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CHAPTER 4. MEASUREMENT OF HUMIDITY

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4.1 GENERAL

The measurement of atmospheric humidity, and often its continuous recording, is an important requirement in most areas of meteorological activity. This chapter deals with the measurement of humidity at or near the Earth's surface. There are many different methods in use, and there is extensive literature on the subject. Accounts of techniques are given in Burt (2012), Harrison (2014) and Sonntag (1994). An older but still useful wide-ranging account of many measurement principles is given in Wexler (1965).

4.1.1 Definitions

Definitions of the most frequently used quantities in humidity measurements are as follows. Further definitions are found in Annex 4.A.

Mixing ratio r : ratio between the mass of water vapour and the mass of dry air;

Specific humidity q : ratio between the mass of water vapour and the mass of moist air;

Dew-point temperature or dew point t_d : The temperature at which moist air saturated with respect to water at a given pressure has a saturation mixing ratio equal to the given mixing ratio. Or more simply, the temperature at which moist air is saturated with water vapour.

Relative humidity U : ratio in % of the observed vapour pressure to the saturation vapour pressure with respect to water at the same temperature and pressure. The term "relative humidity" is often abbreviated to RH;

Vapour pressure e' : The partial pressure of water vapour in air;

Saturation vapour pressures e'_w and e'_i : Vapour pressures in air in equilibrium with the surface of water and ice, respectively.

Annex 4.B provides the formulae for the computation of various measures of humidity. These versions of the formulae and coefficients were adopted by WMO in 1990.¹ They are convenient for computation and sufficiently accurate for all normal meteorological applications, strictly within temperature limitation with $T > -45$ °C for liquid water and $T > -65$ °C for ice (WMO, 1989a). More accurate, extended in range and detailed formulations of these and other quantities may be found in Sonntag (1990, 1994). Other detailed formulations² are presented in WMO (1966, introductions to tables 4.8–10).

4.1.2 Units and scales

The following units and symbols are normally used for expressing the most commonly used quantities associated with water vapour in the atmosphere:

- (a) Mixing ratio r and specific humidity q (dimensionless quotient of masses, in kilogrammes per kilogrammes, kg kg^{-1});

¹ Adopted by the Executive Council at its forty-second session through Resolution 6 (EC-XLII).

² Adopted by the Fourth Congress through Resolution 19 (Cg-IV).

- (b) Vapour pressure in air e' , e'_w , e'_i and pressure p (in units of pressure, such as hectopascals, hPa³);
- (c) Temperature t , wet-bulb temperature t_w , dewpoint temperature t_d , and frost-point temperature t_f (in degrees Celsius, °C);
- (d) Temperature T , wet-bulb temperature T_w , dewpoint temperature T_d , and frost-point temperature T_f (in kelvins, K, as used for certain humidity calculations, and for expressing differences, rather than for general expression of humidity values);
- (e) Relative humidity U (in percent, %. The alternative symbol, %rh, is also often used to avoid confusion with other percentages. It is used throughout this chapter.)

4.1.3 Meteorological requirements

Humidity measurements at the Earth's surface are required for meteorological analysis and forecasting, for climate studies, and for many special applications in hydrology, agriculture, aeronautical services and environmental studies, in general. They are particularly important because of their relevance to the changes of state of water in the atmosphere.

General requirements for the range, resolution and accuracy of humidity measurements are given in Volume I, Chapter 1, Annex 1.A. The uncertainties listed in the table are requirements, not performance of any particular instruments. In practice, these uncertainties are not easy to achieve, even using good quality instruments that are well operated and maintained. In particular, the psychrometer in a thermometer shelter without forced ventilation, still in use, may have significantly worse performance. Even modern electronic humidity instruments can suffer drift that is significant relative to the requirements.

For most purposes, time constants of the order of 1 min are appropriate for humidity measurements. The response times readily available with operational instruments are discussed in 4.8.1.

4.1.4 Methods of measurement and observation

General overviews of humidity instruments for meteorology, and their usage, are given by Burt (2012), Harrison (2014) and Sonntag (1994). Wexler (1965) gives somewhat dated, but still useful, details of many hygrometer principles.

4.1.4.1 Overview of general measurement principles

Any instrument for measuring humidity is known as a hygrometer. The physical principles most widely used for humidity measurement in meteorology are given in the following subsections. Reports of WMO international comparisons of various hygrometers are given in WMO (2011b, 1989b).

The main methods and types of instruments used in meteorology for measuring relative humidity are reviewed here in 4.1.4. Some outdated or no longer used methods and instruments are shortly described in Annex 4.C.

4.1.4.1.1 Electronic sensing

Electronic relative humidity instruments exploit the change in electrical properties of a material on taking up a variable amount water vapour from the air. For relative humidity measurement, the material is commonly a specialised polymer film, coated with electrodes. The measured change in electrical impedance (capacitance or resistance) is scaled to indicate relative humidity. Usually, a compact temperature sensor is also incorporated in the same probe housing.

³ 1 hPa=1mbar

Relative humidity sensor based hygrometers are increasingly the preferred method for remote-reading applications, particularly where a direct reading of relative humidity is required and where data is to be automatically logged.

It is essential to have temperature information alongside humidity observations, because relative humidity is strongly affected by temperature, and because temperature values are needed in order to calculate other humidity quantities (such as dew point) from relative humidity. Meteorological observations do not commonly use the integral temperature sensor in an electronic relative humidity instrument; it is normal to use a separate temperature measurement.

Capacitive polymer hygrometers is the most convenient and leading technology for meteorological applications, as they are easier to produce, maintain and calibrate. More detail about electrical capacitance hygrometers is given in 4.2.

Electrical resistance hygrometers are not really in use in meteorology and described in Annex 4.C.4

4.1.4.1.2 *Psychrometric method*

A psychrometer measures evaporative cooling of a wet surface. The steady-state cooling can be related to the partial pressure of water vapour, and to the relative humidity.

A psychrometer consists essentially of two thermometers exposed side by side, with the surface of the sensing element of one being covered with a sleeve maintaining a thin film of water or ice and termed the wet or ice bulb, as appropriate. The sensing element of the second thermometer is simply exposed to the air and is termed the dry bulb. The measurement is either aspirated or under natural ventilation.

Owing to evaporation of water from the wet bulb, the temperature measured by the wet-bulb thermometer is generally lower than that measured by the dry bulb. The difference in the temperatures measured by the pair of thermometers is a measure of the humidity of the air; the lower the ambient humidity, the greater the rate of evaporation and, consequently, the greater the depression of the wet-bulb temperature below the dry-bulb temperature. The size of the wet-bulb depression is related to the ambient humidity by a psychrometer formula.

Psychrometers remain in use for observational purposes, although increasingly being replaced by electronic sensor based hygrometers. Psychrometers are also sometimes used as working standards.

More detail about this instrument type is given in 4.3.

4.1.4.1.3 *Condensation method*

The temperature of condensation of water vapour (dew point or frost point) is related to the partial pressure of water, and can be measured using a chilled-mirror hygrometer (condensation hygrometer).

When moist air is cooled, it eventually reaches its saturation point with respect to water (or to ice) and condensation can form as dew or frost. The temperature of this saturation point is the dewpoint or frost point.

A typical chilled-mirror hygrometer uses a small mirrored surface, cooled using a Peltier-effect device, to obtain a film of water or ice. Usually, optical detection of the condensed film is used in a feedback loop to control the temperature at the threshold of constant condensation. This temperature is measured using an embedded temperature sensor. Air to be measured is typically sampled through tubing and flowed through the instrument.

Condensation hygrometers are not widely used for meteorological observations but are commonly used as laboratory reference instruments.

More detail about this instrument type is given in 4.4.

4.1.4.1.4 *Water vapour spectrometers*

The water molecule absorbs electromagnetic radiation in a range of wavebands and discrete wavelengths; this property can be exploited to obtain a measure of the molecular concentration of water vapour in a gas. This principle is used in a variety of instruments, using absorption lines of different strengths for different ranges of measurement (stronger absorption for lower concentrations).

In simplest form, an instrument measures the transmission (or absorption) of narrowband infrared radiation from a fixed-intensity source to a calibrated detector, and sometimes compared to a reference wavelength. Certain instruments on this principle can measure in humidity ranges observed at ground level.

For the trace water vapour range, absorption spectrometers measure the absorption of infrared light in multiple reflections through the gas within the measurement cell, giving a long optical path length to extend the range downwards. A particular instrument type is the tunable diode laser spectrometer (TDLAS). The amplitude of light absorption is related to the concentration of water vapour.

Cavity ring-down spectrometers also use infrared absorption through a long path for measuring trace concentrations. A pulse of light is multiply reflected through the gas in a measurement cell. The time taken for the light intensity to decay is measured, and is related to the concentration of water vapour.

Lyman alpha hygrometers operate in the ultraviolet range. UV light from an instrument source is absorbed by water molecules in proportion to the concentration of water vapour. The so-called Lyman alpha line corresponds to radiation emitted or absorbed during an energy transition of atomic hydrogen.

Absorption spectrometers and Lyman alpha instrument are used for some aircraft-borne observations, including measurement of trace levels of water at high flight altitudes. These applications benefit from the relatively fast response time of these instruments.

More detail about this instrument type is given in 4.5.

4.1.4.1.5 *Mechanical methods*

Historically, hygrometers have used the dimensional change of organic materials to indicate relative humidity. Water sorption processes of materials are related to relative humidity because the driving force is chemical potential. Sensing elements have included hair and, more recently, synthetic fibres. The change in length with humidity of the sensing element is amplified using a lever system, moving a pointer to indicate relative humidity on a scale, a chart (as a record for the hygrograph), or less commonly via a transducer to an electrical output.

Only the hair hygrograph is still in use in meteorology, though phasing out. More detail about this instrument is given in 4.6.

4.1.4.2 *Exposure: general comments*

The general requirements for the exposure of humidity instruments are similar to those for temperature sensors, and a suitably positioned thermometer screen can be used for that purpose. Particular requirements include:

- (a) Protection from direct solar radiation, atmospheric contaminants, rain and wind;
- (b) Avoidance of the creation of a local microclimate within the instrument housing structure or sampling device. Note that wood and many synthetic materials will adsorb or desorb water vapour according to the atmospheric humidity.

Exposures appropriate to particular instruments are described in 4.2 to 4.6.

The siting classification for surface observing stations on land (see Volume I, Chapter 1, Annex 1.C of this Guide) provides additional guidance on the selection of a site and the location of a hygrometer within a site to optimize representativeness.

4.1.4.3 Sources of error: general comments

Errors in the measurement of humidity can be caused by any of the following:

- (a) Modification of the air sample: for example, by heat or water-vapour source or sink;
- (b) Contamination of the sensor: for example, by dirt, sea spray, chemical exposure or other pollution;
- (c) Calibration error, including pressure correction, temperature coefficient of sensor, and electrical interface;
- (d) Inappropriate treatment of water/ice phase;
- (e) Intrinsic design weaknesses of instruments: for example, stem heat conduction in the wet-bulb thermometer;
- (f) Slow response time of instrument, or failure to achieve stable equilibrium in operation;
- (g) Inappropriate sampling and/or averaging intervals;
- (h) Hysteresis: Many humidity measuring instruments indicate differently depending on whether they approach the condition after having previously been wetter, or dryer;
- (i) Long-term drift between calibrations, particularly for electronic humidity measuring instruments in high RH environments;
- (j) Radiant heating of the humidity sensor to above the air temperature: for example, due to heating from a radiation screen that is itself warmed by solar radiation;
- (k) Error of any kind in temperature measurement, if the temperature value is used in calculating other humidity quantities (for example, calculating dew point from relative humidity).

The time constant of the sensor (see 4.8.1), the time-averaging of the output and the data requirement should be consistent.

The different types of humidity measuring instruments vary in their susceptibility to, and the significance of, each of the above; further discussion will be found in the appropriate sections of this Chapter.

4.1.4.4 Maintenance: general comments

The vast majority of commercially available hygrometers have operating manuals freely available online. These are generally a good source of guidance for maintenance of instruments, and manufacturers are generally willing and able to advise about particular questions.

The following maintenance procedures should be considered:

- (a) Cleanliness: Instruments and housings should be kept clean. Some humidity measuring instruments, for example, chilled-mirror and hair hygrometers, may be cleaned with distilled water and this should be carried out regularly. Others, notably those having some form of electrolyte coating, but also some with a polymeric substrate, should never be cleaned. The provision of clear instructions for observers and maintenance staff is vital;
- (b) Calibration of field instruments: Regular calibration is required for all humidity measuring instruments in the field. A calibration identifies any errors in readings, by comparison against a reference. Such errors are ideally addressed by applying corrections (for example by

adjustment, for an electronic hygrometer). Any uncorrected errors need to be considered as part of the uncertainty of the measurement. Calibrations should be made using a reference with metrological traceability (JCGM, 2012) to a national standard wherever possible (see Volume I, Chapter 1, Annex 1.B).

- (c) Checking of field instruments is useful in between calibrations. A check against another instrument can be used to assess consistent operation. Results of checks are usually assessed according to a tolerance or criterion based on the uncertainties of the two instruments being compared.

Field hygrometers can conveniently be checked using a calibrated electronic hygrometer. An instrument used for such checks should be equilibrated to the local ambient temperature, and should have a response time well within the period allowed for the check.

Saturated salt solution systems are commercially available to be used for either checking or calibration. However, they must be equilibrated to the ambient temperature, and the salt mixture itself may need additional equilibration time to generate the correct humidity. It is difficult to be confident about their use in the field, unless used together with a transfer standard (calibrated hygrometer).

The use of a standard type of aspirated psychrometer, such as the Assmann, as a field reference has the advantage that some degree of self-check can be made by comparing the dry- and (unsheathed) wet-bulb thermometers, and that adequate aspiration may be expected from a healthy sounding fan. However, psychrometers emit water vapour in operation, and this can affect the humidity condition nearby, possibly limiting the accuracy of the check if it is close to the instrument being compared.

For any calibration or check, the reference instrument should itself be calibrated at intervals that are appropriate to its type.

It is important to check the calibration of electrical interfaces regularly and throughout their operational range. A simulator may be used in place of the sensor for this purpose. However, it will still be necessary to calibrate the ensemble at selected points, since the combination of calibration errors for sensor and interface which are individually within specification may be outside the specification for the ensemble.

Detailed maintenance requirements specific to each class of hygrometer described in this Chapter are included in the appropriate section further below.

4.1.5 Implications of the Minamata Convention for the humidity measurement

The United Nations Environment Programme (UNEP) Minamata Convention on Mercury came into force globally in August 2017, and bans all production, import and export of mercury thermometers (Volume I, Chapter 1, 1.4.1). Therefore humidity instruments based on mercury thermometers are no longer recommended and it is strongly encouraged to take appropriate measures to replace them with modern alternatives, as soon as possible.

4.2 ELECTRICAL CAPACITANCE HYGROMETERS

4.2.1 General considerations

Electronic relative humidity instruments exploit the change in electrical properties of a material on taking up a variable amount water vapour from the air. Water sorption processes of materials are related to relative humidity because the driving force is chemical potential. For relative humidity measurement, the material is commonly a specialised polymer film, coated with electrodes. The measured change in electrical impedance is scaled to indicate relative humidity. Usually, a compact temperature sensor is also incorporated in the same probe housing.

The humidity sensor is typically housed in a probe, and this usually incorporates a compact temperature sensor. The sensor region is normally protected by a cage or a filter. In addition, the humidity sensor itself is often directly encased in a protective porous material.

The instruments typically incorporate linearizing electronics, with temperature compensation if needed, to optimise accurate response to relative humidity. The manufacturers variously supply display, data-processing, or data-logging systems. In some case this is integral to the instrument; in others a cable connects to the supporting electronics unit.

Hygrometers using electrical relative humidity sensors are increasingly used for remote-reading applications, particularly where a direct display of relative humidity is required.

4.2.2 Electrical capacitance hygrometer

The method is based upon the variation of the dielectric properties of a solid, hygroscopic material in relation to the ambient relative humidity. Sensing dielectric materials are chosen or deliberately developed for humidity sensor purposes. Polymers are most widely used for stability, selectivity and water sorption, but also because adequate capacitor properties are achieved with these materials. The water bound in the polymer alters its dielectric properties owing to the large dipole moment of the water molecule.

Typically the humidity sensor is built on ceramic or glass substrate. It is a parallel thin films stack with layer thicknesses from a few nanometers to one micrometer. The active part of the humidity sensor consists of a polymer film sandwiched between two electrodes to form a capacitor. The upper electrode is permeable for water molecules and the polymer absorbs water proportional to RH. The upper electrode may also be covered with a protective layer in order to improve stability in harsh environments.

The capacitance provides a measure of relative humidity. The nominal value of capacitance may be only a few hundred picofarads, depending upon the size of the electrodes and the thickness of the dielectric. This will, in turn, influence the range of excitation frequency used to measure the impedance of the device, which is normally at least several kilohertz and, thus, requires that short connections be made between the sensor and the signal processing electronics to minimize the effect of stray capacitance. Therefore, capacitance sensors often have the signal processing built into the instrument. Typical sensitivity for a 200 pF device is 0.5 pF per percent relative humidity.

In order to prevent condensation when the condition approaches 100 %rh, instrument manufacturers provide different heating options. The sensor may be heated by an integrated heater or the whole probe itself is warmed. The heating is controlled using either temperature difference between ambient temperature and internal temperature or a relative humidity threshold. For good measurement results, it is crucial to measure both the temperature of the humidity sensor and the temperature of the ambient air accurately. By using the RH measured by the sensor, the sensor temperature and the temperature of the air, it is possible to calculate the relative humidity of the air. Even without the known air temperature, heated measurement can be used to determine dew point temperature. Chemical exposure related drift can be reduced by using an integrated heater to heat the humidity sensor, at repeatable intervals, during a short time at high temperature. A drawback is the dead time during heating.

4.2.3 Observation procedure

Hygrometers using electronic relative humidity sensors are frequently used in automatic weather stations, and wherever unattended or data-logged humidity measurements are needed.

Temperature observations are essential alongside humidity observations, since temperature values are used to calculate other humidity quantities (such as dew point) from relative humidity. This normally involves a separate thermometer, not the integral temperature sensor in an electronic relative humidity instrument.

4.2.4 Exposure and siting

Hygrometer probes should be mounted inside a thermometer screen. The manufacturer's advice regarding the mounting of the actual instrument should be followed. The use of a protective filter is essential to minimise contamination which can cause progressive error. Instruments using hygroscopic electrolyte as a sensing element will be damaged by direct contact with liquid. Capacitive sensors that have been wetted can often recover at least partially after drying. However, exposure to high or condensing humidities is associated with long-term drift of some capacitive sensors.

4.2.5 Sources of error

Measurements using relative humidity sensors can be particularly affected by any of the following causes of error.

Calibration error can be present, such that the initial adjustment of the instrument leaves residual uncorrected errors. This error can have the character of non-linearity, or some other form. This can also appear as temperature-dependence, since it is typically not possible to calibrate at multiple temperatures, or to implement temperature-dependent calibrations.

Sensors can suffer contamination; for example, by dirt, sea spray, chemical exposure or other pollution. This type of error can take the form of reduced sensitivity across the whole range, with over-reading at low humidities and under-reading at high humidities, or it can follow some other pattern.

Hysteresis can affect electronic humidity instruments, so that they read differently depending on whether they approach the condition after having previously been wetter, or dryer. Response time can also differ for rising and falling changes in condition.

Long-term drift between calibrations can be significant, particularly for instruments exposed to high or condensing relative humidities (dew, fog or other wetting). Such drift is most typically upwards at high humidity although it can be downwards, and varies greatly (Burt, 2012; Bell *et al.*, 2017). Upwards drift leads to over-reading at high humidity values, for example indicating 100 %rh at a condition of 95 %rh. Heated sensors are potentially less prone to such drift.

Radiant heating of the humidity sensor to above the air temperature can mean that sensor is warmer than the air. This can happen even within a screen if the screen itself is warmed by solar radiation. This can potentially give a falsely low reading of relative humidity.

Error of any kind in temperature measurement is significant with relative humidity if both values are used in calculating other humidity quantities (for example, calculating dewpoint from relative humidity). In such calculations, an error of 0.1 °C near 20 °C has the same magnitude of effect as an error of 0.6 % of relative humidity value. WMO (2011b) details this effect at other temperatures.

4.2.6 Calibration and field inspection

A calibration identifies any errors in readings, by comparison against a reference. Calibration of relative humidity instruments is normally a laboratory process which involves comparison against reference for relative humidity, often in a climatic chamber. Calibrations should be made using a reference with metrological traceability to a national standard wherever possible (see Volume I, Chapter 1, Annex 1.B). Further details are given in 4.7 and Volume V Chapter 4.

Calibrations are ideally implemented by applying corrections (commonly by applying instrument adjustments, for an electronic hygrometer). For some electronic hygrometers, adjustments can be applied using manufacturer software, at the time of calibration. In other cases, adjustments can be made by adjusting potentiometers corresponding to "range" and "zero" of the hygrometer indication. While calibration corrections can be applied arithmetically, this is more useful in a laboratory application than in meteorology settings. Any uncorrected calibration errors need to be considered as part of the uncertainty of the measurement.

Field inspections of electronic relative humidity instruments involve viewing the condition and functioning of the instruments. In particular, the condition of the sensor filter is inspected, and this is cleaned or replaced if it is dirty.

Field checks of hygrometers can conveniently be made using another calibrated electronic hygrometer. An instrument used for such checks should be equilibrated to the local ambient temperature. It should either be calibrated at the temperature of use, or allowance should be made for the different temperatures of operation. The hygrometer used for any field check should have a response time well within the time period allowed for the check. A check will normally have a defined criterion for acceptance.

In principle, field checks of relative humidity instruments can be made using salt-based systems, which are supplied by some instrument manufacturers. These are only reliable after they are fully equilibrated to the local ambient temperature. Therefore it is difficult to be confident about their use in the field. In principle a field humidity generator can be used for checking on site, but these are not widely available. Further details are given at 4.7.6.3.

The use of a standard type of aspirated psychrometer, such as the Assmann, as a field reference has been advocated. However, psychrometers emit water vapour in operation, and this can affect the humidity condition nearby, possibly affecting the accuracy of the check if it is close to the instrument being compared.

For any calibration or check, the reference instrument should itself be calibrated at intervals that are appropriate to its type.

Where relevant, a check of an electronic hygrometer should include checking the data-logging interfaces. A simulator can possibly be used in place of the sensor for this purpose. Depending on the configuration of the system, whole-system checks (hygrometer plus interface) may be needed. For example, on older systems the combination of calibration errors for sensor and interface which are individually within specification could be outside the specification for the ensemble.

4.2.7 Maintenance

Observers should be encouraged to maintain the hygrometer in clean conditions (see 4.1.4.4). Where the hygrometer is fitted with an interchangeable protective filter-cap, this should be visually inspected for evidence of contamination and replaced if necessary. The body of a hygrometer can be cleaned if necessary using a damp cloth taking care not to wet the sensor. Electronic elements must not be cleaned in the field, as this would alter their calibration.

Time intervals for field servicing and calibration of relative humidity instruments will generally depend on the level of long-term stability expected and required, the location, and on the availability of facilities and personnel. The lifetime before failure, for electronic relative humidity instruments in service in weather stations in damp climates, is commonly between six months and two or more years. There is often significant sensor drift on shorter timescales. The cause of failure (especially early failures) is commonly the sensor element. Usually, this can be replaced, and the hygrometer recalibrated before being used again.

In some cases, field servicing of an electronic hygrometer will mean the replacement of a failed instrument. In other cases, field hygrometers are replaced (perhaps annually) with a newly calibrated instrument, and the one taken out of use is sent for servicing, recalibration and (if satisfactory) re-deployment. If a hygrometer has failed, often this can be remedied by the replacement of just the sensor element, followed by recalibration.

In order to address the tendency of sensors to drift, a more intensive management approach can be adopted where resources allow. Sensor drift can be evaluated on return from the field, by comparison against a reference in a calibration facility. Those instruments showing minor drift can be adjusted and then recalibrated for redeployment. However, these can be expected to have worse ongoing reliability than new instruments. Those instruments that are found to have more extreme in-field drift can be refurbished (by buying a new sensing element, changing it in the laboratory and calibrate the renewed instrument). However, after a number of deployments,

performance can be expected to worsen, and a policy of routinely replacing these hygrometers after a defined period can lead to improved overall reliability of the observations.

The vast majority of commercially available hygrometers have operating manuals freely available online. These are generally a good source of guidance for maintenance of instruments, and manufacturers are generally willing and able to advise about particular questions.

4.3 THE PSYCHROMETER

4.3.1 General considerations

4.3.1.1 Psychrometric formulae

The usual practice is to derive the vapour pressure e' under the conditions of observation from the following semi-empirical psychrometric formulae:

$$e' = e'_w(p, t_w) - Ap(t - t_w) \quad (4.1)$$

and:

$$e' = e'_i(p, t_i) - Ap(t - t_i) \quad (4.2)$$

where e'_w is the saturation vapour pressure with respect to water at temperature t_w and pressure p of the wet bulb; e'_i is the saturation vapour pressure with respect to ice at temperature t_i and pressure p of the ice bulb; p is the pressure of the air; t the temperature of the dry bulb; and A is the psychrometer coefficient. (The latter is preferred to the term "psychrometer constant", which is a misnomer.)

The formulae and coefficients appropriate for the various forms of psychrometer are discussed in the following sections.

4.3.1.2 The specification of a psychrometer

The equipment used for psychrometric observations should, as far as practicable, conform to the following recommendations:

- (a) At sea level, and in the case where the thermometers are of the types ordinarily used at meteorological stations, air should be drawn past the thermometer bulbs at a rate of no less than 2.2 m s^{-1} and no greater than 10 m s^{-1} . For appreciably different altitudes, these air speed limits should be adjusted in inverse proportion to the density of the atmosphere;
- (b) The wet and dry bulbs must be protected from radiation, preferably by a minimum of two shields. In a psychrometer with forced ventilation, such as the Assmann, the shields may be of polished, unpainted metal, separated from the rest of the apparatus by insulating material. Thermally insulating material is preferable in principle and must be used in psychrometers which rely on natural ventilation;
- (c) If the psychrometer is exposed in a louvered screen with forced ventilation, separate ventilation ducts should be provided for the two thermometers. The entrance to the ducts should be located so as to yield a measurement of the true ambient temperature, and the air should be exhausted above the screen in such a way as to prevent recirculation;
- (d) The greatest care should be taken to prevent the transfer of significant amounts of heat from an aspirating motor to the thermometers;
- (e) The water reservoir and wick should be arranged in such a way that the water will reach the bulb with sensibly the wet-bulb temperature, so as not to affect the temperature of the dry bulb.

4.3.1.3 *The wet-bulb sleeve*

The wet bulb usually has a cotton wick, or similar fabric, fitting closely around the sensing element in order to maintain an even covering of water, which is either applied directly or by some form of capillary feed from a reservoir. The wick commonly takes the form of a sleeve that has a good fit around the bulb and extends at least 2 cm up the stem of the thermometer in order to give extended cooling, to reduce stem conduction. Distilled water should be used for the wet bulb.

The fabric used to cover the wet bulb should be thin but closely woven. Where the supplier offers a wick designed for the size of the thermometers, this should be used. Before installation, it should be washed thoroughly in an aqueous solution of sodium bicarbonate (NaHCO_3), at a dilution of 5 g per litre, and rinsed several times in distilled water. Alternatively, boiling in a dilute solution of pure detergent in water may be used, followed by boiling in distilled water. Great care should be exercised in handling the clean sleeve or wick to prevent contamination from hands, for example by using tweezers that have been cleaned, or clean plastic residue-free gloves.

The proper management of the wet bulb is particularly important. Any visible contamination of the wick or the wet-bulb sleeve should be considered an absolute indication of the necessity for its immediate replacement. Otherwise, observers should be encouraged to change the wet-bulb sleeve and wick at least once a week for all psychrometers that are continuously exposed. At places near the sea and industrialized districts it may be necessary to replace these items more frequently. The water supply should be checked frequently and replaced or replenished as required.

Under hot, dry conditions, it can be an advantage to wet the covering with water from a porous vessel. This will cause the water to be pre-cooled by evaporation from the porous surface. The vessel should be kept in the shade, but not in the immediate vicinity of the psychrometer.

4.3.1.4 *Operation of the wet bulb below freezing*

The psychrometer is difficult to operate at temperatures below freezing, but it is still used in climates where such temperatures occur. A wick cannot be used to convey water from a reservoir to the wet-bulb sleeve by capillary action when the wick is frozen. Under these conditions, care should be taken to form only a thin layer of ice on the sleeve. It is an absolute necessity that the thermometers be artificially ventilated; if they are not, the management of the wet bulb will be extremely difficult.

The wet bulb of the aspirated and sling psychrometers should be moistened immediately before use. The water should, as far as possible, have a temperature close to freezing point. If a button of ice forms at the lowest part of the bulb, it should be immersed in water long enough to melt the ice.

The time required for the wet bulb to reach a steady reading after the sleeve is wetted depends on the ventilation rate and the actual wet-bulb temperature. An unventilated thermometer usually requires from 15 to 45 min, while an aspirated thermometer will require a much shorter period. It is essential that the formation of a new ice film on the bulb be made at an appropriate time. If hourly observations are being made with a simple psychrometer, it will usually be preferable to form a new coating of ice just after each observation. If the observations are made at longer intervals, the observer should visit the screen sufficiently in advance of each observation to form a new ice film on the bulb.

The evaporation of an ice film between readings can be prevented or slowed by enclosing the wet bulb in a small glass tube, or by stopping the ventilation inlet of the wet bulb between periods of measurement. If so the wet-bulb temperature will not be accurate during these interventions. (Note that the latter course should not be taken if the circumstances are such that the ventilating fan would overheat.)

The effect of supercooled water on the wet bulb may be dealt with in two ways:

- (a) By using different formulae or tables when the wet bulb is coated with ice and with supercooled water, respectively. To find out which table should be used, the wet bulb should

be touched with a snow crystal, a pencil, needle, or other object, just after each observation is completed. Degree of gloss on the surface of the wet-bulb is also useful to check if the wet-bulb is frozen. If the temperature rises towards 0 °C, and then commences to fall again, it can be assumed that the water on the wet bulb was supercooled at the time of the observation;

- (b) By using a formula or table appropriate for an ice-covered wet bulb, and inducing the freezing of supercooled water in the same way as for method (a). In order to save time and to ensure that the wet bulb is ice-covered, the observer should make a point of initiating the freezing of the water at each observation as soon as possible after moistening the bulb. From the behaviour of the wetted thermometer at the freezing point it may usually be determined whether the bulb is covered by ice or by supercooled water. The recommended procedure, however, is to initiate the freezing of the water at each observation when the wet-bulb temperature is assumed to be below 0 °C, regardless of whether the behaviour of the thermometer after moistening has been observed or not.

Although the first method is usually the quickest, it requires two tables and this may cause some confusion.

4.3.1.5 General procedure for making observations

The procedures outlined in Volume I, Chapter 2, for the measurement of temperature should be followed, in addition to the following procedures:

- (a) If the wet-bulb sleeve, wick or water has to be changed, this should be done sufficiently in advance of the observation. The period required for the correct wet-bulb temperature to be attained will depend upon the type of psychrometer;
- (b) The thermometers should be read to the nearest 0.1 degree;
- (c) When making an observation, the readings of the two thermometers should, as far as possible, be taken simultaneously (reading first dry-thermometer, then wet-one, finally the dry-one again is a relevant solution), and it should be ascertained that the wet bulb is receiving a sufficient water supply.

4.3.1.6 Use of electrical resistance thermometers

Precision platinum electrical resistance thermometers are widely used in place of liquid-in-glass thermometers, in particular where remote reading and continuous measurements are required. It is necessary to ensure that the devices, and the related electronics, meet the performance requirements. These are detailed in Volume I, Chapter 2. Particular care should always be taken with regard to self-heating effects in electrical thermometers.

The psychrometric formulae in Annex 4.B used for Assmann aspiration psychrometers are also valid if platinum resistance thermometers are used in place of the mercury-in-glass instruments, with different configurations of elements and thermometers. The formula for water on the wet bulb is also valid for some transversely ventilated psychrometers (WMO, 1989a).

4.3.1.7 Psychrometric formulae and tables

The following paragraphs summarize some existing principles and practice in drawing up psychrometric tables.

The wet-bulb thermometer temperature T_w for most instruments is not identical to the theoretical thermodynamic wet-bulb temperature, defined in Annex 4.A, which depends only upon p , T and r (the humidity mixing ratio). The temperature measured by a practical wet-bulb thermometer depends also upon a number of variables that are influenced by the dynamics of heat transfer across a liquid/gas interface (in which the gas must be characterized in terms of its component laminar and turbulent layers). The description of a satisfactory thermodynamic model is beyond the scope of this publication. The inequality of the thermodynamic and measured wet-bulb

temperatures is resolved in practice through the empirical determination of the psychrometer coefficient A (WMO(1992)).

In general, the coefficient A depends upon the design of the psychrometer (in particular the wet-bulb system), the diameter of the thermometers, the rate of airflow past the wet bulb (termed the ventilation rate), and the air temperature and its humidity. At low rates of ventilation, A depends markedly upon the ventilation rate. However, at ventilation rates of 3 to 5 m s⁻¹ (for thermometers of conventional dimensions) or higher, the value of A becomes substantially independent of the ventilation rate and is practically the same for all well-designed psychrometers. The value of A does not, then, depend very much on temperature or humidity and its dependence on these variables is usually ignored. A is smaller when the wet bulb is coated with ice than when it is covered with water.

4.3.1.8 Sources of error in psychrometry

The following main sources of error must be considered:

- (a) Errors of the thermometers: It is very important in psychrometric measurements that the errors of the thermometers be known over the actual temperature range and that corrections for these errors be applied to the readings before the humidity formulae tables are used. In general, thermometers should be pre-selected to have minimum errors.

Any other errors in the wet-bulb or ice-bulb temperature caused by other influences will appear in the same way as thermometer errors.

Table 4.1 shows the error in relative humidity $\varepsilon(U)$, derived from wet- and ice-bulb measurements having errors $\varepsilon(t_x)$, where x is water for $t > 0$ °C and ice for $t < 0$ °C, respectively of 0.5 and 0.1 K, for a relative humidity U of 50 %rh and a range of true air temperatures (where the dry-bulb reading is assumed to give the true air temperature).

- (b) Thermometer response time coefficients (sometimes called lag coefficients): To obtain the highest accuracy with a psychrometer it is desirable to arrange for the wet and dry bulbs to have approximately the same response time coefficient; with thermometers having the same bulb size, the wet bulb has an appreciably smaller response time than the dry bulb.
- (c) Errors relating to ventilation: Errors due to insufficient ventilation can lead to overestimation of humidity.
- (d) Errors due to the use of inappropriate humidity formulae or tables (see sections covering individual psychrometer types). Other errors can be magnified through inappropriate evaluations.
- (e) Errors due to excessive covering of ice on the wet bulb: Since a thick coating of ice will increase the response time of the thermometer, it should be removed immediately by dipping the bulb into distilled water.
- (f) Errors due to contamination of the wet-bulb sleeve or to impure water: Large errors can be caused by the presence of substances that alter the vapour pressure of water. The wet bulb with its covering sleeve should be washed at regular intervals in distilled water to remove soluble impurities. This procedure is more frequently necessary in some regions than others, for example, at or near the sea or in areas subject to air pollution.
- (g) Errors due to heat conduction from the thermometer stem to the wet-bulb system: The conduction of heat from the thermometer stem to the wet bulb will reduce the wet-bulb depression and lead to determinations of humidity that are too high. The effect is most pronounced at low relative humidity but can be effectively reduced or eliminated by extending the wet-bulb sleeve at least 2 cm beyond the bulb, up the stem of the thermometer.

- (h) Errors due to radiative effects: The wet-bulb temperature will always be colder than the surroundings, and radiation shields will not always protect completely against radiative heating of all parts of the assembly.

It should be noted that psychrometers are generally less accurate at low relative humidities (large wet-bulb depressions).

ELEMENT 1: Floating object (Top)

Table 4.1. Error in derived relative humidity resulting from wet- and ice-bulb index errors $\varepsilon(t_x)$ for $U = 50\%$ rh

TABLE: Table horizontal lines

Air temperature in °C	Error in relative humidity, ε (U) in % due to an error in wet- or ice-bulb temperature	
	$\varepsilon(t_x) = 0.5\text{ K}$	$\varepsilon(t_x) = 0.1\text{ K}$
-30	60	12
-20	27	5
-10	14	3
0	8	2
10	5	1
20	4	0.5
30	3	0.5
40	2	0.5
50	2	0

END ELEMENT

4.3.2 Assmann and other aspirated psychrometers

An alternative instrument to the traditional (mercury-in-glass) Assmann psychrometer is an electrically aspirated psychrometer using two platinum resistance thermometers, instead of two mercury-in-glass thermometers. Newer designs of aspirated psychrometers do not follow the exact pattern of Assmann instruments, and commonly incorporate a reservoir supplying water to the wick over an extended period. Overall, any alternative designs will still require precautions in operation similar to the Assmann types.

This change of instrumentation should be recorded meticulously and "side by side" comparisons for a period of two or more years in line with WMO recommendations. (WMO, 2015; WMO, 2011a)

4.3.2.1 Description

Two thermometers, mounted vertically side by side in a chromium- or nickel-plated polished metal frame, are connected by ducts to an aspirator (fan). The aspirator may be driven by a spring or an electric motor. In the traditional Assmann design, mercury-in-glass thermometers were used, but updated designs could in principle use suitably characterised alternatives (resistance thermometers, or other liquid-in-glass types) of suitable diameter and measuring range. One

thermometer has a well-fitting muslin wick which, before use, is moistened with distilled water. The wick covers the sensing part of the thermometer (for a liquid-in-glass thermometer this is the bulb) and a defined additional length of the thermometer stem. Where a resistance thermometer is used for the "wet-bulb", it is important that the wick covers and extends beyond the region of the sensing element; this region is not usually obvious by inspection of a thermometer but will be based on knowledge of its internal structure.

Each thermometer is located inside a pair of coaxial metal tubes, highly polished inside and out, which screen the bulbs from external thermal radiation. The tubes are all thermally insulated from each other.

A WMO international intercomparison of Assmann-type psychrometers from 10 countries (WMO, 1989a) showed that there is good agreement between dry- and wet-bulb temperatures of psychrometers with the dimensional specifications close to the original specification, and with aspiration rates above 2.2 m s^{-1} . Not all commercially available instruments fully comply. A more detailed discussion is found in WMO (1989a). It has been suggested that the performance of the Assmann psychrometer in the field may be as good as the achievable accuracy stated in Volume I, Chapter 1, Annex 1.F of this Guide, but this level of accuracy will not reliably be achieved, due to possible errors of airflow, contamination and radiant heat transfer, among others. As for all types of psychrometer, calibration of the instrument, as in 4.3.2.4 below, is the best way to ensure accuracy. This will be especially important for any emerging designs where alternatives are used in place of mercury-in-glass thermometers.

Annex 4.B lists standard formulae for the computation of measures of humidity using an Assmann psychrometer,⁴ and these formulae are also used for some of the other artificially ventilated psychrometers, in the absence of well-established alternatives.

4.3.2.2 Observation procedure

The wick, which must be free of grease, is moistened with distilled water. Dirty or crusty wicks should be replaced. Care should be taken not to introduce a water bridge between the wick and the radiation shield.

The instrument is normally operated with the thermometers held vertically, ideally by mounting it on a stand. The thermometer stems should be protected from solar radiation by turning the instrument so that the lateral shields are in line with the sun. If the instrument is hand-held, it should be tilted so that the inlet ducts open into the wind, but care should be taken so that solar radiation does not fall on the thermometer bulbs. A wind screen is necessary in very windy conditions when the rotation of the aspirator is otherwise affected.

The psychrometer should be in thermal equilibrium with the surrounding air. At air temperatures above $0 \text{ }^{\circ}\text{C}$, at least three measurements at 1 min intervals should be taken following an aspiration period. Below $0 \text{ }^{\circ}\text{C}$ it is necessary to wait until the freezing process has finished, and to observe whether there is water or ice on the wick. During the freezing and thawing processes the wet-bulb temperature remains constant at $0 \text{ }^{\circ}\text{C}$. In the case of outdoor measurements, several measurements should be taken and the average taken. Thermometer readings should be made with a resolution of 0.1 K or better.

A summary of the observation procedure is as follows:

- (a) Moisten the wet bulb;
- (b) Wind the clockwork motor (or start the electric motor);
- (c) Wait 2 or 3 min or until the wet-bulb reading has become steady;

⁴ Recommended by the Commission for Instruments and Methods of Observation at its tenth session (1989).

- (d) Read the dry bulb;
- (e) Read the wet bulb;
- (f) Check the reading of the dry bulb.

4.3.2.3 Exposure and siting

Observations should be made in an open area. The instrument is either suspended from a clamp or attached using a bracket to a thin post, or held with one hand at arm's length with the inlets slightly inclined into the wind. The inlets should be at a height of 1.25 to 2 m above ground for normal measurements of air temperature and humidity.

Great care should be taken to prevent the presence of the observer or any other nearby sources of heat and water vapour, such as the exhaust pipe of a motor vehicle, from having an influence on the readings.

4.3.2.4 Calibration

Calibration of a psychrometer has two aspects: calibration of the thermometers, and calibration of the whole instrument functioning as a hygrometer. Maintenance steps (particularly for wick and fan) should be performed before an instrument is calibrated.

Calibration of the thermometers is recommended at regular intervals according to the thermometer type and quality, and the degree of handling or other stresses on the thermometers. For further information, see Volume I, Chapter 2.

For resistance thermometers, calibration corrections can be applied by applying different coefficients in the formula for converting resistance to temperature (see Volume I, Chapter 2). If calibration-specific coefficients are not applied, then the calibration process is used to confirm accuracy of the thermometers to within a given tolerance. If thermometers do not meet the tolerance, they should be replaced.

For liquid-in-glass thermometers, calibration corrections can in principle be applied arithmetically; otherwise, again, the calibration process is used to confirm accuracy of the thermometers to within a given tolerance. If thermometers do not meet the tolerance, they can be replaced.

After temperature calibration is applied, the whole psychrometer is calibrated as a hygrometer, usually against a reference in terms of relative humidity. This reference may be a reference dewpoint hygrometer or one or more reference thermometers. The calibration may be undertaken in ambient air - or in a humidity- and temperature-controlled chamber for remote-reading (PRT) psychrometers. The possibility of calibration in a chamber at multiple temperatures and humidities is a strongly advised for psychrometers using electrical thermometers.

Ideally, where a psychrometer calibration can be carried out at a range of temperature and humidity conditions, it is possible to use the results to evaluate a psychrometer coefficient, or a corresponding function, specific to the psychrometer. The function is typically a constant plus a second term representing a slight temperature dependence. The coefficient or function derived from calibration can replace the value of A in the psychrometer equation, if this can be implemented (for example in software). This approach to implementing calibration provides better accuracy than using the generalized default psychrometer coefficient.

If temperature calibration is neglected before humidity calibration, the uncorrected temperature values will usually cause larger errors in humidity values than if temperature corrections are applied (or tolerances met).

Pressure is normally reported for calibration of psychrometers, since evaluation of the psychrometer equation uses pressure, and the psychrometric effect has some pressure dependence.

4.3.2.5 Maintenance

The calibration of the thermometers should be checked regularly. The two may be compared together, with both thermometers measuring the dry-bulb temperature. The ventilation system should be checked, at least once per month, or before use if that is a longer interval. Checks of thermometers by comparison against a reference thermometer are useful at intervals, for example annually.

Mercury instruments should no longer be used. But as long as any remains, the mercury columns of the thermometers should be inspected for breaks, which should be closed up or the instrument should be replaced.

Between uses, the instrument should be stored in an unheated room or be otherwise protected from precipitation and strong insolation. When not in use, the instrument should be stored indoors in a sturdy packing case such as that supplied by the manufacturer.

4.3.3 Screen psychrometer

Traditionally mercury in glass thermometers have been used as screen psychrometers. Alternative instruments are psychrometers using two platinum resistance thermometers with appropriate instrumentation, or two liquid-in-glass thermometers of other type, instead of two mercury-in-glass thermometers.

This change of instrumentation should be recorded meticulously and "side by side" comparisons for a period of two or more years in line with WMO recommendations. (WMO, 2015; WMO, 2011a)

4.3.3.1 Description

Two thermometers are mounted vertically in a thermometer screen. One thermometer sensing element (for a liquid-in-glass thermometer this is the bulb) is fitted with a cotton or muslin wick sleeve generally known as the "wet-bulb sleeve", which should fit closely, covering and extending past the sensing part of the thermometer. Where a resistance thermometer is used for the "wet-bulb", it is important that the wick covers and extends beyond the region of the sensing element; this region is not usually obvious by inspection of a thermometer but will be based on knowledge of its internal structure. If a wick and water reservoir are used to keep the wet-bulb sleeve in a moist condition, the reservoir should preferably be placed to the side of the thermometer and with the mouth at the same level as, or slightly lower than, the top of the sensing element. The wick should be kept as straight as possible and its length should be such that water reaches the sensing element with sensibly the wet-bulb temperature and in sufficient (but not excessive) quantity. If no wick is used, the wet bulb should be protected from dirt by enclosing the bulb in a small glass tube between readings.

The performance of a screen psychrometer can be expected to be much worse than that shown in Volume I, Chapter 1, Annex 1.F of this Guide, especially in light winds if the screen is not artificially ventilated.

It is therefore desirable that screen psychrometers be artificially aspirated where possible. Both thermometers should be aspirated at an air speed of about 3 m s^{-1} . The air should be drawn in horizontally across the bulbs, rather than vertically, and exhausted in such a way as to avoid recirculation.

The psychrometric formulae given in 4.3.1.1 apply to screen psychrometers, but the coefficients are quite uncertain, and the following summary indicates varied practices going back many years. If there is artificial ventilation at 3 m s^{-1} or more across the wet bulb, the formulae may be applied, using a psychrometer coefficient of $6.53 \cdot 10^{-4} \text{ K}^{-1}$ for water. However, values from 6.50 to $6.78 \cdot 10^{-4} \text{ K}^{-1}$ have been used for wet bulbs above $0 \text{ }^\circ\text{C}$, and 5.70 to $6.53 \cdot 10^{-4} \text{ K}^{-1}$ for below $0 \text{ }^\circ\text{C}$. For a naturally ventilated screen psychrometer, coefficients in the range from 7.7 to $8.0 \cdot 10^{-4} \text{ K}^{-1}$ above freezing and 6.8 to $7.2 \cdot 10^{-4} \text{ K}^{-1}$ for below freezing have been used when there is some air movement in the screen, which is probably nearly always the case. However, coefficients up to $12 \cdot 10^{-4} \text{ K}^{-1}$ for water and $10.6 \cdot 10^{-4} \text{ K}^{-1}$ for ice have been advocated for when there is no air movement. As for all types of psychrometer, calibration of the instrument, as in

4.3.2.4 above, would be the best way to determine the choice of psychrometer coefficient or function, although for screen psychrometers this is less straightforward than for other psychrometer types.

4.3.3.2 Observation procedure

The procedures described in 4.3.1.5 apply to the screen psychrometer.

In the case of a naturally aspirated wet bulb, provided that the water reservoir has about the same temperature as the air, a stable wet-bulb temperature will be attained approximately 15 minutes after fitting a new sleeve; if the water temperature differs substantially from that of the air, it may be necessary to wait for 30 minutes.

4.3.3.3 Exposure and siting

The exposure and siting of the screen are described in Volume I, Chapter 2.

4.3.3.4 Calibration

Calibration principles for a screen psychrometer are in principle similar to those for an Assmann or other aspirated psychrometer. However, removal of a screen psychrometer to a climatic chamber or other laboratory setting is unlikely to be representative of normal operation, while calibration in-situ will probably not provide a range of temperature and humidity conditions.

The psychrometer coefficient appropriate for a particular configuration of screen, shape of wet bulb and degree of ventilation can be determined by comparison with a suitable working or reference standard, as described for Assmann psychrometers in 4.3.2.4 above. However, a large dataset (ideally in a humidity- and temperature-controlled chamber) would be necessary, and wide scatter in the data might be expected. This evaluation is not commonly performed for this basic type of instrument, and there would be little justification for departing from established national practices.

4.3.3.5 Maintenance

The calibration of the thermometers should be checked regularly. The two may be compared together, with both thermometers measuring the dry-bulb temperature. Checks of thermometers by comparison against a reference thermometer are useful at intervals, for example annually.

The liquid-in-glass columns of the thermometers should be inspected for breaks, which should be closed up or the thermometer should be replaced.

4.3.4 Sling or whirling psychrometers

These instruments are still in use, mainly on board ships.

4.3.4.1 Description

A small portable type of whirling or sling psychrometer consists of two liquid-in-glass thermometers mounted on a sturdy frame, which is provided with a handle and spindle, and located at the furthest end from the thermometer bulbs, by means of which the frame and thermometers may be rotated rapidly about a horizontal axis.

The wet-bulb arrangement varies according to individual design. Some designs shield the thermometer bulbs from direct insolation, and these are to be preferred for meteorological measurements.

The psychrometric formulae in Annex 4.B may be used. However, these hygrometers suffer the same sources of error as other psychrometers, while being difficult to calibrate against a humidity reference. In addition, the need to cease aspiration in order to take a reading is a particular source of error, leading to probable over-readings of wet-bulb temperature. For these reasons, measurements using whirling or sling psychrometers tend to have significant uncertainty.

4.3.4.2 Observation procedure

The following guidelines should be applied:

- (a) All instructions with regard to the handling of Assmann aspirated psychrometers apply also to sling psychrometers;
- (b) Sling psychrometers lacking radiation shields for the thermometer bulbs should be shielded from direct insolation in some other way;
- (c) Thermometers should be read at once after aspiration ceases because the wet-bulb temperature will begin to rise immediately, and the thermometers are likely to be subject to insolation effects.

4.4 THE CHILLED-MIRROR DEWPOINT HYGROMETER

4.4.1 General considerations

4.4.1.1 Theory

The dewpoint (or frost-point) hygrometer is used to measure the temperature at which moist air, when cooled, reaches saturation and a deposit of dew (or ice) can be detected on a solid surface, which usually is a mirror. The deposit is normally detected optically. The principle of the measurement is described in 4.1.4.1.3 and below.

The thermodynamic dew point is defined for a plane surface of pure water. In practice, water droplets have curved surfaces, over which the saturation vapour pressure is higher than for the plane surface (known as the Kelvin effect). Hydrophobic contaminants will exaggerate the effect, while soluble ones will have the opposite effect and lower the saturation vapour pressure (the Raoult effect). The Kelvin and Raoult effects (which, respectively, raise and lower the apparent dewpoint) are minimized if the critical droplet size adopted is large rather than small; this reduces the curvature effect directly and reduces the Raoult effect by lowering the concentration of a soluble contaminant. Contaminants are minimised by suitable care in operation (see 4.4.3.), and general influences of Raoult and Kelvin effects are taken into account by calibration (see 4.4.5.).

4.4.1.2 Principles

When moist air at temperature T , pressure p and mixing ratio r_w (or r_i) is cooled, it eventually reaches its saturation point with respect to a free water surface (or to a free ice surface) and a deposit of dew (or frost) can be formed on a non-hygroscopic surface. The temperature of this saturation point is called the dewpoint temperature T_d (or the frost-point temperature T_f). The corresponding saturation vapour pressure with respect to water e'_w (or ice e'_i) is a function of T_d (or T_f), as shown in the following equations:

$$e'_w(p, T_d) = f(p) \cdot e_w(T_d) = \frac{r \cdot p}{0.62198 + r} \quad (4.3)$$

$$e'_i(p, T_f) = f(p) \cdot e_i(T_f) = \frac{r \cdot p}{0.62198 + r} \quad (4.4)$$

The hygrometer measures T_d or T_f . Despite the great dynamic range of moisture in the troposphere, this instrument is capable of detecting both very high and very low concentrations of water vapour.

It is important to determine whether the deposit is supercooled liquid or ice when the surface temperature is at or below freezing point. For a given condensation temperature, the vapour pressure over supercooled water is higher than over ice.

The chilled-mirror hygrometer is used occasionally for meteorological measurements and as a reference instrument both in the field and in the laboratory.

4.4.2 Description

4.4.2.1 Sensor assembly

The most widely used systems employ a small polished-metal reflecting surface, cooled electrically using a Peltier-effect device. The sensor consists of a thin metallic mirror of small (approximately 5 mm to 10 mm) diameter that is thermally regulated using a cooling assembly (and usually a heater), with a temperature sensor (usually a miniature platinum resistance thermometer) embedded on the underside of the mirror. The mirror should have a high thermal conductance, optical reflectivity and corrosion resistance combined with a low permeability to water vapour. Materials used include gold, rhodium-plated silver, chromium-plated copper and stainless steel.

The mirror may be equipped with an optical detection assembly part to automatically detect contaminants that may increase or decrease the apparent dew point (see 4.4.2.2), so that they may be removed.

4.4.2.2 Optical detection assembly

An electro-optical system is usually employed to detect the formation of condensate and to provide the input to the servo-control system to regulate the temperature of the mirror. A narrow beam of light is directed at the mirror at an angle of incidence of about 55°. The light source may be incandescent or a light-emitting diode. In simple systems, the intensity of the directly reflected light is detected by a photodetector that regulates the cooling and heating assembly through a servo-control. The specular reflectivity of the surface decreases as the thickness of the deposit increases; cooling should reduce while the deposit is thin, with a reduction in reflectance in the range of 5 % to 40 %. More elaborate systems use an auxiliary photodetector which additionally detects the light scattered by the deposit; the two detectors are capable of very precise control. A second, uncooled, mirror may be used to improve the control system.

Greatest precision is obtained by controlling the mirror to a temperature at which condensate neither accumulates nor dissipates; however, in practice, the servo-system will oscillate around this temperature. The response time of the mirror to heating and cooling is critical in respect of the amplitude of the oscillation, and should be of the order of 1 to 2 s. Airflow rate needs to be reasonably stable, simply avoiding sudden changes for maintaining a stable deposit on the mirror. It is possible to determine the temperature at which condensation occurs with a resolution of 1 mK in some cases, and an overall uncertainty of 0.1 K (at coverage probability of 95 %, coverage factor $k=2$), or more, depending on the calibration uncertainty as well as other factors.

Historical types of dew-point hygrometer with manual control of temperature are largely obsolete.

4.4.2.3 Thermal control assembly

A Peltier-effect thermo-junction device provides a simple reversible heat pump; the polarity of direct current energization determines whether heat is pumped to, or from, the mirror. The device is bonded to, and in good thermal contact with, the underside of the mirror. Commonly, a multistage Peltier device is used, with the greatest cooling requiring the most stages. When measuring relatively dry gases, initial cooling is needed to several degrees below the condensation temperature, in order to form a detectable film of droplets or ice particles.

Thermal control is achieved by using an electrical servo-system that takes as input the signal from the optical detector subsystem. Modern systems operate under microprocessor control.

Integral supplementary cooling is commonly provided in order to control overall temperature at the instrument head, and to extract heat generated by the Peltier element. This can take the form

of forced air cooling, or a closed-cycle refrigerant system. Alternatively, some instrument types use a sterling engine for supplementary temperature control. In older instruments, a low-boiling-point fluid, such as ethanol, is used with external refrigeration to provide supplementary cooling, but this becoming less common. In addition, supplementary heating (and in some regimes a heated sampling tube) is used to protect against unwanted condensation.

4.4.2.4 Temperature display system

The mirror temperature, as measured by the electrical thermometer embedded beneath the mirror surface, is output as the dewpoint of the air sample. Commercial instruments normally include an electrical interface for the mirror thermometer and a digital display, but may also provide digital and analogue electrical outputs for use with data-logging equipment. A chart recorder can be used for continuous monitoring of an analogue output of the mirror thermometer signal, but this is becoming less common. Some hygrometers provide a separate PRT output, distinct from the PRT that is used for temperature control, of the mirror.

4.4.2.5 Instrument format

Commonly, laboratory dewpoint hygrometers are bench-top or rack-mounted instruments used with tubing to sample air from a chosen location. The sample tubing is heated if used in a range where there is a risk of condensation

An alternative format has a remote sensor head containing the Peltier, mirror, optics and temperature sensing systems. In some cases the remote head is designed to measure in free air, without forced ventilation.

4.4.2.6 Auxiliary systems

A microscope may be incorporated to provide a visual method to discriminate between supercooled water droplets and ice crystals for mirror temperatures below 0 °C. Some instruments have a detector mounted on the mirror surface to provide an automatic procedure for this purpose, while others employ a method based on reflectance.

A microprocessor-based system may incorporate algorithms to calculate and display relative humidity. In this case, it is important that the instrument should discriminate correctly between a water and an ice deposit. In addition, the calibration and placement of the external thermometer will be critical for obtaining correct and representative relative humidity values. If other humidity quantities are calculated, such as volume fraction or ratio, the result also depends on pressure, which is either measured, or based on a set value.

Many instruments provide an automatic procedure for minimizing the effects of contamination. This may be a regular heating cycle in which volatile contaminants are evaporated and removed in the air stream. During such a heating cycle, the instrument either will give elevated readings, or will output a fixed recent value until normal readings resume. Systems with a wiper to automatically clean the mirror are also in use. Visual inspection, where possible, can confirm the quality of the water or ice film as an indication of cleanliness.

For meteorological measurements, and in most laboratory applications, a small pump is required to draw the sampled air through the measuring chamber. A regulating device is also required to set the flow at a rate that is consistent with the stable operation of the mirror temperature servo-control system and at an acceptable rate of response to changes in humidity. This can usually be achieved by using a needle valve between the hygrometer outlet and the pump. In some instruments an internal pump is provided. The optimum flow rate is dependent upon the moisture content of the air sample and is normally within the range of 0.25 l min⁻¹ to 1 l min⁻¹.

4.4.3 Observation procedure

The correct operation of a dewpoint hygrometer requires an appropriate volume airflow rate through the measuring chamber, although the exact flowrate is not usually critical. The setting of a needle valve for this purpose, usually located downstream of the measuring chamber, is likely to require adjustment to accommodate diurnal variations in air temperature. Sudden adjustment of

the airflow can momentarily disturb the operation of the hygrometer. Any adjustment should be made with sufficient time in order for a stable operation to be achieved before a reading is taken. The amount of time required will depend upon the control cycle of the individual instrument. The manufacturer's instructions should be consulted to provide appropriate guidance on the airflow rate to be set and on details of the instrument's control cycle.

The condition of the mirror should be checked frequently; the mirror should be cleaned as necessary. The stable operation of the instrument does not necessarily imply that the mirror is clean. It should be washed with distilled water and dried carefully by wiping it with a soft cloth or cotton bud to remove any soluble contaminant. Alternatively, instead of wiping dry, a generous drop of water on the mirror can be pulled away using the cotton bud. It is a sign of a clean mirror if the drop pulls away cleanly. If the mirror is not visually clean and free from tide-marks, then cleaning should be repeated. Care must be taken not to scratch the surface of the mirror, most particularly where the surface has a thin plating to protect the substrate or where an ice/liquid detector is incorporated. However, an isolated surface scratch will not typically prevent the instrument from operating. If an air filter is not in use, cleaning should be performed at least daily. If an air filter is in use, its condition should be inspected at each observation. The observer should take care not to stand next to the air inlet or to allow the outlet to become blocked.

For readings at, or below, 0 °C the observer should determine whether the mirror condensate is supercooled water or ice. If no automatic indication is given, the mirror must be observed. From time to time the operation of any automatic system should be verified.

An uncertainty of ± 0.1 K over a wide dewpoint range (-60 °C to $+50$ °C) is specified for the best instruments. The uncertainty in use will depend on the uncertainty of calibration, and on other factors.

4.4.4 Exposure and siting

The criteria for the siting of the sensor unit are similar to those for any aspirated hygrometer. They tend to be less stringent than for either a psychrometer or a relative humidity sensor. This is because the dew or frost point of an air sample is unaffected by changes to the ambient temperature provided that it remains above the dew point at all times. For this reason, a temperature screen is not required. The sensor should be exposed in an open space and may be mounted on a post, within a protective housing structure, with an air inlet at the required level.

For hygrometers requiring a flow of gas through the instrument, an air-sampling system is required. This is normally a small pump that must draw air from the outlet port of the measuring chamber and eject it away from the inlet duct. In some cases, the pump is integral to the hygrometer. Recirculation of the airflow should be avoided as this represents a poor sampling technique, although under stable operation the water-vapour content at the outlet should be effectively identical to that at the inlet. Recirculation may be avoided by fixing the outlet above the inlet, although this may not be effective under radiative atmospheric conditions when a negative air temperature lapse rate exists.

An air filter should be provided for continuous outdoor operations. It must be capable of allowing an adequate throughflow of air without a large blocking factor, as this may result in a significant drop in air pressure and affect the condensation temperature in the measuring chamber. A sintered metal filter may be used in this application to capture all but the smallest aerosol particles. A metal filter has the advantage that it may be heated easily by an electrical element in order to keep it dry under all conditions. It is more robust than the membrane-type filter and more suited to passing the relatively high airflow rates required by the chilled-mirror method as compared with the sorption method. On the other hand, a metallic filter may be more susceptible to corrosion by atmospheric pollutants than some membrane filters.

Instruments requiring an air sampling system need to pay attention to possible pressure changes during the air sampling. Where a filter or lengthy sample tubing causes a pressure drop, this can lead to an underestimate of dew point. If the air pressure in the sensing volume above the mirror is significantly different from the ambient pressure, this needs to be measured and the change in dewpoint temperature must be properly considered.

4.4.5 Calibration and field inspection

4.4.5.1 Calibration

A dew-point hygrometer should be calibrated in terms of dewpoint temperature, against a dewpoint reference, usually in a laboratory. A calibration can be made directly against a primary dewpoint generator, or by comparison against a traceably calibrated dew-point hygrometer, using as a transfer medium any stable source of humid gas sampled by both of them simultaneously. To apply the calibration, in some cases the dew-point hygrometer readings can be adjusted (for example in software). In other cases, an adjustment to electronics can partly or fully implement the calibration. Alternatively, corrections are applied arithmetically, particularly in laboratory usage. To whatever extent calibration corrections or functions are applied, any residual error needs to be taken into account as a component of uncertainty in using the instrument.

If any associated air temperature sensor is used, it too needs to be calibrated. General guidance on calibration of thermometers is given in Volume I, Chapter 2. For use in air, either the thermometer is calibrated in air or, if calibrated in a liquid bath, suitable additional uncertainty is allowed for applying this calibration to measurements in air. This would include components due to the different self-heating in air, the different thermal exchange with air, and radiative effects.

If a hygrometer derives relative humidity from measured dew point and temperature, calibration of the relative humidity output is also relevant. Although, in principle, this output can be calibrated directly in terms of relative humidity, this will normally be temperature-dependent and will therefore require an extensive matrix of calibration values. A better approach is to ensure that the relative humidity is evaluated from dew point and temperature values whose calibration corrections have already been applied - whether this is done wholly arithmetically, or in corrections applied within the instrument.

4.4.5.2 Field inspection

Regular comparisons should be made against a reference instrument, such as an Assmann psychrometer or another chilled-mirror hygrometer, or even a relative humidity instrument, as the operation of a field chilled mirror is subject to a number of influences which may degrade its performance. An instrument operating continuously in the field should be the subject of weekly check measurements. As the opportunity arises, its operation at both dew and frost points should be verified. When the mirror temperature is below 0 °C the deposit should be inspected visually, if this is possible, to determine whether it is of supercooled water or ice.

A possible check is to compare the mirror temperature measurement with the air temperature while the thermal control system of the hygrometer is inactive. The check is best done with the mirror as openly exposed as possible to ambient air, by removing any head cover. Checking is best performed under stable, non-condensing conditions. In bright sunshine, the sensor and duct should be shaded and allowed to come to equilibrium. For the check to be meaningful, it is essential that the mirror and its housing reach ambient temperature. This can take considerable time after switching off normal operation.

An independent field check of the mirror thermometer interface can be performed by simulating the thermometer signal. In the case of a platinum resistance thermometer, a standard platinum resistance simulation box, or a decade resistance box and a set of appropriate tables, may be used. A special simulator interface for the hygrometer control unit may also be required.

HYGROMETERS USING ABSORPTION OF ELECTROMAGNETIC RADIATION

The water molecule absorbs electromagnetic radiation (EMR) in a range of wavebands and discrete wavelengths; this property can be exploited to obtain a measure of the molecular concentration of water vapour in a gas. The most useful regions of the electromagnetic spectrum, for this purpose, lie in the ultraviolet and infrared regions. Therefore, the techniques are often classified as optical hygrometry or, more correctly, EMR absorption hygrometry.

The method makes use of measurements of the attenuation of radiation in a waveband specific to water-vapour absorption, along the path between a source of the radiation and a detector. There are two principal methods for determining the degree of attenuation of the radiation as follows:

- (a) Transmission of radiation at two wavelengths, one of which is strongly absorbed by water vapour and the other being either not absorbed or only very weakly absorbed. If a single source is used to generate the radiation at both wavelengths, the ratio of their emitted intensities may be accurately known, so that the attenuation at the absorbed wavelength can be determined by measuring the ratio of their intensities at the receiver. The most widely used source for this technique is a tungsten lamp, filtered to isolate a pair of wavelengths in the infrared region. The measuring path is normally greater than 1 m;
- (b) Transmission of narrowband radiation at a fixed intensity to a calibrated detector. The most commonly used source of radiation is hydrogen gas; the emission spectrum of hydrogen includes the Lyman-Alpha line at 121.6 nm, which coincides with a water-vapour absorption band in the ultraviolet region where there is little absorption by other common atmospheric gases. The measuring path is typically a few centimetres in length.

Both types of EMR absorption hygrometers require frequent calibration and are more suitable for measuring changes in vapour concentration than absolute levels. The most widespread application of the EMR absorption hygrometer is to monitor very high-frequency variations in humidity since the method does not require the detector to achieve vapour-pressure equilibrium with the sample. The time constant of an optical hygrometer is typically just a few milliseconds. The use of optical hygrometers remains restricted to research activities.

4.6 THE HAIR HYGROGRAPH

4.6.1 General considerations

The change in the length of hair has been found to be a function primarily of the change in relative humidity with respect to liquid water (both above and below an air temperature of 0 °C), with an increase of about 2 % to 2.5 % when the humidity changes from 0 %rh to 100 %rh. By rolling the hairs to produce an elliptical cross-section and by dissolving out the fatty substances with alcohol, the ratio of the surface area to the enclosed volume increases and yields a decreased lag coefficient which is particularly relevant for use at low air temperatures. This procedure also results in a more linear response function, although the tensile strength is reduced. For accurate measurements, a single hair element is to be preferred, but a bundle of hairs is commonly used to provide a degree of ruggedness. Chemical treatment with barium (BaS) or sodium sulphide (Na₂S) yields further linearity of response.

The hair hygrometer is considered to be a satisfactory though not very precise instrument for use in situations or during periods where extreme and very low humidities are seldom or never found. The mechanism of the instrument should be as simple as possible, even if this makes it necessary to have a non-linear scale. This is especially important in industrial regions, since air pollutants may act on the surface of the moving parts of the mechanism and increase friction between them.

The rate of response of the hair hygrometer is very dependent on air temperature. At -10 °C the lag of the instrument is approximately three times greater than the lag at 10 °C. For air temperatures between 0 °C and 30 °C and relative humidities between 20 %rh and 80 %rh, a good hygrometer should indicate 90 % of a sudden change in humidity within about 3 min.

A good hygrograph in perfect condition should be capable of recording relative humidity at moderate temperatures with an uncertainty of ± 3 %rh. At low temperatures, the uncertainty will be greater.

Using hair pre-treated by rolling (as described above) is a requirement if useful information is to be obtained at low temperatures.

4.6.2 Description

The detailed mechanism of hair hygrographs varies according to the manufacturer. Some instruments incorporate a transducer to provide an electrical signal, and these may also provide a linearizing function so that the overall response of the instrument is linear with respect to changes in relative humidity.

The hair hygrograph uses a bundle of hairs held under slight tension by a small spring and connected to a pen arm in such a way as to magnify a change in the length of the bundle. A pen at the end of the pen arm is in contact with a paper chart fitted around a metal cylinder and registers the angular displacement of the arm. The cylinder rotates about its axis at a constant rate determined by a mechanical clock movement. The rate of rotation is usually one revolution either per week or per day. The chart has a scaled time axis that extends round the circumference of the cylinder and a scaled humidity axis parallel to the axis of the cylinder. The cylinder normally stands vertically.

The mechanism connecting the pen arm to the hair bundle may incorporate specially designed cams that translate the non-linear extension of the hair in response to humidity changes into a linear angular displacement of the arm.

The hair used in hair hygrographs may be of synthetic fibre. Where human hair is used, it is normally first treated as described in 4.6.1 to improve both the linearity of its response and the response lag, although this does result in lower tensile strength.

The pen arm and clock assembly are normally housed in a box with glass panels which allow the registered humidity to be observed without disturbing the instrument, and with one end open to allow the hair element to be exposed in free space outside the limits of the box. The sides of the box are separate from the solid base, but the end opposite the hair element is attached to it by a hinge. This arrangement allows free access to the clock cylinder and hair element. The element may be protected by an open mesh cage.

4.6.3 Observation procedure

The hair hygrograph should always be tapped lightly before being read in order to free any tension in the mechanical system. The hygrograph should, as far as possible, not be touched between changes of the charts except in order to make time marks.

The hair hygrograph can normally be read to the nearest 1 %rh. Attention is drawn to the fact that the instrument measures relative humidity with respect to saturation over liquid water even at air temperatures below 0 °C.

The humidity of the air may change very rapidly and, therefore, accurate setting of time marks on a hygrograph is very important. In making the marks, the pen arm should be moved only in the direction of decreasing humidity on the chart. This is done so that the hairs are slackened by the displacement and, to bring the pen back to its correct position, the restoring force is applied by the tensioning spring. However, the effect of hysteresis may be evidenced in the failure of the pen to return to its original position.

4.6.4 Exposure and siting

The hygrograph should be exposed in a thermometer screen. Ammonia is very destructive to natural hair. Exposure in the immediate vicinity of stables and industrial plants using ammonia should be avoided.

4.6.5 Sources of error

4.6.5.1 Changes in zero offset

For various reasons which are poorly understood, the hygrograph is liable to change its zero. The most likely cause is that excess tension has been induced in the hairs. For instance, the hairs may be stretched if time marks are made in the direction of increasing humidity on the chart or if the hygrograph mechanism sticks during decreasing humidity. The zero may also change if the hygrograph is kept in very dry air for a long time, but the change may be reversed by placing the instrument in a saturated atmosphere for a sufficient length of time.

4.6.5.2 Errors due to contamination of the hair

Most kinds of dust will cause appreciable errors in observations (perhaps as much as 15 %rh). In most cases this may be eliminated, or at least reduced, by cleaning and washing the hairs. However, the harmful substances found in dust may also be destructive to hair (see 4.6.4).

4.6.5.3 Hysteresis

Hysteresis is exhibited both in the response of the hair element and in the recording mechanism of the hair hygrometer. Hysteresis in the recording mechanism is reduced through the use of a hair bundle, which allows a greater loading force to overcome friction. It should be remembered that the displacement magnification of the pen arm lever applies also to the frictional force between the pen and paper, and to overcome this force it requires a proportionately higher tension in the hair. The correct setting of the tensioning spring is also required to minimize hysteresis, as is the correct operation of all parts of the transducing linkage. The main fulcrum and any linearizing mechanism in the linkage introduce much of the total friction.

Hysteresis in the hair element is normally a short-term effect related to the absorption-desorption processes and is not a large source of error once vapour pressure equilibrium is established (see 4.6.5.1 in respect of prolonged exposure at low humidity).

4.6.6 Calibration and field inspection

The readings of a hygrograph should be checked as frequently as is practical. In the case where wet- and dry-bulb thermometers are housed in the same thermometer screen, these may be used to provide a comparison whenever suitable steady conditions prevail, but otherwise field comparisons have limited value due to the difference in response rate of the instruments.

Accurate calibration can only be obtained through the use of an environmental chamber and by comparison with reference instruments.

The 100 %rh point may be checked, preferably indoors with a steady air temperature, by surrounding the instrument with a saturated cloth (though the correct reading will not be obtained if a significant mass of liquid water droplets forms on the hairs).

The ambient indoor humidity may provide a low relative humidity checkpoint for comparison against a reference aspirated psychrometer. A series of readings should be obtained.

Long-term stability and bias may be appraised by presenting comparisons with a reference aspirated psychrometer in terms of a correlation function.

4.6.7 Maintenance

Observers should be encouraged to keep the hair hygrograph clean.

The hair should be washed at frequent intervals using distilled water on a soft brush to remove accumulated dust or soluble contaminants. At no time should the hair be touched by fingers. The bearings of the mechanism should be kept clean and a small amount of clock oil should be applied occasionally. The bearing surfaces of any linearizing mechanism will contribute largely to the total

friction in the linkage, which may be minimized by polishing the surfaces with graphite. This procedure may be carried out by using a piece of blotting paper rubbed with a lead pencil.

With proper care, the hairs may last for several years in a temperate climate and when not subject to severe atmospheric pollution. Recalibration and adjustment will be required when hairs are replaced.

4.7 TRACEABILITY ASSURANCE AND CALIBRATION

4.7.1 Principles involved in the calibration of hygrometers

Precision in the calibration of humidity measuring instruments entails special problems, to a great extent owing to the relatively small quantity of water vapour which can exist in an air sample at normal temperatures, but also due to the general difficulty of isolating and containing gases and, more particularly, vapour. An ordered hierarchy of international traceability in humidity standards is only now emerging.

Table 4.2 shows a summary of humidity standard instruments and their performances.

ELEMENT 2: Floating object (Automatic)

Table 4.2. Standard instruments for the measurement of humidity

TABLE: Table horizontal lines

<i>Standard instrument</i>	<i>Dewpoint temperature</i>		<i>Relative humidity (%rh)</i>	
	<i>Range (°C)</i>	<i>Uncertainty (K)</i>	<i>Range</i>	<i>Uncertainty</i>
<i>Primary standard</i>				
Requirement	-60 to -15 -15 to +40	0.3 0.1	5 to 100 5 to 100	0.2 0.2
Gravimetric hygrometer	-60 to -35 -35 to +35 +35 to +60	0.25 0.03 0.25		
Standard two-temperature humidity generator	-75 to -15 -15 to +30 +30 to +80	0.25 0.1 0.2		
Standard two-pressure humidity generator	-75 to +30	0.2		
<i>Secondary standard</i>				
Requirement	-80 to -15 -15 to +40	0.75 0.25	5 to 100	0.5
Chilled-mirror hygrometer	-60 to +40	0.15		
Reference psychrometer			5 to 100	0.6
<i>Reference standard</i>				

Requirement	-80 to -15 -15 to 40	1.0 0.3	5 to 100	1.5
Reference psychrometer			5 to 100	0.6
Chilled-mirror hygrometer	-60 to 40	0.3		
<i>Working standard</i>				
Requirement	-15 to 40	0.5	5 to 100	2
Assmann psychrometer	-10 to 25		40 to 90	1
Chilled-mirror hygrometer	-10 to 30	0.5		
Electrical capacitive hygrometer (<i>for regularly calibrated and carefully maintained high performance instruments</i>)	-20 to 40		5 to 95	2
	15 to 30		5 to 95	1

END ELEMENT

4.7.2 Primary standards

4.7.2.1 Gravimetric hygrometry

This instrument type is only rarely used in a small number of national metrology institutes, but the description below is given for information.

The gravimetric method yields an absolute measure of the water-vapour content of an air sample in terms of the proposition of water vapour to air – either as a ratio of the two components (mixing ratio) or as a fraction of the total. This is expressed in terms of masses of water and air, or sometimes as volume fraction (or rarely as amount fraction, in moles, if the composition of air can be known). This is obtained by first removing the water vapour from the sample using a known mass of a drying agent, such as anhydrous phosphorous pentoxide (P_2O_5) or magnesium perchlorate ($Mg(ClO_4)_2$). The mass of the water vapour is determined by weighing the drying agent before and after absorbing the vapour. The mass of the dry sample is determined either by weighing (after liquefaction to render the volume of the sample manageable) or by measuring its volume (and having knowledge of its density).

The complexity of the apparatus required to accurately carry out the procedure described limits the application of this method to the laboratory environment. In addition, a substantial volume sample of air is required for accurate measurements to be taken and a practical apparatus requires a steady flow of the humid gas for a number of hours, depending upon the humidity, in order to remove a sufficient mass of water vapour for an accurate weighing measurement. As a consequence, the method is restricted to providing an absolute calibration reference standard. Such an apparatus is found mostly in national metrological institutes (NMIs).

4.7.2.2 Dynamic two-pressure standard humidity generator

This laboratory apparatus serves to provide a source of humid gas whose relative humidity is determined on an absolute basis. A stream of the carrier gas is passed through a saturating chamber at pressure P_1 and allowed to expand isothermally in a second chamber at a lower pressure P_2 . Both chambers are maintained at the same temperature in an oil bath. The relative humidity of the water vapour-gas mixture is straightforwardly related to the total pressures in each of the two chambers through Dalton's law of partial pressures. The partial pressure e' of the

vapour in the low-pressure chamber will have the same relation to the saturation vapour pressure e'_w as the total pressure in the high-pressure saturator has to the total pressure in the low-pressure chamber. Thus, the relative humidity U_w is given by:

$$U_w = 100 \cdot e'/e'_w = 100 \cdot P_1/P_2 \quad (4.5)$$

The relation also holds for the solid phase if the gas is saturated with respect to ice at pressure P_1 :

$$U_i = 100 \cdot e'/e'_i = 100 \cdot P_1/P_2 \quad (4.6)$$

4.7.2.3 *Dynamic two-temperature standard humidity generator*

This laboratory apparatus provides a stream of humid gas at temperature T_1 having a dew- or frost-point temperature T_2 . Two temperature-controlled baths, each equipped with heat exchangers and one with a saturator containing either water or ice, are used first to saturate the air-stream at temperature T_1 and then to heat it isobarically to temperature T_2 . In practical designs, the air-stream is continuously circulated to ensure saturation. Test instruments draw off air at temperature T_2 and a flow rate that is small in proportion to the main circulation.

4.7.3 **Secondary standards**

A secondary standard instrument should be carefully maintained and removed from the calibration laboratory only for calibration with a primary standard or for intercomparison with other secondary standards. Secondary standards may be used as transfer standards from the primary standards.

A chilled-mirror hygrometer may be used as a secondary standard instrument under controlled conditions of air temperature, humidity and pressure. For this purpose, it should be calibrated from a recognized accredited laboratory, giving uncertainty limits throughout the operational range of the instrument. This calibration must be directly traceable to a primary standard and should be renewed at an appropriate interval (usually once every 12 to 24 months).

General considerations for chilled-mirror hygrometers are discussed in 4.4. This method presents a fundamental technique for determining atmospheric humidity, and any change of the air pressure resulting from the sampling technique must be taken into account by using the equations given in 4.4.1.2.

High-performance capacitive hygrometers can also be used as secondary standards. They must be traceable and regularly calibrated against a primary standard in a laboratory, typically every 12 months.

4.7.4 **Working standards (and field reference instruments)**

A chilled-mirror hygrometer or an Assmann psychrometer may be used as a working standard for comparisons under ambient conditions in the field or the laboratory. For this purpose, it is necessary to have performed comparisons at least at the reference standard level. The comparisons should be performed at least once every 12 months under stable room conditions. The working standard will require a suitable aspiration device to sample the air.

High-performance capacitive hygrometers can also be used as working standards or field reference instruments. They must be traceable and regularly calibrated against a traceable standard in a laboratory, typically every 12 months. For additional caution, they may be checked quarterly or monthly against other standards.

4.7.5 **Salt solutions**

A salt solution creates characteristic values of the relative humidity in the air above it. The values of relative humidity are dependent on the chemical structure of the salt, the salt concentration and the temperature. Two types of salt solutions are available:

- (a) Unsaturated salt solution, which comes in the form of ampoules of the solution, generates an atmosphere with a certain relative humidity. These ampoules are generally used to soak a pad in a housing designed for exposing a sensor to the humidity produced.
- (b) Saturated salt solution maintains a stable concentration of relative humidity if both phases of the salt exist: if the solution is saturated with salt and some salt remains in the solid phase. In this case, the vapour pressure depends only on temperature.

Vessels containing saturated solutions of appropriate salts may be used to calibrate relative humidity measuring instruments. Commonly used salts and their saturation relative humidities at 25 °C are as follows:

Potassium sulfate (K_2SO_4) :	97.0 %rh
Barium chloride ($BaCl_2$):	90.3 %rh
Sodium chloride ($NaCl$):	75.3 %rh
Magnesium nitrate ($Mg(NO_3)_2$):	52.9 %rh
Magnesium chloride ($MgCl$) :	33.0 %rh
Calcium chloride ($CaCl_2$):	29.0 %rh
Lithium chloride ($LiCl$):	11.1 %rh

Potassium Sulfate and Lithium chloride are convenient saturated salt solutions and provide easy and extended range of relative humidity environments at 11 %rh and 97 %rh.

It is important that the surface area of the solution is large compared to that of the sensor element and the enclosed volume of air so that equilibrium may be achieved quickly; an airtight access port is required for the test sensor. The temperature of the vessel should be measured and maintained at a constant level as the saturation humidity for most salts has a significant temperature coefficient. The homogeneity of the relative humidity above the solutions is improved by mixing the air with a fan in the airtight volume.

Care should be taken when using saturated salt solutions. The degree of toxicity and corrosivity of salt solutions should be known to the personnel dealing with them. The salts listed above may all be used quite safely, but it is nevertheless important to avoid contact with the skin, and to avoid ingestion and splashing into the eyes. The salts should always be kept in secure and clearly labelled containers which detail any hazards involved. Care should be taken when dissolving calcium chloride crystals in water, as much heat is evolved. Chemical hazards are described in 4.8.3 in greater detail.

Saturated salt solutions provide a practical method for adjusting a certain type of hygrometer (capacitive). But for calibration purposes, a traceable relative humidity reference instrument should also be used in the air tight volume above the saturated salt solutions.

4.7.6 Calibration methods

4.7.6.1 General comments

Humidity calibrations are normally carried out by comparing the instrument against a calibrated humidity reference, in a suitable humidity environment.

Environments for humidity calibration are most commonly provided using a humidity generator or a humidity-controlled (and temperature-controlled) chamber.

A humidity generator, a precision chilled mirror hygrometer, a carefully designed psychrometer or a high-performance capacitive hygrometer is used as a standard in NMHS laboratory.

4.7.6.2 Laboratory calibration

Laboratory calibration is essential for maintaining accuracy in the following ways:

- (a) Calibration method

The method for calibrating an hygrometer uses as a standard, either a humidity generator or a hygrometer.

(i) Using a humidity generator as a standard

The hygrometer to be calibrated is placed in the chamber of the humidity generator, or alternatively, the moist air generated by the humidity generator is led to the hygrometer to be calibrated. The humidity value indicated by the humidity generator is then compared with the indication value of the hygrometer to be calibrated.

(ii) Using a hygrometer as a standard

The humidity value indicated by the hygrometer to be calibrated is compared with the standard hygrometer, while both hygrometers are placed in a chamber of humidity generator, or alternatively while the moist air generated by the humidity generator is led to both hygrometers.

(b) Humidity generation method

The main methods of humidity generation are as follows:

- (i) Two-pressure generator
- (ii) Two-temperature generator
- (iii) Two-pressure and two-temperature generator
- (iv) Mixed-flow generator
- (v) Salt solution
- (vi) Humidity chamber

- (c) Reference and standard instruments: Laboratory calibration of reference and standard instruments requires a precision humidity generator and a suitable transfer standard hygrometer. Two-pressure and two-temperature humidity generators can deliver a suitably controlled flow of air at a predetermined temperature and dew point. The calibration should be performed at least every 12 months and over the full range of the reference application for the instrument. The calibration of the mirror thermometer and the temperature display system could be performed independently at least once every 12 months.
- (d) Field and working standard instruments: Laboratory calibration of field and working standard instruments should be carried out on the same regular basis as for other operational thermometers. For this purpose, the chilled-mirror sensor device may be considered separately from the control unit. The mirror thermometer should be calibrated independently and the control unit could be calibrated on the same regular basis as other items of precision electronic equipment. The calibration of a field instrument in a humidity generator is not strictly necessary if the components have been calibrated separately, as described previously.

The correct operation of an instrument may be verified under stable room conditions by comparison with a reference instrument, such as a standard chilled-mirror hygrometer or an Assmann psychrometer. If the field instrument incorporates an ice detector, the correct operation of this system should be verified.

4.7.6.3 Field calibration

Regular calibration is required for all humidity instruments in the field. Depending on instruments, calibration is done in the field only, in the laboratory only, or alternatively.

For psychrometers and dewpoint hygrometers that use a temperature detector, calibration can be checked whenever a regular maintenance routine is performed. Comparison with a working standard, such as an Assmann psychrometer, should be performed very regularly.

The use of a standard type of aspirated psychrometer, such as the Assmann, as a working standard has the advantage that its integrity can be verified by comparing the dry- and wet-bulb thermometers, and that adequate aspiration may be expected from a healthy sounding fan. The reference instrument should itself be calibrated at an interval appropriate to its type.

A practical field inspection is most frequently achieved using well-designed aspirated psychrometers and dewpoint measuring instruments or capacitive hygrometers as working

standards. These specific types of standards must be traceable to the higher levels of standards by careful calibrations. Any instrument used as a standard must be individually calibrated for all variables involved in calculating humidity (air temperature, wet-bulb temperature, dewpoint temperature, and so forth). Other factors affecting performance, such as airflow, must also be checked.

Saturated salt solutions can be applied with humidity measuring instruments that require only a small-volume sample. A very stable ambient temperature is required and it is difficult to be confident about their use in the field. This limitation can be overcome by careful comparison with a working standard above the saturated salt solutions. This method can also be applied in the laboratory for humidity measuring instruments used in the field.

When using salt solutions for control purposes, it should be borne in mind that the nominal humidity value given for the salt solution itself is not traceable to any primary standard.

Another option is to generate some points of specific humidity using a portable humidity generator at a field and calibrate with a working standard hygrometer.

4.8 TIME CONSTANTS, PROTECTIVE FILTERS AND SAFETY

4.8.1 Time constants of humidity sensors

The specification of the time constant for a humidity sensor implies that the response of the sensor to a step change in humidity is consistent with a known function. In general usage, the term refers to the time taken for the sensor to indicate 63.2 % ($1/e$) of a step change in the measurand (in this case humidity), and assumes that the sensor has a first-order response to changes in the measurand (namely, the rate of change of the measurement is proportional to the difference between the measurement and the measurand). It is then possible to predict that 99.3 % of the change will take place after a period of five time constants in duration.

Table 4.3 gives $1/e$ time-constant values typical for various types of humidity sensor.

ELEMENT 3: Floating object (Top)

Table 4.3. Time constants for humidity sensors

TABLE: Table horizontal lines

85 % relative humidity	1/e time constant (s)		
	20 °C	0 °C	-20 °C
Sensor type			
Ordinary human hair	32	75	440
Rolled hair	10	10	12
Electrical capacitance	1-10	1-10	1-10
Electrical resistance	1-10	—	—
Assmann psychrometer			
Condensation hygrometers }	30-50	30-50	30-50
Electrolytic hygrometers			
Optical hygrometer	< 0.01	< 0.01	< 0.01

Note: The first-order relation does not hold particularly well for sorption sensors since the forcing agent for vapour equilibrium, the local gradient of vapour pressure, is dependent upon the local migration of water vapour molecules

within the body of a solid humidity element. In general, a first-order response will be most closely exhibited by those sensors having a thin active element.

END ELEMENT

4.8.2 Protective filters

A protective filter is commonly used to protect a humidity sensor from contaminants that may adversely affect its performance. Where a sensor is not artificially aspirated, the use of a filter tends to slow the response rate of the sensor by preventing the bulk movement of air and by relying upon molecular diffusion through the filter material. Although the diffusion of water vapour through some materials, such as some cellulose products, is theoretically more rapid than for still air, porous hydrophobic membranes achieve better diffusion rates in practice. The pore size should be sufficiently small to trap harmful aerosol particles (in a maritime environment sea-salt particles may be present in significant quantity down to a diameter of $0.1 \mu\text{m}$) and the porosity should be sufficient to allow an adequate diffusion rate.

The size of the filter as well as its porosity affects the overall diffusion rate. Diffusion is enhanced by aspiration, but it must be remembered that this technique relies upon maintaining low air pressure on the sensing side of the filter, and that this can have a significant effect on the measurement.

Non-aspirated sensors should, in general, be protected using a hydrophobic, inert material. High-porosity polymer membranes made from an expanded form of polytetrafluoroethylene have been used successfully for this purpose in a variety of situations and are fairly robust.

Sintered metal filters may be used, but they should be heated to avoid problems with condensation within the material. This is not normally appropriate for a relative humidity sensor, but is quite acceptable for a dewpoint sensor. Sintered metal filters are robust and well suited for aspirated applications, which allow the use of a filter having a large surface area and, consequently, an acceptably small pressure differential.

Where diffusion is not enhanced by artificial aspiration, the relation of the surface area of the filter to the volume of the air being sampled by the sensor must be considered. In the case of a typical sorption sensor composed of a flat substrate, a flat membrane positioned close to the sensor surface will provide the optimum configuration. In the case of a cylindrical sensing surface, a cylindrical filter is appropriate.

4.8.3 Safety

Chemical agents are widely used in the measurement of humidity. The properties of such agents should always be made known to the personnel handling them. All chemicals should be kept in secure and clearly labelled containers and stored in an appropriate environment. Instructions concerning the use of toxic materials may be prescribed by local authorities.

Safety Data Sheet (SDS), also called Material Safety Data Sheet (MSDS) should be carefully read and understood before handling chemicals. This compulsory document provided by the manufacturer for each chemicals or salt details all relevant information on the composition, properties, potential danger, safety measures, handling and storage of the said chemicals.

Saturated salt solutions are widely used in the measurement of humidity. The notes that follow give some guidance for the safe use of some commonly used salts:

- (a) Barium chloride (BaCl_2): Colourless crystals; very soluble in water; stable, but may emit toxic fumes in a fire; no hazardous reaction with water, acids, bases, oxidizers or with combustible materials; ingestion causes nausea, vomiting, stomach pains and diarrhoea; harmful if inhaled as dust and if it comes into contact with the skin; irritating to eyes; treat with copious amounts of water and obtain medical attention if ingested;

- (b) Calcium chloride (CaCl_2): Colourless crystals; deliquescent; very soluble in water, dissolves with increase in heat; will initiate exothermic polymerization of methyl vinyl ether; can react with zinc to liberate hydrogen; no hazardous reactions with acids, bases, oxidizers or combustibles; irritating to the skin, eyes and respiratory system; ingestion causes gastric irritation; ingestion of large amounts can lead to hypercalcaemia, dehydration and renal damage; treat with copious amounts of water and obtain medical attention;
- (c) Lithium chloride (LiCl): Colourless crystals; stable if kept dry; very soluble in water; may emit toxic fumes in a fire; ingestion may affect ionic balance of blood leading to anorexia, diarrhoea, vomiting, dizziness and central nervous system disturbances; kidney damage may result if sodium intake is low (provide plenty of drinking water and obtain medical attention); no hazardous reactions with water, acids, bases, oxidizers or combustibles;
- (d) Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$): Colourless crystals; deliquescent; very soluble in water; may ignite combustible material; can react vigorously with deoxidizers, can decompose spontaneously in dimethylformamide; may emit toxic fumes in a fire (fight the fire with a water spray); ingestion of large quantities can have fatal effects (provide plenty of drinking water and obtain medical attention); may irritate the skin and eyes (wash with water);
- (e) Potassium nitrate (KNO_3): White crystals or crystalline powder; very soluble in water; stable but may emit toxic fumes in a fire (fight the fire with a water spray); ingestion of large quantities causes vomiting, but it is rapidly excreted in urine (provide plenty of drinking water); may irritate eyes (wash with water); no hazardous reaction with water, acids, bases, oxidizers or combustibles;
- (f) Sodium chloride (NaCl): Colourless crystals or white powder; very soluble in water; stable; no hazardous reaction with water, acids, bases, oxidizers or combustibles; ingestion of large amounts may cause diarrhoea, nausea, vomiting, deep and rapid breathing and convulsions (in severe cases obtain medical attention).

Advice concerning the safe use of mercury is given in Volume I, Chapter 3, Annex A, A.2.8.

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ANNEX 4.A. DEFINITIONS AND SPECIFICATIONS OF WATER VAPOUR IN THE ATMOSPHERE

(1) **The mixing ratio r** of moist air is the ratio of the mass m_v of water vapour to the mass m_a of dry air with which the water vapour is associated:

$$r = \frac{m_v}{m_a} \quad (4.A.1)$$

(2) **The specific humidity, mass concentration or moisture content q** of moist air is the ratio of the mass m_v of water vapour to the mass $m_v + m_a$ of moist air in which the mass of water vapour m_v is contained:

$$q = \frac{m_v}{m_v + m_a} \quad (4.A.2)$$

(3) **Vapour concentration (density of water vapour in a mixture) or absolute humidity:** For a mixture of water vapour and dry air the vapour concentration ρ_v is defined as the ratio of the mass of vapour m_v to the volume V occupied by the mixture:

$$\rho_v = \frac{m_v}{V} \quad (4.A.3)$$

(4) **Mole fraction of the water vapour of a sample of moist air:** The mole fraction x_v of the water vapour of a sample of moist air, composed of a mass m_a of dry air and a mass m_v of water vapour, is defined by the ratio of the number of moles of water vapour ($n_v = m_v/M_v$) to the total number of moles of the sample $n_v + n_a$, where n_a indicates the number of moles of dry air ($n_a = m_a/M_a$) of the sample concerned. This gives:

$$x_v = \frac{n_v}{n_a + n_v} \quad (4.A.4)$$

or:

$$x_v = \frac{r}{0.62198 + r} \quad (4.A.5)$$

where r is merely the mixing ratio ($r = m_v/m_a$) of the water vapour of the sample of moist air.

(5) **The vapour pressure e'** of water vapour in moist air at total pressure p and with mixing ratio r is defined by:

$$e' = \frac{r}{0.62198 + r} p = x_v \cdot p \quad (4.A.6)$$

(6) **Saturation:** Moist air at a given temperature and pressure is said to be saturated if its mixing ratio is such that the moist air can coexist in neutral equilibrium with an associated

condensed phase (liquid or solid) at the same temperature and pressure, the surface of separation being plane.

(7) **Saturation mixing ratio:** The symbol r_w denotes the saturation mixing ratio of moist air with respect to a plane surface of the associated liquid phase. The symbol r_i denotes the saturation mixing ratio of moist air with respect to a plane surface of the associated solid phase. The associated liquid and solid phases referred to consist of almost pure water and almost pure ice, respectively, there being some dissolved air in each.

(8) **Saturation vapour pressure in the pure phase:** The saturation vapour pressure e_w of pure aqueous vapour with respect to water, is the pressure of the vapour when in a state of neutral equilibrium with a plane surface of pure water at the same temperature and pressure; similarly for e_i with respect to ice; e_w and e_i are temperature-dependent functions only, namely:

$$e_w = e_w(T) \quad (4.A.7)$$

$$e_i = e_i(T) \quad (4.A.8)$$

(9) **Mole fraction of water vapour in moist air saturated with respect to water:** The mole fraction of water vapour in moist air saturated with respect to water, at pressure p and temperature T , is the mole fraction x_{vw} of the water vapour of a sample of moist air, at the same pressure p and the same temperature T , that is in stable equilibrium in the presence of a plane surface of water containing the amount of dissolved air corresponding to equilibrium. Similarly, x_{vi} will be used to indicate the saturation mole fraction with respect to a plane surface of ice containing the amount of dissolved air corresponding to equilibrium.

(10) **Saturation vapour pressure of moist air:** The saturation vapour pressure with respect to water e'_w of moist air at pressure p and temperature T is defined by:

$$e'_w = \frac{r_w}{0.62198 + r_w} p = x_{vw} \cdot p \quad (4.A.9)$$

Similarly, the saturation vapour pressure with respect to ice e'_i of moist air at pressure p and temperature T is defined by:

$$e'_i = \frac{r_i}{0.62198 + r_i} p = x_{vi} \cdot p \quad (4.A.10)$$

(11) **Relations between saturation vapour pressures of the pure phase and of moist air:** In the meteorological range of pressure and temperature the following relations hold with an error of 0.5 % or less:

$$e'_w = e_w \quad (4.A.11)$$

$$e'_i = e_i \quad (4.A.12)$$

(12) **The thermodynamic dewpoint temperature T_d** of moist air at pressure p and with mixing ratio r is the temperature at which moist air, saturated with respect to water at the given pressure, has a saturation mixing ratio r_w equal to the given mixing ratio r .

(13) **The thermodynamic frost-point temperature T_f** of moist air at pressure p and mixing ratio r is the temperature at which moist air, saturated with respect to ice at the given pressure, has a saturation mixing ratio r_i equal to the given ratio r .

(14) **The dewpoint and frost-point temperatures** so defined are related to the mixing ratio r and pressure p by the respective equations:

$$e'_w(p, T_d) = f(p) \cdot e_w(T_d) = x_v \cdot p = \frac{r \cdot p}{0.62198 + r} \quad (4.A.13)$$

$$e'_i(p, T_f) = f(p) \cdot e_i(T_f) = x_v \cdot p = \frac{r \cdot p}{0.62198 + r} \quad (4.A.14)$$

(15)¹ **The relative humidity U_w with respect to water of moist air** at pressure p and temperature T is the ratio in % of the vapour mole fraction x_v to the vapour mole fraction x_{vw} which the air would have if it were saturated with respect to water at the same pressure p and temperature T . Accordingly:

$$U_w = 100 \left(\frac{x_v}{x_{vw}} \right)_{p,T} = 100 \left(\frac{px_v}{px_{vw}} \right)_{p,T} = 100 \left(\frac{e'}{e'_w} \right)_{p,T} \quad (4.A.15)$$

where subscripts p, T indicate that each term is subject to identical conditions of pressure and temperature. The last expression is formally similar to the classic definition based on the assumption of Dalton's law of partial pressures.

U_w is also related to the mixing ratio r by:

$$U_w = 100 \frac{r}{r_w} \cdot \frac{0.62198 + r_w}{0.62198 + r} \quad (4.A.16)$$

where r_w is the saturation mixing ratio at the pressure and temperature of the moist air.

(16)⁵ **The relative humidity U_i with respect to ice of moist air** at pressure p and temperature T is the ratio in % of the vapour mole fraction x_v to the vapour mole fraction x_{vi} which the air would have if it were saturated with respect to ice at the same pressure p and temperature T . Corresponding to the defining equation in paragraph 15:

$$U_i = 100 \left(\frac{x_v}{x_{vi}} \right)_{p,T} = 100 \left(\frac{px_v}{px_{vi}} \right)_{p,T} = 100 \left(\frac{e'}{e'_i} \right)_{p,T} \quad (4.A.17)$$

(17) **Relative humidity at temperatures less than 0 °C** is to be evaluated with respect to water. The advantages of this procedure are as follows:

- Most hygrometers which are essentially responsive to the relative humidity indicate relative humidity with respect to water at all temperatures;
- The majority of clouds at temperatures below 0 °C consist of water, or mainly of water;
- Relative humidities greater than 100 %rh would in general not be observed. This is of particular importance in synoptic weather messages, since the atmosphere is often supersaturated with respect to ice at temperatures below 0 °C;
- The majority of existing records of relative humidity at temperatures below 0 °C are expressed on a basis of saturation with respect to water.

(18) **The thermodynamic wet-bulb temperature of moist air** at pressure p , temperature T and mixing ratio r is the temperature T_w attained by the moist air when brought adiabatically to saturation at pressure p by the evaporation into the moist air of liquid water at

⁵ Equations 4.A.15 and 4.A.17 do not apply to moist air when pressure p is less than the saturation vapour pressure of pure water and ice, respectively, at temperature T .

pressure p and temperature T_w and containing the amount of dissolved air corresponding to equilibrium with saturated air of the same pressure and temperature. T_w is defined by the equation:

$$h(p, T, r) + [r_w(p, T_w) - r]h_w(p, T_w) = h(p, T_w, r_w(p, T_w)) \quad (4.A.18)$$

where $r_w(p, T_w)$ is the mixing ratio of saturated moist air at pressure p and temperature T_w ; $h_w(p, T_w)$ is the enthalpy⁶ of 1 gram of pure water at pressure p and temperature T_w ; $h(p, T, r)$ is the enthalpy of $1 + r_w$ grams of moist air, composed of 1 gram of dry air and r grams of water vapour, at pressure p and temperature T ; and $h(p, T_w, r_w(p, T_w))$ is the enthalpy of $1 + r_w$ grams of saturated air, composed of 1 gram of dry air and r_w grams of water vapour, at pressure p and temperature T_w . (This is a function of p and T_w only and may appropriately be denoted by $h_{sw}(p, T_w)$.)

If air and water vapour are regarded as ideal gases with constant specific heats, the above equation becomes:

$$T - T_w = \frac{[r_w(p, T_w) - r]L_v(T_w)}{c_{pa} + rc_{pv}} \quad (4.A.19)$$

where $L_v(T_w)$ is the heat of vaporization of water at temperature T_w ; c_{pa} is the specific heat of dry air at constant pressure; and c_{pv} is the specific heat of water vapour at constant pressure.

Note: Thermodynamic wet-bulb temperature as here defined has for some time been called "temperature of adiabatic saturation" by air-conditioning engineers.

(19) **The thermodynamic ice-bulb temperature of moist air** at pressure p , temperature T and mixing ratio r is the temperature T_i at which pure ice at pressure p must be evaporated into the moist air in order to saturate it adiabatically at pressure p and temperature T_i . The saturation is with respect to ice. T_i is defined by the equation:

$$h(p, T, r) + [r_i(p, T_i) - r]h_i(p, T_i) = h(p, T_i, r_i(p, T_i)) \quad (4.A.20)$$

where $r_i(p, T_i)$ is the mixing ratio of saturated moist air at pressure p and temperature T_i ; $h_i(p, T_i)$ is the enthalpy of 1 gram of pure ice at pressure p and temperature T_i ; $h(p, T, r)$ is the enthalpy of $1 + r$ grams of moist air, composed of 1 gram of dry air and r grams of water vapour, at pressure p and temperature T ; and $h(p, T_i, r_i(p, T_i))$ is the enthalpy of $1 + r_i$ grams of saturated air, composed of 1 gram of dry air and r_i grams of water vapour, at pressure p and temperature T_i . (This is a function of p and T_i only, and may appropriately be denoted by $h_{si}(p, T_i)$.)

If air and water vapour are regarded as ideal gases with constant specific heats, the above equation becomes:

$$T - T_i = \frac{[r_i(p, T_i) - r]L_s(T_i)}{c_p + rc_{pv}} \quad (4.A.21)$$

where $L_s(T_i)$ is the heat of sublimation of ice at temperature T_i .

The relationship between T_w and T_i as defined and the wet-bulb or ice-bulb temperature as indicated by a particular psychrometer is a matter to be determined by carefully controlled

⁶ The enthalpy of a system in equilibrium at pressure p and temperature T is defined as $E + pV$, where E is the internal energy of the system and V is its volume. The sum of the enthalpies of the phases of a closed system is conserved in adiabatic isobaric processes.

experiment, taking into account the various variables concerned, for example, ventilation, size of thermometer bulb and radiation.

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ANNEX 4.B. FORMULAE FOR THE COMPUTATION OF MEASURES OF HUMIDITY

These formulae are convenient for computation and sufficiently accurate for all normal meteorological applications, limited to temperature $T > -45^{\circ}\text{C}$ for liquid water and $T > -65^{\circ}\text{C}$ for ice. These formulae are not suitable at all below the stated temperature thresholds.

More accurate, extended in range and detailed formulations of these and other quantities may be found in Sonntag (1990, 1994). With respect to their limits, they are adequate for normal meteorological applications with a lower temperature range extension, and are specifically relevant for radiosonde purposes.

TABLE: Table as text

Saturation vapour pressure:

$$e_w(t) = 6.112 \exp [17.62 t / (243.12 + t)] \quad (4.B.1) \quad \text{Water } (-45^{\circ}\text{C to } 60^{\circ}\text{C}) \text{ (pure phase)}$$

$$e'_w(p, t) = f(p) \cdot e_w(t) \quad (4.B.2) \quad \text{Moist air}$$

$$e_i(t) = 6.112 \exp [22.46 t / (272.62 + t)] \quad (4.B.3) \quad \text{Ice } (-65^{\circ}\text{C to } 0^{\circ}\text{C}) \text{ (pure phase)}$$

$$e'_i(p, t) = f(p) \cdot e_i(t) \quad (4.B.4) \quad \text{Moist air}$$

$$f(p) = 1.0016 + 3.15 \cdot 10^{-6} p - 0.074 p^{-1} \quad (4.B.5) \quad [\text{see note}]$$

Dewpoint and frost point:

$$t_d = \frac{243.12 \cdot \ln [e' / 6.112 f(p)]}{17.62 - \ln [e' / 6.112 f(p)]} \quad (4.B.6) \quad \text{Water } (-45^{\circ}\text{C to } 60^{\circ}\text{C})$$

$$t_f = \frac{272.62 \cdot \ln [e' / 6.112 f(p)]}{22.46 - \ln [e' / 6.112 f(p)]} \quad (4.B.7) \quad \text{Ice } (-65^{\circ}\text{C to } 0^{\circ}\text{C})$$

Psychrometric formulae for the Assmann psychrometer:

$$e' = e'_w(p, t_w) - 6.53 \cdot 10^{-4} \cdot (1 + 0.000944 t_w) \cdot p \cdot (t - t_w) \quad (4.B.8) \quad \text{Water}$$

$$e' = e'_i(p, t_i) - 5.75 \cdot 10^{-4} \cdot p \cdot (t - t_i) \quad (4.B.9) \quad \text{Ice}$$

Relative humidity:

$$U = 100 e' / e'_w(p, t) \text{ \%rh} \quad (4.B.10)$$

$$U = 100 e'_w(p, t_d) / e'_w(p, t) \text{ \%rh} \quad (4.B.11)$$

Symbols applied:

TABLE: Table as text

- t = air temperature (dry-bulb temperature);
- t_w = wet-bulb temperature;
- t_i = ice-bulb temperature;
- t_d = dewpoint temperature;
- t_f = frost-point temperature;
- p = pressure of moist air;
- $e_w(t)$ = saturation vapour pressure in the pure phase with regard to water at the dry-bulb temperature;
- $e_w(t_w)$ = saturation vapour pressure in the pure phase with regard to water at the wet-bulb temperature;
- $e_i(t)$ = saturation vapour pressure in the pure phase with regard to ice at the dry-bulb temperature;
- $e_i(t_i)$ = saturation vapour pressure in the pure phase with regard to ice at the ice-bulb temperature;
- $e'_w(t)$ = saturation vapour pressure of moist air with regard to water at the dry-bulb temperature;
- $e'_w(t_w)$ = saturation vapour pressure of moist air with regard to water at the wet-bulb temperature;
- $e'_i(t)$ = saturation vapour pressure of moist air with regard to ice at the dry-bulb temperature;
- $e'_i(t_i)$ = saturation vapour pressure of moist air with regard to ice at the ice-bulb temperature;
- U = relative humidity.

Note: In fact, f is a function of both pressure and temperature, i.e. $f = f(p, t)$, as explained in WMO (1966) in the introduction to Table 4.10. In practice, the temperature dependency (± 0.1 %) is much lower with respect to pressure (0 % to +0.6 %). Therefore, the temperature dependency may be omitted in the formula above (see also WMO (1989a), Chapter 10). This formula, however, should be used only for pressure around 1 000 hPa (i.e. surface measurements) and not for upper-air measurements, for which WMO (1966), Table 4.10 should be used.

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ANNEX 4.C. INSTRUMENTS AND METHODS IN LIMITED USE, OR NO LONGER USED

4.C.1 MECHANICAL INSTRUMENTS USING ORGANIC MATERIALS

4.C.1.1 The hair hygrometer

The change in the length of hair due to changes in the air relative humidity has been used to measure humidity in hygrometers. All types of hair hygrometers have fallen out of use in meteorology except for the hair hygrograph described in 4.6, which is progressively being phased out.

4.C.1.2 Other mechanical methods

Mechanical methods using dimensional change of organic materials to indicate relative humidity have in earlier times used sensing elements made of animal tissue, such as Goldbeater's skin (an

organic membrane obtained from the gut of domestic animals). These sensing elements are no longer used.

4.C.2 THE LITHIUM CHLORIDE HEATED CONDENSATION HYGROMETER (DEW CELL)

4.C.2.1 General considerations

4.C.2.1.1 Principles

The equilibrium vapour pressure at the surface of a saturated lithium chloride solution is exceptionally low. As a consequence, a solution of lithium chloride is extremely hygroscopic under typical conditions of surface atmospheric humidity; if the ambient vapour pressure exceeds the equilibrium vapour pressure of the solution, water vapour will condense over it (for example, at 0 °C water vapour condenses over a plane surface of a saturated solution of lithium chloride to only 15 %rh).

A thermodynamically self-regulating device may be achieved if the solution is heated directly by passing an electrical current through it from a constant-voltage device. An alternating current should be used to prevent polarization of the solution. As the electrical conductivity decreases, so will the heating current, and an equilibrium point will be reached whereby a constant temperature is maintained; any cooling of the solution will result in the condensation of water vapour, thus causing an increase in conductivity and an increase in heating current, which will reverse the cooling trend. Heating beyond the balance point will evaporate water vapour until the consequent fall in conductivity reduces the electrical heating to the point where it is exceeded by heat losses, and cooling ensues.

It follows from the above that there is a lower limit to the ambient vapour pressure that may be measured in this way at any given temperature. Below this value, the salt solution would have to be cooled in order for water vapour to condense. This would be equivalent to the chilled-mirror method except that, in the latter case, condensation takes place at a lower temperature when saturation is achieved with respect to a pure water surface, namely, at the ambient dewpoint.

A degree of uncertainty is inherent in the method due to the existence of four different hydrates of lithium chloride. At certain critical temperatures, two of the hydrates may be in equilibrium with the aqueous phase, and the equilibrium temperature achieved by heating is affected according to the hydrate transition that follows. The most serious ambiguity for meteorological purposes occurs for ambient dewpoint temperatures below -12 °C. For an ambient dewpoint of -23 °C, the potential difference in equilibrium temperature, according to which one of the two hydrate-solution transitions takes place, results in an uncertainty of ± 3.5 K in the derived dewpoint value.

4.C.2.1.2 Description

The dew-cell hygrometer measures the temperature at which the equilibrium vapour pressure for a saturated solution of lithium chloride is equal to the ambient water-vapour pressure. Empirical transformation equations, based on saturation vapour pressure data for lithium chloride solution and for pure water, provide for the derivation of the ambient water vapour and dewpoint with respect to a plane surface of pure water. The dewpoint temperature range of -12 °C to 25 °C results in dew-cell temperatures in the range of 17 °C to 71 °C.

4.C.2.1.3 Sensors with direct heating

The sensor consists of a tube, or bobbin, with a resistance thermometer fitted axially within. The external surface of the tube is covered with a glass fibre material (usually tape wound around and along the tube) that is soaked with an aqueous solution of lithium chloride, sometimes combined with potassium chloride. Bifilar silver or gold wire is wound over the covering of the bobbin, with equal spacing between the turns. An alternating electrical current source is connected to the two ends of the bifilar winding; this is commonly derived from the normal electrical supply (50 or 60 Hz). The lithium chloride solution is electrically conductive to a degree determined by the concentration of solute. A current passes between adjacent bifilar windings, which act as electrodes, and through the solution. The current heats the solution, which increases in

temperature.

Except under conditions of extremely low humidity, the ambient vapour pressure will be higher than the equilibrium vapour pressure over the solution of lithium chloride at ambient air temperature, and water vapour will condense onto the solution. As the solution is heated by the electrical current, a temperature will eventually be reached above which the equilibrium vapour pressure exceeds the ambient vapour pressure, evaporation will begin, and the concentration of the solution will increase.

An operational equilibrium temperature exists for the instrument, depending upon the ambient water-vapour pressure. Above the equilibrium temperature, evaporation will increase the concentration of the solution, and the electrical current and the heating will decrease and allow heat losses to cause the temperature of the solution to fall. Below the equilibrium temperature, condensation will decrease the concentration of the solution, and the electrical current and the heating will increase and cause the temperature of the solution to rise. At the equilibrium temperature, neither evaporation nor condensation occurs because the equilibrium vapour pressure and the ambient vapour pressure are equal.

In practice, the equilibrium temperature measured is influenced by individual characteristics of sensor construction and has a tendency to be higher than that predicted from equilibrium vapour-pressure data for a saturated solution of lithium chloride. However, reproducibility is sufficiently good to allow the use of a standard transfer function for all sensors constructed to a given specification.

Strong ventilation affects the heat transfer characteristics of the sensor, and fluctuations in ventilation lead to unstable operation.

In order to minimize the risk of excessive current when switching on the hygrometer (as the resistance of the solution at ambient temperature is rather low), a current-limiting device, in the form of a small lamp, is normally connected to the heater element. The lamp is chosen so that, at normal bobbin-operating currents, the filament resistance will be low enough for the hygrometer to function properly, while the operating current for the incandescent lamp (even allowing for a bobbin-offering no electrical resistance) is below a value that might damage the heating element.

The equilibrium vapour pressure for saturated lithium chloride depends upon the hydrate being in equilibrium with the aqueous solution. In the range of solution temperatures corresponding to dewpoints of $-12\text{ }^{\circ}\text{C}$ to $41\text{ }^{\circ}\text{C}$ monohydrate normally occurs. Below $-12\text{ }^{\circ}\text{C}$, dihydrate forms, and above $41\text{ }^{\circ}\text{C}$, anhydrous lithium chloride forms. Close to the transition points, the operation of the hygrometer is unstable and the readings ambiguous. However, the $-12\text{ }^{\circ}\text{C}$ lower dewpoint limit may be extended to $-30\text{ }^{\circ}\text{C}$ by the addition of a small amount of potassium chloride (KCl).

4.C.2.1.4 Sensors with indirect heating

Improved accuracy may be obtained when a solution of lithium chloride is heated indirectly. The conductance of the solution is measured between two platinum electrodes and provides control of a heating coil.

4.C.2.2 Operational procedure

Readings of the equilibrium temperature of the bobbin are taken and a transfer function applied to obtain the dewpoint temperature.

Disturbing the sensor should be avoided as the equilibrium temperature is sensitive to changes in heat losses at the bobbin surface.

The instrument should be energized continuously. If allowed to cool below the equilibrium temperature for any length of time, condensation will occur and the electrolyte will drip off.

Check measurements with a working reference hygrometer must be taken at regular intervals and the instrument must be cleaned and retreated with a lithium chloride solution, as necessary.

A current-limiting device should be installed if not provided by the manufacturer, otherwise the high current may damage the sensor when the instrument is powered-up.

4.C.2.3 Exposure and siting

The hygrometer should be located in an open area in a housing structure which protects it from the effects of wind and rain. A system for providing a steady aspiration rate is required.

The heat from the hygrometer may affect other instruments; this should be taken into account when choosing its location.

The operation of the instrument will be affected by atmospheric pollutants, particularly substances which dissociate in solutions and produce a significant ion concentration.

4.C.2.4 Sources of error

An electrical resistance thermometer is required for measuring the equilibrium temperature; the usual sources of error for thermometry are present.

The equilibrium temperature achieved is determined by the properties of the solute, and significant amounts of contaminant will have an unpredictable effect.

Variations in aspiration affect the heat exchange mechanisms and, thus, the stability of operation of the instrument. A steady aspiration rate is required for a stable operation.

4.C.2.5 Calibration and field inspection

A field inspection should be performed at least once a month, by means of comparison with a working standard instrument.

Calibration of the bobbin thermometer and temperature display should be performed regularly, as for other operational thermometers and display systems.

4.C.2.6 Maintenance

The lithium chloride should be renewed regularly. This may be required once a month, but will depend upon the level of atmospheric pollution. When renewing the solution, the bobbin should be washed with distilled water and fresh solution subsequently applied. The housing structure should be cleaned at the same time.

Fresh solution may be prepared by mixing five parts by weight of anhydrous lithium chloride with 100 parts by weight of distilled water. This is equivalent to 1 g of anhydrous lithium chloride to 20 ml of water.

The temperature-sensing apparatus should be maintained in accordance with the recommendations for electrical instruments used for making air temperature measurements, but bearing in mind the difference in the range of temperatures measured.

4.C.3 HEATED PSYCHROMETER

This instrument type is not used for observations, but the description below is given for information.

The principle of the heated psychrometer is that the water-vapour content of an air mass does not change if it is heated. This property may be exploited to the advantage of the psychrometer by avoiding the need to maintain an ice bulb under freezing conditions.

4.C.3.1 Description

Air is drawn into a duct where it passes over an electrical heating element and then into a

measuring chamber containing both dry- and wet-bulb thermometers and a water reservoir. The heating element control circuit ensures that the air temperature does not fall below a certain level, which might typically be 10 °C. The temperature of the water reservoir is maintained in a similar way. Thus, neither the water in the reservoir nor the water at the wick should freeze, provided that the wet-bulb depression is less than 10 K, and that the continuous operation of the psychrometer is secured even if the air temperature is below 0 °C. At temperatures above 10 °C the heater may be automatically switched off, when the instrument reverts to normal psychrometric operation.

Electrical thermometers are used so that they may be entirely enclosed within the measuring chamber and without the need for visual readings.

A second dry-bulb thermometer is located at the inlet of the duct to provide a measurement of the ambient air temperature. Thus, the ambient relative humidity may be determined.

The psychrometric thermometer bulbs are axially aspirated at an air velocity in the region of 3 m s⁻¹.

4.C.3.2 Observation procedure

A heated psychrometer could be suitable for automatic weather stations.

4.C.3.3 Exposure and siting

The instrument itself should be mounted outside a thermometer screen. The air inlet, where ambient air temperature is measured, should be inside the screen.

4.C.4 ELECTRICAL RESISTANCE HYGROMETERS

Most of section 4.2 on electrical capacitance hygrometers (outside specific 4.2.2) is also relevant to electrical resistance hygrometers.

Resistive humidity instruments feature chemically treated plastic material having an electrically conductive surface layer on the non-conductive substrate. The surface resistivity varies according uptake of water vapour depending on the ambient relative humidity. The process of adsorption, rather than absorption, is dominant because the humidity-sensitive part of such a sensor is restricted to the surface layer. As a result, this type of sensor is capable of responding rapidly to a change in ambient humidity.

This class of sensor includes various electrolytic types in which the availability of conductive ions in a hygroscopic electrolyte is a function of the amount of adsorbed water vapour. The electrolyte may take various physical forms, such as liquid or gel solutions, or an ion-exchange resin. The change in impedance to an alternating current, rather than to a direct current, is measured in order to avoid polarization of the electrolyte. Low-frequency supply can be used, given that the DC resistance is to be measured, and therefore it is possible to employ quite long leads between the sensor and its electrical interface.

SECTION: Chapter_book

Chapter title in running head: CHAPTER 4. MEASUREMENT OF HUMIDITY

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Part title in running head: PART I. MEASUREMENT OF METEOROLOGICAL VARI...

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