The study of the effect of water vapour in methane and helium on humidity sensing

A thesis submitted for the degree of Master of Philosophy

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Abstract

The calibration of humidity sensors is usually carried out in air and at near ambient pressure. In many industries, humidity sensors are sometimes used to make measurements in carrier gases other than air and this can give rise to errors. It is presumed that humidity sensors have responses that differ depending upon gas species–i.e. they are gas species dependent. The number of atoms in a gas molecule is called its *Atomicity*. A gas with a high atomicity can remove more heat out of a sensor than a gas with a small atomicity. The gases chosen in this research were methane and helium.

The Flow Mixing Generator (FMG) has been developed to generate humid gas. The operation relies on the basis of mixing *wet gas* and *dry gas*. The major component was dry gas, >95% by volume. The experimental dew point temperature range was around -30 °C at a pressure of 1.5 bar A with this wet gas and dry gas ratio. The FMG was controlled to generate humid gases with the same dew point, although the dry gas' dew points were not equal. Therefore, the gas flow rates were adjusted. The mass flow controller that was a part of the FMG used to measure and control the gas flow rate was calibrated in air. When the other gases were used, the gas correction factor had to be applied in order to obtain the actual flow rate. The correction factor's uncertainty was not reported and presumably, this quantity may be included with the instrument's uncertainty (0.25% of value).

Humidity quantities may be stated in various units. Water vapour is directly sensed by a humidity sensor. This quantity is thus important and usually reported in terms of water vapour pressure. Based on Dalton's partial pressure, total pressure is the sum of the pressures of gases in the mixture including water vapour pressure. However, this is only valid for gas at low pressure with no molecular interaction. The ideal condition does not

exist – even in ambient air. The actual water vapour pressures need to be corrected by the enhancement factor. The present equations for the enhancement factor are valid for air at pressures up to 20 bar. The equations of states with respect to molecular interaction were chosen to calculate the enhancement factor. Nevertheless, the equations of state were insufficient.

The overall uncertainty evaluation for the standard hygrometers, the FMG and the test humidity sensors have been presented. The FMG gives an acceptable uncertainty of ±0.3 °C at the 95% confidence level ($k = 2$). Weak reproducibility gave the largest source of uncertainty. The polymer sensor showed a difference of 1.2 °C between air and methane, but the difference was insignificant in the aluminium oxide sensors. It can be concluded that gas species has an effect on a polymer sensor.

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1 Introduction

1.1 Background

Water in its gaseous state is referred to as water vapour and the humidity of a gas is the quantity of water vapour in that gas (eg air). In the Earth's atmosphere, approximately 0.5% is water vapour. In industry, the accurate measurement of humidity can have important implications – it affects the quality and cost of products, ranging from food to pharmaceutical items to the production of nuclear energy.

An instrument that measures humidity is called a *hygrometer* and there are at least ten different types of sensor. Each sensor type has a different principle of operation and a description is given in *A Guide to the Measurement of Humidity* by the Institute of Measurement and Control (published in 1996). For several decades new technology has been developing ever higher accuracy sensors.

Humidity generators, used for generating humid air in the laboratory, have also undergone substantial development. The Standard Humidity Generators (SHGs) at the *National Physical Laboratory* (NPL) in the UK were designed to operate with air and/or nitrogen only and can produce dew points between -100 °C and +100 °C, and relative humidities in the range 0% to 98%, for ambient pressures less than 5 bar. Basically, the SHGs work by taking dry gas (air or nitrogen) and humidifying it (in a generator saturator) by passing it over an ice or water surface several times.

At present, sensors are calibrated only in air and at nominally atmospheric pressure – no facility currently exists for calibrating sensors under any other conditions. In response to a questionnaire, Stevens (2005) reported however, that many industries have requirements for humidity measurement in environments other than air or nitrogen at atmospheric pressure. Ideally, a sensor should be calibrated under the same conditions it will be in when in use. At present, however, when a humidity sensor is used to make a measurement in a gas other than air or nitrogen, or at higher pressures, a *correction factor* is usually applied to the reading. These correction factors have *not* been established through calibrating the sensor however and are inadequate for several applications where errors in measurement are undesirable – for example in industries where measurement errors could have financial implications or in health related applications where there are safety critical issues.

Further examples of the need for humidity measurement in carrier gases other than air or nitrogen and at non-atmospheric pressure include: military applications using argon for leak testing from atmospheric pressure up to 20 bar; carbon dioxide in the power industry; natural gas in high-pressure operations up to 200 bar; SF_6 (Sulphur Hexafluoride) used by the switch gear industry and air/nitrogen in compressed air facilities at pressures between 10 and 20 bar.

1.2 Research Objective

For the reasons given above, there is an important need to extend the use of SHGs to cope and the research presented in this thesis has been to develop (build and characterise) a Flow Mixing Generator (FMG) for use with helium and methane as the carrier gases. The work has included validating the performance of the FMG by comparing it with the standard chilled-mirror hygrometers held at NPL and also by the calibration of other sensors on helium, methane and, as a benchmark, air. An uncertainty budget for the FMG has also been produced.

In addition, the equations of state used to calculate absolute humidity have also been studied since the ones in current use are inadequate due to them being only valid for air and nitrogen. This work includes a theoretical study to predict the water content in a variety of gases as a function of pressure, temperature and volume. The reason for the choice of gases used in this work was that they each possess different numbers of atoms in their molecules – ie helium is a monatomic molecule, air includes mostly diatomic molecules and methane represents a polyatomic molecule. The effect of these gases on various types of humidity sensor is also studied.

1.3 Overview

The experimental work undertaken in this research has been based on the concept of taking wet gas generated by the SHG, passing it through a Mass Flow Controller (MFC) and then mixing it with a carrier gas passed through another MFC.

The SHG (referred to as SHG1) is one of three humidity generators that form the National Standards for humidity in the UK. The SHG1 can generate dew points in the range 82 °C down to -75 °C with a corresponding uncertainty ranging from ±0.04 °C to ±0.10 °C.

The three hygrometer sensors used for this research have operating principles based on electrical impedance and formation of condensation. They have been used to measure the dew point at approximately -30 °C at slightly above atmospheric pressure. Prior to use in the research, all three humidity sensors were benchmarked by calibrating them in dry air against two standard hygrometers and the FMG.

The widely accepted Sonntag formula is highly accurate when applied to water vapour. However, it is only applicable to water vapour without other gases present. In a gas mixture, e.g. water vapour in air, the pure saturation vapour pressure must be multiplied by something that is known as the ‘enhancement factor’ to give the actual vapour pressure. The water vapour enhancement factor equations derived by Bögel (BS 1339-1, 2002) will be applied for the calculations. The enhancement factor equations are valid at near ambient pressure and were first introduced by Hyland and Wexler (1973). They were then modified by Hardy and are valid only for moist air up to 10 bar. The equation’s accuracies are dependent on the second virial coefficients that are usually obtained from experiments.

The equations of state are an alternative method for calculating the enhancement factor and water vapour pressure in a gas mixture at any pressure. The interaction between molecules is included in the equations. A large number of equations of state have been proposed and they are each designed with different purposes. The semi-empirical, or cubic equations of state, have been derived for many other applications where gases other than air or nitrogen have been used. For example the Soave-Redlich-Kwong and Peng-Robinson equation of state are famous for natural gas dew point calculation. The GasVLe software package (Advantica Ltd.), HumiCalc (Thunder Scientific Cooperation) and an Excel spreadsheet were the software used to calculate the water dew point in gases.

2 Theoretical Method

To start off with, the fundamentals of the properties of water are presented. Water vapour is water in its gaseous state and is what humidity is concerned with. The enhancement factors are the relationships between the saturation vapour pressures and the actual water vapour pressure. These quantities are only valid for ambient air at pressures slightly higher than ambient. The investigation of the enhancement factors for further ranges should be performed. Numerous equations of states have been proposed and the empirical equations of state with respect to intermolecular interaction have been chosen to make a prediction on the enhancement factor in other gas species.

2.1 Water properties

A water molecule is tri-atomic and consists of one oxygen atom bonded with two hydrogen atoms and has the chemical formula H_2O. The oxygen and hydrogen atoms are attracted by the covalent bond whereby these atoms share their valence electrons–i.e. covalently bonded. Oxygen has an electronic configuration of $1s^2$ $2s^2$ $2p^4$ and hydrogen has an electronic configuration of $1s^1$. By sharing their valence electrons each atom can fill its outer shell to complete the Octet rule as shown on Figure 2-1. The two hydrogen atoms bond to one oxygen atom to form a 'V' shape with the hydrogen atoms at an angle of ~104.5° and this is due to the lone pairs of electrons in the oxygen atom.

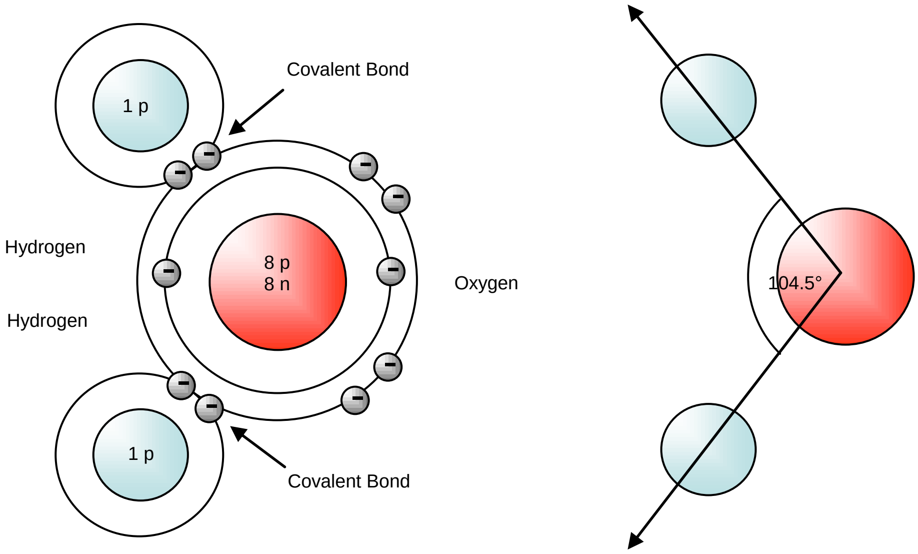

Figure 2-1 Diagram of a water molecule shows oxygen atom bonded with two hydrogen atoms by the covalent bond. Water has a strong polarity because of large electronegativity between oxygen atom and hydrogen atoms. The unpaired electrons cause the water molecule shape to bend 104.5 °.

Electronegativity is defined as the ability of an atom in a molecule to attract an electron itself. Oxygen has a higher electronegativity than hydrogen and therefore the side of the molecule with the oxygen atom has a partial negative charge, while the other side has positive charge. The large difference in electronegativity between oxygen and hydrogen leads to the strong polarity of a water molecule. As a result water vapour is everywhere because it attracts every substance and liquid water has high surface tension.

Water vapour is the gaseous form of water found over liquid water and ice surfaces because of evaporation. The triple point temperature of water is 0.01 °C, where the solid, liquid and vapour phases of water co-exist in thermal equilibrium. Water vapour is not a gas. Water does not have to heat up to its boiling point, which depends on the ambient pressure, to supply water vapour.

Water vapour can exist in ambient air as a single molecule due to the free energy possessed in its molecule. In spite of the hydrogen bond attracting water molecules together, water vapour will not form a greater molecule. The hydrogen bond has a large, significant effect to the liquid and solid phase of water. The forms of water other than the gaseous phase will not be studied.

2.2 Humidity definition

The presence of water vapour in air or other gases is defined as humidity and it occurs because of evaporation over water and ice surfaces. Humidity is influenced by numerous factors: Temperature is the most important variable for humidity because more water vapour can be contained in air at high temperature-humidity increases with temperature. The condensation of water occurs in the opposite way to evaporation.

2.3 Humidity units

Humidity can be reported as an absolute value and a relative value. Humidity in terms of absolute values is dew point and in terms of relative value are mole fraction, mixing ratio, and specific humidity. In very low water concentration, the humidity measurement is usually expressed in parts per million. Parts per million is mole fraction $\times 10^6$. At higher humidities it is more likely to specify dewpoint or partial pressure of water vapour. Concerning the effect of water vapour on materials, it is usual to state the measurement as relative humidity. There is a wide diversity of humidity units in use and care must be taken when converting between units.

There seems to be some confusion over the use of water content and moisture content. Water content is a ratio of mass of water vapour per volume of dry air (mg/m^3), whilst moisture content is used only in descriptive or qualitative expressions and was used in the meaning of both mixing ratio and specific humidity. Nowadays, mixing ratio is defined as mass of water vapour per unit mass of associated dry air, whereas specific humidity means mass of water per unit mass of humid air (The Institute of Measurement and Control, 1996). Moisture content should be avoided.

2.4 Dew point and condensation point

Water condensation occurs all the time in the environment. It is the presence of a water film on a substance’s surface whose temperature is colder than the temperature of the surrounding air. Water vapour condenses at an exact temperature and at a given pressure. The principle is extensive in the development of humidity measuring instruments. It is defined in the publication *A Guide* (the Institute of Measurement and Control, 1996) that *dew point* is the temperature at which dew, or condensation, forms on cooling a gas – and this is the temperature at which air becomes saturated in equilibrium with water. The *Frost point* is defined as the temperature at which frost forms on a cooling gas or the temperature at which air is saturated in equilibrium with ice.

Dew/Frost point is more specific than condensation point and is usually only applicable for water condensation, while condensation point is for any substance. The term *dew point* is often used for supercooled water when it is measured below 0 °C. The definition of supercooled water is water remaining in a liquid phase at below 0 °C and this is because that water is so pure that there is no particle to start the formation of an ice crystal.

2.5 Saturation water vapour pressure

The saturation vapour pressure of water is defined as the maximum pressure of water vapour that can exist at a given temperature (BS 1339-1, 2002). In other words, the pressure at which only water vapour exists over an ice or water liquid surface without any gas, whilst water vapour pressure is considered as a partial pressure co-existing with another substance such as air in its vapour phase. The saturation vapour pressure of water also increases with temperature as a logarithmic function.

Wexler (1976) proposed the formulations for saturation vapour pressure of water in the range 0 °C to 100 °C and for the saturation vapour pressure of water over ice in the range -100 °C to 0 °C based on the temperature scale IPTS-68. These equations were derived from the Clausius-Clapeyron equation based on phase equilibrium (The chemical potential of the substance in each phase is equal when a vapour is in equilibrium with its condensed phase.). The Clausius-Clapeyron equation is concerned with the vapour pressure increasing as the temperature increases. Later, Sonntag modified those equations to fit with the temperature scale IPTS-90 and they have been widely used in hygrometry and air conditioning. The Magnus formula and Antonine equation are simple forms compared with that of Sonntag.

2.6 Water vapour enhancement factor and the second-cross virial coefficients

The ideal gas law cannot precisely predict the water vapour content of gas non-ideality, and of air with known temperature and pressure. For this reason, it was suggested to multiply the saturation vapour pressure of water by an enhancement factor and this is:

$$f(p,T)=\frac{e}{e_s}$$ **Equation 2-1**

Where e is the partial pressure of pure water and e_s is the saturation water vapour pressure. The enhancement factor is a function of temperature and pressure. At temperatures ranging from -80 °C to +80 °C, at ambient pressure between 1.05 at 10 bar, the enhancement factor for water vapour in air is around 1.006.

The enhancement factor equations are theoretically derived form the virial equation. The virial equation of state is a development of the compressibility factor in series. The series is expanded in powers of the molar density with density-independent coefficients, *B*, *C* and *D*.

$$Z = \frac{pV}{RT} = 1 + B(T)v + C(T)v^2 + D(T)v^3 \qquad \textbf{Equation 2-2}$$

Z is the compressibility factor. The density-independent coefficients are known as virial coefficients. (*B* is called the second virial coefficient, *C* the third and so on). In practice, the third and fourth virial coefficients are less significant than the second. With a basis for the virial equation in statistical thermodynamics, relationships have been provided between the virial coefficients and the interactions between molecules. Thus, the second virial coefficient depends on the interaction between two molecules, the third between three molecules, etc.

The enhancement factor accuracy is dependent on the second-cross virial coefficient for air and water vapour mixture. The second-cross virial coefficient is of the interaction between water and air mixture. The measurements cannot be made directly on the second-cross virial coefficients. Inversely, these are derived back to the enhancement data. This is a check on the quality of the data. Experimental measurements of the enhancement factors for air were proposed by Hyland (1975) and the enhancement factor equation was derived by fitting the experimental data. The equation contains thirteen terms and is large and complex. Greenspan (1976) obtained values based on data given by Hyland (1975) to fit the enhancement factor to a more simplified equation, the form of which is due to Goff and Gratch (1949). Hardy (1996) improved values of enhancement factor to agree with the International Practical Temperature Scale of 1990 (IPTS-1990). The Bögel enhancement factor equation is valid at near ambient pressure, where as the Hardy enhancement factor equation is applicable from ambient pressure to 10 bar. The uncertainties of these have also been included. It is of no surprise that the uncertainties of the equation increases at a low water concentration and higher pressures. The enhancement factor varies depending on gas species. For example, the thermodynamic properties of air and nitrogen are similar, but the predicted enhancement factor values between air and nitrogen should differ by around 0.01%. This value was placed as the systematic difference for the gravimetric hygrometer (Bell, 1995).

The second-cross virial coefficient formulation for water vapour and gas was proposed by Rigby and Prausnitz (1967). The water vapour mole fractions have been measured in nitrogen, methane and argon and the results were used to calculate the cross-second virial coefficients. At low pressure, the water vapour mole fraction can be approximated by calculating from the ratio of water vapour pressure and total pressure as mentioned in Raoult's law. The solubility of a liquid in a gas at low pressure may be calculated from the vapour pressure of the liquid. At high pressure approaching the critical pressure of the mixture, however, the non-ideality of the liquid phase becomes important in determining the vapour phase solubility. In equilibrium, the chemical potential of vapour and liquid phase is equal as well as the fugacity of the two phases. In 1929 G.N. Lewis introduced the fugacity, which is equivalent to the chemical potential and is expressed in units of pressure. Measurements of mole fraction of water vapour yield values of the fugacity coefficient through the proposed equation by Rigby and Prausnitz (1967) and it is, therefore, possible to derive values of the second-cross virial coefficient. The 1% uncertainty of water vapour mole fraction causes an uncertainty in the second-cross virial coefficient of around ±6 ml/mole at 20 bar and ±3 ml/mole at 40 bar. The temperature range is between +20 °C and +100 °C. It does not cover the range in the humidity measurement (-100 °C to +100 °C).

The second-cross virial coefficients for air and other gases should therefore be studied when being applied to lower water concentration and higher pressures.

2.7 The equation of state for pure compounds

The equation of state has been developed to describe gas behaviour. The equation of state presents the relationships between the three main parameters of gas properties; pressure, volume and temperature. The ideal gas model is the simplest form of the equation of state. The assumptions are that molecules do not interact with each other and their inherent volume is negligible. The ideal gas model is valid for low-density gas only. It is insufficient to predict the non-ideal gas behaviour and it is assumed that there are attractive forces between gas molecules.

Van der Waals was the first person who proposed the interactive terms into the equation to predict the non-ideal gas behaviour. A wide range of equations have been developed since the appearance of the Van der Waals equation of state. The equation of state can be approximately separated into four groups, but the most well known could be the semi-empirical equation of state. The semi-empirical equation of state is apparently obtained by fitting the experimental data. The advantages of this equation are the accuracy and the simple form, while the theoretical equations are complex and inconvenient to use. This is the reason why the semi-empirical equation of state is widely acceptable.

A highly successful equation of states has been developed by Soave, Redlich and Kwong knows as SRK-eqaution of state (SRK-eos). Later, Peng and Robinson reported that the SRK-eos has failed to predict the liquid density at approaching the critical point and proposed a new equation of state known as Peng-Robinson equation of state (PR-eos). The two equations of state are extensively applied in the natural gas industry. Brown et al

(2007) reported that the SRK equation of state gives good agreement to predict water dew point in natural gas of -10 °C at 85 bar, but a large difference is by the ISO equation of state. The SRK equation of state assumes water to be in liquid phase, but the ISO equation of state gives the condensed phase of water below 0 °C as ice. The *ISO 18453* (2004) states the modification of the PR-eos as a conversion between water content and water dew point for natural gas. The *Group Europeen De Recherches Gazieres* (GERG) modified the PR-eos as a conversion between water dew point and water content in natural gas. The range of dew point is in the medium range between -20 °C and +20 °C with an uncertainty of around ±2 K at pressures to 100 bar.

At present, there are the high accuracy formulas for saturation water vapour pressure proposed by Hyland and Wexler (1983), and later developed by Sonntag. To accurately determine the water vapour pressure in non-ideal gas, the enhancement factor is invented and multiplied by the saturation water vapour pressure as in the previous section. The emphasis is on the enhancement factor variation with gas species, the overall pressure and the dew-point temperature. The equation of state will probably be an alternative for humidity calculation in the gas non-ideality. The enhancement factor can be calculated by using the equation of state.

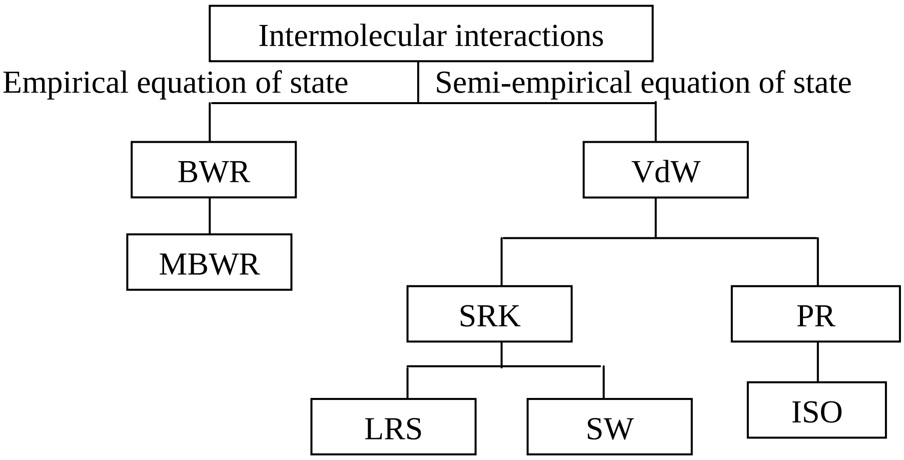

Figure 2-2 the subdivision of the equation of state is illustrated concerned with intermolecular interactions. The empirical of state is such as the Benedict-Webb-Rubin equation of state (BWR) and its modification (MBWR). The semi-empirical equations of state are Van der Waals (VdW), Soave-Redlich-Kwong (SRK), London Research Station (LRS), Schmidt-Wenzel (SW), Peng-Robinson (PR), and ISO (ISO 18453).

A group of equations of state with respect to the interaction between molecular connections is illustrated in Figure 2-2. The Modified Benedict Webb and Rubin equation of state is an empirical equation of state. The empirical equation of state is developed based on theory, whilst the semi-empirical of state is based on experimental data. Van der Waals proposed the first semi-empirical equation of state. Later, some parameters have been modified and the PR and SRK-eos are provided in many applications. The other approach of the equation of state will be briefly given, such as the London Research Station (LRS), and Schmidt and Wenzel (SW). The two equations are developed from the SRK-eos. The ISO-eos is chosen for the prediction of water dew point in gases for this research. Some of these equations are provide by the Gas VLe software package developed by Advantica Ltd.

Equation of state	Equation form
Simple ideal gas	$PV = RT$
van der Waals (1873)	$P = \frac{RT}{V-b} - \frac{a}{V^2}$
Redlich-Kwong (1949)	$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$
Soave-Redlich-Kwong (1972)	$P = \frac{RT}{V-b} - \frac{a(T)}{RT(V+b)}$
Peng-Robinson (1976)	$P = \frac{RT}{V-b} - \frac{a(T)}{RT\left[V(V+b)+v(V-b)\right]}$
Schmidt-Wenzel (1980)	$P = \frac{RT}{V-b} - \frac{a(T)}{RT(V^2+ubV+wb^2)}$

Table 2-1: The equations of state with the equation form are presented. The first equation of state was proposed by Van der Waals (1873) where parameters *a* and *b* were added into the ideal gas equation. Since then, a number of equations of state has been developed.

The equation of state form is shown in Table 2-1. The parameter *a*, is an attractive term between gas molecules and *b*, is a volumetric function. Van der Waals is the first to propose these two parameters to make the correction for gas non-idealility. Redlich and Kwong introduced $a/T^{1/2}$ instead of *a*, and then Soave replaced it as a function of temperature. The parameter *a*, remained as a function of temperature in PR-eos. The SW-eos has four parameters, whilst the MBWR-eos is excessively complex and has more than four parameters.

2.8 Semi-empirical equation of state for mixture

The mixing rule was first proposed by Van der Waals for a gas mixture. The parameters *a* and *b* for the pure compounds are substituted by mixing parameters a_M and b_M for example. The assumption is based on that a pure fluid has a similar behaviour to the mixture or *one-fluid* theory (ISO 18453, 2004). The mole fraction of the components in the mixture is used as a weighting factor for the parameters. The cross coefficients of parameter *a*, are corrected with a binary interaction parameter. A pair of gases has an individual value. The binary interaction coefficients are significant in the mixing rule. These values are presented in the ISO 18453 without the uncertainty reported.

In conclusion, humidity measurement is a complicated subject because the fundamental properties of a water molecule have strong polarity. Although the present saturation vapour pressure of water formula are highly precise, their accuracy decreases in air or other gas mixtures and correction values have been proposed. Enhancement factors are successful to improve the water vapour pressure in air at pressures up to 10 bar. Due to the fact that the operational range in industry is much greater than this, this is the reason why the enhancement factors need to be developed. The second-cross viral coefficients are the variables of importance for the enhancement factor corrections in theory, but lack of data prevents the improvement of enhancement factor in other gas species. The equation of state is another approach for enhancement factor development and the semi-empirical equations of state are of concern in the study. Equation development is mostly for natural gas applications.

3 Experimental investigation

The purpose of this chapter is to make a comparison between the results from the experimental investigation to measure humidity for a range of water-gas mixtures and the published experiments for water content in carrier gases. The experimental techniques used are described and compared with the experimental results as appropriate. This chapter also provides an examination of the humidity generators, sensors and incorporated devices as well as the practical methodology of flow mixing used in this research. An outline of the configuration of instrumentation used to build a mass flow-mixing generator is also given.

3.1 Experimental review

Many researchers have studied water content in natural gas because it has a large effect on the quality of the product. Condensation and blockages in natural gas pipelines are a result of excessive water vapour.

Dry gas (nitrogen, methane and argon) flows directly through the saturation and condensation units. In experiments proposed by GERG TM-14 (2004), the Blanco et al (1999) and Folas (2007) Karl-Fischer titration technique was used to measure water content and chilled-mirror hygrometers were used to measure water vapour dew point. The experimental temperature range was in the medium-high region, but the pressure range was quite high (Figure 3-1).

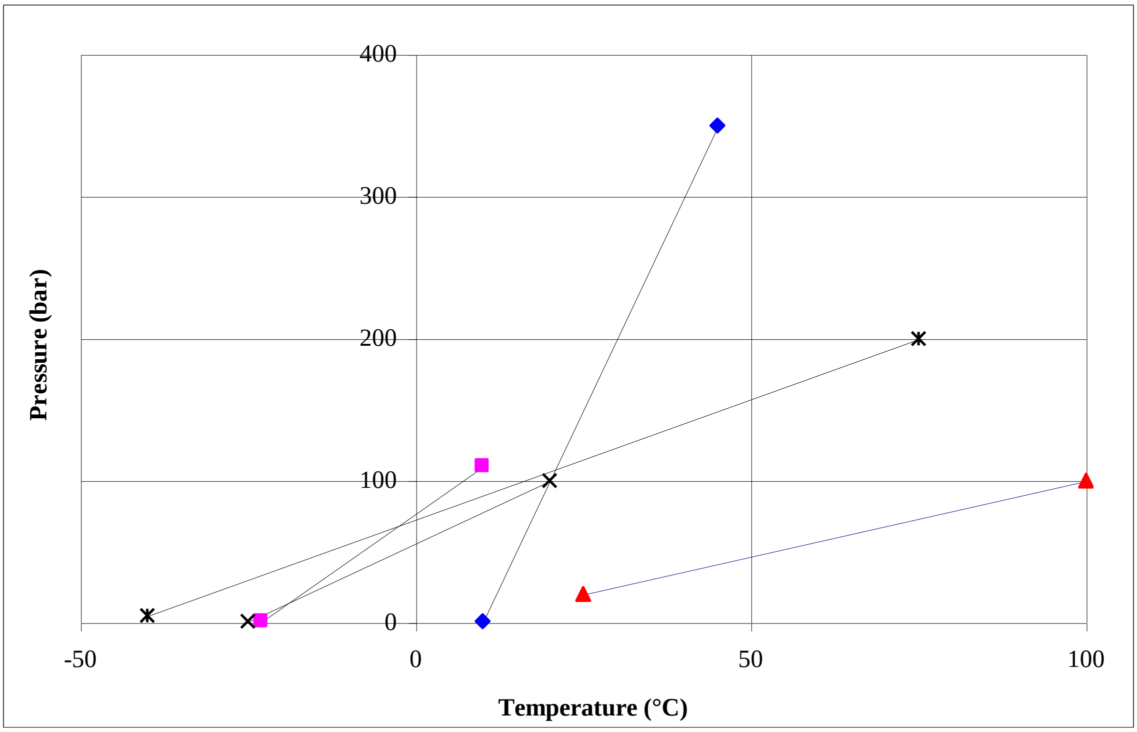

Figure 3-1: The temperature and pressure range of five experiments by ▲:Rigby and Prausnitz (1967), ■ :Blanco (1999), ◆:Chapoy (2003), ×:GERG (2004) and ✳: Folas (2007)

Rigby and Prausnitz (1967) reported the solubility of water vapour in nitrogen, argon and methane in the range +25 °C to +100 °C and between 20 and 100 bar. Two equilibrium cells were submerged in a fluid bath with dry gas flowing through them. Water vapour was fed via a needle expansion valve which reduced the pressure to 1 bar. After expansion, the water vapour in the gas mixture was passed through a desiccant. The gas was then saturated with water and passed through a calibrated wet test meter, after which it was vented to the atmosphere. The overall uncertainty of the experiment was reported to be within ±1% of the water vapour mole fraction.

GERG TM-14 (2004) proposed an experiment for water content in natural gas whereby the gas was saturated with water in a saturator at near room temperature. Thereafter, the gas was cooled down in two condensers to the required dew point temperature and the excess water was removed. The experimental set up can be divided into four main parts: gas supply and pressure control, saturation unit, condenser unit and analytical unit. The experimental set up therefore is suited for saturated water content measurements between 1 and 100 bar and temperatures between -25 °C and +20 °C. The water contents (mg/m^3) and water dew points have been measure by a Karl-Fischer coulometer and a chilled-mirror hygrometer respectively. The uncertainty is up to 20% of water content at $\leq$100 mg/m^3 and is less than 2.5% of water content at >100 mg/m^3. The dew point uncertainty was ±2 K.

Water content in gas mixtures was focused on the experiments proposed by Folas et al (2007). The experimental set-up consisted of flow equipment similar to the GERG TM-14 (2004) with four main units, but the temperature range was wider at between -40 °C and +75 °C with pressures between 5 and 200 bar. The overall uncertainty was not reported.

Blanco et al (1999) reported water dew point in natural gas. The experiment set-up was with temperatures between -23 °C and +10 °C and at pressures from ambient to 110 bar. The uncertainty for water content in natural gases measured by the Karl-Fischer titration technique was ±0.2% of value and for water dew point was better than ±0.4 K.

Chapoy (2003) studied the solubility of water vapour in methane at near the hydrate formation condition. The water vapour in methane for the system was measured at between +10 °C and +45 °C and at pressures up to 350 bar. A gas chromatograph equipped with a pair of detectors was used as the analytical unit for examining water vapour concentration in methane. The overall uncertainty for the system was not reported.

For the measurement of humidity, the water vapour in air or any gas needs to be known, but most natural gas industries, as mentioned above, are different because they focus on water content and water dew point. It is possible to use the Karl-Fischer titration technique to measure water content in this experiment because the amount of water content is in units of mass – it does not vary as pressure changes. This technique is however more suitable for water vapour chemical analysis than physical analysis and condensation is probably sufficient to evaluate water vapour in gases. The titration technique's uncertainty is dependent on the chemical reaction between the water vapour and the Karl-Fischer solution.

Most of the experiments reported the water concentration in mg/m^3 but it would be more useful if water vapour pressure had been reported because it leads to the gas enhancement factor. Another approach is that the experimental data from the various researches could be converted to partial water vapour pressure by using the GasVLe software package containing many equations of state. However, it is known that the calculated results will not be accurate because the equations of state are not designed for water vapour calculation in gases and the partial vapour pressure in a gas at high pressure is concerned with non-ideality conditions. Total pressure is not equal to the sum of gas pressure and water vapour pressure. The study by Rigby and Prausnitz (1967) stated that the partial pressure of water can be evaluated from chemical potential and McCartney (2008), proposed the notes on partial pressure with respect to the equation of state for the molar Gibbs energy. The two approaches would be useful concerning the energy of the system, but the enhancement factor is more relevant to thermodynamic properties of gases rather than an energy basis.

3.2 Literature Survey for humidity generator

Evaluation of trace moisture sensors-final report by Bell et al (2004) and *A Guide* (the Institute of Measurement and Control, 1996) refer to the national standard humidity generators used at NPL. These being: the dew point generator, the two-pressure generator and the coulometric generator. Each has a different and individual design.

The operation of a two-temperature generator is presented. Gas is humidified in a first saturator and then fed to another saturator. The temperature of the second saturator is higher than that of the first generator, but the pressures of these two saturators are not different and they operate at ambient pressure. The temperature can be varied in one saturator or both. Therefore, the two-temperature generator can generate dew points and relative humidity, but again at ambient pressure.

A two-pressure generator is designed to have a pressure difference between two saturators whereby the first saturator pressure is higher than that of the second saturator. Gas is humidified in the first elevated saturator and pushed to expand in the second saturator. By knowing the initial humidity, the humidity after expansion can be found. The two-pressure generator can generate both dew points and relative humidity.

At NPL, the Standard Humidity Generator 1 (SHG 1) is a dew point generator that operates from -75 °C to +82 °C and the Low Frost-point Generator (LFG) combined with the Standard Humidity Generator 2 (SHG 2)is a two-temperature generator that operates from - 90 °C to +90 °C. The High Dew-point Generator (HDG) operates from +1 °C to +82 °C. SHG 1, LFG+SHG 2 and HDG have overlapping temperature ranges. The designs of the saturator coils are both based on similar principles, but the pipe diameter, shape and size are all different. The HDG has a larger pipe diameter so there is greater surface area for the supply to be humidified more easily. When NPL's humidity generators were designed, the calculations for the shape and length of the saturator coil were concerned with the gas's thermodynamic properties. The principle of operation behind the saturator coil is that a coil of pipe, approximately half a metre in length, is submerged in a temperature controlled liquid bath and gas is flowed though it from top to bottom. At the lowest part of the coil the gas flows over a liquid water or ice surface. The pressure at which the gas is supplied has an effect on the humidity of the gas at the outlet and the pressure condition in the saturator is monitored. All three generators operate at ambient pressure. The LFG & SHG 2 and HDG can be used to measure dew point and relative humidity because they are two-temperature generators at a single pressure.

The NPL Humidity Group is planning to extend its capability in order to enable it to calibrate hygrometers at higher pressures and a commercial two-temperature two-pressure generator has been purchased (Thunder Scientific Model 3900). The design is based on humidifying gas by flowing it over the water/ice surfaces contained at levels inside the generator's saturator. At a given saturator condition, temperatures and pressures may be different. The maximum flow to the system is five litres per minute and the pressure will be up to 20 bar. The generator's uncertainty will get larger at very low moisture content. The two-temperature two-pressure generator will possibly operate faster than the dew point generator. The external flow controller was mounted to bypass that generator. The maximum flow rate can be extended from 5 litres per minute to 35 litres per minute. The saturator is effective up to about 20 litres per minute and then the efficiency decreases. The 3900 generator can possibly generate at very low moistures down to -90 °C and its uncertainty is ±0.1 °C at -75 °C. The expansion valve is a cause of uncertainty because it does not function properly. Soleyn (2006) reported that the uncertainty of a Thunder

Scientific Model 3900 Frost point Generator as being between ±0.002 °C and ±0.01 °C. Tests were performed at 1, 3 and 7 bar and from -80 °C to +10°C.

There is a variety of combinations in a flow-mixing generator. The change from one flow rate to another is faster, but the stabilisation time is as usual depending on the level of water vapour dew point. Achieving a low water vapour dew point will take a longer than that of a high water vapour dew point. Dew points at near room temperature may take less than an hour to stabilise. Scace et al (2006) proposed the hybrid humidity generator. This is a combination of the primary two-pressure generator and the flow-mixing generator and this idea is not new. The maximum flow rate is 150 litres per minute. The flow-mixing generator used to be connected to the LFG but since the cooler was set up, the flow mixing system has not been used.

3.2.1 Mass flow mixing generator

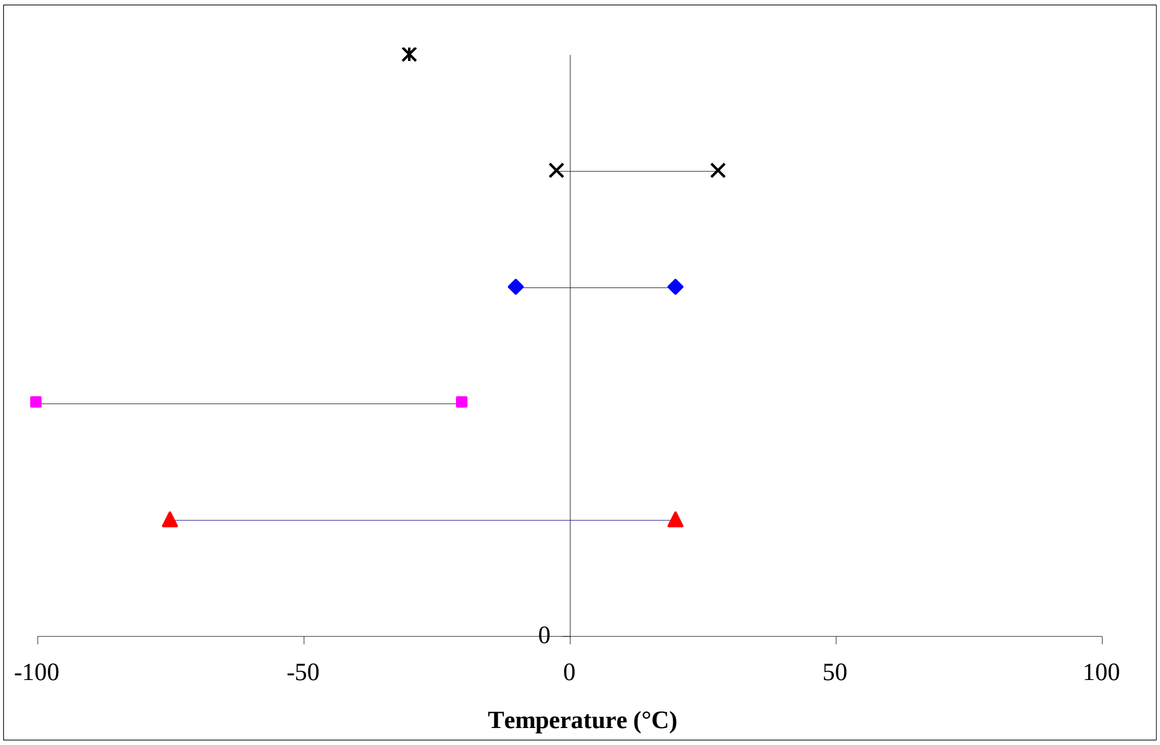

Figure 3-2: The flow-mixing generators operating range presented by national laboratory humidity department ▲:NPL, ■:France, ◆:Japan, ×:Taiwan and ✳: this research

Basically, in a flow-mixing generator, wet gas is mixed, or diluted, with dry gas. Bell (1999) reported that the flow-mixing generator operating with the Low Frost point Generator (LFG) at NPL could lower the dew point down to -85 °C (±0.2 ppm) ±0.5 °C equal to ±10% uncertainty. However, the LFG itself was later improved to generate the dew point at -90 °C ±0.5 °C (0.1 ±0.05 ppm) and -85 °C ±0.3 °C (4.5 ±0.03 ppm).

The Bureau National de Métrologie (BNM) accredited the 4-stage dilution flow-mixing generator at Air Liquid, France for the range of dew points from -20 °C to -100 °C (approximately 1000 ppm to 15 ppb). The sources of uncertainty are pressure, flow and saturator temperature, while neglecting the uncertainties in moisture content of dry and wet inlet gases. The uncertainty analysis assumes that an upper limit of dryness of the dry gas is about 0.1 ppb, but without the uncertainty values assigned. Despite having the uncertainty in moisture content of wet gas, its significance is reduced in proportion to dilution. However, this conclusion for the flow-mixing generator is invalid.

Takahashi et al (1996) proposed the standard calibration for the mass flow generator. The generator combines dry and wet gas in a simple way. The generator’s uncertainty for relative humidity and dew point and the water vapour pressure formulations were given. A flow rate error of 1% full scale causes an error in relative humidity of up to 1% rh. No formal abbreviation for relative humidity is given, but it is widely accepted to use % rh to represent of percentage of relative humidity. Critical flow nozzles were used as flow controllers, but these are not compatible with a single pressure generator. As a result, when using the flow nozzles as a flow controller, the feedback will disturb the system pressure that affects dew point temperature in a single pressure generator.

Su et al (2004) stated that the temperature range of their mass flow-mixing generator is from 15 to 35 °C with 30-90% rh. The expanded uncertainty is 0.6% rh. The minimum range is, for example, at 15 °C and at 30% rh and this corresponds to -2.5 °C ±0.2 °C dew point. Their temperature range is not low.

Goody et al (2002) proposed a high accuracy gas flow dilutor. The method of mass flow calibration was self-referring and the uncertainty is ±0.4% at the 95% confidence level ($k = 2$). The uncertainty could be improved by reducing setting errors in the MFC drivers by increasing the resolution of the flow meter and removing any bias during the calibration sequence.

3.3 Mass flow controller

There are many methods for measuring gas flow and the devices used were: A volumetric flow meter, a mass flow meter and a bubble flow meter. Volumetric flow measurements are inaccurate because the gas volume is dependent on pressure and temperature – with different conditions; the flow rate of gas varies. Mass flow measurements although usually express as a volume flow such as litres per minute, its sensor responses to (specific) heat capacity. As a result mass flow measurements are dependent upon gas species are independent of pressure and temperature. (Goody and Milton, 2002) Bubble flow measurements are not affected by gas composition. Caution should be taken however, because some gases may have a chemical reaction with the substance used to make the bubble solution.

3.3.1 Mass flow controller

A mass flow controller consists of four main units: a sensor, the electronics, a shunt and a valve. The sensor measures the flow rate from 0 to 10 cc/min of gas to be measured. The shunt divides the flow such that the flow through the sensor is a precise percentage of the flow through the shunt. The electronics unit amplifies the sensor's output and this output is used to control the valve position. The valve is an automatic solenoid and the voltage in its coil controls the valve's seat level.

Thermal sensors are used to detect the gas flow in the mass flow meter and heat transfer rate is proportional to the mass flow rate. The sensor detects the change in the thermocouples. The thermocouples are wired at two ends of a capillary tube. The heater is wound around the middle of the capillary tube and heats up the bled gas. The sample gas is bled from 0 to 10 cc/min. The difference in the gas's upstream and downstream temperatures causes the temperature of TC-1 and TC-2 to become unequal as shown in

Figure 3-3. With a constant power input, the change in the thermocouples is dependent on the mass flow rate and the specific heat capacity of the gas. The sensor detects the change and the signal is sent to the electronics unit and then to the valve control.

A mass flow meter/controller is usually calibrated in air or nitrogen. The gas correction factor is a parameter used to obtain the actual flow rate when the mass flow meter is used in gases other than air or nitrogen. The correction factor for different gases varies form manufacturer to manufacturer and is derived from different sources (3.4).

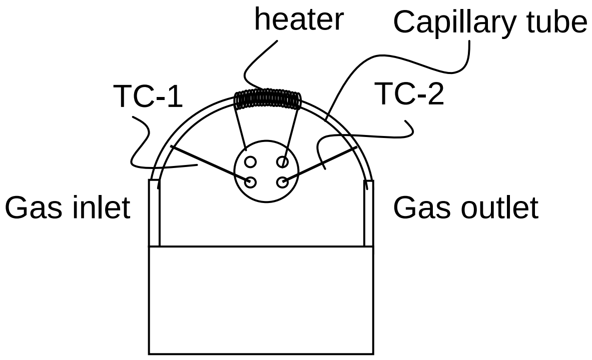

Figure 3-3: A diagram of the sensing unit of the mass flow controller consists of a metallic capillary tube, thermocouples TC-1 and TC-2 and a heater. The sensor measures the flow rate from 0 to 10 sccm of the gas to be measured

The Mass Flow Controller's (MFC) principle of operation is based on a single thermal electronic principle whereby a capillary tube is heated up by the resister winding attached to the middle part of the capillary. Thermocouples TC-1 and TC-2 are connected to the ends of the capillary to sense the change in the gas temperature (Figure 3-3).

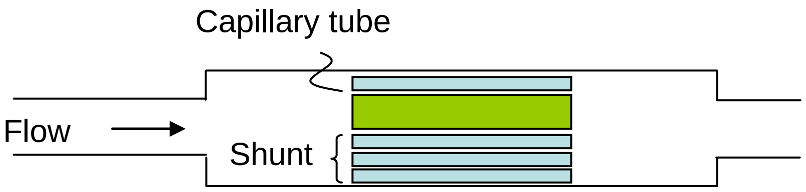

Figure 3-4: A Laminar Flow Element arrangement (LFE) consists of capillary tubes that are parallel placed with similar channels.

A fixed ratio arrangement is made to measure gas flow rates higher than 10 cc/min by dividing the flow with a fixed ratio shunting arrangement (Figure 3-4). This is done by placing the measuring capillary tube parallel with one or more dimensionally similar channels and is called a Laminar Flow Element (LFE). The low range shunt and medium range shunt are provided for the HFC-202. The shunt is adjustable to allow the gas flow to be divided.

3.4 Gas correction factor

The gas correction factor is multiplied by the flow rate generated by the mass flow controller where the mass flow controller is usually calibrated in air or nitrogen. Errors will occur if the mass flow controller is used to control gases other than air or nitrogen. Gas correction factors values are derived from many sources and Tison (1996) stated that the correction factor is instrument specific and may vary by as much as 10% between instruments of different designs. Correction factor values may vary from 0.2 to 1.5. The HFC-202 series data sheet gives the gas correction factor without values of uncertainty and these are obtained from experiments and theory. In theory, the gas correction factor values are derived from the virial coefficient fitted to empirical data from various researches and the gases specific heat capacity.

The units of flow used in a mass flow controller is usually expressed as units of volume per units of time (eg litres per minute), but the flow sensor responds to the thermal properties of the flowing gas. A high flow of gas contains a greater number of gas molecules and therefore mass than a low flow of gas. The heat generated by a resistor within a mass flow controller is taken away by the gas flow. The greater the gas flow, the more heat will be taken away from the resistor and the sensor will sense this change. A unit of volume is widely used by many manufacturers and it is possible to convert this unit into a mass unit. Values of gas density at 0 °C and 25 °C STP are given with the manufacturer's data sheet.

According to the HFC's manual, the gas correction factors of air, methane and helium are 1.0015, 0.7787 and 1.4005 respectively (no units). The value of correction factor for nitrogen is, as a reference, 1.0000. These correction factors applied to the experiment are obtained from the manufacturer's empirical determination. For example, take two litres of dry air per minute flowing from MFC 1. To obtain the same flow rate as for air, the mass flow meter will be: $2 \div 0.7787 = 2.568$ litres per minute for methane and at $2 \div 1.4005 = 1.428$ litres per minute for helium. 2 litres per minute of dry air, 2.568 litre per minute of methane flow to mixed with wet 0.1 litres per minute of wet air and 1.4005 litres per minute of helium was also did the same way. Without considering the gas species and atomicity effects STANDARD 2 was theoretically expected to read the same dew point ~-30°C, but measured dew points were different. Deviation was found between experimental values and the given values of the gas correction factor. It was 3.4% for methane and 3.0% for helium. This should be accounted for as a source of uncertainty and allowed for in further studies.

3.5 Humidity sensors

Humidity sensor development has been with a diversity of technologies. The natural properties of substances will change due to water vapour and sensors can detect that change. This section is intended to outline the operating principles of humidity sensors and the use of the sensors in this research is discussed.

The ten types of humidity sensor are shown in Table 3-1.

The quantities of interest will be relative humidity, dew point and water concentration. It is known that humidity sensors are developed for only one unit of measurement and so another would have to be obtained from conversion. For this reason, the intended measurement purpose should be considered.

The typical, in use uncertainty of each type of humidity sensor is shown in Table 3-1. These uncertainties will be minimised by calibration and will vary with temperature. For example, the uncertainty of NPL's standard humidity sensor based on condensation is around ±0.1 to ±0.4 °C from -75 °C to +90 °C (NPL's Excel spreadsheet for STANDARD 1, 2007). Because of its high precision, a condensation type is used as the standard, but it usually requires skill to operate and is expensive. The capacitive, resistive and impedance sensors are widely used because mostly are portable and with acceptable accuracy. This can be observed from the records of customers who have sent their instruments to NPL for calibration. In contrast to the capacitive type, other types of sensor such as psychrometer and lithium chloride are rarely sent to NPL for calibration. The colour change type may be of use in less demanding applications, where larger uncertainties are acceptable.

Sensor type	Absolute humidity or relative humidity	Uncertainties for typical uses
Mechanical	R	5 to 15% rh
Psychrometer	R	2 to 5% rh
Resistive	R	2 to 3% rh
Capacitive	R	2 to 3% rh
Impedance dew-point types	A	2 to 5 °C
Condensation	A	0.2 to 1.0 °C
Lithium chloride	A	2 to 4 °C
Phosphorus pentaoxide	A	3 to 10% of reading
Spectroscopic	A	3 to 10% of reading
Colour change	R	10 to 20% rh

Table 3-1 Humidity sensor types classified into relative and absolute humidity measurement including with typical uncertainty in uses (The Institute of Measurement and Control, 1996)

In this research, the condensation capacitive sensor type has been chosen. The humidity sensor type based on condensation is sometimes called a chilled-mirror hygrometer. The principle of operation is as following.

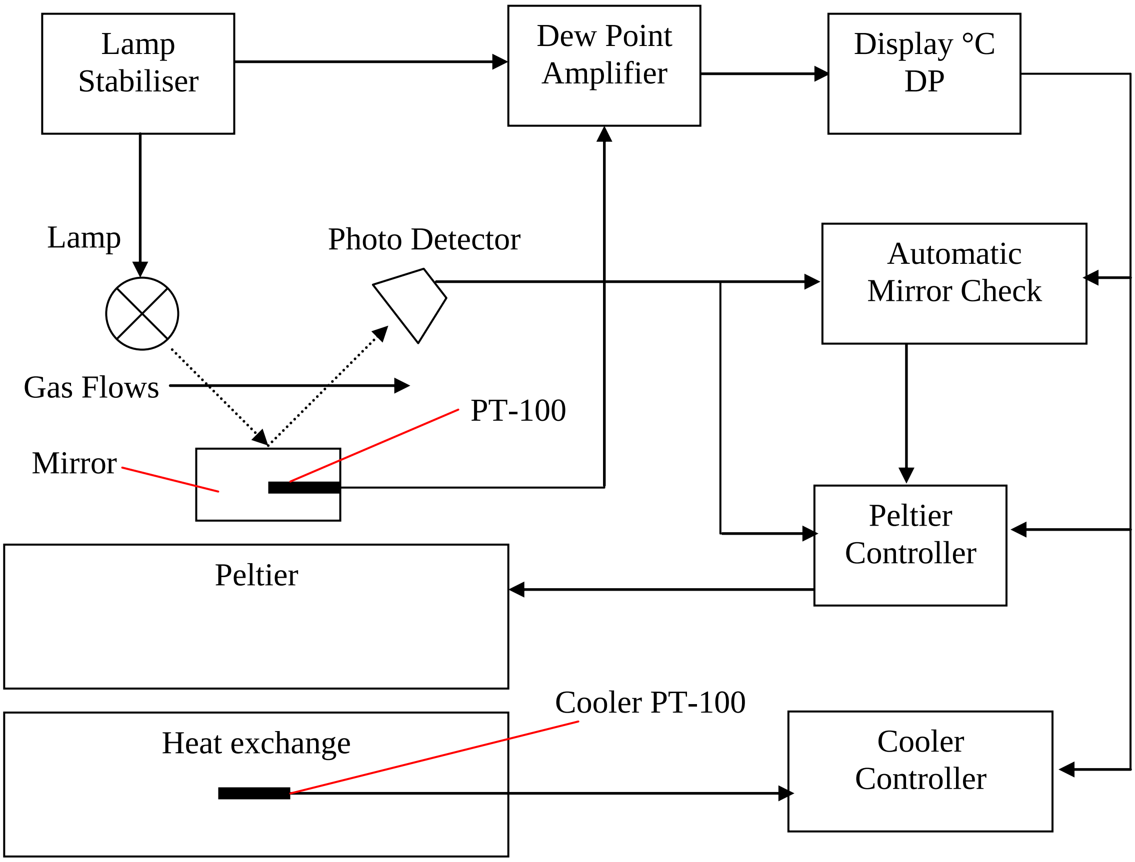

Figure 3-5: Condensation is formed on small mirror surface and is detected by an optical sensing bridge. A platinum resistance thermometer PT-100, detects the temperature of the mirror when dew has formed. A thermoelectric cooler controls the layer of dew. (MBW dew-point measuring instrument DP3-D-B/C user guide, 1985)

The measurement head essentially consists of the Peltier on the cold side of the dew point mirror. The PT-100 mirror temperature sensor is embedded within the dew point mirror. Excess heat from the Peltier is carried away by the exchange of heat. The cooler temperature is measured with the cooler temperature PT-100 sensor. Dew formation is regulated by the optical system consisting of a lamp and a photo detector. The signal from the photo detector is processed in the Peltier-controller. The Peltier-current is adjusted so that a constant layer of dew forms on the mirror. The mirror temperature PT-100 sensor signal is amplified in the temperature amplifier and shown on the digital display. As the slightest differences in the lamp's luminance would immediately alter the measuring results, the mirror check indicator shows how much light from the measuring-head lamp is reflected on the mirror and transmitted to the photo detector. The signals from the lamp and PT-100 are sent to the dew point display and feedback from these controls the mirror temperature.

Figure 3-6 TD 1 sensor is a capacitive sensor Vaisala DMT347 based on DRYCAP technology (Vaisala user guide)

The capacitive sensor used in this research is a Vaisala DMP347 (Figure 3-6). It is based on DRYCAP technology whereby the change in capacitance is as its thin polymer film absorbs water molecules together with a combined temperature measurement with a PT-100. It should be pointed out that the capacitive sensor is suitable for relative humidity measurement, so conversion is needed.

$$T_d = \frac{T_n}{\dfrac{m}{\log\left(\dfrac{P_w}{A}\right)} - 1}$$

Equation 3-1

The parameters A, m, and T_n depend on temperature according to the data sheet supplied by the manufacturer. This equation is a conversion obtained from the Hyland-Wexler formula.

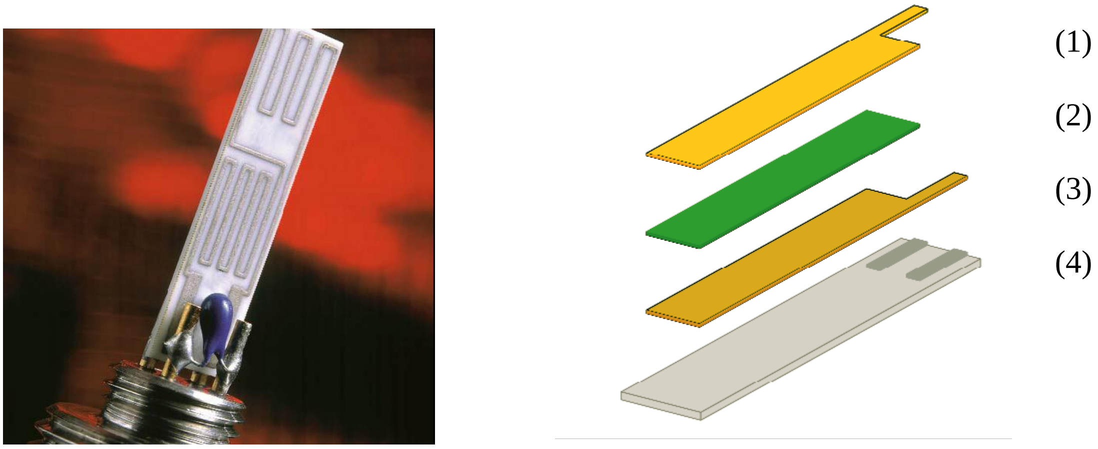

Figure 3-7 TD 2 sensor is an aluminium oxide sensor Michell series 2000 (Michell instrument user guide)

An example of a dew point impedance sensor is the Michell instrument. The principle of operation is based on the absorption of water vapour onto a porous, non-conducting substance packed in-between conductive layers built on top of a ceramic substrate base (Figure 3-7). The impedance layers for the Michell ceramic sensor are (1) Surface conductive layer, (2) Hygroscopic active layer (3) Conductive layer and (4) Ceramic substrate. Figure 3-8 shows another aluminium oxide sensor developed by Alpha moisture system used in the experiment.

Figure 3-8 TD 3 sensor is an aluminium oxide sensor Alpha DS2000 (Alpha moisture system user guide)

In conclusion, there are at least ten different types of humidity sensor. Out of these, three were selected in this research. Chilled-mirror hygrometers, based on the condensation principle, have the highest precision and so are used as national standard hygrometers. However, this type of sensor is not designed to be portable and is less tolerant. Capacitive sensors are more suitable for measuring relative humidity than absolute humidity, although dew point temperature is focused on in this research. The calculation to convert dew point to relative humidity should be investigated and accounted for as a source of uncertainty. Aluminium oxide sensors are used to measure dew point and have quite a wide range of usage. Compared with chilled-mirror hygrometer, they have a larger uncertainty, but are portable. Water vapour pressure has to be measured and this is described in the next section.

3.6 Pressure sensor

Pressure is a highly important variable in humidity measurement because it affects the water vapour pressure in gases. Pressure can be measured by many techniques using both direct and indirect methods. One of the direct methods uses the resistive principle and is widely used in most control systems operating with electrical signals. This research is to measure water content and dew point in gases, so the selected pressure sensor must be gas species independent. For that reason, a strain gauge sensor, based on the resistive principle, is studied in this section.

In a resistive sensor, pressure causes a change in the resistance by mechanically deforming the sensor, enabling the resistor in a bridge circuit, for example, to detect pressure as a proportionally different voltage across the bridge. Conventional resistive pressure measurement devices include film resistors, strain gauges, metal alloys and polycrystalline semiconductors.

Strain gauges are devices whereby their electrical resistance changes when they are strained; either by extending or compressing them. These gauges are bonded to, or embodied in, a diaphragm and can be used to measure the pressure induced movement of the diaphragm in a pressure sensor. Four gauges: A, B, C and D are connected in a Wheatstone bridge circuit as shown in

Figure 3-9. The phenomenon of a change in resistivity due to strain, induced by mechanical force, is known as piezo-resistivity and this effect is exhibited by most conductors and semiconductors.

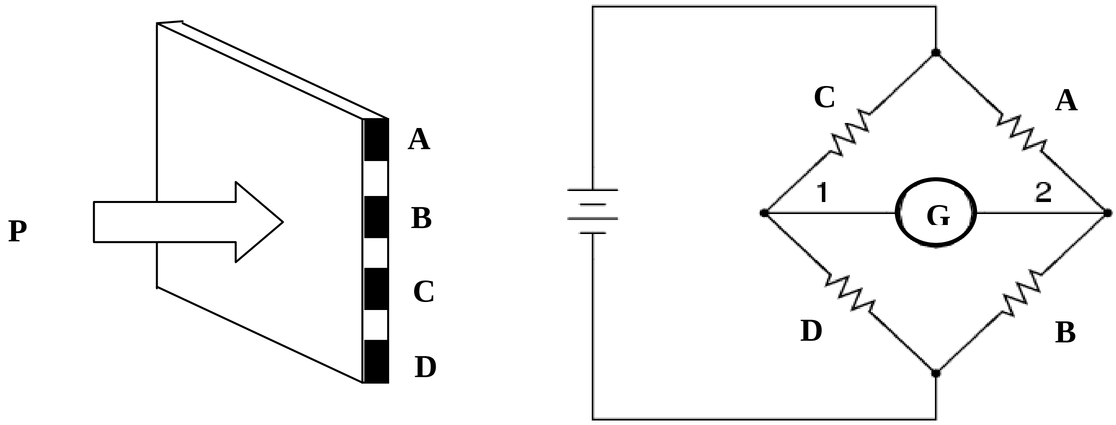

Figure 3-9: The pressure sensor with the Wheatstone bridge

When a gauge’s wire is stretched, because of the change in the diaphragm, its resistance will increase by an amount related to geometry and piezo-resistivity and can be expressed as:

$$\frac{\Delta R}{R} = \Sigma \frac{\Delta L}{L}$$ **Equation 3-2**

Where R is the resistance of the wire, Σ is the constant of proportionality (known as the gauge factor) and L is the length of the wire. The gauge factor in a semiconductor is typically about fifty times greater than that in a metal. This makes semiconductor sensors far more sensitive and suitable for use as strain gauges (Guide to the measurement of pressure and vacuum, 1998).

Figure 3-10: The pressure transducer Sensor Technics series CTE8000 used in the mass flow-mixing generator.

The four pressure transducers, based on the resistive principle, are used in the experimental system as shown in Figure 3-10. Pressure transducers P 1 and P 2 are used to measure the inlet pressure of wet gas and dry gas respectively in the range up to 10 bar. P 3 is used to measure pressure at the mixing unit and P4 is to measure the pressure of the bled gas from the first dilution with a 2 bar pressure range. In addition, P 3 operates as a pressure controller, whilst P 1, P 2 and P 4 are for measurement only. The uncertainty of these sensors, as stated in the manufacturer’s data sheets, is ±0.5% full scale of pressure. This is a source of uncertainty for the mass flow-mixing generator.

In conclusion, because the research was intended to find the difference in humidity sensors for various gases, the pressure sensor selected must be gas species independent. A strain gauge type is suitable not only it operates independent of gas species, but also because of its convenience of use. The flow-mixing generator will be studied in the following section.

3.7 Experimental set-up

The mass flow-mixing generator is assembled for the experiment of humidity measurement in water-methane and water-helium mixtures. The system can be separated into three main parts, namely: inlet, mixing, and outlet units. A description of the system and discussion of the device combinations are presented in this section.

	Instrument list	Range
1.	Wet gas unit	
	MFC N	2 l/m
	MFC (H_2O)	1 l/m
	P1	10 bar
	V1	-
	CMD1	4 channel
	SHG1	-75°C to
	Bleeding unit	
	Hygro 1	-60 °C
	Hygro 2	
	P 4	2 bar
	Dry gas unit	
	MFC 2	5 l/m
	P 2	10 bar
	CMD 2	4 channel
	V2	-
	Gas cylinder (He, CH_4)	285 l
	Compressed air	
	GE	-70 °C, 7 bar
2.	Mixing unit	
	STANDARD 1/STANDARD 3	
	Test Device 1 (TD1)	
	Test Device 2 (TD2)	
	Test Device 4 (TD4)	
	P3	
	MFC 3	
	CMD	
	V 3	
	Multimeter	
	PC	
3.	Outlet unit	
	STANDARD 2	
	MFC (dilutor)	

Table 3-2: The instrument list assembled within the FMG was arranged in three units including the instrument's range. These units were wet gas, mixing and outlet.

Table 3-2 and Table 3-3 outline the instruments and hygrometers gathered in the mass flow-mixing generator.

Humidity sensors	Sensor type	Dew point range	Pressure range
1. STANDARD 1	Chilled-mirror	-100 to +20°C	2 bar
2. STANDARD 2	Chilled-mirror	-100 to +20°C	2 bar
3. STANDARD 3	Chilled-mirror	-75 to +80°C	1 bar
4. Test Device 1 (TD 1)	Polymer	-60 to +20°C	10 bar
5. Test Device 2 (TD 2)	Aluminium oxide	-80 to +20°C	300 bar
6. Test Device 3 (TD 3)	Aluminium oxide	-110 to +20°C	400 bar
7. Test Device 4 (TD 4)	Aluminium oxide	-100 to +20°C	34 bar
8. Hygro 1	Polymer	-60 to +80°C	-

Table 3-3 The hygrometer sensor specification used to measure dew point of the mass flow-mixing generator

The mass-flow mixing generator consists of three units, namely the inlet, mixing and outlet units. The inlet unit includes the standard humidity generator (SHG 1), dry air supply and gas bottles. The outlet unit contains the standard chilled-mirror hygrometer and a flow dilutor. The mixing unit is composed of four mass flow controllers, four pressure transducers and the standard chilled-mirror hygrometer. Stainless steel pipe is used to connect all these instruments (Figure 3-11).

3.7.1 The inlet unit

The standard humidity generator (SHG 1) produces wet gas into the system. The uncertainty of the generator is ±0.10 °C at -75 °C, ±0.06 °C at -70 °C, ±0.03 °C from -60 °C to 60 °C and ±0.04 °C from 70 °C to 82 °C. The gas generated from SHG1 to the flow generator is at 15 °C and at 4.5 bar G through PTFE pipe between five and ten metres in length (because SHG1 and the flow mixing generator are not in the same room). Although PTFE is suitable for air above -20 °C, the inlet pressure will drop because of the length of the PTFE pipe. This pressure drop at the inlet is probably insignificant to the flow generator system as long as the wet and dry gas inlet pressures are balanced. The

International Standard for compressed air quality has a simple form of classification for the three main contaminants present in any compressed air system (dirt, water and oil). The dry gas is supplied by the NPL compressed air supply. The Pneudri DM002 is classed for contaminants: dirt 1 micron, water -40 °C to -70 °C dew point and oil 0.01 mg/m^3. The dew point of dry gas is -73.15 °C as measured by the standard hygrometer MBW E and the uncertainty for that hygrometer is ±0.05 °C.

3.7.2 The mixing unit

The mixing unit consists of mass flow controllers (MFCs), pressure transducers, test hygrometers and a standard chilled-mirror hygrometer. There were two steps of dilution. 1.0 litre per minute of wet gas flows from SHG 1 to MFC N and 0.9 litres per minute was bled to measure dew point and pressure of wet air at atmospheric pressure. Two hygrometers, Hygro 1 and Hygro 2, were used to measure dew points and relative humidity of wet gas in the first step dilution. Pressure transducers P1 and P2 measured the pressure at the wet and dry gas inlets. The 0.1 litres per minute of wet gas flows through MFC1 and the dry gas flows through MFC 2 in the second step dilution. The MFC 1 and MFC 2 range was 1 litre per minute and 5 litres per minute. The flow rate setting should be no lower than 2% of full scale because of large errors, so the set point of MFC 1 and MFC 2 is 0.1 litres per minute and 2 litres per minute. The test hygrometers are connected in series and were in parallel to the standard chilled-mirror hygrometer. The test hygrometers were: TD 1, TD 2 and TD 3. The TD 1 sensor was a capacitance type with an operating range from -20 °C to +60 °C and up to 10 bar, whereas TD 2 and TD 3 are aluminium oxide type sensors. The operating range of TD 2 was from -80 °C to +20 °C and up to 300 bar, and for TD 3 was from -110 °C to +20 °C and up to 400 bar. STANDARD 1 was a standard hygrometer based on the condensation principle with an operating range from -100 °C to +20 °C and up to 10 bar. The maximum pressure that the generator could produce was 2 bar. A regulating valve is at the inlet to MFC2 in order to control the dry gas from the methane and helium gas cylinders. The cylinders contain ~200 litres at 4 bar. The dew points of methane and helium are -73.56 °C and -62.25 °C respectively. In theory, the dew point of these gases should be the same for a comparison, so this should be included as a source of uncertainty in measurement.

3.7.3 The outlet unit

The outlet unit contains the standard hygrometers STANDARD 2 and MFM. STANDARD 2 measured the mixed gas at ambient pressure and the range of STANDARD 2 is similar to that of STANDARD 1. MFM is to dilute the mixed gas to the atmosphere with a flow rate up to 30 litres per minute.

In summary, the experimental set-up was separated into three main parts: The inlet unit was where the wet gas generated by SHG 1 and the dry gas supplied by the compressed air and gas cylinders was mixed. Methane and helium, supplied by the gas cylinders, were used as the carrier gases in the humidity measurement for the hygrometers. Wet and dry gas flows from MFC1 and MFC2 to mix in the mixing unit where the pressure was adjustable up to 50 atmospheres. Three test hygrometers and a standard hygrometer measured the mixed gas dew point and afterwards it was released to the atmosphere. The mixed gas was measured by STANDARD 1 at the inlet at atmospheric pressure and the MFM was to dilute that gas mixture. The protocols for the experiments are outlined in the following section.

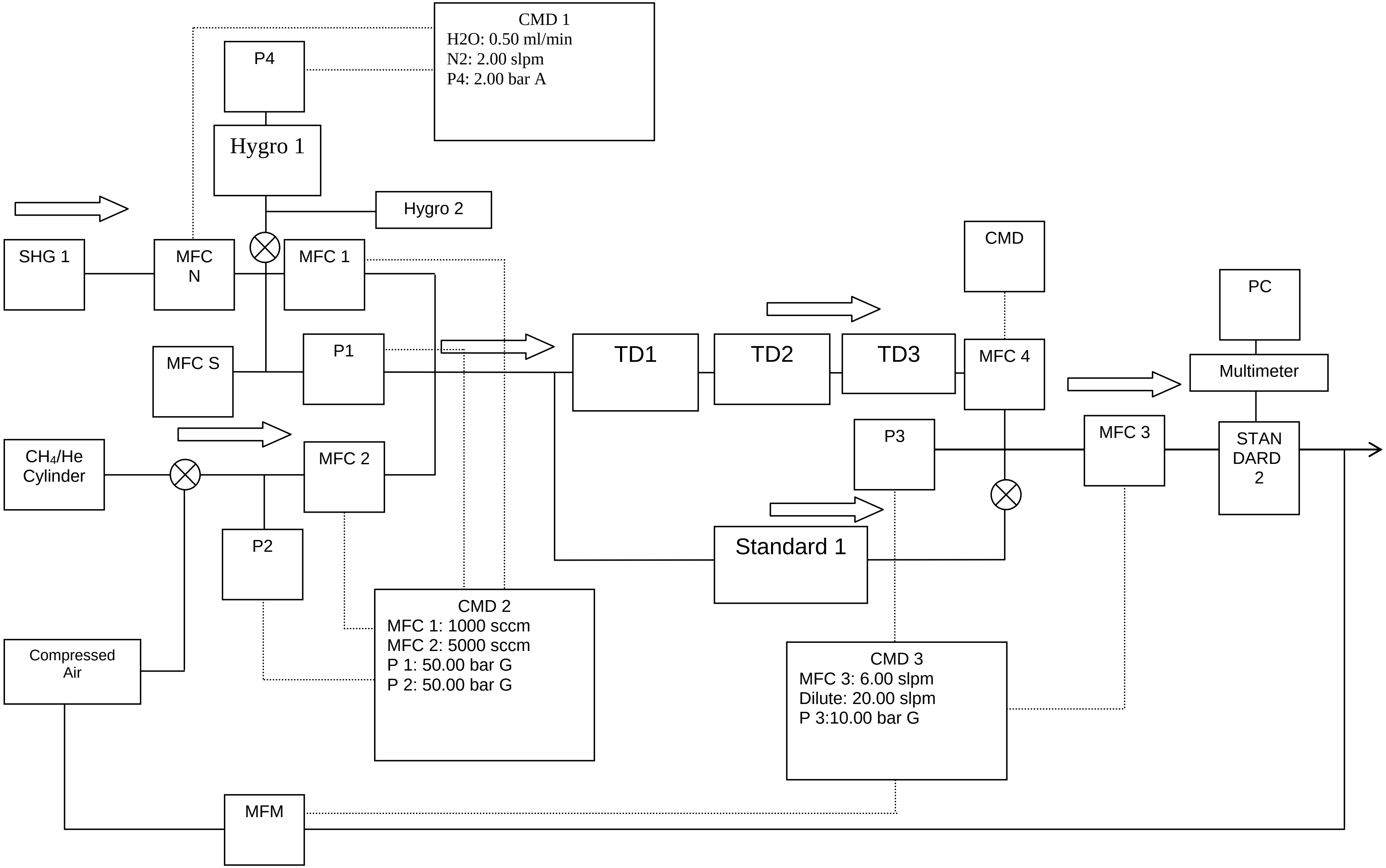

Figure 3-11: The FMG consists of the inlet, mixing, and outlet units. The two-step dilution includes five mass flow controllers and two pressure sensors in the inlet unit. Three test hygrometers TD 1, TD 2 and TD 3 are connected in series and parallel with STANDARD 1 in the mixing unit. In the outlet unit STANDARD 2 will measure humid gas dew points and the gas will be released to atmosphere.

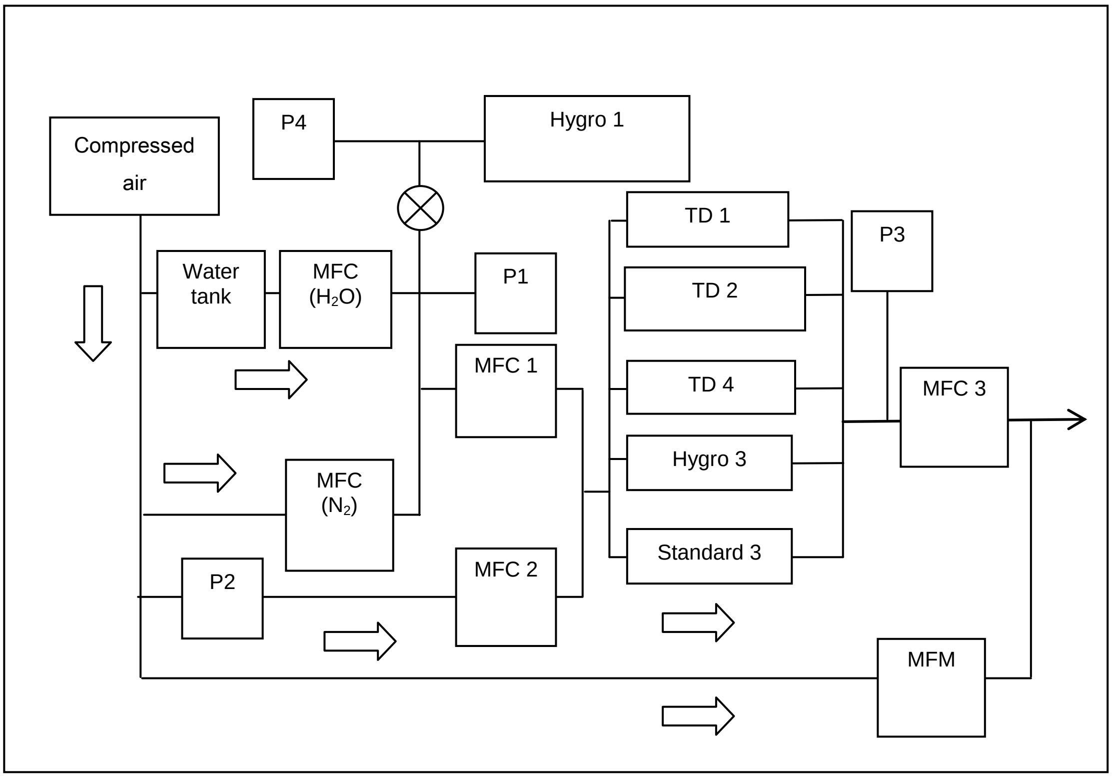

Figure 3-12 The FMG first protocol shows water tank that was mounted to generate liquid water to the system. The test hygrometers and STANDARD 3 are connected in parallel to measure humid gas dew point.

The set-up shown in Figure 3-12 this was used to study the mass flow-mixing generator. As in the previous set-up there were three main units: inlet, mixing and outlet units. The water tank supplies liquid water. Dry gas was provided by the laboratory's compressed air supply via an air dryer. Test hygrometers and the standard hygrometer were connected in parallel in the mixing unit. All the mixed gas was released to the atmosphere when the measurement was completed.

The inlet unit consists of compressed air and a water tank. Liquid water was pressurised by compressed air at -55 °C dew point passing through MFC (H_2O). Dry gas, provided by the laboratory's compressed air supply via Pneudri DM2000, flows through MFC N and MFC 2.

Liquid water controlled by MFC (H_2O) and dry gas from MFC N are mixed in the first dilution. Wet gas is bled to atmospheric pressure so that TD1 measures its dew point at atmospheric pressure. To prevent condensation, the heated line and heated box are insulated from MFC (H_2O) to MFC 1. The wet gas from MFC 1 and dry gas from MFC 2 are mixed in the second stage dilution. TD1, TD2, TD4, Hygro 3 and the standard hygrometer STANDARD 3 were connected in parallel. TD 2, TD 4 and Hygro 3 hygrometers were aluminium oxide sensors. TD1 was a capacitance sensor and STANDARD 3 was a chilled-mirror hygrometer.

After measuring the mixed gas, the total gas flows through MFC 3 and MFM which will dilute that gas before releasing to the atmosphere.

3.7.4 The first protocol

Several points should be discussed about this protocol (Figure 3-12) and these are: The liquid water used, an MFC blockage and sensor connection. This research was intended to measure dew point in humid gas. To generate humid gas, dry gas (air, methane and helium) and liquid water has been mixed by flowing through MFC (N_2) and MFC (H_2O). However, this method did not work because there was no flow through MFC 1. It was presumed that water condensed inside MFC 1 and prevented the gas flow.

The MFC (H_2O) range is 0.5 millilitres per minute. It has been found that the small amount of water required is difficult to control. Practically, these results are not consistent because the MFC 1 flow did not occur. It was assumed that a water droplet was causing a blockage inside the capillary tube of MFC 1. Without flow sensing, the MFC 1 valve was automatically closed and to solve this problem MFC 1 was heated up to remove the water droplet. An unnecessary spring above a plunger seat to control the gap flow of the MFC 1 was present and caused the flow to stop, but this was solved after the spring was removed. The parallel connection was practically effective because the mixed gas runs directly through each sensor, where the values were more accurately measured than that of sensor connection in series. An unequal flow occurred however, when the sensors were connected in parallel. A mechanical flow meter could be mounted, but the mixed gas will diffuse and will be uncontrollable. Also, the pressure cannot rise because that gas escapes to atmosphere. Thus, these sensors were connected in series for the final protocol.

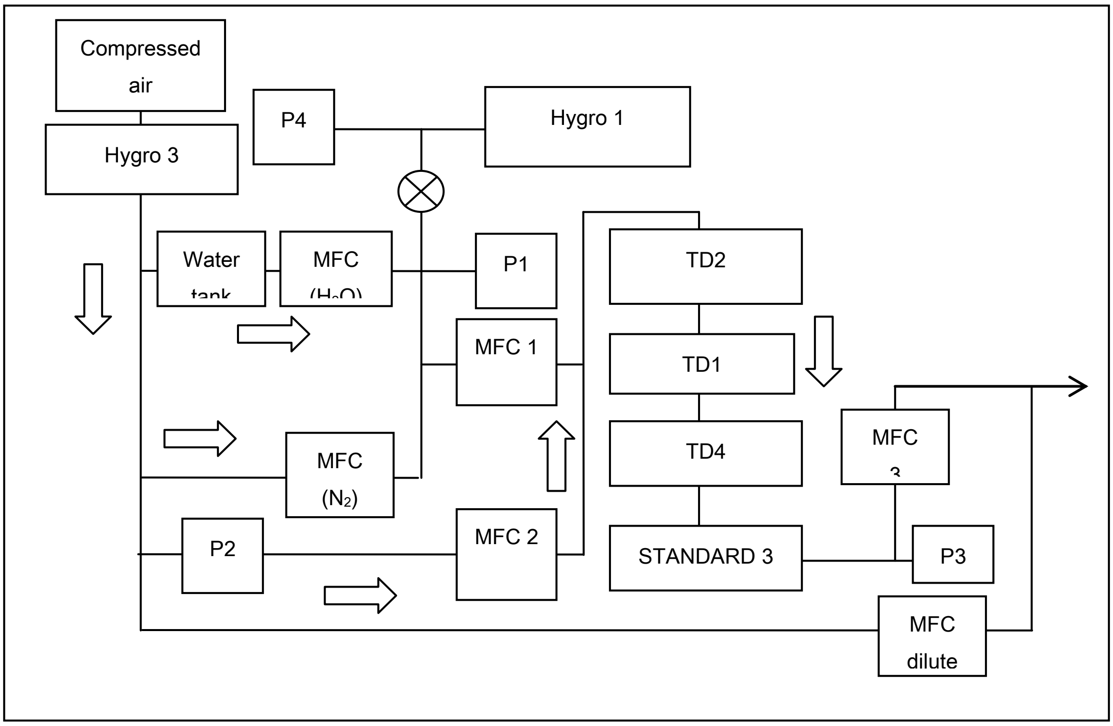

Figure 3-13 The second FMG protocol shows the series connection in TD1, TD2, TD4, and STANDARD 3.

3.7.5 The second protocol

The protocol for the mass flow-mixing generator was connection in series for sensors as shown in Figure 3-13. There are still three main units: inlet, mixing and outlet units. To control the pressure in the mixing unit, TD 2, TD 1, TD 4 and STANDARD 3 were connected in series. The Hygro 1 was replaced to measure dry gas dew point.

Since the large fluctuation was in MFC (H_2O) causing the erroneous results, the water tank and MFC (H_2O) was removed. Therefore, SHG 1 was used to generate wet air instead. Despite the fact that SHG1 has minimum changeability, it results in less than 5% of air composition in water-methane and water-helium mixtures and its maximum pressure is no more than 3 bar A – this is unsuitable for very high pressure experimental conditions.

STANDARD 1 replaced STANDARD 3 because it was not working. STANDARD 1 was the standard chilled-mirror hygrometer in addition to STANDARD 3. TD4 was exchanged for TD3 because it was unusable. It should be pointed out that STANDARD 1 was not designed to measure dew points at pressures greater than 3 bar in the mixing unit. The experiment showed that gas leaks at the measurement head. Therefore, STANDARD 1 should be capped off before the pressure rises above 3 bar. It was found that MFC 3 could not control pressure at the mixing unit because of the wrong size orifice and so the problem was corrected. Also, STANDARD 2 has been located at the outlet to measure the mixed gas at atmospheric pressure.

In summary for this section, the three main parts for the mass flow-mixing generator were the inlet, mixing and outlet units. Wet gas was generated from SHG 1 instead of flowing liquid water to the system as this caused large fluctuations in a flow controller. Dry gas was provided by the laboratory’s compressed air supply, whereas methane and helium were obtained from gas cylinders. The first protocol was to arrange the sensor connection in parallel, whereas the second was in series. It was found that the series connection is slightly better for this simple system at present in spite of leading to inaccurate measurements within the sensors. The mixed gas was measured by the first sensor and repeatedly measured by the second sensor. The second sensor results will not be exactly correct. The calculation for the flow-mixing generator is studied in the next section.

3.8 Flow rate calculation

The flow rate calculation is based on mass conservation principle as follows:

$$Mass\ of\ \ wet\ gas + Mass\ of\ \ dry\ gas = Mass\ of\ \ humid\ gas$$ **Equation 3-3**

The dew point of wet gas and dry air must be known to calculate the mixed gas dew point. The wet gas dew point measured at atmospheric pressure is -3.2 °C. To convert the dew point to saturation vapour pressure of water, the Sonntag formula over ice is applied as in equation 7-2 and that comes out as 468 Pa. This value has to be converted into specific humidity (kg/kg). Specific humidity is defined as a mass of water vapour per unit mass of humid air, which is:

$$Y_w = \frac{\frac{M_v}{M_g} p'}{\left(P - p' + \frac{M_v}{M_g} p' \right)}$$ **Equation 3-4**

Its value for wet gas at -3.2 °C will be 2.9×10^{-3} where M_v and M_g are molecular weight of water and dry air, p' is saturation water vapour pressure, P is total pressure and Y_w is specific humidity. This value is converted to density of humid gas as in the following equation:

$$\rho_g = \frac{M_g}{RT} \left(P - p' + \frac{M_v}{M_g} p' \right)$$ **Equation 3-5**

The value for density of humid gas is 1.2 kg/m^3 where ρ_g is humid gas density. The absolute humidity is evaluated as:

$$d_v = Y_w \rho_g$$ **Equation 3-6**

The equations 3-3 and 3-6 lead to:

$$\left(Absolutehumidity \times flowrate\right)_{wet\ gas} + \left(Absolutehumidity \times flowrate\right)_{dry\ air} =$$

$$\left(Absolutehumidity \times total\ flowrate\right)_{mixed\ gas}$$ **Equation 3-7**

The absolute humidity for wet gas and dry air are 3.46 g/m^3 and 1.2×10^{-3} g/m^3 respectively. The flow rate for wet gas and dry gas are 0.1 litres per minute (4.7% of total mixture) and 2.0 litres per minute (93.7% of total mixture) respectively. The sum of wet gas and dry gas flow rates is total gas flow rate. Therefore, the absolute humidity for mixed gas is calculated and that is approximately 0.17 g/m^3, equal to -35.0 °C dew point of mixed gas. The use of the Magnus formula to convert saturation vapour pressure to dew point is easier than using the Sonntag formula.

Equation 3-3 can, however, be used in methane and helium. The ISO equation of state is alternatively chosen to calculate the flow of the system. The ratio of wet gas and dry gas remain similar by adjusting the flow rate of methane and helium to produce the same water concentration at the outlet. These are ~4.7% of wet gas and ~93.7% of dry gas. The dew point of dry air is -73.15 °C (1.67 ppm), methane is -73.56 °C (1.52 ppm) and helium is -65.73 °C (4.86 ppm).

In conclusion, the literature survey of published experiments shows that there were overlapping regions for water-nitrogen and water-methane. The similar range of data will be compared in the following chapter. In some published results the water content and water dew point were not accurate – it was presumed that either the chosen conversion formula is not suitable for the operation range or there are experimental mistakes. In addition, the flow-mixing generator was easy to make various combinations, but it has too many dependent variables. The dew point, and two-pressure and two-temperature generators benefit from high precision, although they are complicated practically. The chilled-mirror hygrometer was used as a standard hygrometer for the flow-mixing generator and the three tested hygrometers based on capacitive sensor types were included in the experiment. The flow mixing generator uncertainty and calibration results for the test hygrometers will be given in the next section.

4 Analysis of results

This section will present the results obtained by the standard hygrometers STANDARD 1, STANDARD 2 and the FMG. The measurement uncertainty associated with STANDARD 1, STANDARD 2 and the FMG is presented. Three hygrometer sensors TD 1, TD 2 and TD 3 were calibrated against the standard hygrometers and FMG to see how they responded to different gases.

The carrier gases used in this research have different atomicity. Atomicity is defined as the number of atom in a molecule. It may have an effect on the humidity sensors when the experiment is operated under non-ideal conditions. Non-ideality condition is about the interaction between gas molecules and happens even under ambient air conditions. The formulae used in the humidity calculations, therefore, need to consider these interaction parameters named the virial coefficients. The molecular interaction may be dependent on gas atomicity. (Equation 2-2)

The ISO equation of state was chosen to calculate water vapour pressures and the enhancement factors in the carrier gases. The results were compared with the values calculated by Bögel’s and Hardy’s equations.

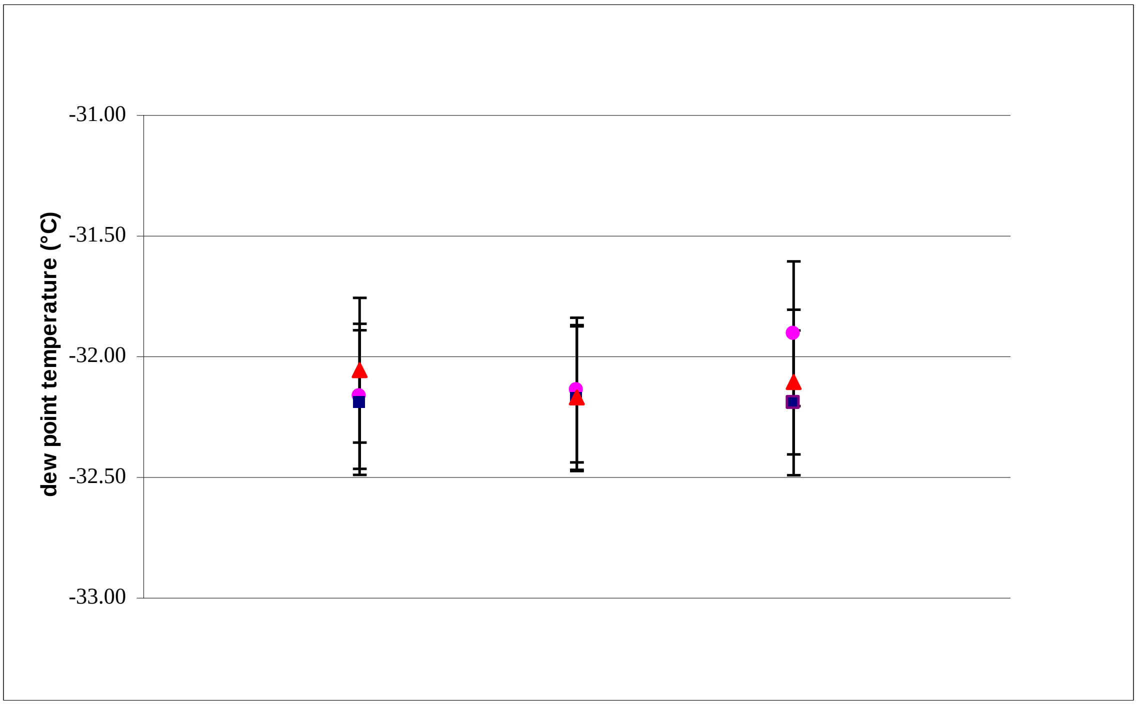

Figure 4-1: Water dew point in air, methane and helium measured by STANDARD 1 (●), STANDARD 2 (■), and the FMG (▲) with the error bars at 1.5 bar A.

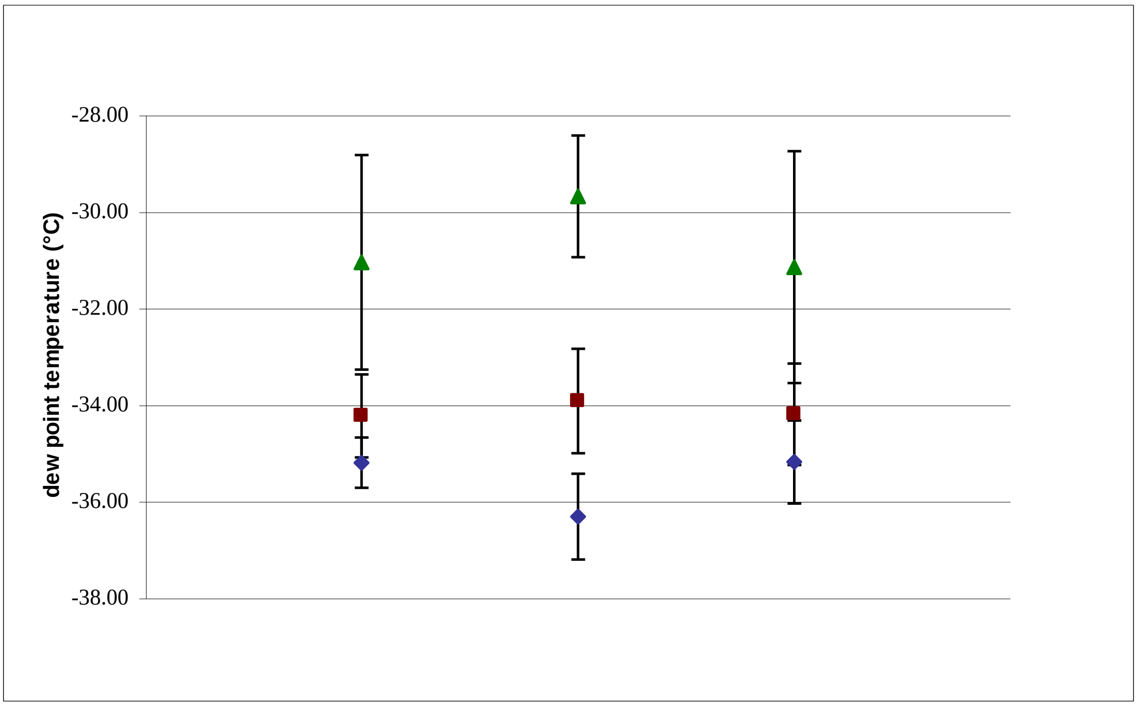

Figure 4-2: Water dew point in air, methane and helium measured by TD 1 (◆), TD 2 (■) and TD 3 (▲) with the error bars at 1.5 bar A.

The results of water dew point measurement in air, methane and helium as measured by the standard hygrometer (Figure 4-1) and the test hygrometers (Figure 4-2) are shown. Two points are to be considered: Firstly, the calculated water dew point value of humid gas generated by the FMG is investigated and the comparison of the results has been made against the standard hygrometers. The uncertainty of the FMG and the standard hygrometers are also evaluated. Secondly, the calibration of the three test hygrometers; TD 1, TD 2 and TD 3 are made against the standard hygrometer STANDARD 1 and the FMG in the different gases.

The calculation of the water dew point in humid gas generated by the FMG is completed by the Sonntag formula (over ice) Equation 7-2 for air and the ISO equation of state for methane and helium. Although the Humidity conversion software, HumiCalc, has the provision to allow for carrier gases other than air using Sonntag's and Hardy's formulas, in actual fact it is invalid for other gases. The use of Sonntag's and Hardy's formulas with complex molecules like methane will lead to large errors in calculation of humidity. So, instead the ISO equation of state can be applied to convert between water content (in ppm) and water dew point (°C). Helium is a monatomic molecule and is less complex than air or methane. Sonntag's and Hardy's formulas and the ISO equation might not be appropriate for humidity calculation in a monatomic gas like helium. However, the ISO equation was applied in argon.

The agreement between the theoretically calculated dew point values for the FMG and the experimental dew point values measured by the standard hygrometers STANDARD 1 and STANDARD 2 will ensure that the FMG is valid for generating humid gas. The dryness of wet gas is measured by Hygro 1 and the dryness of dry gas (air, methane and helium) has been measured by the standard hygrometer STANDARD 2 in terms of dew point. The dew point of mixed gas is not equal to the sum of wet gas and dry gas dew point. Therefore, it must be changed to another unit – hence this is the reason why the conversion equations are essential. From Figure 4-1 and Figure 4-2 it could be superficially concluded that the measured and calculated values are in agreement since the calculated dew points overlap in the range of the measured values. However, an uncertainty evaluation for the standard hygrometers STANDARD 1, STANDARD 2 and the FMG must be made first. The uncertainty evaluation will verify agreement between the measured and calculated dew point values.

Although, the four repeated measurements are apparently small in methane and helium, they are assured to be reproducible. Reproducibility of the Standard Hygrometer (4.1.3) and the test sensors (4.4.3 and 4.5.1) was evaluated from the standard deviation of only four actual measuring. This is why the hygrometer sensors' reproducibility of was too large than it was expected. The large number of measurement will minimise the uncertainty due to reproducibility of these sensors.

These hygrometer sensors have been calibrated, so their uncertainty will be small or smaller than before calibrating because a correction value was added to the hygrometers.

4.1 Uncertainty evaluation of the standard hygrometer STANDARD 1

STANDARD 1 has been calibrated against the NPL Low Frost-point Generator (LFG) where dew point measured values have been collected between June 2003 and January 2007 (Figure 4-3). The range of dew point measurement is from -75 °C to +20 °C. The error bars are to show the measured values at the 95% confidence level (~±0.13 °C). The equation and the curve are estimated from the entire measuring range and are obtained from Excel.

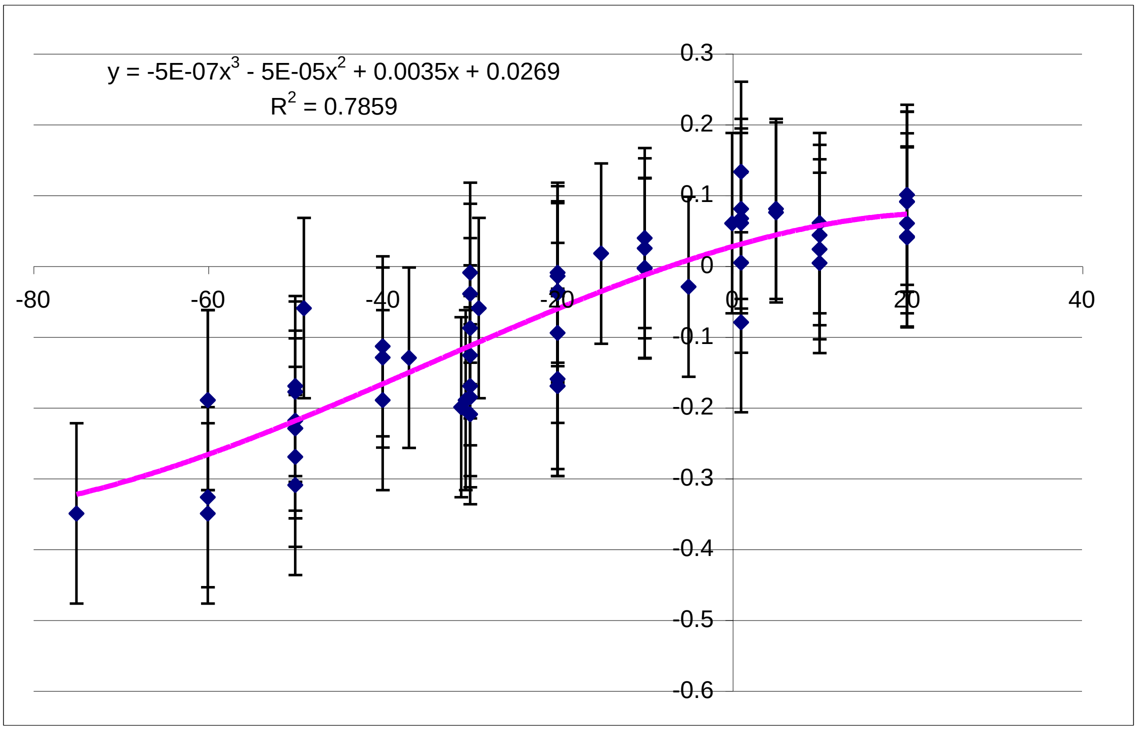

Figure 4-3: The calibration correction value (◆) for the standard hygrometer STANDARD 1 with dew point from -75 °C to +20 °C. The curve shows the correction trend of STANDARD 1 for the whole range of dew point. The error bar of the correction value shows the uncertainty of value at the 95% confidence level (k=2). The x-axis represents the dew point temperature range and the y-axis is for the correction values against the LFG. (NPL the standard hygrometer STANDARD 1 Excel spreadsheet, 2008)

4.1.1 Calibration of the standard

The standard hygrometer STANDARD 1 has been calibrated against the Low Frost-point Generator (LFG) at NPL from -75 °C to +20 °C and the calibration correction dew point values for STANDARD 1 is shown in Figure 4-3. The LFG is a humidity generator used for the low range dew point humidity standard generator over the range -90 °C to +90 °C. The expanded uncertainty of calibration of the LFG is reported in the document *Operation and Maintenance Manual for the Dew point Generator LFG and SHG 2* (Stevens, 2004) with a coverage factor *k*=2 or at the 95% confidence level at –30 °C is ±0.03 °C. The probability distribution for the calibration of the standard is a normal distribution (divisor = 2). The standard uncertainty is ±0.02 °C.

4.1.2 Long-term stability

The change in an instrument’s measurement performance with respect to time will be as a result of gradual drift and/or sudden shift. It can occur in the measurement characteristics of any instrument. Stability can be quantified by calibrating the instrument at regular intervals. The drift of the LFG as reported in the NPL data sheet is between ±0.1 °C at -75 °C and ±0.05 °C at +20 °C. The drift figure for the standard has been obtained from the difference between two recent calibrations and it can be estimated that the STANDARD 1 drift will be ±0.10 °C at ~-30 °C. The probability distribution of long-term stability is treated as a rectangular distribution (divisor = √3), and gives a standard uncertainty of ±0.06 °C.

4.1.3 Reproducibility

Reproducibility is the ability of an instrument to reproduce the previous measurement and is the largest (dominant) source of uncertainty. The reproducibility of STANDARD 1 is obtained from the standard deviation of repeated actual measurements. The standard uncertainty is different in each carrier gas as shown in Figure 4-1. The standard uncertainties are ±0.08 °C for air, ±0.12 °C for methane and ±0.08 °C for helium.

4.1.4 Non-linearity

It can be pointed out that the STANDARD 1 non-linearity can be evaluated directly from the measured dew point value shown in Figure 4-3. The probability distribution is normal (divisor = 1). The standard uncertainty for non-linearity is ±0.07 °C.

4.1.5 Contamination

Stevens (2004) reported in the document *Operation and Maintenance Manual for the Dew point Generator LFG and SHG 2* that any contamination will affect the generated dew point. Contaminants will enter the system with water or with air. The level of contamination may be made by measurement of the conductivity of the water. Based on Raoult's law, 10 μS cm^{-1} of water conductivity will give a reduction in vapour pressure equivalent to 0.002 °C dew point. The level of contamination has been estimated as not being larger than the resolution of MBW A. The contamination could be estimated not larger than its resolution. The uncertainty of the water and air contamination is assumed to be ±0.01 °C and therefore the standard uncertainty is ±0.006 °C.

4.1.6 Temperature gradients in the mirror

The Peltier is designed to transfer heat from the mirror in the chilled-mirror hygrometer and it causes unbalancing of the temperature gradient in the mirror. The temperature gradients in the mirror can be considered in two regions-the top surface and the contact surface between the mirror and the Peltier. The temperature at the boundary is colder than the top surface because of the Peltier. The PRT that is embedded underneath the mirror surface may not measure the actual temperature of the mirror because there is a temperature difference between the two regions. The effect of temperature gradients in the mirror can be measured, but may be as small at ~10 mK. The temperature gradient need not be taken into account if the temperature difference is constant across the whole range of measured dew points. However, in practice, though, the temperature gradient is dependent on the dew point. The temperature gradient uncertainty should not be greater than the resolution of STANDARD 1, and gives a standard uncertainty contribution of ±0.006 °C.

4.1.7 Temperature gradient in condensate

The temperature gradient in the condensate may be considered in the same way as the temperature gradient in the mirror. The condensate is the condensed material (i.e. liquid water or ice). The temperature of the water or ice film may not be uniformly distributed and the water or ice film contact surface with the mirror is colder than the top surface.

The temperature gradient in the condensate could have a very small effect with the limit of variation that is not larger than the resolution of STANDARD 1 (±0.01 °C). This gives a standard uncertainty of ±0.006 °C.

4.1.8 Pressure gradients in the mixing unit

A difference in pressure between a humidity generator and a calibrated sensor can cause a flow of gas, and the water dew point at the generator to be higher than the dew point at the sensor. Any pressure difference between the LFG and STANDARD 1 sensor could be the cause of changes in the dew point. The effect of pressure drop depends on the flow rate and the length/diameter of the pipe that is used to connect the generator and the sensor together. Measuring the pressure at the generator and at the sensor can be used to determine the pressure drop effect. The pressure drop in the hygrometer can also occur if something restricts the flow. The flow meter used that measures the flow rate should not constrict the flow so as not to prevent the pressure drop in a hygrometer and an external instrument should control the flow. The limit of pressure drop in STANDARD 1 is estimated to be ±0.02 °C at -75 °C and ±0.03 °C at +20 °C. It can be assumed that the uncertainty of the pressure difference at around -30 °C should be no more than ±0.02 °C. STANDARD 1 was connected in parallel with the test hygrometers where the mixing unit pressure condition was controlled by the external pressure controller P 3. There is a needle valve to divide the flow between STANDARD 1 and the test hygrometers and it may cause the pressure drop in the measuring unit. The limit of pressure drop in STANDARD 1 is estimated to be ±0.01 °C. The standard uncertainty due to the pressure gradient is ±0.006 °C.

4.1.9 Temperature fluctuation in the mirror

The optical detection feedback to the Peltier of the chilled-mirror hygrometer causes temperature fluctuation in the mirror. When the water or ice film is formed on the mirror surface, the automatic film detection system will heat up and the film will melt down. The sensor detection system will send a signal to the peltier and the peltier will cool down the mirror and form a new water or ice film. The limit of variation is assumed to be ±0.01 °C and is not larger than the resolution of STANDARD 1. The standard uncertainty will therefore be ±0.006 °C.

4.1.10 Desorption in the pipework

The desorption effect will be dominant at very low moisture content. Water vapour can get trapped within the pipework. The dew point of gas will increase due to any remaining water vapour. For STANDARD 1, it is reported that the effect is assumed to be ±0.29 °C at -75 °C. At higher dew points this effect is negligible (e.g. +20 °C). The limit of variation is assumed to be ±0.05 °C, and gives the standard uncertainty ±0.03 °C.

4.1.11 Self-heating effect

The hygrometer sensor will heat up due to the electrical current supplied to it. Excessive heat will cause measurement errors and this is known as self-heating effect. Downs et al (1990) stated that magnitude of self-heating in PRT has resulted in changes in the dimensions of the sensor involved and the rated value of circulation of the air. Pramanik et al (2004) proposed the idea for calculating the self-heating effect in the pressure sensor. Their results are on very large scale where the temperature is up to 30 °C in twenty hours, whilst the calibrated PRT in the laboratory will be affected by 0.5 °C per milliwatt. The effect can be measured by plotting a graph of gas velocity (m/s) against another measure quantity (ie dew point, relative humidity etc). If the measured value varies as the gas velocity, the sensor will suffer from self-heating effect. The effect will be decreased when the compensated gas flowing is added up. The uncertainty of the self-heating effect will not be larger than the instrument’s resolution (±0.01 °C). The standard uncertainty for the self-heating effect therefore is ±0.006 °C.

4.1.12 Resistance Bridge and DVM uncertainty evaluation

The uncertainty of the resistance bridge and of the digital voltmeter (DVM) used to convert the humidity data measured by the hygrometer into an electric signal should be evaluated. Although, the effect of the resistance bridge and the DVM uncertainty is very small, it is good practice to take them into account. In the future however, it is foreseeable that the resistance bridge and the DVM be replaced by something else (e.g. PC interface card modern, computer control systems) and the uncertainty contribution of these instruments need not be included.

4.1.13 Combination uncertainty

The combined standard uncertainty is obtained from taking the square root of the sum of the squares of the individual standard uncertainties of the contributory components – a method often referred to as “adding in quadrature”. The standard uncertainties are assumed to be un-correlated. However, some standard uncertainties may be related to others and will have an effect on the overall uncertainty. There is a need for some statement of confidence in most fields of measurement that are associated with a calculated total measurement uncertainty. The expanded uncertainties are based on the combined standard uncertainties multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95%.

In conclusion then at around -30 °C the combined standard uncertainty of STANDARD 1 is ±0.13 °C for air, ±0.15 °C for methane and ±0.13 °C for helium (Table 7-1). The expanded uncertainty, with the coverage factor of $k = 2$ or 95% confidence level, is ±0.3 °C for water dew point measurement in air, methane and helium.

4.2 The uncertainty evaluation of the standard hygrometer STANDARD 2

It can be assumed that the uncertainty evaluation of STANDARD 2 can be approached in a similar way to that for STANDARD 1. However, reproducibility of the two hygrometers should be considered individually. The reproducibility of STANDARD 2 is calculated from the standard uncertainty of the actual measurements of dew point in the carrier gases. The standard uncertainty for reproducibility of STANDARD 2 is ±0.13 °C for air, ±0.11 °C for methane and ±0.08 °C for helium.

4.2.1 Combination of uncertainty

The expanded uncertainty of STANDARD 2 is ±0.3 °C for air, ±0.3 °C for methane and ±0.3 °C for helium (Table 7-2).

The largest source of uncertainty for STANDARD 1 and STANDARD 2 is reproducibility. Reproducibility is classified as a random uncertainty. To reduce or eliminate the random uncertainty the average of a large number of readings needs to be obtained. Some of the individual uncertainties that have only a small effect on the overall uncertainty can be reduced or eliminated altogether by calibration and, in spite of having only a small effect, these sources of uncertainties carefully should be stated to ensure that all eventualities are included. The cause of the large figure for reproducibility is because only a small number of measurements were taken in this research. Ten repeated readings were taken at each measurement point. At each measurement point, readings were taken after a stabilisation time of four hours. The long stabilisation time prevented large numbers of repeat measurements.

Three repeated readings by STANDARD 2 were -36.10 °C, -35.88 °C and –35.72 °C and standard deviation of these values is 0.19 °C. The standard deviation of actual measure is the standard uncertainty (where the divisor = 1). It is pessimistic because of small number of readings. A chilled-mirror hygrometer used as a national standard hygrometer usually have the expanded uncertainty less than ±0.1 °C. The two approaches are to be concerned with this situation. Firstly, a spurious error should be excluded from the data set as a result it leads to a large standard uncertainty. However, the large standard uncertainty of three reading values is caused by random errors. Alternately the possible solution is to take more reading. It is stated that random errors can be minimise and eliminate by a large number of reading.

The expanded uncertainty for STANDARD 1, STANDARD 2 and the FMG is expected to be less than ±0.3 °C at -30 °C, 1.5 bar.

4.3 The uncertainty evaluation of the Flow Mixing Generator (FMG)

The uncertainty evaluation of the FMG is considered on a basis of sensitivity. Small variations to the input of equation 3.3, within the limits of the parameters listed in the uncertainty budget, causes the changes in the water dew point or other units of water content results. It is not possible to sum the dew points of a wet gas and a dry gas in order to obtain the dew point of a mixed gas. In order to obtain the dew point of a mixed gas the value, in units of temperature, must be converted into another unit of water vapour pressure. Also, the water dew point, as measured by the hygrometers, should be converted to the units of mole fraction to avoid the effect of pressure dependency. Equation 3-3, 7-2 and HumiCalc are therefore needed to calculate the FMG uncertainty. Equation 3-3 is based upon mass being constant at any pressures and is designed to calculate the total flow of the FMG. Not only can equation 3-3 calculate water vapour pressure and mole fraction, but also absolute humidity and humid gas density can be multiplied by the flow rate. Equation 7-2 (or 7-1) is needed when these units are to be converted to the unit of temperature. As mentioned above the unit of temperature is still required because it is one of the SI units and widely used, but is not possible to add temperatures up together. A commercial software (HumiCalc) is used as a reference to ensure that the author's calculated results is right.

The setting for the calculation is at ambient pressure around 1.1 bar A, in order to make the calculation more simple, despite the fact that water content in mole fraction is independent of the environmental pressure.

4.3.1 Calibration of the standard

The FMG is calibrated against STANDARD 2. It is reported in the Certificate of Calibration that the uncertainty will be ±0.1 °C at around -30 °C. That value of uncertainty in degrees Celsius is equivalent to 2.0 ppm. The probability distribution is normally distributed and the divisor is 2. The standard uncertainty of the STANDARD 2 is at *k*=2, or at a confidence level of 95% and is thus ±1.0 ppm.

4.3.2 The dew point measurement in wet gas

It can be stated that all the humidity generators at NPL use only air or nitrogen as the carrier gas. Any other carrier gas can cause changes in the humidity generator performance. The wet gas stated in this research means air that is humidified by water vapour. Hygro 1 is a hygrometer based on polymer technology to measure the wet gas dew point that is generated by the Standard Humidity Generator (SHG 1). Hygro 1 is calibrated against STANDARD 2 and the uncertainty will be ±0.1 °C at -3.2 °C (equivalent to 4292 ppm ±36.2 ppm). The standard uncertainty resulting from equation 3.3 is ±0.86 ppm.

4.3.3 The dew point measurement in dry gas

The NPL compressed air system generates dry gas ~-75 °C as measured by STANDARD 2. As reported in the STANDARD 1 data sheet uncertainty evaluation, the uncertainty at -75 °C is ±0.4 °C. The uncertainty evaluation for STANDARD 1 and MBW E should not be much different and the uncertainty at -75 °C is ±0.4 °C. The standard uncertainty for the dryness of the dry gas is ±0.05 ppm.

4.3.4 The flow controller MFC 1 for wet gas

The Certificate of Calibration for the flow controller stated that the instrument's uncertainty should be not larger than ±0.25% of the flow. 10% full scale of flow was set for MFC 1. The standard uncertainty is ±2.43 ppm.

4.3.5 The flow controller MFC 2 for dry gas

The flow rate of MFC 2 was set at 40% of the maximum flow. The standard uncertainty for MFC 2 is ±0.24 ppm.

4.3.6 The water vapour concentration

Bell (1999) reported in the study of the design of the flow mixing stage that the fractional uncertainty in moisture content of dry gas will be much larger than that of wet gas and the effect is significant at very low moisture content. The moisture content of dry gas is 0.02 ±0.01 ppm and the output uncertainty is 5% of value. However, the effect is less significant at higher water content conditions. The moisture content in the range of this research is 202 ppm ±0.01 ppm. The output uncertainty will be very small (0.05%) and the standard uncertainty will be ±0.005 ppm.

4.3.7 Desorption and leaks

Water vapour adheres easily to the surface of objects because of its module’s strong polarity. Water vapour remaining on the inner surfaces of the pipe-work of the humidity generator and hygrometer causes the increase of the water dew point. The water vapour could sometimes be trapped in the joints and cracks of the system’s pipe-work. Also, the effect may be dependent on the area of the wetted surfaces, the material the pipe is made from and the complexity of the arrangement. This is known as the desorption effect. Desorption usually is the largest source of uncertainty at very low moisture content.

The uncertainty evaluations of the humidity generators at NPL reported that the effect of desorption in the pipe-work can be reduced by purging with dry gas for several hours to remove remaining moisture. The purging time is dependent on the level of moisture content in the gas and it will take at least twelve hours of purging to measure the dew point at -75 °C.

The leak effect can be detected by measuring the effect of the water vapour that leaks into the system. Covering the system’s joints with a damp cloth can test the leak effect. If the dew point of the system is increasing, it can be assumed that the water vapour will leak through the system. With constant experimental conditions and moisture content in the system, the effect of a leak will remain constant with time, but the effect of desorption would be decrease with time.

Purging is performed to eliminate the effect of desorption and leak effect. The dew point of the purging gas should be lower than dew point of the experimental gas.

Stainless steel tubing is mostly used in the system to prevent desorption and leaks effect. Stainless steel and PTFE tube are common in the laboratory in two sizes: ¼” and 6 mm in diameter. *A guide* states that stainless steel tubing is suitable to use at dew points below -70 °C.

The mixing unit was set at 1.5 bar A to avoid the leak effect, where the pressure was controlled by P 3. External water vapour can leak into the system if the generator pressure is lower than the environmental pressure.

Desorption and leak effect will be limited to ±0.01 °C (0.2 ppm) at ~-30 °C. The figure is estimated from the LFG and the flow mixing stage uncertainty evaluation (Bell, 1999). The standard uncertainty will be ±0.005 ppm.

4.3.8 Combination of uncertainty

The combined standard uncertainty for the mass flow-mixing generator is ±2.82 ppm and is obtained by taking the square root of the sum of squares of the contributing components. The expanded uncertainty value, with the coverage factor at *k*=2 (95% confidence level), is ±5.64 ppm. In conclusion, the FMG uncertainty evaluation is -35.69 ±0.25 °C (Table 7-3).

The uncertainty evaluation for STANDARD 1, STANDARD 2 and the FMG will prove that they are in agreement with a coverage factor *k*=2 (95% confidence level).

The largest source of uncertainty for the FMG is the flow controller MFC 1 for the wet air. The uncertainty in the flow metering is increased if the MFC is operated at low flows. However, the NPL report of the flow mixing design stated that the proportion of wet gas and dry is the main cause of uncertainty.

The uncertainty of the gas correction factor should be evaluated. This situation is similar to the hygrometer sensors that are calibrated in air, but are used to make measurements in gases other than air. The gas correction factor is usually dependent on the specific heat capacity of the carrier gas.

The pressure drop will affect the experimental results if the water vapour pressure is used in the calculations. Takahashi (1996) proposed the equations used to calculate the water vapour pressure of the NRLM flow mixing generator and the uncertainty. The approach used for the uncertainty evaluation of the equations is similar to the equation that is used in this research, but the uncertainty of the proposed equations is a function of the vapour pressure and many variables are involved. The benefit of Takahashi's work is that all sources of uncertainty contribution are accounted for in the equations. The equations were developed for the NRLM flow mixing generator however, and the FMG arrangement is not identical to the NRLM flow mixing generator. It is possible to adapt the equations for use in the FMG, but there is not necessity. The FMG uncertainty of the pressure drop is not the focus of attention because the outlet moisture content is independent of the pressure variable.

Calibration is the process of comparing a measuring instrument against an authoritative reference used for the same type of measurement, to identify any bias or systematic error in the measuring instrument. STANDARD 1, STANDARD 2 and FMG are used as the standard humidity hygrometers and generators where the test hygrometers TD 1, TD 2 and TD 3 were calibrated against the standard hygrometers and the generator. They are in the same conditions at a pressure slightly higher than ambient pressure.

4.4 The uncertainty evaluation of TD 1

TD 1 is a capacitive sensor that operates on polymer technology. The operating range (especially pressure) is not as wide as the metal oxide sensor and the instrument was calibrated prior to the experiments.

4.4.1 Calibration of the standard

TD 1 has been calibrated against STANDARD 1. In the experiment, the uncertainty evaluation for STANDARD 1 for air, methane and helium is ±0.2 °C, ±0.3 °C and ±0.2 °C respectively. The probability distribution is normal (Gaussian), so the divisor = 2 and gives a standard uncertainty of ±0.1 °C for both air and helium and ±0.2 °C for methane.

4.4.2 Long-term drift

Long-term drift can be quantified by calibrating instruments at regular intervals. The limit of long-term drift for TD 1 has been approximately established as being no more than ±0.1 °C. As the hygrometer was calibrated not long before being used to make the measurements (i.e. a time much shorter than the period over which the drift figure is for), the effect of drift will not be more significant than the effect of resolution. Therefore, the standard uncertainty is ±0.06 °C dew point for long–term drift.

4.4.3 Reproducibility

It can be pointed out that reproducibility is the largest source of uncertainty and is dependent on the carrier gas. The standard deviation of dew point measurements on water-air, -methane and helium mixtures is ±0.2 °C, ±0.4 °C and ±0.4 °C dew point. The reproducibility is considered as a normal distribution (divisor = 1) and the standard uncertainty for reproducibility for TD 1 is ±0.2 °C, ±0.4 °C and ±0.4 °C for air, methane and helium respectively.

4.4.4 Short-term stability or noise

Ten repeated readings have been collected at one dew-point and the short-term stability is calculated from the standard deviation of those ten readings. It is found that the standard deviation for short-term stability of TD 1 is insignificant: <0.01 °C dew point. The probability distribution for this source of uncertainty is considered the same as for the reproducibility evaluation and is normally distributed (divisor = 1). However, the standard uncertainty for TD 1 is insignificant.

4.4.5 Non-linearity

An instruments non-linearity can be determined by plotting a graph of measured values against actual values, and then putting a best–fit straight line (i.e. a linear-fit) through the data. The non-linearity of the instrument may then be taken as the standard deviation of the fit through the data. Actual values of dew point measurement are collected from STANDARD 1 and measured values obtain from a test hygrometer. TD 1's specification covers the range from - 30 °C down to - 60 °C of dew point and the part of the range that is of interest is at around - 30 °C. Despite measurements being taken in the range - 30 °C to - 60 °C, the system was not completely stable. After changing to a new set point, a reading could not be taken for at least two hours. Therefore, to avoid large errors, measurements taken before allowing the system to stabilise should be rejected. The limit of value is approximately equal to the instrument's resolution (±0.1 °C), giving the standard uncertainty as ±0.06 °C.

4.4.6 Hysteresis

The uncertainty evaluation for hysteresis is similar to that for non-linearity. However, hysteresis is a measurement error dependent upon whether the previous measurement was above or below the current one and is why a calibration comprises of a rising and falling series of measurements. Hygrometers are notorious for being prone to hysteresis. The limit of variation is ±0.1 °C, giving the standard uncertainty for hysteresis to be ±0.06 °C.

4.4.7 Self-heating

The sensor will suffer from what is known as a self-heating effect. The cause of this effect is because the gas surrounding it cannot remove excessive heat from the sensor. The effect is not helped by the sensor's protective cap or that the sensor is inside a small, enclosed chamber. The probability distribution applied for self-heating effect is rectangular and the devisor equals √3. The standard uncertainty estimation for self-heating effect of TD 1 is ±0.06 °C dew point for water gas mixture.

4.4.8 Resolution

The resolution of an instrument is always a contribution to overall uncertainty. If the instrument's display is to one decimal place then values between 20.45 °C and 20.54 °C are rounded to 20.5 °C. The 0.09 °C difference results in a value of uncertainty for resolution of ±0.05 °C (ie half-way). The probability distribution is rectangular (divisor = √3) and so gives a standard uncertainty equal to ±0.03 °C for the water-gas mixture.

4.4.9 Combination of uncertainties

The standard uncertainties are combined by taking the positive square root of the sum of the squares of the contributing component standard uncertainties in terms of generated dew point. The result is multiplied by the appropriate coverage factor (Appendix C) to give the expanded uncertainty. The expanded uncertainties of TD 1 are ±0.5 °C, ±0.9 °C and ±0.9 °C for water-air (Table 7-4) , -methane (Table 7-5) and -helium (Table 7-6) mixtures respectively.

4.5 Uncertainty evaluation of the TD 2

The TD 2 sensor is one of the metal oxide sensors used in the experiment. It is widely known that metal oxide sensors are especially designed for detecting water vapour. The range of operation of the TD 2 is much wider than polymer sensors for dew point temperature down to -120 °C and pressures up to 300-400 bar. In actual fact though, the TD 2 could not reach the dew point as low as the dew point in its specification.

The approach taken for the uncertainty evaluation of the TD 2 sensor could, quite plausibly, be similar to that for TD 1. The sources of standard uncertainty analysed from actual measurements are mostly calibration of the standard, reproducibility and short-term stability. Apart from these sources of uncertainty, the other sources are approximations made according to the instrument's resolution.

4.5.1 Reproducibility

The reproducibility of the TD 2 was evaluated from taking the standard deviation of seven readings for water-air mixture, four readings of water-methane mixture and four readings of water-helium mixture at the same dew point of interest (~-30 °C). With a normal probability distribution (divisor = 1), the standard uncertainty of reproducibility for air, methane and helium mixtures of the TD 2 is ±0.4 °C, ±0.5 °C and ±0.5 °C respectively. It should be noted that although the spurious errors have been rejected, they are shown on Figure 4-1 for information.

4.5.2 Drift

The TD 2 has been in use for over 20 years and during that time has been calibrated regularly against the standard hygrometers. From its history of calibrations, the value for drift is ±0.1 °C (equivalent to its resolution) and yields a standard uncertainty of ±0.06 °C.

Non-linearity, hysteresis and other sources of uncertainty are sometimes obtained by estimation. Although they can be eliminated by calibration, they should remain in the list in order to show that they have been included already. The TD 2 limit of variation for non-linearity, hysteresis and self-heating effect should not be more than its ±0.1 °C resolution. The probability distribution will be rectangular and the divisor will be √3. The standard uncertainty is ±0.06 °C for each source of uncertainty.

4.5.3 Combination of uncertainties

In conclusion, the combined uncertainty for water-air mixture is ±0.43 °C, water-methane is ±0.54 °C and for water-helium is ±0.53 °C. The expanded uncertainty with a coverage factor $k = 2$ and 95% confidence level for water–air (Table 7-7) mixture is ±0.86 °C, for water–methane (Table 7-8) is ±1.08 °C and water-helium (Table 7-9) is ±1.05 °C at ~-30 °C and 1.5 bar A.

4.6 Uncertainty evaluation of the TD 3

The TD 3 sensor is another metal oxide sensor. It is a new instrument and has been calibrated against the standard chilled-mirror hygrometer. Initially, the sensor’s indicated dew point differed greatly from the standard chilled-mirror hygrometer (-3 °C) and it took a long time to respond to change in dew point. The sensor’s performance improved slightly after being left to warm up for a couple of hours.

The approach taken for the uncertainty evaluation of the TD 3 sensor is similar to that taken for the TD 1 and TD 2 sensors. The standard uncertainty of reproducibility for humidity measurement in air is ±2.2 °C, for measuring in methane is ±0.6 °C and for measuring in helium is ±1.2 °C. The expanded uncertainty of the TD 3 sensor at *k*=2, or at a confidence level of 95% for humidity measurement in air is ±2.2 °C (Table 7-10), in methane is ±1.3 °C (Table 7-11) and in helium is ±2.4 °C (Table 7-12). An aluminium oxide sensor's uncertainty should not typically be larger than ±2.0 °C however and the excessive time to take a measurement using this sensor makes it impractical.

4.7 Correction values of dew point for the test hygrometers

Sensor	Carrier gas		
	air	methane	helium
TD1	+3.0	+4.2	+3.3
TD2	+2.1	+1.8	+2.3
TD3	+3.6	+3.8	+3.9

Table 4-1: Dew point correction values (°C) given to the test sensors at around -30 °C and 1.5 bar A

Correction values of dew point for the test hygrometer are given in Table 4-1. These values were obtained from the subtraction of the measured values of dew point between STANDARD 1 and the test hygrometers. For TD1's sensor, the correction value of measuring in air is +3.0 °C and in methane is +4.2 °C. The difference between these two values (1.2 °C) is larger than TD1 sensor's uncertainty (<±0.9 °C). This is significant because it shows the effect of gas species on TD1. Gas species did not have an effect on TD2. The difference between the correction values is not significant. The results for TD3's sensor should be discarded because it has poor sensitivity. Before a measurement could be taken, TD3 had to be left to stabilise for at least four hours.

4.8 The effect of gas atomicity on the sensor

For each of the sensors, the experiments show insignificantly different response to gas species. Any electrical sensor will suffer from self-heating effect where the carrier gas can take the heat away from the sensor at different rates and this can be explained by the gas atomicity, thermal conductivity and temperature coefficient.

Atomicity has an effect on the sensors. Atomicity is defined as a number of atoms in a molecule. A relationship between gas atomicity, heat capacity and the degree of freedom will be studied. The capability of a molecule to keep heat energy in it is known as the heat capacity. Large numbers of atoms in a molecule can retain heat energy more than small numbers of atoms in a molecule.

The idea of degree of freedom of a gas can be explained simply: A degree of freedom of a molecule is a process in which it can possess energy. A monatomic molecule that moves in three dimension x, y and z has kinetic energy in three directions and so has three degrees of freedom in terms of gas phase. A diatomic molecule has kinetic energy of translation, vibration, rotation and potential energy of vibration. As a result, a diatomic gas molecule has greater degree of freedom than a monatomic molecule.

The relationship between heat capacity and degree of freedom is plausibly simplified

$$\gamma = 1 + \frac{2}{p}$$ **Equation 4-1**

where γ is the ratio of the heat capacity at constant pressure and constant volume and p is the number of degrees of freedom per molecule.

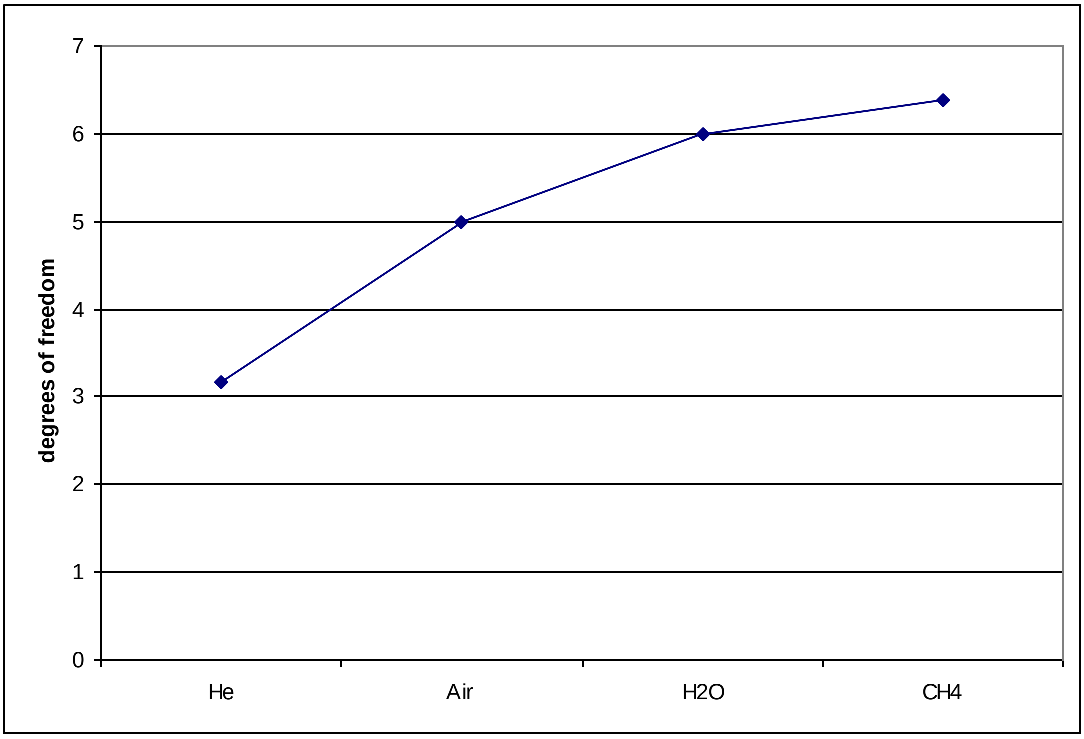

Figure 4-4: The degrees of freedom of helium, air, water and methane ordering from low to high gas atomicity at near room temperature. The degrees of freedom of these gases are obtained from the experiment (de Podesta, 1996).

Figure 4-4 shows the number of accessible degrees of freedom that is dependent on the atomicity. The degree of freedom is also dependent on the gas molecule arrangement, temperature and pressure.

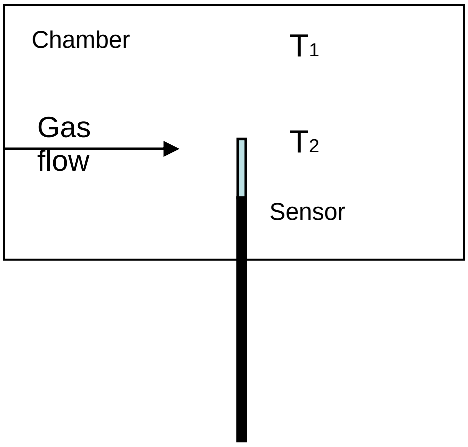

Figure 4-5: The sensor is in the chamber with T_1 and T_2 showing the different temperature between two places inside the chamber. A laminar flow removes heat out of the sensor.

The sensor is installed inside the chamber to measure the dew point in the gases. Figure 4-5 shows the sensor heated up by electric current. Inside the chamber heat will flow around the space surrounding the sensor. The processes of heat transfer are conduction, convection and radiation. In a system with laminar flow convection will be absent whereas in a system with turbulent flow it will be present, although only to a very small ignorable amount.

Thermal conductivity is related to the process of heat transfer. It increases with temperature, but not linearly. A graph (de Podesta, 1996) of thermal conductivity plotted against temperature shows that monatomic and diatomic gases have similar tendencies, whilst the absolute magnitude of conductivity significantly changes with gas species. Thermal conductivity is proportional to the number of accessible degrees of freedom, but inversely varies with the square of the atomic diameter of gas molecule. The two variables must be known to work out the thermal conductivity value.

The carrier gas will remove some heat from the humidity sensor. The amount of heat may vary depending on the gas atomicity. Large gas atomicity has more ability to remove heat from the sensor than small gas atomicity as explained above. The thermal conductivity of a gas is a variable that is dependent on gas species. This means that the rate of heat transfer will vary depending on the carrier gas. Therefore, the sensor should give a different response in different carrier gases.

The heat energy retained in a carrier gas and water vapour can exchange when they have an interaction. It can be presumed that a carrier gas with a high atomicity molecule may transfer more energy to water vapour than a low atomicity molecule. Hypothetically, the gas removes the excessive heat in a sensor. A high atomicity gas can contain more heat than a low atomicity gas.

It was claimed by a polymer sensor manufacturing company that the accuracy of the sensor is dependent on gas species and the effect is greater at higher pressures. In gases that have a high boiling point, such as methane and carbon dioxide, large measurement errors can be seen with polymer sensors. Polymer sensor types are intended for making measurements in gases like nitrogen and oxygen. Pressure compensation is allowed for in the device when measuring humidity in air at high pressures and it could be used to compensate in nitrogen and oxygen, but it is not suitable for gases with low boiling points such as helium and hydrogen. The pressure compensation in polymer sensors is not suitable for gases with high boiling point (e.g. methane) and it is suggested that a correction factor be applied.

Some carrier gases such as methanol and oxides of sulphur can affect the aluminium oxide sensors sensitivity. Not all aluminium oxide sensors perform the same – they are dependent on the pore structure. The pore structure of the metal oxide sensors has a different response depending on the carrier gas. The sensors are easily destroyed when Cl_2 and HCl are measured at high moisture concentration.

In conclusion, the atomicity of a gas has effects on the sensor and can take excessive heat away from the sensor. The information from the manufacturer shows that their product accuracy is dependent on gas species. Further investigation into the technology of this type of sensor should be carried out in order to achieve higher accuracy measurement of humidity.

4.9 Enhancement factor comparisons

The ISO equation of state is used to calculate the water vapour pressures and the enhancement factors in gases. The values of water vapour pressure are put into the enhancement factor equations.

The water vapour pressure values in gases have been calculated by the equation of state. The enhancement factor values are calculated in two different ways. In the first way the water vapour pressure is put into the Bögel equation (Equation 7-3) to yield the enhancement factor values. The second way is that the water vapour pressure values are divided by the saturation vapour pressure. The comparison between the two values has been made at 1.01325 bar.

The enhancement factor values in gases have also been compared with the enhancement factor values in air based on the Hardy equation. The enhancement factor equation at high pressures is more complicated than at lower pressures because there are too many unknowns in the interaction parameters in the equation. Greenspan (1975) developed the simple equation for enhancement factor for air (only) that was later modified by Hardy (1990) Equations 7-4, 7-5 and 7-6. A comparison between the enhancement factor values calculated by the ISO equation of state and the Hardy equation was made.

The comparison between the results for the enhancement factor values for air is presented. The deviation at 1.01325 bar is <0.6% of value for temperatures from 0 °C to 90 °C and <1.0% of value for temperatures from -50 °C to 0 °C. The deviation at 10 bar is <7% of value for temperatures from 0 °C to 100 °C and <10% of value for temperatures from –50 °C to 0 °C. *A Guide* reports that the uncertainty of the enhancement factor proposed by Bögel at 1.01325 bar is less than 0.1% and by Hardy at 10 bar is less than 1.0% at the 95% confidence level.

At 1.01325 bar the deviation for methane and helium is <0.3% from 0 °C to 90 °C, for methane is <2.0% from -70 °C to 0 °C. At 10 bar the deviation for methane and helium is around 2% - 3% from 0 °C to 90 °C.

The ISO equation of state gives a large deviation of enhancement factor in air because it is specifically designed for calculating moisture content and dew point in natural gases. Apparently, the difference between the three gases may not be significant compared with the uncertainty of the ISO equation of state. In addition, it is reported that the GasVLe software's uncertainty is between ±1.0 °C to ±2.0 °C. This systematic error needs to be improved. Furthermore, the method of calculation of the enhancement factor was not completely accurate. The water vapour pressure results in this experiment should be treated with caution because they were calculated based on Dalton's partial pressure law. The application of the ISO equation of state to calculate the enhancement factor should be studied further.

4.10 The use of the equations of state to predict the dew point in the experiments

A comparison was made between the equations of state provided in the GasVLe software package and the experimental results. The five equations of state are PR, ISO, SRK, LRS and SW equations of state. The ISO equation of state gives the best prediction of water dew point in air (deviation = 0.2%), in methane (deviation = 0.1%) and in helium (deviation = 0.6%) at around -30 °C and at 1.5 bar A. The remaining equations of state should be discarded because they give very large deviation as shown on Table 7-19

The ISO equation of state gives very good prediction of water dew point in gases in this experiment, but the GERG experimental results show large deviation in the calculation. The GERG experiment has been done in the medium moisture content range and at very high pressures. The ISO equation of state can be used to predict water dew point in nitrogen at high pressures and it gives very small deviations – less than 2% at 60 bar. The equation is good for calculating water dew point in methane, but at higher pressures the error increases and it is not suitable for predicting water dew point in argon at high pressures (Table 7-20).

In conclusion, the equations of state are not sufficient to accurately predict humidity in gas at high pressures at the present time and needs more development.

The FMG system requires software to log the data and although its writing was in development, it was not completed before the experiments were carried out. Data will be plotted against time for ease of viewing. At the moment, there are three CMDs used to display data from the MFCs and the pressure sensors. However, these were only good enough to obtain the results because this research was in the early stages.

There were four measurement points each for methane and helium and it would have been better if more measurements could have been taken. However, because of the time taken to stabilise, each measurement was time consuming. The stabilisation time was moisture dependent and at very low moisture content, the system should be left for several hours.

Helium is a good example of an ideal gas, but it is difficult to use. The measurements fluctuated more than for air and methane (Figure 4-1 and Figure 4-2). Although the Gas VLe software can be used to calculate water content and water dew point, its uncertainty is quite large (±2.0 °C). It has been suggested to calculate water vapour pressure via the fugacity parameter instead. However, this variable is of little interest. The use of the equations of state to calculate water vapour pressure should be studied further.

5 Conclusions

5.1 Experimental results

The FMG gives good agreement with the standard hygrometers. The uncertainty of the FMG is satisfactory: ±0.3 °C at ~-30 °C. The FMG has a simple construction and can be used in various combinations. However, the flow controller generates the gas flow depending on gas species. The gas correction factors need to be applied and this may increase the unknown error in the experiment. Low flow rate less than 10% full scale should be avoided or otherwise a large uncertainty of the outlet flow will arise.

The effect of gas species can be seen on the polymer sensor. The effect can be seen on the aluminium oxide sensor, but it is not significant. The carrier gas can remove heat from the sensor which had been generated by the supply current. This effect is dependent on gas atomicity, heat capacity and accessible degrees of freedom. This provides a good explanation why humidity sensors have different responses to gas species.

The ISO equation of state, developed from the PR equation of state, was used to predict dew point of humid gas, with methane as the carrier gas. Good agreement between the experimental values and the measured value were shown (Figure 4-1). However, this equation of state should be insufficient for calculating water dew point in air and helium. Also, the software’s uncertainty is significantly large at ±2.0 °C, so caution should be taken when making any calculation.

5.2 Recommendation

The reproducibility of the standard hygrometers measuring water dew point in helium is slightly high (~0.3 °C). The cause of the large fluctuation has not been established. Helium is a light and small atom gas that is used to detect leaks in pipework. The FMG pressure was higher than ambient to prevent water vapour pressure from the environment entering the system. It is suggested that helium may be replaced by argon to reduce the leak effect. Both are inert gases, but argon is cheaper than helium. Also, there is a lot of published research data on measured water content and water dew point in argon. Therefore, argon should be used in the experiment as a next step.

SHG 1 was used to generate humid air to supply FMG at the wet gas inlet MFC 1. In measuring water dew point in methane and helium, there was less than 5% by volume of air component. This contamination causes the change in heat capacities of methane + water vapour, and helium + water vapour. The heat capacity of mixture with air contamination is 1.2% higher than methane + water vapour and is 22.3% lower than helium + water vapour. These values are estimated by using the ISO equation of state. Air contamination could be included in the FMG's uncertainty budget. However, it is insignificant because the level of contaminant was equal in both methane and helium in the experiment.

To prevent gas flow back to SHG 1, the pressure at the wet gas inlet and dry gas inlet should be the same. Regulators controlled these pressures and these were connected with SHG 1 and the gas cylinder. The inlet pressures have to be higher than the pressure in the FMG's mixing unit and P 1 and P 2 pressure sensors were to monitor these inlet pressures. Due to the limitations of the laboratory facilities, the FMG pressure conditions could only be up to 8 bar g. To extend the experimental pressure ranges the two-pressure two-temperature humidity generator, that generates wet gas up to 20 bar, will be connected between SHG 1 and MFC 1. In order to reach the pressure range of the two-pressure two-temperature humidity generator the pressure regulator will have to be replaced with one intended for higher pressures and a compressed-air cylinder used in place of the compressed-air supply. For pressures higher than 20 bar, a gas cylinder will be used to provide all gases. The standard hygrometer STANDARD 1 will have to be removed because it can only operate up to 10 bar, but STANDARD 2 can remain on the system.

In the mixing unit the test hygrometers were arranged in series and this was not ideal. Although a parallel connection makes the system more complicated, it is possible to implement. A flow meter will be inserted to measure and balance the flow to each test hygrometer. The series arrangement might have a significant effect for very low moisture contents, but it may not be significant at temperatures around -30 °C.

The mass flow controller should be replaced, or checked, by the bubble flow meter because it is gas species dependent. In order to achieve this, some variables in the experiment will have their uncertainty decreased–such as a MFC gas correction factor.

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7 Appendixes

7.1 Appendix A

Sontag formulae for saturation water vapour pressure

Sonntag (1990) updated the formulae given by Wexler (1976 and 1977), for saturation water vapour pressure *e_w(t)* (in pascals) from dew point temperature *T* (in Kelvin) is as follow the saturation water vapour pressure over water.

$$\begin{aligned}\ln e_w(T) = {}& -6096.9385T^{-1} + 21.2409642 - 2.711193\times 10^{-2}T \\ & + 1.673952\times 10^{-5}T^2 + 2.433502\ln T\end{aligned}$$ **Equation 7-1**

For the range 0 °C to +100 °C, the uncertainties are less than ±0.01% of value at the 95% confidence level. The formula for saturation water vapour pressure over ice is

$$\begin{aligned}\ln e_i(T) = {}& -6024.5282T^{-1} + 29.32707 + 1.0613868\times 10^{-2}T \\ & - 1.3198825\times 10^{-5}T^2 - 0.493382577\ln T\end{aligned}$$ **Equation 7-2**

For the range -100°C to 0 °C, the uncertainties with this equation are less than 1.0% of value at the 95% confidence level.

7.2 Appendix B

Water vapour enhancement factor equations

The enhancement factor in terms of water vapour was proposed by Bögel (1977) in the temperature range -50°C to +6°C at pressure in the range 3 kPa to 110 kPa with the uncertainty of less than ±0.08% of value.

$$\begin{aligned}f_w(p,t) = 1 + \frac{10^{-4}\cdot e_w(t)}{273+t}\Bigg[&\left(38+173e^{\frac{-t}{43}}\right)\left(1-\frac{e_w(t)}{p}\right) \\ & + \left(6.39+4.8e^{\frac{-t}{107}}\right)\left(\frac{p}{e_w(t)}-1\right)\Bigg]\end{aligned}$$ **Equation 7-3**

For pressure from atmosphere up to 2 bar, f can be given by the equation by Greenspan.

$$f = \exp\left[\alpha\left(1 - \frac{e_s}{P}\right) + \beta\left(\frac{P}{e_s} - 1\right)\right]$$ **Equation 7-4**

Greenspan utilised the two following equations with a series of coefficients based on the IPTS-1968 temperature scale. Hardy has updated the coefficients based on the ITS-90 temperature scale.

$$\alpha = \sum_{i=1}^{4} A_i t^{(i-1)}$$ **Equation 7-5**

$$\ln\beta = \exp\sum_{i=1}^{4} B_i t^{(i-1)}$$ **Equation 7-6**

7.3 Appendix C

For each item of input uncertainty, there is an associated *standard uncertainty*, u. These are at one standard deviation and are evaluated by dividing the value of that individual input uncertainty by a number (the *divisor*) that is associated with an assumed probability distribution.

According to the publication *The Expression of Uncertainty and Confidence in Measurement* (1997, United Kingdom Accreditation Service), there are what is referred to as *Type A* and *Type B* input uncertainties.

The type A uncertainty is obtained by taking the standard deviation of a set of several repeat measurements (usually at least 10 readings) whereas type B uncertainties are based on other sources of information such as manufacturer’s data sheets, Certificates of Calibration and so on.

The *combined standard uncertainty* u_c is the addition of all the individual standard uncertainties by root-sum-of-squares (RSS) summation. That is, taking the square root of the sum of the squares of all the individual standard uncertainties.

Certificates of Calibration state an *expanded uncertainty* and a *coverage factor*. The expanded uncertainty, U is simply the combined uncertainty multiplied by a number, the coverage factor (*k*). A coverage factor associated with the expanded uncertainty is necessary to represent the *level of confidence* of a measurement. The coverage factor is a statement of how sure the results in the Certificate lie between ±U. Usually on Certificates *k*=2 and this corresponds to a reported level of confidence of 95%.

The type A input uncertainty, with normal probability distribution, is already at one standard deviation and therefore has divisor = 1. The type B input uncertainty obtained from a Certificate of Calibration will have divisor = 2 (see Table 7-1). The other levels are *k*=2.58 for 99% confidence and *k*=3 for 99.7% confidence.

When the type B input uncertainties are evaluated from an instrument's specification, most manufacturers declare confidence levels for tolerance. Rectangular probability distributions can be assumed and have divisor = √3. Also, triangular and U-shaped probability distributions have divisor = √6 and √2 respectively. Uncertainty evaluation is detailed in *The Expression of Uncertainty and Confidence in Measurement*. (1997, United Kingdom Accreditation Service)

7.4 Appendix D

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.03	Normal	2	0.02
2	Long-term stability	0.10	Rectangular	1.732	0.06
3	Reproducibility	0.08	Normal	1	0.08
4	Non-linearity	0.07	Normal	1	0.07
5	Contamination	0.01	Rectangular	1.732	0.006
6	Temperature gradient in mirror	0.01	Rectangular	1.732	0.006
7	Temperature gradient in condensate	0.01	Rectangular	1.732	0.006
8	Pressure gradients	0.01	Rectangular	1.732	0.006
9	Temperature fluctuations in mirror	0.01	Rectangular	1.732	0.006
10	Desorption in the pipework	0.05	Rectangular	1.732	0.03
11	Self-heating effect	0.01	Rectangular	1.732	0.006
	Combined standard uncertainty with k=2				0.13
	Expanded uncertainty				0.25

Table 7-1: Combined standard uncertainty and expanded uncertainty of STANDARD 1 in terms of dew point temperature with humidity measuring in air

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.07	Normal	2	0.04
2	Long-term stability	0.03	Rectangular	1.732	0.02
3	Reproducibility	0.13	Normal	1	
4	Non-linearity	0.07	Normal	1	0.07
5	Contamination	0.01	Rectangular	1.732	0.006
6	Temperature gradient in mirror	0.01	Rectangular	1.732	0.006
7	Temperature gradient in condensate	0.01	Rectangular	1.732	0.006
8	Pressure difference	0.01	Rectangular	1.732	0.006
9	Temperature fluctuations in mirror	0.01	Rectangular	1.732	0.006
10	Desorption in the pipework	0.05	Rectangular	1.732	0.03
11	Self-heating effect	0.01	Rectangular	1.732	0.006
	Combined standard uncertainty				0.16
	Expanded uncertainty				0.32

Table 7-2: Combined standard uncertainty and expanded uncertainty of STANDARD 2 in terms of dew point temperature with humidity measuring in air

	Source of uncertainty	Value (ppm)	Probability distribution	Divisor	Standard uncertainty (ppm)
1	Calibration of standard	2.2	Normal	2	1.1
2	Wet Gas	1.73	Normal	2	0.86
3	Dry gas	0.1	Normal	2	0.05
4	MFC 1	4.87	Normal	2	2.43
5	MFC 2	0.48	Normal	2	0.24
	Combined standard uncertainty (*k*=2)				2.82
	Expanded uncertainty				5.6

Table 7-3: Combined standard uncertainty and expanded uncertainty of the FMG in terms of ppm with humidity measuring in gas

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.2	Normal	2	0.10
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.2	Normal	1	0.20
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self- heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.26
	Expanded uncertainty				0.52

Table 7-4: Combined standard uncertainty and expanded uncertainty of TD 1 in terms of dew point temperature with humidity measuring in air

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.3	Normal	2	0.15
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.4	Normal	1	0.40
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.45
	Expanded uncertainty				0.89

Table 7-5: Combined standard uncertainty and expanded uncertainty of TD 1 in terms of dew point temperature with humidity measuring in methane

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.2	Normal	2	0.10
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.4	Normal	1	0.40
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.43
	Expanded uncertainty				0.86

Table 7-6: Combined standard uncertainty and expanded uncertainty of TD 1 in terms of dew point temperature with humidity measuring in helium

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.2	Normal	2	0.10
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.4	Normal	1	0.40
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.43
	Expanded uncertainty				0.86

Table 7-7: Combined standard uncertainty and expanded uncertainty of TD 2 in terms of dew point temperature with humidity measuring in air

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.3	Normal	2	0.15
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.5	Normal	1	0.50
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.54
	Expanded uncertainty				1.08

Table 7-8: Combined standard uncertainty and expanded uncertainty of TD 2 in terms of dew point temperature with humidity measuring in methane

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.2	Normal	2	0.10
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.5	Normal	1	0.50
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.53
	Expanded uncertainty				1.05

Table 7-9: Combined standard uncertainty and expanded uncertainty of TD 2 in terms of dew point temperature with humidity measuring in helium

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.2	Normal	2	0.10
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	1.1	Normal	1	1.10
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				1.11
	Expanded uncertainty				2.22

Table 7-10: Combined standard uncertainty and expanded uncertainty of TD 3 in terms of dew point temperature with humidity measuring in air

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.3	Normal	2	0.15
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	0.6	Normal	1	0.60
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				0.63
	Expanded uncertainty				1.26

Table 7-11: Combined standard uncertainty and expanded uncertainty of TD 3 in terms of dew point temperature with humidity measuring in methane

	Source of uncertainty	Value (°C)	Probability distribution	Divisor	Standard uncertainty (°C)
1	Calibration of standard	0.2	Normal	2	0.20
2	Long-term stability	0.1	Rectangular	1.732	0.06
3	Reproducibility	2.0	Rectangular	1.732	1.15
4	Short-term stability	0.0	Normal	1	0.00
5	Non-linearity	0.1	Rectangular	1.732	0.06
6	Self-heating effect	0.1	Rectangular	1.732	0.06
7	Hysterisis	0.1	Rectangular	1.732	0.06
8	Resolution display	0.1	Rectangular	1.732	0.06
	Combined standard uncertainty (*k*=2)				1.18
	Expanded uncertainty				2.36

Table 7-12: Combined standard uncertainty and expanded uncertainty of TD 3 in terms of dew point temperature with humidity measuring in helium

7.5 Appendix E

Temperature	Enhancement factor (Bögel)	Enhancement factor (ISO-eos)	Absolute value of % Deviation
Over water			
100			
90	1.00422	1.00262	0.16
80	1.00592	1.00418	0.17
70	1.00630	1.00517	0.11
60	1.00606	1.00591	0.02
50	1.00561	1.00656	0.09
40	1.00514	1.00722	0.21
30	1.00476	1.00793	0.31
20	1.00451	1.00871	0.42
10	1.00440	1.00954	0.51
0	1.00441	1.01025	0.58
Over ice			
-10	1.00461	1.01472	1.00
-20	1.00483	1.01497	1.00
-30	1.00516	1.01242	0.72
-40	1.00558	1.00915	0.35
-50	1.00609	1.00816	0.21
-60	1.00669	1.01367	0.69
-70	1.00739	1.03189	2.37
-80	1.00819	1.07217	5.97
-90	1.00911	1.14994	12.25
-100	1.01017	1.27580	20.82

Table 7-13: The comparison of the enhancement factor value for air calculated by Bögel equation and the ISO equation of state at 1.01325 bar

Temperature	Enhancement factor (Bögel)	Enhancement factor (ISO–eos)	Absolute value of % Deviation
Over water			
100			
90	1.00422	1.00265	0.16
80	1.00592	1.00413	0.18
70	1.00630	1.00482	0.15
60	1.00606	1.00501	0.10
50	1.00560	1.00491	0.07
40	1.00513	1.00463	0.05
30	1.00476	1.00424	0.05
20	1.00451	1.00375	0.07
10	1.00439	1.00314	0.12
0	1.00441	1.00221	0.22
Over ice			
-10	1.00461	1.00473	0.01
-20	1.00483	1.00274	0.21
-30	1.00516	0.99764	0.75
-40	1.00558	0.99139	1.43
-50	1.00609	0.98684	1.95
-60	1.00669	0.98796	1.90
-70	1.00739	1.00054	0.68
-80	1.00819	1.03317	2.42
-90	1.00911	1.09983	8.25
-100	1.01017	1.20908	16.45

Table 7-14: The comparison of the enhancement factor value for methane calculated by Bögel equation and the ISO equation of state at 1.01325 bar

Temperature	Enhancement factor (Bögel)	Enhancement factor (ISO-eos)	Absolute value of % Deviation
Over water			
100			
90	1.00422	1.00244	0.18
80	1.00592	1.00359	0.23
70	1.00630	1.00408	0.22
60	1.00606	1.00429	0.18
50	1.00560	1.00443	0.12
40	1.00513	1.00460	0.05
30	1.00476	1.00484	0.01
20	1.00451	1.00515	0.06
10	1.00439	1.00549	0.11
0	1.00441	1.00568	0.13
Over ice			
-10	1.00461	1.00916	0.45
-20	1.00483	1.00862	0.38
-30	1.00516	1.00521	0.01
-40	1.00558	1.00094	0.46
-50	1.00609	0.99877	0.73
-60	1.00669	1.00285	0.38
-70	1.00739	1.01921	1.16
-80	1.00819	1.05695	4.61
-90	1.00911	1.13102	10.78
-100	1.01017	1.25135	19.27

Table 7-15: The comparison of the enhancement factor value for methane calculated by Bögel equation and the ISO equation of state at 1.01325 bar

Temperature	Enhancement factor (Hardy)	Enhancement factor (ISO-eos)	Absolute value of % Deviation
Over water			
100	1.02915	1.04625	1.7
90	1.02797	1.04986	2.1
80	1.02710	1.05374	2.6
70	1.02661	1.05800	3.1
60	1.02655	1.06275	3.5
50	1.02694	1.06808	4.0
40	1.02776	1.07409	4.5
30	1.02903	1.08088	5.0
20	1.03075	1.08854	5.6
10	1.03296	1.09719	6.2
0	1.03643	1.11489	7.6
Over ice			
-10	1.03963	1.12235	8.0
-20	1.04347	1.13485	8.8
-30	1.04797	1.14616	9.4
-40	1.05321	1.15891	10.0
-50	1.05943	1.17709	11.1
-60	1.06672	1.20653	13.1
-70	1.07561	1.25619	16.8
-80	1.08629	1.34037	23.4
-90	1.09941	1.48373	35.0
-100	1.11660	1.70975	53.1

Table 7-16: The comparison of the enhancement factor value for air calculated by Hardy equation and the ISO equation of state at 10 bar

Temperature	Enhancement factor (Hardy)	Enhancement factor (ISO-eos)	Absolute value of % Deviation
Over water			
100	1.02915	1.05281	2.3
90	1.02797	1.05312	2.4
80	1.02710	1.05258	2.5
70	1.02661	1.05133	2.4
60	1.02655	1.04944	2.2
50	1.02694	1.04693	1.9
40	1.02776	1.04379	1.6
30	1.02903	1.03993	1.1
20	1.03075	1.03521	0.4
10	1.03296	1.02944	0.3
0	1.03643	1.02308	1.3
Over ice			
-10	1.03963	1.01737	2.1
-20	1.04347	1.00627	3.6
-30	1.04797	0.99008	5.5
-40	1.05321	0.97045	7.9
-50	1.05943	0.94966	10.4
-60	1.06672	0.93077	12.7
-70	1.07561	0.91787	14.7
-80	1.08629	0.91647	15.6
-90	1.09941	0.93465	15.0
-100	1.11660		

Table 7-17: The comparison of the enhancement factor value for methane calculated by Hardy equation and the ISO equation of state at 10 bar

Temperature	Enhancement factor (Hardy)	Enhancement factor (ISO-eos)	Absolute value of % Deviation
Over water			
100	1.02915	1.03340	0.4
90	1.02797	1.03446	0.6
80	1.02710	1.03562	0.8
70	1.02661	1.03699	1.0
60	1.02655	1.03861	1.2
50	1.02694	1.04053	1.3
40	1.02776	1.04276	1.5
30	1.02903	1.04532	1.6
20	1.03075	1.04821	1.7
10	1.03296	1.05141	1.8
0	1.03643	1.05564	1.9
Over ice			
-10	1.03963	1.06255	2.2
-20	1.04347	1.06625	2.2
-30	1.04797	1.06741	1.9
-40	1.05321	1.06823	1.4
-50	1.05943	1.07195	1.2
-60	1.06672	1.08319	1.5
-70	1.07561	1.10884	3.1
-80	1.08629	1.15940	6.7
-90	1.09941	1.25237	13.9
-100	1.11660	1.40074	25.4

Table 7-18: The comparison of the enhancement factor value for helium calculated by Hardy equation and the ISO equation of state at 10 bar

7.6 Appendix F

Carrier gas	Measured dew point (°C)	% Deviation				
		ISO	PR	SRK	LRS	SW
Air	-32.17	0.2	1.7	6.1	14.2	9.3
Methane	-32.14	0.1	1.4	6.3	13.5	9.7
Helium	-31.91	0.6	2.0	6.2	14.2	9.2

Table 7-19: A comparison between the equations of state and the measured dew point in the carrier gases.

7.7 Appendix G

Pressure (bar) \Carrier gas	nitrogen measured at -25 °C	methane measured at -20 °C	argon measured at -15 °C
5	1.2%	2%	-
15	1.6%	2%	5%
40	-	3%	19%
60	1.2%	9%	35%
80	-	19%	59%
100	-	19%	66%

Table 7-20: Percentage deviation of using the ISO equation of state to predict water dew point in the gases at pressures made against the GERG experimental results. (GERG-TM14, 2004)