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REPORT

Assessment of fundamental data used in humidity metrology

Steven Boyes and Stephanie A Bell

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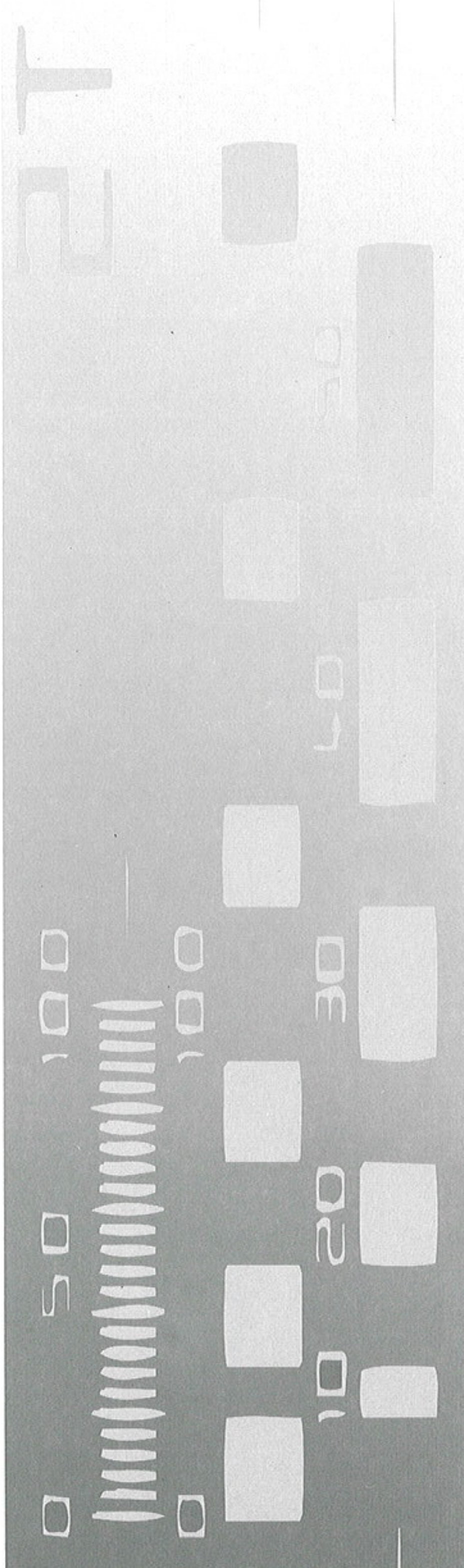

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Assessment of fundamental data used in humidity metrology

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ABSTRACT

Published measured data and the derived formulae have been reviewed for the pure saturation vapour pressure over water and ice, and for the water vapour enhancement factor in air. The measurements of the leading workers are compared, with discussion of the weaknesses and strengths of different methods, leading to conclusions about the possible errors in the results obtained. The data are viewed alongside the published formulae for vapour pressure and enhancement factor. By considering which are the most soundly based formulae, recommendations are made for preferred equations for saturation vapour pressure over water and over ice, and for water vapour enhancement factor.

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EXECUTIVE SUMMARY

Humidity is measured in a variety of ways, including gravimetric analysis, condensation detection, electrical sensing, psychrometry, and many other methods. Values of humidity are expressed in terms of various quantities, including mole fraction, dew point, relative humidity, and others, which are different but are in principle related. In practice, there are questions over the reliability of the data which are the basis of conversion between different units of humidity measurement. These data relate to two quantities - firstly, the values of the vapour pressure of water at a given temperature, and secondly the effect of the non-ideal behaviour of gas and liquid mixtures on the partial pressure of water (the so-called water vapour enhancement factor). Over most of the range of temperatures relevant to NPL humidity standards, the vapour pressures of water have been measured relatively infrequently and in some regions the data are very sparse. Measurements of enhancement factor are equally rare and often of lower precision than the vapour pressure measurements. A thorough study of the fundamental data has been undertaken and the results of this investigation are presented here.

The report falls into four main parts. The first assesses the vapour pressure over the liquid phase of water and the second the vapour pressure over ice. Both of these sections consider experimental results and the equations used to represent them. The third section considers the water vapour enhancement factor of the vapour pressure of water in the presence of air. Measurements of the enhancement factor and aspects of the underlying theory are discussed. In the final section a discussion of the pertinent points is given along with some recommendations and conclusions.

Any assessment of the fundamental data used in humidity metrology must refer back to the original measurements. However, in recent work the focus of attention has been on the equations used to represent the data in a continuous fashion over various regions of the coexistence curve. There are numerous representations, each slightly different, and this has led to confusion. Differences between these representations have been identified as inconsistencies in the underlying vapour pressure data but in the case of (liquid) water this is not always true. In particular, confusion has arisen from the use of formulations such as that of Goff and Gratch [1], based around integrations of the Clausius-Clapeyron equation. When developed in full rigour, such integrations require additional information which is in short supply. Over the years, more precise measurements of the vapour pressure of water have been made, as have more recent integrations of the Clausius-Clapeyron equation. In short the Goff-Gratch equations are a product of their time and have now been superseded. The more recent equations clearly differ from the Goff-Gratch formulations and are in better agreement with the underlying vapour pressure data. For some fields of study the differences are insignificant, but for metrology this is not the case. This report identifies the reliable vapour pressure data and the most suitable representations of them. Uncertainty estimates of the data are noted. Preferred equations for use in humidity metrology are given.

The situation regarding the enhancement factor is less satisfactory. Again the focus of attention has been on the representations, while the quality of the underlying data has often been overlooked. In this work the data are reviewed in order to identify the most reliable measurements. Only then can the representations of the data be considered. The conclusion of this work is that no measurements have been published for the enhancement factor below -35 °C, and that extrapolation of the formulae currently in use is unreliable below this temperature.

1. INTRODUCTION

Humidity denotes the presence of water vapour in air or other gases. It arises from the evaporation of water or ice and the extent to which this happens depends on a number of factors, the most important of which is temperature. The presence of water vapour influences a vast range of physical, chemical and biological processes and therefore humidity measurements are important for a wide range of industries and many different techniques of measurement have been developed. Because of this very wide interest and the multiplicity of techniques of measurement, humidity is expressed in many different but inter-related ways, and some of these relationships can be confusing. Those interested in very low concentrations would probably express their measurements in parts per million; those concerned with higher humidities are more likely to specify dew-point or partial pressure of water vapour; and those interested in the effects of water vapour on materials usually use measurements of relative humidity. Wherever conversions are made between humidity quantities of dew point (or frost point), relative humidity, mole fraction, etc., the accuracy of the conversion relies critically on the accuracy of the formula used to represent the vapour pressure curve of water.

It is not the purpose of this report to discuss all the quantities of interest but to focus on those of central importance to the metrological community - saturation vapour pressure, and water vapour enhancement factor - and to give a thorough assessment of the fundamental data underlying these quantities. In what follows, temperature data are variously reported in terms of degrees Celsius and Kelvin. Conversions are given in some places for clarity.

1.1. STUDY METHODOLOGY

Any assessment of the fundamental data must refer back to the original experimental measurements. For the purpose of this investigation a most important aspect is the accuracy of the measurements. Information supplied by the authors regarding estimated uncertainties, precision of measurement and any assessment of systematic influences must be used. However, since this is a critical assessment of the measurements, comparison with additional data and measurements is important. This can be difficult because in some regions of interest there is only one set of reliable data and where there is more than one data set the range of overlap is small. However, for the case of water above 0 °C, there is sufficient information to allow a reliable assessment of the underlying data. Some aspects of the effect of impurities on the measurement of vapour pressure are discussed, since all measurements use different samples and the effect of impurities must be known to allow an accurate assessment of the level of agreement between various data sets. Where there is disagreement, the possibility of contamination must be explored to see if an explanation for the disagreement can be found.

In the discussion of measured data, the uncertainties are classed as Type A uncertainties (those evaluated by statistical methods) or Type B (those evaluated by other means) in line with the recommendations of the ISO Guide to the Expression of Uncertainty in Measurement [2].

1.2. QUANTITIES OF INTEREST

The ideal physical standard of humidity would be a device enabling one to measure humidity in accordance with its definition. A suitable definition is based on mole fraction. That is, for a sample of moist air, the mole fraction, x_w, of the water vapour is defined by

$$x_w = \frac{n_w}{n_a + n_w},$$

where n_w is the number of moles of water and n_a the number of moles of air in the sample. A gravimetric analyser, which measures the mixing ratio, probably comes closest to fulfilling this ideal. The mixing ratio, r, is defined by

$$r = \frac{m_w}{m_a} = \frac{M_w x_w}{M_a(1 - x_w)},$$

in which m_w is the mass of water and m_a the mass of air in the sample. This equation allows one to relate the measured masses of the gases in the sample to the definition given above through the relative molar masses of water and air, M_w and M_a respectively. The gravimetric hygrometer is of high accuracy but is a complex and expensive device. It is used mainly to calibrate humidity generators which are the most common top-level humidity standard. Humidity generators condition a stream of air to an accurately known dew-point and are essentially devices which bring water at a given temperature into contact with a gas stream at the same temperature, with elaborate construction to ensure saturation occurs. When pure water is in equilibrium with its vapour it exerts a pressure known as the saturation vapour pressure, which is a function of temperature only. In the presence of a gas, say air, the partial pressure of water vapour in the saturated gas, p_w , is not necessarily equal to the vapour pressure. That is,

$$p_w = x_w p = f_w(p,T)e_w(T),$$

in which we have introduced the enhancement factor f, which is a function of temperature T and overall pressure p, and e_w is the vapour pressure of pure water. At atmospheric pressure and 20 °C the enhancement factor is about 1.004.

Since x_w must lie between 0 and 1, it follows that

$$p \geq f_w e_w.$$

The quantities of interest are those relating to water in the last two equations. That is the vapour pressure of water as a function of temperature, and the enhancement factor when water is in contact with a gas other than its vapour. It is these quantities which are assessed in this report.

1.3. PHASE EQUILIBRIA

When a vapour is in equilibrium with its condensed phase the chemical potential of the substance in each phase is equal. From this can be derived the Clapeyron equation [3],

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m},$$

in which ΔS_m and ΔV_m are the differences of molar entropy and volume between the two phases. This result defines the rate at which pressure must change with temperature for the two phases to remain in equilibrium (i.e. the slope of the phase boundary). It is exact and applies to any phase transition of a pure substance. However, integration of this equation to calculate vapour pressure information is not straightforward and requires information which is in short supply and often known only with limited precision. Therefore actual measurements of p and T, where they can be made accurately, are more useful.

An important consequence of the phase rule is that for an isotopically pure substance there are no degrees of freedom at the triple point. That is, the temperature and pressure are fixed and invariant. Since the definition of the Kelvin assigns a temperature of 273.16 K to the triple point of water, the only requirement for a measurement of the vapour pressure at this point is the adequate realisation of the condition. If this is achievable a measurement of the pressure alone is all that is required. When the phase rule is applied to the equilibrium between two phases of a pure substance we find that there is one degree of freedom. That is, the temperature and pressure cannot be varied independently: a choice of temperature fixes the pressure and vice versa. Which is regarded as the independent variable is in fact determined by which is the more accurately known.

1.4. APPROACHES TO MEASUREMENT OF VAPOUR PRESSURE

Vapour pressures can be measured in a number of ways but they essentially reduce to two methodologies: static methods and methods which depend on boiling.

1.4.1. Static Methods

In static methods a sample of water is confined in a vessel connected to a pressure gauge, and the pressure exerted by the sample when it is maintained at a fixed temperature is measured. Key points about the method are:

1) The measured pressure will be too high if dissolved air is present. For a volatile gaseous impurity dissolved in a liquid the distribution coefficient between the liquid and vapour phases is given approximately by

$$x \approx \frac{K_A\, y}{p},$$

in which x is the mole fraction in the vapour phase, y is the mole fraction in the liquid phase, p is the pressure and K_A is the Henry's law constant for the impurity-liquid mixture. For nitrogen dissolved in water at 25 °C, K_A is about 8.7×10^9 which implies x is about $2.7 \times 10^6 y$. The impurity is therefore almost entirely in the vapour phase and for static measurements the effect on the vapour pressure may be calculated with sufficient precision from

$$\delta p \approx \frac{RT\rho z}{1 - \dfrac{\rho}{3\rho_c} + \dfrac{RT\rho}{K_A}} ,$$

in which δp is the increase in the pressure, ρ is the average density of the water, ρ_c is the critical density of water, R is the gas constant, T is the kelvin temperature, K_A is Henry's constant for the impurity dissolved in water and z is the mole fraction of the impurity in the sample. A considerable advantage for static methods is the repeated degassing of the liquid throughout the course of the measurements, hence removing gaseous impurities.

2) The measured pressure will be too high if any low-boiling point impurity is present and too low if any high-boiling impurity is present. The effect of non-volatile impurities is to suppress evaporation, and so elevate the boiling point of the mixture , as well as to depress the freezing point. The boiling point elevation is given by

$$\delta T_b \approx \frac{RT^2}{\Delta H_l^v}\, x$$

and the freezing point depression by

$$\delta T_f \approx \frac{RT^2}{\Delta H_s^l} x,$$

where δT_f is negative (for a depression). In these expressions δT is the change in temperature at a fixed pressure, x the mole fraction of impurity in the liquid, R the gas constant, T the temperature and ΔH the enthalpy associated with the phase change. Absence of impurities to the required degree can be demonstrated if the pressure can be measured for different vapour volumes and is found to be unchanged.

1.4.2 Boiling point methods

It is sometimes suggested that methods which depend on boiling (ebulliometry) are less accurate than static methods This is because the temperature measured is that of the boiling liquid and, since a liquid must be to some extent superheated for it to boil, it is difficult to ensure that the temperature measured is that truly corresponding to the prevailing pressure. If, however, the condensation temperature is measured this difficulty does not arise.

In addition, for the case of a less- or non-volatile impurity (B dissolved in A), for example, Raoult's law implies

$$x_{B,v} \approx \frac{p_B x_{B,l}}{p},$$

in which $x_{B,v}$ is the impurity fraction in the vapour phase, $x_{B,l}$ is the impurity fraction in the liquid phase, p is the vapour pressure of the mixture and p_B is the vapour pressure of the pure substance B (since $p_B < p$, because it is less volatile). This implies, as expected, that the amount of impurity in the vapour phase is reduced, and if the condensation temperature is measured then the method is less susceptible to the presence of these impurities.

In ebulliometric methods a second component is always present: the gas by which the pressure in the system is controlled. It is assumed that at low pressures this gas does not affect the behaviour of the substance under study. This assumption is borne out in practice. Ambrose, Sprake and Townsend [4] used the method and found no difference between the values obtained when helium was used as the buffer gas and those obtained when nitrogen was used. Presumably this results from the fact that boiling continually degasses the sample of liquid and additionally sweeps the buffer gas to a well defined vapour-gas boundary at the condenser. This will confine any interaction between vapour and buffer to this small volume only, which is generally well removed from the thermometer and pressure systems. In ebulliometric methods the difference between the boiling and condensing temperatures may indicate whether an impurity is present. However, if the temperature measuring equipment is sufficiently precise the behaviour of the condensing temperature alone may reveal inadequacy of the sample and it is the opinion of Ambrose that there is little advantage to measuring the boiling temperature as well as the condensing temperature.

1.5. WATER VAPOUR ENHANCEMENT FACTOR

When an inert (non-reacting) gas is added to a system in which a liquid or solid is in equilibrium with its vapour, the vapour pressure of the condensed substance changes. This change in the vapour pressure is attributable to three effects: 1) the chemical potential of the condensed substance is increased because of the rise in the applied pressure, the so-called Poynting effect [5]; 2) if the gas is soluble in the condensed substance then the chemical potential of the solution is different from that of the pure solvent; and 3) the chemical potential of the vapour is changed because of interactions between the vapour and the inert gas. For water vapour, the resulting effect is expressed in terms of the so-called "water vapour enhancement factor", f,

$$f = \frac{x_w p}{e_w},$$

in which x_w is the mole fraction of water in the gas phase, p is the total system pressure and e_w is the vapour pressure of the condensed phase. The quantity $x_w p$ may be thought of as an effective vapour pressure of the water substance in a real gas mixture analagous to a partial pressure in an ideal gas mixture. As p approaches e_w, x_w approaches unity, and at $p = e_w$ and $x_w = 1$, the enhancement factor f becomes unity.

The enhancement factor is, in principle, calculable from the expression given by Hyland [6]. Hyland's formula is a cumbersome 13-term polynomial function of many thermodynamical quantities. In practice, however, evaluation is not always possible because the additional information required to evaluate the expression with sufficient precision is in short supply over wide ranges of temperature and pressure. The virial coefficients of the gases under consideration are not always known beyond the second and this is especially true for the interaction virial coefficients. Estimates can be obtained from physically realistic models but their accuracy is hard to evaluate. The various contributions to the enhancement factor are numerous and an alternative approach is to compare direct measurements of the enhancement factor with values obtained theoretically. In practice this is done by utilising all available information in the theory, and using the experimental values to extract estimates of the remaining parameters, in particular the second interaction virial coefficient of the water-gas mixture. The outcome from this is a theoretically based correlation derived from experimental measurements. The reliability of such a correlation depends critically on the precision and accuracy of the underlying data and in a later section an assessment of the available data is given.

2. REVIEW OF DATA FOR LIQUID-VAPOUR EQUILIBRIUM

The starting point for a critical examination of experimental measurements is the recent paper by Sato et al [7]. This evaluates various thermodynamic property data for water including vapour pressure measurements. From this paper we consider only those measurements of the highest precision in the temperature interval 273 K to about 373 K: this includes the measurement at the triple point of water by Guildner, Johnson and Jones [8], the data of Stimson [9], and the measurements of Douslin [10]. Two additional sets of measurements which are of high precision are those of Besley and Bottomley [11] between 273 K and 298 K and those of Beattie and Blaisdell [12] between 369 K and 376 K. We have restricted our attention to temperatures above the triple point temperature: supercooled water is not considered in the context of this report. A more detailed discussion of the selected measurements is given below.

2.1. DATA OF GUILDNER, JOHNSON AND JONES

For the measurements of Guildner et al [8], a modified triple point cell was constructed and filled with very pure water. The modifications allowed water from the triple point section to be transferred by a percolator to a reservoir. The water was distilled from the reservoir through a trap and allowed to flow over the ice mantle. This permitted realisation of triple point conditions over a large area, providing high stability to the observed pressure. Circulating and distilling the water drives off any residual air dissolved in the liquid and the distillate which is passed over the triple point cell is also virtually free of involatile contaminants. The arrangement of the apparatus also ensured that the ice mantle was not in contact with water containing dissolved involatile materials. The absence of a significant residue of contaminating gases was demonstrated in the extensive experimental procedures. The vapour pressure at the triple point was measured on three occasions. The results from the first series were used to analyse the process to improve techniques and procedures. The results from the second series established p_t = 611.636 ± 0.061 Pa (at a "3σ" level of uncertainty). The random uncertainty was much reduced by further improvements and the third series of measurements established p_t = 611.657 ± 0.010 Pa. Systematic uncertainties were identified and discussed and were concluded to be relatively insignificant.

2.2. DATA OF STIMSON

Stimson [9] measured the vapour pressure of water at seven temperatures in the range 25 °C to 100 °C using a boiler and precision manometer used in the calibration of standard platinum resistance thermometers. At the time of the measurements the normal boiling point was a fixed point on the ITS-48 and was defined as the temperature of equilibrium between liquid water and its vapour under the pressure of 101325 Pa, the assigned value of temperature at this point being 100°C. The experimental protocol of Stimson was to determine the coefficients of the thermometers at this temperature and then to make measurements at various other temperatures. The measurements reported by him are therefore of the temperature at a series of super-imposed pressures established in a precision manometer.

Additionally, his measurements were of the condensing temperature of the vapour. This is a subtle, but important, point because it means his measurements were less susceptible to non-volatile impurities and super-heating than measurements of the boiling temperature. The measurements were very extensive and spanned a period of 7 years. The Type A uncertainties, in pascals, given by Stimson are well represented by

$$\sigma(p) = [(0.1384)^2 + [\delta T \frac{dp}{dT}(\frac{t}{100})]^2]^{1/2} ,$$

in which δT = 0.44 mK is the random uncertainty in the calibration of the thermometers at the steam point. This error propagates to other temperatures over the range of measurement. The constant term can be thought of as the limiting uncertainty of the measurements and corresponds roughly to 0.1 Pa. Assessments of other sources of error are not expounded in great detail by the author. The rms deviation of the experimental results from a fiducial line is about 0.21 Pa, which is consistent with his estimated Type A uncertainty.

2.3. DATA OF BEATTIE AND BLAISDELL

The measurements of Beattie and Blaisdell [12] pre-date those of Stimson but utilise a similar methodology and apparatus . They are very extensive and thorough but cover only the limited temperature interval 96-103 °C. Temperatures were measured on the ITS-27. Information provided by the authors allows a thorough assessment of the Type A uncertainties. The estimated total Type A uncertainty from all sources was about 0.52 mK at the steam point. This value is in good agreement with the 0.43 mK rms deviation of the results from a fiducial line. A very thorough assessment of Type B uncertainties is given including the effects of contamination, isotopic composition, radiation losses and overheating of the boiler and its impact on the water vapour condensation boundary. The estimated total Type B uncertainty is 0.45 mK. The total uncertainty at the steam point is therefore about 0.68 mK, equivalent to about 2.4 Pa.

2.4. DATA OF BESLEY AND BOTTOMLEY

These authors made a very extensive series of measurements of the vapour pressure of water in the range 273-298 K [11]. The measurements were based on the static method. The apparatus consisted of purified water, at a temperature measured by a platinum resistance thermometer on the IPTS-68, exerting its equilibrium vapour pressure on a mercury manometer. Great pains were taken to remove residual air and prevent contamination from organic and involatile materials. Information given by the authors allows the estimation of the Type A uncertainty as follows: the pressure error was estimated at 0.13 Pa; the temperature uncertainty was estimated at 1 mK, which corresponds to a pressure uncertainty which varies between 0.04 and 0.19 Pa (the temperature error is scaled by the derivative of the vapour pressure at that temperature). This leads to a total Type A uncertainty which varies between 0.14 and 0.23 Pa. This should be compared with the 0.23 Pa rms deviation from their fiducial line. Additional information given by the authors relates to their determination of the pressure at the triple point of water. Numerous direct measurements were taken before the apparatus, the techniques and the purification procedures were finalised and we can take the spread of these measurements as an estimate of possible Type B uncertainties in their measurements. The variance of the measurements led to an estimate of 0.24 Pa for their Type B uncertainty. An additional Type B uncertainty can be estimated from the difference of 0.19 Pa between their direct determination of the triple point pressure and the value interpolated from their equation. The total uncertainty in their measurements is therefore estimated to range between 0.34 Pa and 0.38 Pa.

2.5. DATA OF DOUSLIN

The measurements reported by Douslin [10] span the temperature interval 273-293 K and use the static method. An inclined piston gauge designed and built by the author was used to measure the pressure, rather than a manometer. Water vapour contacted the piston directly and the liquid sample was contained in a pyrex glass bulb immersed in a small mercury vat, which was in turn immersed in a temperature controlled bath. The mercury was determined to be free of gradients or variations in temperature greater than 0.5 mK. A platinum resistance thermometer calibrated on the IPTS-68 was immersed in the mercury in the vessel and the temperature of the water was inferred from the temperature of the mercury. Of all the measurements discussed here these are the least precise with uncertainties ranging from 0.33 Pa at 273 K to 0.81 Pa at 293 K. The results were analysed individually for maximum cumulative error based on the specifications given for the piston gauge, and the estimated uncertainty in the temperature of the sample, which was given as 1 mK. Douslin states that the uncertainties given are the calculated maximum systematic uncertainties and include all known sources of error except possible non-equilibrium errors.

2.6. CONCLUSIONS FROM DATA FOR LIQUID WATER

Figure 1 shows selected data as deviations from the equation of Sonntag [13] and the comparison is discussed below. Sonntag's equations for saturation vapour pressure are adaptations to ITS-90 of the formulae of Wexler [14], and currently have widespread acceptance among humidity metrologists. Here, Sonntag's formulae provide a useful basis for comparison of the other data and formulations. For plotting on the graph in Figure 1, the data have been converted to the ITS-90 and so are all based on a common temperature scale. The uncertainty associated with such a conversion is of the order of 1 mK. The fine dotted line shows the "$\pm 1\sigma$" uncertainty of Sonntag.

The data of Douslin et al (filled squares) show positive deviations from the baseline. This behaviour is consistent with the presence of a volatile impurity and we note that his measurements are based on a static method which is susceptible to this effect. It is also of note that this set of measurements superseded an earlier set which he concluded were affected by the presence of air. One suspects the same to be true here. The solid curve is based on a fit to Douslin's data. Although there is considerable scatter the deviation of the data are accommodated reasonably well by the equations describing the presence of air. The short-dashed line shows the effect of a superimposed temperature error of 6 mK. This does not accommodate the data nearly so well.

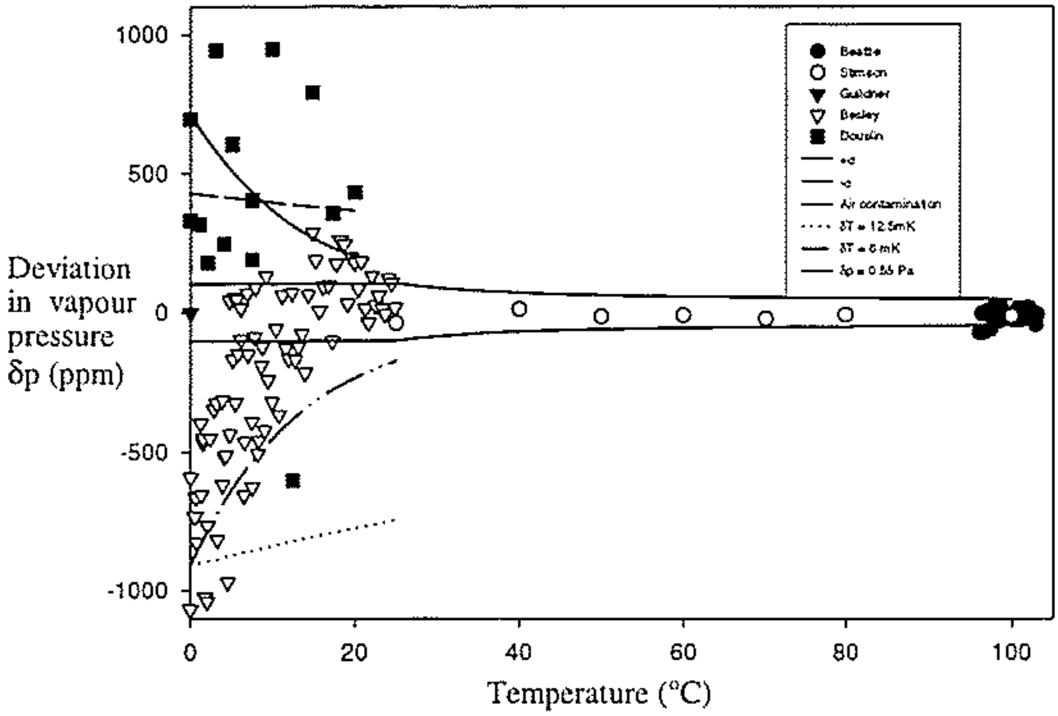

Figure 1: **Deviation in vapour pressure (δp) of selected data for water from the equation of Sonntag [13]**

The data of Besley and Bottomley (open triangles) show negative deviations. This is not consistent with the presence of air impurity and the presence of non-volatile materials is unlikely as the authors took great pains to ensure that the water was free from contamination. A superimposed pressure error (dashed-double dot line) does not accommodate the data and neither does a superimposed temperature error (dotted line). An alternative explanation is the mechanism of adsorption. This is a dynamic process but in a uniform temperature enclosure the process will reach equilibrium and it is unlikely that a large pressure gradient could be supported. However, a more likely explanation would be the presence of a cold spot. At such a point, condensation-evaporation cycles could occur leading to oscillations and an overall lowering of the pressure in the system. This is consistent with the experimental observations being low and showing more scatter than expected. Besley and Bottomley noted the increased scatter and were disappointed with the results.

The remaining sets of data, those of Stimson (open circles), Guildner et al (filled triangle),and Beattie and Blaisdell (filled circles) are all in good agreement with the equation of Sonntag. This is not surprising, as the data were used in the construction of Sonntag's equation. However, the internal consistency of the data sets is remarkable. In particular the agreement between the data of Stimson and Beattie and Blaisdell is within experimental uncertainty. The difference between the data sets is about 2 ppm (0.21 Pa) at the normal boiling point of water. Both measurements used a mercury manometer to determine the pressure and this difference may well reflect a Type B uncertainty associated with the measurement data sets.

2.7. FORMULATIONS FOR SATURATION VAPOUR PRESSURE WITH RESPECT TO WATER ABOVE 0 °C

The remaining problem is how to represent the vapour pressure as a function of temperature. This is not as straight forward as it sounds as the data are at discrete points, unevenly distributed, and varying uncertainty, and the equation is required to represent the whole coexistence curve, or at least the region of interest, in a continuous fashion.

One method is to use least squares regression analysis to generate the coefficients of a polynomial of some order. This leads to a multitude of equations, typically one for each author who performs measurements, and a great deal of confusion.

Gibbins [15] has recently reviewed all the equations in use up to 1990 but falls short of critically assessing them on the basis of the best representation of the coexistence curve. He merely compares them and concludes that there are large differences.

The best approach to equations of this type is that advocated by Wagner [17]. He has developed an equation that can represent the entire coexistence curve of water from the triple point to the critical point. The equation has theoretical justification and has been adopted by the International Association for the Properties of Water and Steam (IAPWS). The great advantage of this equation is that it utilises all the available vapour pressure data over the entire coexistence region. This is particularly advantageous for water as there is a great deal of high quality data for temperatures greater than 373 K.

Semi-theoretical derivations can be produced for water but these are valid at fairly low pressures only and there are no theoretically based equations which relate vapour pressure to temperature over the whole range from the triple point to the critical point. Equations can be written in terms of other thermodynamic properties which allow the consistency between vapour-pressure and heat-capacity measurements to be checked, but they do not bring us any closer to a theoretical equation because the manner of variation with temperature of the related properties is no better known than is that of the vapour pressure itself. Integrations of the equations relating the other thermodynamic properties to vapour pressure can be performed if the parameters entering into the integration are completely independent and known sufficiently accurately. This would enable calculation of the vapour pressure to be compared with direct measurements. This was the approach adopted by Goff and Gratch [1]. Since their equation was developed additional information has become available and the process has been repeated by Wexler and Hyland [16]. They concluded that the Goff-Gratch equation was inadequate in the region of 273-293 K. In addition they concluded that the additional information must be known to an accuracy that is 1 or 2 orders of magnitude better than they are now known for thermodynamic calculations of vapour pressure to have an uncertainty comparable to the best available experimental measurements. Their approach was modified therefore to utilise the best available additional information along with actual vapour pressure measurements to ensure internal consistency. The compromise equations are presented, not as accurate theoretical representations of the properties of water, but as smoothing functions that have a theoretical basis.

The equations mentioned above are shown as deviations from the Sonntag equation in Figure 2.

Wagner's equation is in close agreement with the equation of Sonntag over the entire range of overlap, and the temperature range of its validity extends beyond that of Sonntag's equation. It is concluded that Wagner's equation is the best available representation of the coexistence curve of water, with the most sound basis in the data.

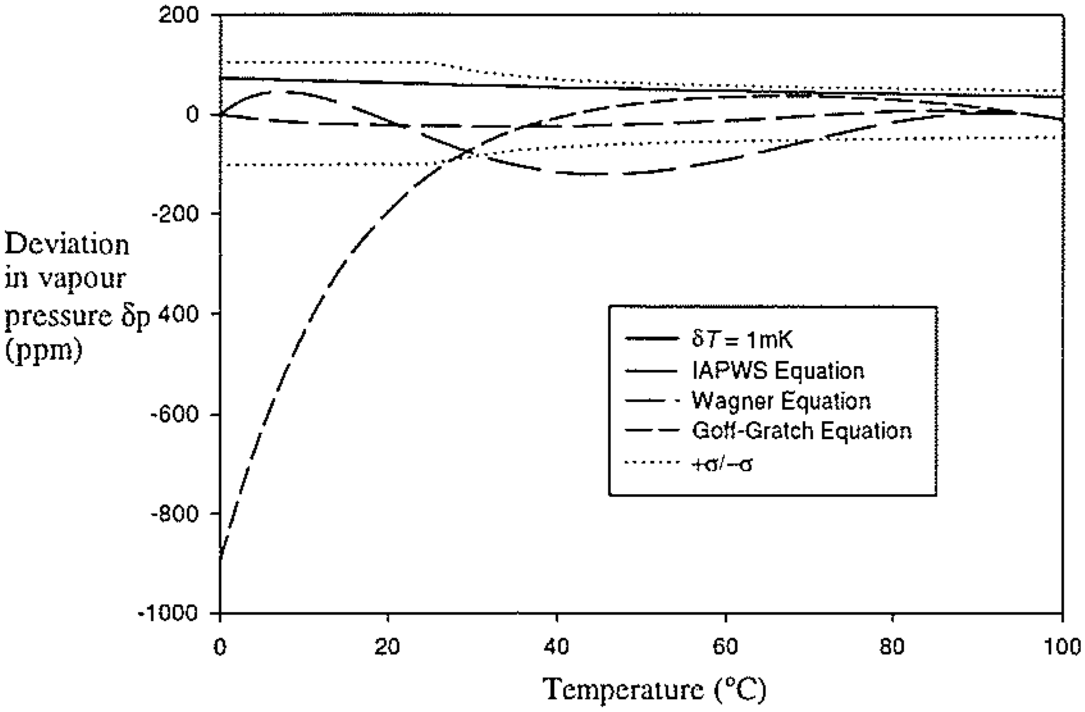

Figure 2: Deviations of alternative equations for water from Sonntag [13]

3. REVIEW OF DATA FOR SOLID-VAPOUR EQUILIBRIUM

The starting point for the discussion of vapour pressure measurements over ice is the recent paper of Marti and Mauersberger [19]. This paper examined studies of the vapour pressure of ice made since 1970, in addition to reporting independent experimental measurements. We restrict our attention to those measurements made on hexagonal crystalline ice. Other forms of ice do exist at these temperatures but the hexagonal form is generally taken to be the stable form at temperatures above about 170 K. The measurements discussed and assessed in detail are: the measurements of Jancso and co-workers [20], the measurements of Douslin and Osborn [21], and the measurements of Marti and Mauersberger [19]. The definitive measurement of Guildner et al [8], made at the triple point temperature, has already been discussed.

3.1. DATA OF JANCSO, PUPEZIN AND VAN HOOK

The measurements of Jancso et al [20] were very extensive and cover the temperature range 195 K to 273 K. Temperatures were measured on the IPTS-48 and pressures were measured relative to the triple point pressure using a capacitance manometer. The values of the experimental sublimation pressures had to be corrected since the value adopted for the triple point pressure differed from that measured directly by Guildner et al [8]. The Type A uncertainty estimates given by the author were 0.04 Pa at temperatures below 255 K and 0.4 Pa at temperatures above 255 K.

3.2. DATA OF DOUSLIN ET AL

The measurements reported by Douslin et al [21] span the temperature interval 242-271 K and used the static method. An inclined piston gauge designed and built by the author was used to measure the pressure (rather than a manometer). Water vapour contacted the piston directly. Temperatures were measured on the IPTS-48 and the estimated uncertainty in the temperature of the sample was given as 1 mK. The pressure measurements had an uncertainty which varied from 0.15 Pa at 242 K to 0.28 Pa at 271 K.

3.3. DATA OF MARTI AND MAUERSBERGER

The measurements reported by Marti and Mauersberger [19] spanned the temperature interval 170 K to 273 K and used the static method. The apparatus consisted of a small glass sample cell connected to a gold plated sphere, to which were connected a pressure sensor, a mass spectrometer system and the gas handling lines. Pressures were measured to 0.2 % using a precision capacitance manometer for pressures above 20 Pa. For pressures below 10^{-2} Pa a mass spectrometer was used and the estimated uncetainty was 1 %. For the pressure interval 10^{-2} - 20 Pa no information is given as to how the measurements were made. Temperatures are assumed to have been measured on the IPTS-68 (the authors do not state which scale was used) and the estimated uncertainty in the temperature of the sample was given as 10 mK.

3.4. CONCLUSIONS FROM DATA FOR ICE

Figure 3 shows the selected data as deviations from the equation of Sonntag [13]. Here, the data have been converted to the ITS-90 and so are all comparable. The uncertainty associated with such a conversion is of the order of 1 mK.

The data of Douslin et al [21] (open circles) agree with the baseline to within 0.5 % at temperatures above 250 K. Below this temperature the data show positive deviations from the baseline. This behaviour is consistent with the presence of a volatile impurity and we note that his measurements are based on a static method which are susceptible to this effect. It is of note that this set of measurements is based on the earlier set, mentioned above in relation to the

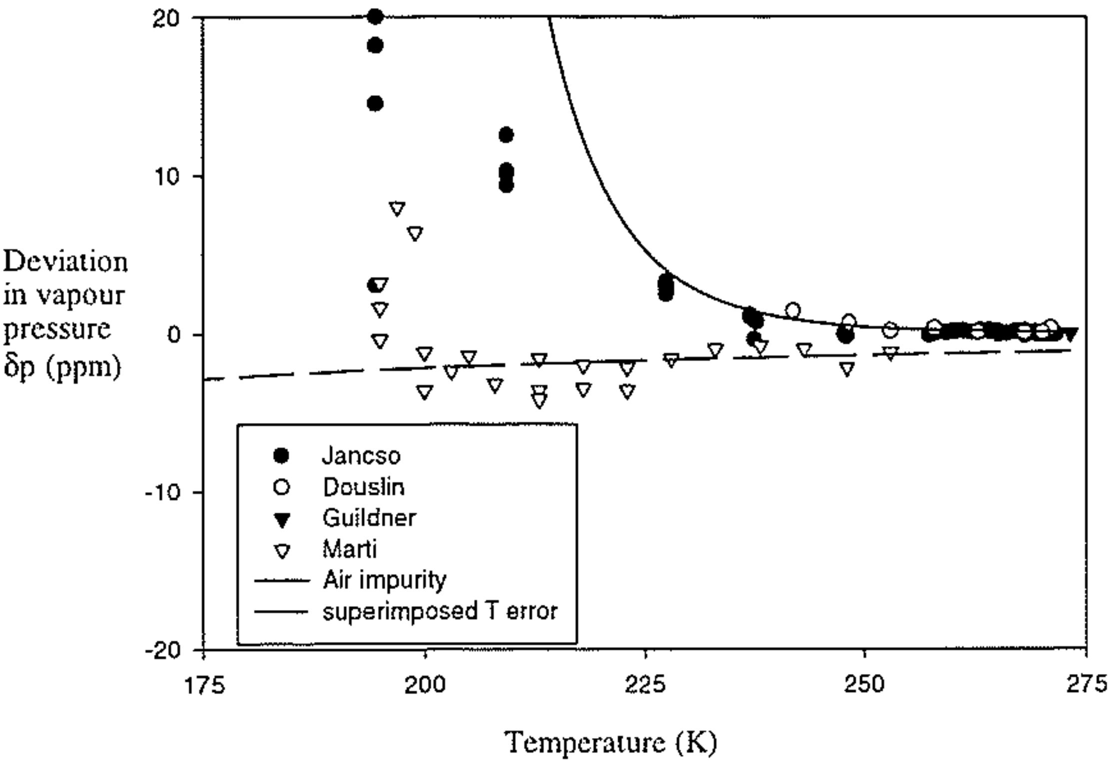

Figure 3: **Deviation in vapour pressure (δp) of selected data for ice from the equation of Sonntag [13]**

liquid-vapour equilibrium, which he concluded in a later paper were affected by the presence of air. The solid curve is an estimate of the effect of air on the vapour pressure measurements of ice. Although there is considerable scatter the deviation of the data are accommodated reasonably well by the equations describing the presence of air.

The Jancso et al data (filled circles) [20] show agreement to better than 0.5 % at temperatures above about 250 K. Below this temperature, their data also show positive deviations, which is not entirely consistent with the effect of a volatile impurity (as seen by the not-so-good agreement with the solid curve). The situation regarding the Jancso data is complicated by the fact that some instrumental range changes were required to make measurements over the range they studied.

The data of Marti and Mauersberger [19] (open triangles) show significant scatter and negative deviations from the baseline on the order of 2 % over most of the range. (The scatter below 200 K is too great to be included on a graph at this scale and so is not shown.) However, the measurements are rendered almost useless by poor reporting and the data shown in figure 3 have been estimated from their graph. The dashed line represents a superimposed temperature error, and we see that it gives a good representation of the deviations from the baseline. It is concluded that the data of Marti and Mauersberger contain a systematic temperature.

3.5. FORMULATIONS FOR SATURATION VAPOUR PRESSURE WITH RESPECT TO ICE

For ice, as for water, to represent the vapour pressure data, least squares regression analysis can be used to generate the coefficients of a polynomial. Gibbins' review of the equations in use up to 1990 included those for ice, but merely compared them and concluded that there are large differences.

Wagner [22] has generated an equation for ice which gives a good representation of the data. This equation has been adopted by the International Association for the Properties of Water and Steam (IAPWS). However, an earlier equation of Wagner for ice which gave a good representation of the experimental data yielded values for the derivatives which were inaccurate leading to physically unrealistic values for the heat capacity of ice. This point is discussed further below, in relation to the equation of Sonntag.

Integrations of the equations relating the other thermodynamic properties to vapour pressure can be performed if the parameters entering into the integration are completely independent and known sufficiently accurately. This would enable calculation of the vapour pressure to be compared with direct measurements. This was the approach adopted by Goff and Gratch [1]. Since that equation was developed additional information has become available and the process repeated by Wexler [18]. In contrast to the situation with the liquid phase the additional information for ice is known with sufficient precision to enable thermodynamic calculations of vapour pressure to have an uncertainty better than the best available experimental measurements. The Wexler formulations have been updated to the ITS-90 by Sonntag [13]. It is the opinion of this author that Sonntag's 1990 equation gives the best estimates of the sublimation pressures for ice and the reader is referred to that article for a fuller discussion. However, a word of caution is necessary. As mentioned above the heat capacity of ice can be estimated from the derivatives of the vapour pressure curve. Such a calculation is a severe test of any proposed equation. Calculations here suggest that the derived values are in reasonable agreement with experimentally determined values, but the agreement is not close and it is important to realise that values of the derivatives of Sonntag's 1990 equation may be inaccurate.

4. REVIEW OF DATA FOR WATER VAPOUR ENHANCEMENT FACTOR

The water vapour content of real gases, and of air in particular, saturated under known conditions of temperature and pressure, is not predicted adequately by ideal gas laws. On any isotherm, the saturated water vapour content increases with pressure. It is possible to derive theoretically an expression for the saturation water vapour content of the gas mixture as a function of the mole fraction of the constituents, the parameters of state and the virial coefficients. In such a formulation, the air-water interactions are in large part characterised by the second cross-virial coefficient for the air and water molecules.

Measurements of the enhancement factors for air-water mixtures can be analysed to yield values of the interaction virial coefficients and a review of such data follows below.

4.1. DATA OF HYLAND AND WEXLER, AND HYLAND

The most extensive series of measurements of enhancement factor were made at the NBS (now NIST). The data relate to measurements of air-water mixtures and are of high precision. The work is reported in two papers by Hyland and Wexler [23], and Hyland [24], and the results are at 6 temperatures spanning the range from 253 K to 343 K (-20 °C to +70 °C). The data have been analysed to yield values for the interaction virial coefficients with uncertainties ranging from 0.7 cm^3mol^{-1} at 343 K to 1 cm^3mol^{-1} at 253 K (i.e. between 2 %

and 4 % of the value of B_{AW}). The uncertainties include all known random and systematic influences.

4.2. DATA OF WYLIE AND FISHER

Wylie and Fisher (at the NSL, Australia) made measurements of the enhancement factor of air-water mixtures at three temperatures in the interval 293 K to 348 K (20 °C to 75 °C) [25]. The measurements and analysis of results have been reported in two papers. The measurements have been analysed to yield values of the interaction virial coefficient with uncertainties ranging from 0.7 cm^3mol^{-1} at 293 K to 2 cm^3mol^{-1} (i.e. between 2 % and 10 %) at 348 K.

4.3. DATA OF POLITZER AND STREBEL

Politzer and Strebel performed single saturation isotherm experiments at 50 and 70 °C [26]. Values of the interaction virial coefficient were derived from the results by Hyland and Wexler [23]. The measurements at 70 °C were found to contain a systematic error and were excluded on this basis. The Type A experimental uncertainty associated with the measurement at 50 °C is 0.4 cm^3mol^{-1} (i.e. about 1.6 %). No assessment of the Type B uncertainties associated with these measurements was given.

4.4. DATA OF WEBSTER

Webster obtained values of the enhancement factor at four temperatures between 238 K and 288 K (-36 °C to +15 °C) [27]. These results were analysed by Hyland and Wexler [23] to obtain values of the interaction virial coefficient. The Type A uncertainties derived from these measurements ranged from 7.5 cm^3mol^{-1} (about 11 %) at 238 K to 2 cm^3mol^{-1} (about 5 %) at 273 K. No assessment of the Type B uncertainties associated with these measurements was given.

4.5. CONCLUSIONS FROM DATA FOR WATER VAPOUR ENHANCEMENT FACTOR

In Figure 4, the available data for interaction virial coefficients B_{AW} are plotted as a function of temperature along with a number of equations representing the data. A curve based on a square well potential is also shown for comparison. Above 273 K the data are in good agreement and generally overlap within two standard deviations. Below 273 K the agreement is not good. (The two data sets which are available differ by up to 20 cm^3mol^{-1}.)

The most extensive series of measurements were those of the NBS. However, the data are inconsistent with a physically meaningful temperature dependence expected for virial coefficients. Specifically, the data show no deviations, outside their standard uncertainties, from a straight line. (This is shown in more clearly in Figure 5, where the virial coefficients are plotted as deviations from a linear model.) This linearity of the NBS curve is unrealistic and raises a question mark over the lower temperature data, given that the higher temperature data are in good agreement with independent measurements. The NBS low temperature data are based on three measurements of the enhancement factor. The imposed temperature dependences of the other virial coefficients used in the analysis could conspire to leave the apparent cross-virials with a linear temperature dependence but this is extremely unlikely. It is concluded therefore that the lower temperature data obtained at the NBS are in error.

Those equations which use the low temperature NBS virial coefficients are likely to be suspect for temperatures below 273 K and should be treated with caution. Of the published equations this leaves the earlier work of Hyland and Wexler [23] as the most reliable representation at the lower temperatures. Unfortunately, this equation is seen to be unreliable at temperatures above 343 K, but in the interval 238 K to 343K it gives the best representation of the data.

It is of interest to compare calculated values of the enhancement factor using different estimates of the interaction virial coefficient, as this is a check of the quality of the data. We chose in this work to use estimates of the virials based on the equation of Hyland and Wexler [23], and that of Hyland [24]. These represent the extremes of the available estimates. Values of *f* derived using these equations differ by 0.15 % at 238 K (-35 °C) reducing to just 0.02 % at 273 K (0 °C). Above this temperature the agreement becomes progressively better. Below 273 K the values of *f* differ by an amount in excess of the estimated uncertainty in the value. This is not surprising given the discrepancies in the virial coefficients noted above, but has important consequences for the humidity community. The main consequence is that values of *f* based on equations which incorporate the low temperature NBS data are likely to be in error at temperatures below 273 K by an amount exceeding their estimated uncertainty. Additionally, the common practice of extrapolating such values to even lower temperatures is likely to be very suspect and it is recommended that values calculated for temperatures below 238 K be treated with caution.

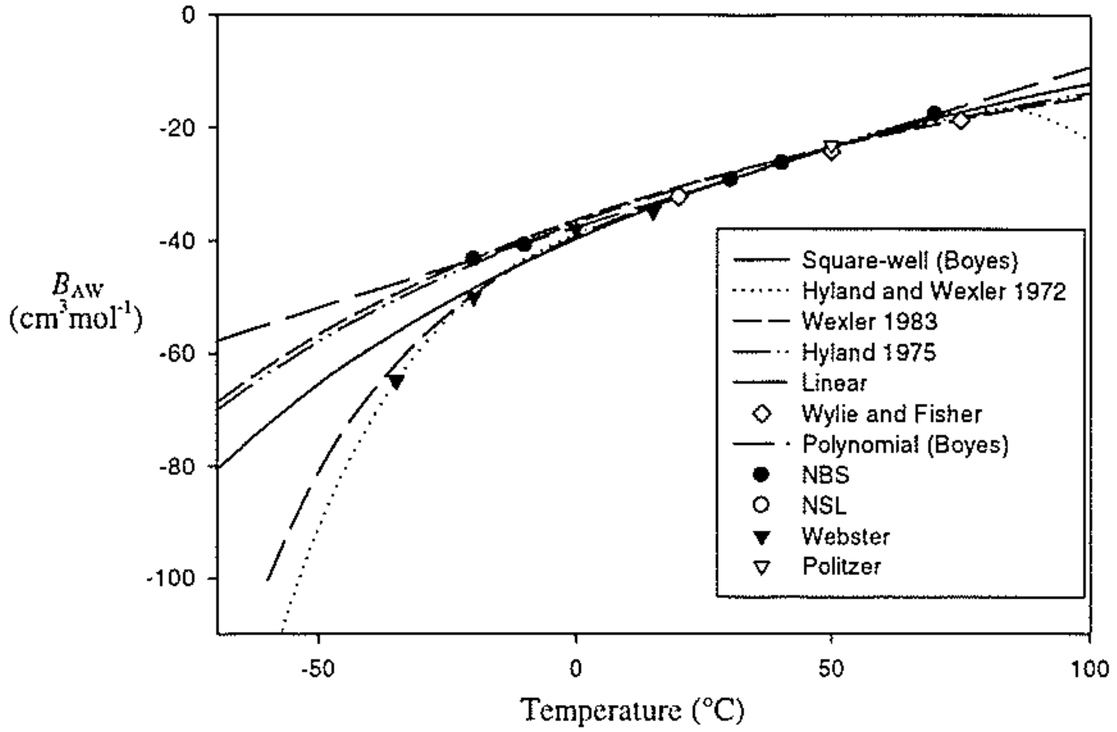

Figure 4: **Interaction virial coefficients B_{AW}**

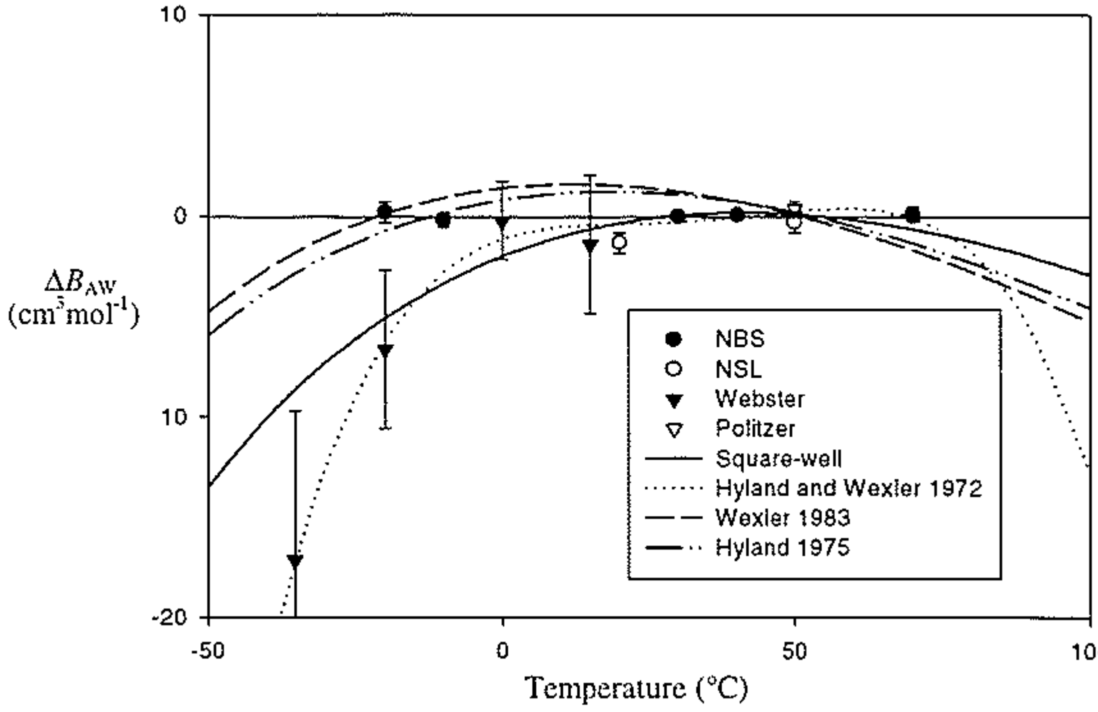

Figure 5: **Interaction virial coefficients plotted as deviations from a linear model**

5. OVERALL CONCLUSIONS

This study has looked at the published data and formulations for saturation vapour pressure over water above 0 °C, and over ice, and for water vapour enhancement factor. The quality of the measurement approach, consistency of the data and quality of the uncertainty analysis have all been considered. As a result, recommendations can be made as follows.

For saturation vapour pressure, p_s over water above 0 °C, the most strongly recommended formulation is that of Wagner [22],

$$\ln\,(p_s\,/\,p_c) = (T_c\,/\,T)\,(a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5}),$$

where

p_c is 22.064 MPa
T_c is 647.096 K
T is temperature in kelvin
$\tau = 1\text{-}T/T_c$
a_1=-7.85951783
a_2=1.84408259
a_3=-11.7866497
a_4=22.6807811
a_5=-15.9618719
a_6=1.80122502.

For saturation vapour pressure over ice, in pascals, the most recommended is that of Sonntag [13],

$$\ln p = -6024.5282T^{-1} + 29.32707 + 1.0613868\times10^{-2}T - 1.3198825\times10^{-5}T^{-2} - 0.49382577\ln T\,.$$

Formulations for saturation vapour pressure over water have a sound foundation on the data, which are experimentally more well known than the theoretical estimates. For ice, the measured data are not considered as reliable as the theoretical estimates of the quantities. It should also be noted that derivation of other data from these formulations (e.g. derivatives of the vapour pressure curve) may be unreliable.

For water vapour enhancement factor the most recommended formulation is that of Hyland and Wexler [23]. The lengthy formula and supporting calculations are not listed here, but are given in Hyland's paper [24]. The paper also gives a detailed tabulation of the values of enhancement factor given by the formula for temperatures from -80 °C to +90 °C and for air (total) pressures between 0.25 bar and 100 bars (0.025 MPa to 10 MPa). Interpolation of these tables may represent the most practical way to use Hyland's formulation. Published in 1975, Hyland's formula refers to temperatures on the scale of IPTS-68, and not ITS-90. However, enhancement factor varies only slowly with temperature, and errors due to differences between the temperature scales have an effect of less than one part in 10^6, and are thus insignificant. More significantly, Hyland's formula for enhancement factor should be used with caution below -35 °C as this is the limit of the measured data. The use of this formula outside its range of validity would be an extrapolation which is likely to magnify errors to an unacceptably high level.

Overall, the choice of which formulations to use depends in the end upon the uncertainty required. Where the smallest uncertainty is not needed, formulae other than those recommended above may reasonably be used.

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