A NEW ABSOLUTE METHOD OF HYGROMETRY

I. The General Principles of the Method

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Summary

This paper is the first of two which give a detailed treatment of a new method of hygrometry. In this method an ionic single crystal is surrounded by the gas which is the subject of measurement, and the temperature of the whole is so adjusted that a very thin layer of saturated solution is formed on the crystal surface and is brought to a constant thickness as determined electrically. The temperature thus established provides a measure of the absolute humidity of the gas.

In this first paper the general principles and theory of the method are dealt with and the observed performance is outlined. The method is compared with the conventional condensation method, the basic limitations of which are considered, and is shown to be considerably more accurate; it is also more convenient and can be at least as rapid in response.

I. Introduction

This paper is the first of two dealing with a new method of hygrometry which is quasi-absolute, accurate, and convenient to apply. The method has already been described in general terms elsewhere (Wylie 1955).

This paper gives a general account of the method and its relationship to conventional hygrometric instruments and derives values for the sensitivity to be expected. The second paper will be devoted to an experimental study of the properties of a particular type of crystal element and the interpretation of the results.

The design of practical forms of the hygrometer will be considered elsewhere.

(a) Conventional Hygrometry

A generally unsatisfactory situation exists in the subject of hygrometry, especially as regards precise absolute measurements. Apart from the use of inconvenient chemical methods requiring very careful technique, an *absolute* accuracy of better than $0 \cdot 1$ °C in the dew-point temperature can be obtained probably only with the dew-point hygrometer. No conventional method of hygrometry can provide either an accurate and rapidly responding instrument for general use or a convenient instrument of greater than usual accuracy for use as a standard.

The present method of hygrometry is related to the conventional condensation method (dew- or frost-point method) and certain methods involving electrolytic conduction. These will consequently be considered here.

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(b) The Condensation Method

The conventional condensation method is based on the detection of a surface condensate of nominally pure water (or ice) by means of the light which it scatters. The condensate has a complex detailed structure and possesses complex thermo-dynamic and optical properties. Theoretical and experimental investigations of these properties have revealed that, far from being capable of an arbitrarily high accuracy as is often assumed, the condensation method is subject to significant fundamental limitations. In the case of a dew-point these result from the effect of the high internal pressure of a small water droplet on its vapour pressure and the vapour pressure lowering which extremely small quantities of water-soluble matter, present on the dew-condensing surface, can produce.

It can be shown that a dew deposit first becomes detectable when the basal radius of the individual droplets is about 8×10^{-6} cm. If the droplets are hemispherical, this corresponds to a vapour pressure increase of $1 \cdot 5$ per cent. and, at ordinary temperatures, to an observed dew-point about $0 \cdot 2$ °C too low. An effect of comparable magnitude but opposite sense would be contributed if a uniform concentration of sodium chloride of only about 6×10^{-8} g/cm^2 were present on the condensing surface. Such a layer of salt possesses a theoretical thickness of about 3 Å, the interionic distance in the sodium chloride crystal lattice. If as is usual in practice the contaminant is not uniformly distributed, far smaller quantities can produce a marked effect. The practical significance of these facts is that dew-point measurements made using a really clean surface could easily be in error by $0 \cdot 1$ °C and that, in the usual case, where the amount of soluble contamination is sufficient to produce significant effects, not only can errors larger than this easily occur without the observer's knowledge, but the dew-point temperature will not be sharply defined. This latter phenomenon was observed, although incorrectly interpreted, by Hixson and White (1938) when they attempted a particularly accurate determination of the dew-point under carefully controlled conditions. Its occurrence has been confirmed by the author. An observed frost-point can be affected by the elevation of the vapour pressure of small ice crystals which results from their surface-free energy but is unaffected by traces of water-soluble matter.

A practical aspect which should be mentioned is that the sharp temperature gradient which exists between a condensing surface and the neighbouring gas represents a load on the cooling system and necessitates careful design of the means for measuring the temperature.

Measurements made with a conventional condensation hygrometer could rarely be assigned an absolute accuracy of $0 \cdot 05$ °C with confidence. The attain-ment in practice of even a relative accuracy of this magnitude is not easy.

(c) Devices depending on Electrolytic Conduction

Humidity sensitive elements which employ a solid salt have been described by Todd and Bousfield (1920), Anderson (1922), and Fiene (1936). Anderson used his elements only in a qualitative way and the others presented no experi-mental evidence that a sharp change in the electrical behaviour of their elements

at a definite relative humidity actually occurs.   Indeed, Fiene has made claims which would indicate that he had observed only a diffuse change.

The elements of Weaver and Ledig (1923), which were produced to avoid the disadvantages of those which had already been described and which involve an electrolytic coating on a glass surface, and the elements of Hickes (1947), which involve the impregnation of lithium chloride into a woven glass fabric, might both have been expected to provide a sharply defined transition humidity. The former elements actually provide only a continuous relationship between electrical resistance and humidity, whilst the latter provide a transition insufficiently sharp to allow an accuracy much better than 1 °C in the dew-point.

Lichtgarn (1947) attempted to plot the electrical resistance of small ionic single crystals against relative humidity, with indifferent results.   That he should have sought and apparently found such a one-to-one relationship is symptomatic of a general disbelief that the dissolution of a solid salt, as detected electrically, begins at a sharply defined relative humidity.

The conclusions reached by previous writers show that their experiments have been complicated by effects due to surface and capillary adsorption, the surface tension of the forming liquid, and the presence of traces of soluble contamination.   By the appropriate design of elements utilizing single crystals these effects can be reduced to such an extent that the phase change occurs over a humidity range corresponding to a range of dew-point of no more than a few thousandths of a centigrade degree.

(d) The New Hygrometer

The present hygrometer may be regarded as derived in principle from the condensation hygrometer by substitution of a water-soluble ionic single crystal for the condensing surface.   The temperature is determined at which a very thin layer of saturated solution, formed on the surface of the crystal and observed by virtue of its electrical properties, is in equilibrium with the gas which is the subject of measurement.   The conducting layer, unlike a deposit of dew or frost, is easily maintained in equilibrium with the gas.   Since the layer possesses a plane free surface, its thermodynamic properties are practically identical with those of the bulk saturated solution.   This is so even down to thicknesses of less than 100 Å.   The change in electrical resistance with layer thickness follows a very simple law, whereas it can be shown that the optical properties of a dew or frost deposit are complex, involving gross hysteresis.

The thickness of the conducting layer can be chosen arbitrarily within wide limits ;   this represents a valuable degree of freedom which has no effective analogue in the conventional condensation method, and provides a simple but stringent test for the presence of foreign water-soluble matter on the crystal surface.   If necessary, accurate results can be deduced when contamination is present by making measurements at two or more layer thicknesses.

An absolute accuracy of 0·01 °C can readily be attained.   The accuracy is at present limited to about this level by factors which are believed to be technical rather than fundamental.   The crystal element can be housed in a

truly isothermal environment and provision for the accurate measurement of temperature is easy.

The method has a number of advantages over the conventional condensation method. Some of these are of a fundamental character, while others are essentially practical, such as the facility with which the operation can be made automatic by simple electrical means and the convenience with which measurements can be made on gases at very high pressures.

II. THE PHYSICAL BASIS OF THE METHOD
(a) The Principle

The term *saturated solution* will be used to denote a solution which remains just saturated irrespective of any variation of temperature. Also, with the neglect of deviations from perfect gas behaviour and smaller effects due to other causes, the ratio of the saturation vapour pressure of a solution to that of water will be referred to as the *relative vapour pressure* of the solution.

The relative vapour pressures of saturated salt solutions generally depend little upon the temperature, whereas the relative humidity of a gas of constant composition changes markedly with temperature. Therefore, an *equilibrium temperature* usually exists at which the relative humidity of a particular gas is equal to the relative vapour pressure of the saturated solution of a particular salt. When a clean ionic crystal and a surrounding atmosphere of constant composition are cooled below the equilibrium temperature the surface of the crystal dissolves in water provided by the surrounding gas. If, once a surface layer of saturated solution has been formed, the temperature is brought to, and held at the equilibrium value, the thickness of the layer will remain constant except in so far as liquid is drained off by gravity or surface-tension forces. If the temperature is raised slowly from the equilibrium value, water evaporates from the layer and the solute grows back onto the crystal.

Whereas, at ordinary temperatures, the ionic crystal is a good electrical insulator, the layer of saturated solution is a good conductor. Consequently, the presence of the layer and changes in its thickness may be detected by electrical methods.

In the present hygrometer, which has been termed the " electrolytic condensation hygrometer ", a single crystal of a stable salt is surrounded by an atmosphere of the gas the humidity of which is to be measured and the temperature of the whole is so adjusted that a layer of saturated solution, formed on the crystal surface, is of constant thickness as determined electrically. The gas is most conveniently cooled at constant pressure and will be assumed to be so cooled in all that follows. If the vapour pressure of water at temperature T is denoted by $p_w(T)$, and the relative vapour pressure of the saturated solution, expressed as a fraction, is $S(T)$, then, since the relative humidity at the equilibrium temperature T_e is $100S(T_e)$, the partial pressure of water vapour in the gas, p, is given by

$$p = S(T_e) \cdot p_w(T_e). \quad \dots\dots\dots\dots\dots\dots (1)$$

The equilibrium temperature is always higher than the dew-point.   Below 0 °C the equilibrium temperature is also higher than the frost-point unless it lies in the metastable zone just below the eutectic temperature of the water-salt system.

(b) The Crystal Element

Whereas with elements such as those of Dunmore (1938, 1939) a one-to-one relationship exists between electrical resistance and relative humidity, with those now to be described the electrical conductance varies, in principle, as the time-integral of the deviation from equilibrium.   It is clear that this valuable property is not obtained with permeable aggregates of crystals or with thin deposits formed on an electrical insulator as described by Weaver and Ledig (1923).   It has been found that suitably designed elements, utilizing single crystals, do in fact possess the integrating property with high accuracy.

The surfaces of a single crystal may be regarded as impervious, or, having regard to the fact that the substance is interlaced with dislocation lines, practically so.   The structure of the surface will depend on its history, and particularly the
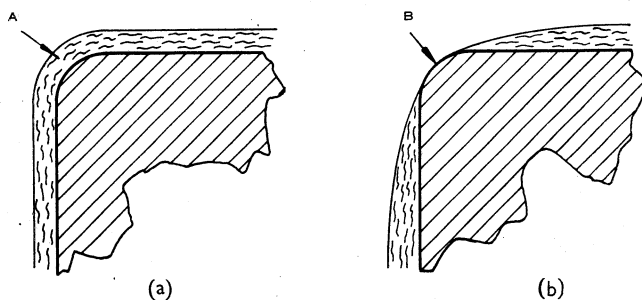

Fig. 1.—Layer of solution on a cubic crystal (for explanation, see text).

method of production of the crystal, but will undoubtedly be crossed by terraces and intersecting steps.   It has been shown by Frank (1949) that surface defects are necessary if the crystal is to grow for small degrees of supersaturation of the surrounding medium.

It has been found very desirable to extend the electrodes of a crystal element onto its actual conduction faces, in order to avoid detrimental edge effects.   The origin of these can be understood by reference to Figure 1, which shows, consider-ably magnified, part of a cubic crystal bounded by (100)-like planes and with the edge rounded as could result from partial dissolution in a solvent.   Clearly, a uniform layer of solution such as is shown in Figure 1 (a) cannot persist, because there is excess pressure in the region A due to surface tension.   The actual equilibrium form, assuming the solution makes zero contact angle with the crystal, is as shown in Figure 1 (b).   The area B has been denuded of liquid but possesses an adsorbed layer.   If the path of electrical conduction passes over such an edge, a substantial conductance can be maintained only if the temperature is held below the true equilibrium value so that a dynamical equilibrium is established, liquid being removed from area B as fast as it is being formed.

A similar situation exists in the neighbourhood of multimolecular steps or irregularities on an otherwise plane surface and for this reason the conduction faces should be habit faces for normal crystal growth from the aqueous solution. On other than habit faces etching could occur, especially with successive superficial dissolution and regrowth of the crystal.

In general, the effect of surface tension forces is much greater than that of gravity. It is easily shown on the basis of the work of Caw (unpublished data) that the drainage under the influence of gravity of the layer from a vertical surface a few millimetres in height is, in the present context, entirely negligible for layer thicknesses of less than 5000 Å, and hence for any thickness of importance here.

It will be shown in the second paper that the most advantageous thickness of the conducting surface layer is about 200 Å. At ordinary temperatures the corresponding resistance of the crystal element is of the order of 1 MΩ. A 200 Å layer can be reduced to half thickness very rapidly (certainly in less than 1 sec) without the nucleation of new crystals within it. On the other hand, if an unduly thick layer is allowed to develop, the crystal must be dried slowly if the formation of large numbers of microcrystals and a consequent marked deterioration of performance of the hygrometer are to be avoided. In practice the formation of microcrystals on the actual conducting surfaces of a crystal is easily avoided.

The properties of different crystal substances differ greatly as do the methods most suitable for the production of the corresponding crystal elements. In particular, hydrated substances are usually more soluble, have lower eutectic temperatures, and crystallize more conveniently from solution than anhydrous substances. The range of equilibrium temperature provided by any particular substance is from the eutectic temperature of the water-salt system to the melting point of the crystal, unless phase transitions, usually between different hydrates of the salt, intervene. Data for some useful crystal substances are given in Table 1.

To indicate what is involved in producing suitable crystal elements, the preparation of elements of potassium chloride and calcium nitrate tetrahydrate, which are more or less representative, will be outlined here. It has been found convenient to use crystals which are roughly equiaxed and 2–3 mm in linear size.

Potassium chloride is anhydrous over the whole range from the eutectic point, at −10·65 °C, to its melting point of over 700 °C. The substance is chemically stable and easily obtained in a sufficiently pure state, say, A.R. grade. It crystallizes in a cubic structure. Elements of accurate rectangular shape can be prepared by cleavage on (100) and equivalent planes. The (100) face is the habit face for normal growth from aqueous solution. The crystals may be coated on two opposite faces and just around the adjacent edges with gold or graphite. Gold may be applied in the form of leaf or by vacuum deposition. Graphite may be applied in colloidal suspension in ethyl alcohol either by brushing, using a soft hair brush, or by spraying, using an artist's air brush. The finished crystals can be washed in pure ethyl alcohol if desired,

some care being necessary with those end-coated with graphite. As explained in the second paper, both freshly cleft and freshly washed surfaces of potassium chloride should be allowed to stand for some hours before being used for hygrometric purposes.

Calcium nitrate tetrahydrate is stable from the eutectic point of the water-salt system, at $-27 \cdot 9$ °C, to a hydrate transition point at approximately 42 °C. At the latter point a transition occurs in a simple way so that the crystal appears to melt to form a liquid of the same composition. In such a case, as the temperature approaches the " melting point " the solubility of the crystal tends practically to infinity ; as will be seen below, the sensitivity of the present method of hygrometry then also tends practically to infinity. Efflorescence, which occurs with hydrated crystals at sufficiently low relative humidities, necessitates some precautions when using elements of this material. The substance can be crystallized from solution after dissolving A.R. grade calcium carbonate in pure nitric acid. The structure is monoclinic and the crystals exhibit no useful cleavage properties. The procedure which has been used to prepare the elements is to grow prismatic crystals of the desired thickness and, after breaking them into short lengths, to grind the broken ends flat and square to the prism axis using a rotating abrasive disk. They are best end-coated by spraying with colloidal graphite in ethyl alcohol suspension. Vacuum deposition of gold is obviously impracticable. The finished elements can be washed in pure propyl alcohol.

III. The General Form of the Hygrometer
(a) The Essential Components

In order to achieve a high performance, the practical hygrometer must be designed carefully.

Figure 2 shows diagrammatically two convenient general forms. These have in common an isothermal enclosure B which houses the crystal element C, an inlet heat exchanger E_1 by means of which the incoming gas is brought to the temperature of B before it enters the crystal cavity, provision for controlled heating, H, and cooling, R, and some means of indicating an electrical characteristic of the crystal, M_c, and of indicating the temperature of the enclosure, TH. Although often only cooling or heating will be required, the provision of both is desirable, especially when the instrument is to be operated automatically.

In the arrangement of Figure 2 (a), the isothermal enclosure is provided by a block of metal, preferably of silver or copper, which may conveniently be cylindrical and about an inch in size and which is thermally isolated by the insulation I.

Cooling is obtained by passing a refrigerant directly through channels E_2 cut in the metal or by conducting heat from the enclosure either along a slender metal bridge or across a narrow gas-filled space communicating with a cold reservoir. An electrical heater may be wound directly onto the enclosure. The resistance of the crystal element between suitable electrodes is the simplest electrical quantity of which to take account and is easily indicated on a meter

with the aid of a suitable circuit.   To avoid polarization effects and the formation
of impurities by electrolysis, alternating current is used, the magnitude of the
current being such that no significant heating of the crystal occurs for any desired
resistance value. Currents of the order of 1 μA have been used. The temperature
may be measured using a thermometer inserted in a well in the enclosure, or,
better, using a resistance thermometer wound directly on the enclosure.

The arrangement of Figure 2 (*b*), which utilizes a Dewar vessel, *D*, is capable
of no less accuracy but is not nearly as amenable to automatic operation or to
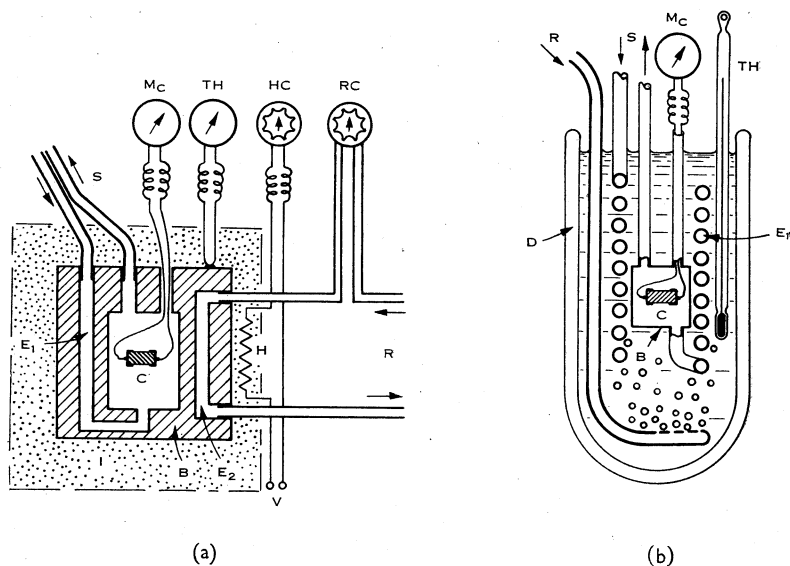easy manipulation of the crystal element.   The inlet heat exchanger may consist

(a)   (b)

Fig. 2.—Two forms of the electrolytic condensation hygrometer.   (*a*) Type
suitable for automatic operation, (*b*) an easily improvised type. *B*, Isothermal
enclosure ;   *C*, crystal element ; *D*, Dewar vessel ; E_1, inlet heat exchanger ;
E_2, cooling channels; *H*, heater; *HC*, heater control; *I*, thermal insulation;
M_c, meter indicating an electrical characteristic of crystal element ; *R*, cooling
circuit ; *RC*, control for cooling ; *S*, gas inlet and outlet tubes ; *TH*, thermo-
meter ;   *V*, heater power source.

of a coil of metal tube E_1.   Cooling may be achieved either by passing a refrigerant
through another coil immersed in the liquid or, if the liquid is sufficiently volatile,
by bubbling a gas through it as shown.   With this arrangement there is little
disadvantage in using an ordinary liquid-in-glass thermometer.

(*b*) *Methods of Operation*

When the hygrometer is operated manually, the operations performed by
the observer are largely analogous to those performed in using a visual dew-
point hygrometer.   The main differences are that the operator makes use of
purely objective observations of the crystal-resistance indicator instead of
attempting to observe visually the onset of condensation, and that equilibrium

between the gaseous and liquid phases may be established accurately and maintained. By adjusting the temperature judiciously within a range of about 0·2 °C the crystal resistance may be brought to any desired value within a wide range; it is then easily maintained almost constant.

The observer inevitably causes small and irregular variations of the temperature about the equilibrium value and consequently small variations of resistance about the chosen value. These are much diminished when, with experience, the observer pays almost equal attention to the temperature and resistance indicators. It is particularly desirable to observe both indicators if the dynamical properties of the system are unfavourable, as when there is an appreciable lag in the temperature indication or in the communication of a temperature change from the enclosure B (see Fig. 2) to the element C. This aspect will be considered in detail elsewhere where a double-loop controller will be described which takes account of the temperature of the enclosure as well as the resistance of the crystal element.

The hygrometer is easily operated semi-automatically or wholly automatically. In semi-automatic operation the temperature of the enclosure B is brought automatically to any value set by the observer, the resistance indicator still being observed visually. Provided that the temperature setting is not changed too rapidly, a one-to-one relationship between control setting and temperature exists and the equilibrium temperature can be located with accuracy and with ease.

Wholly automatic operation is obtained when the temperature of the enclosure is controlled by the resistance of the crystal element. In this case the temperature may be continuously recorded. Details of apparatus capable of semi-automatic and automatic operation will be given elsewhere.

IV. General Quantitative Aspects

In order to appreciate and to be able to predict the behaviour of the crystal element, some properties of the conducting layer must be considered quantitatively.

(a) The Thickness of the Liquid Layer

In practice the layer thickness must be chosen between a lower limit which depends on the allowable systematic temperature error and an upper limit which is set by lag effects due to surface flow. For potassium chloride at ordinary temperatures, and for a systematic error of 0·01 °C the lower limit is about 100 Å. Irrespective of the origin of temperature errors with thinner layers, the correct generalization, for all crystal substances, is almost certainly expressed in terms of layer thickness. Consequently, when, in the following, a value of the layer thickness must be adopted, the value 100 Å will be used. Results given in the second paper show that, even at this thickness, the layer may be regarded in all relevant respects as a continuous sheet of the bulk saturated solution.

(b) The Diffusion of Salt through the Layer

The layer changes thickness by taking up or losing water at its outer surface where some dilution or supersaturation must occur as a consequence. When the

temperature is constant at the equilibrium value, any non-uniformity of composition in the layer disappears through diffusion of the salt in a time of the order of

$$t = d^2/4D, \quad \dots\dots\dots\dots\dots\dots\dots \quad (2)$$

where d is the layer thickness and D is the appropriate diffusion coefficient. For salts in aqueous solution D is about 10^{-5} cm^2/sec, so that, for $d = 100$ Å, the time is of the order of 3×10^{-8} sec. Clearly the diffusion time will never be significant.

(c) The Rate of Transport of Water to and from the Layer

If a temperature slightly different from the equilibrium value is established, a steady transport of water to or from the layer occurs in proportion to the difference between the water vapour pressure of the gas sample and that of the layer itself. As a first step in determining theoretically the sensitivity of the method, the transport rate per unit vapour pressure difference will be computed for conditions typical of the experimental work, namely, a linear crystal size of approximately $2 \cdot 5$ mm and a mean gas velocity in the crystal cavity of approximately 9 cm/sec (flow rate $2 \cdot 5$ cm^3/sec). Since the gas adjacent to the surface layer may be regarded as being in complete equilibrium with that layer, the transport rate for a given vapour pressure difference is the same as for a free water surface.

Because the transit time of the gas in passing the crystal is of the same order as the diffusion time corresponding to the width of the annular space surrounding the crystal the deduction of an accurate water vapour transfer coefficient is difficult. For present purposes this coefficient is best obtained from what amounts to an accurate extension of the Reynolds analogy, by making use of the psychrometer equation (Wylie 1949), which reduces the problem to the determination of a heat-transfer coefficient. This gives the water vapour transfer coefficient f in the form

$$f = (h + h_r)/APL, \quad \dots\dots\dots\dots\dots\dots \quad (3)$$

where h is the convective heat-transfer coefficient, h_r is the radiative heat-transfer coefficient, L is the latent heat of vaporization of water, P is the total pressure, and A is the usual psychrometer constant. The appropriate value of A is $7 \cdot 2 \times 10^{-4}$ (°C)$^{-1}$. The value of h must correspond to zero flow of heat between the gas and the enveloping metal surface. For the present Reynolds number of approximately 8 the value of h will be slightly less than $5 \cdot 5 \times 10^{-4}$ cal sec^{-1} cm^{-2} (°C)$^{-1}$ and practically independent of the temperature (McAdams 1954). Substitution in (3) gives values for f, corresponding to atmospheric pressure, which range from $1 \cdot 75 \times 10^{-6}$ to $2 \cdot 25 \times 10^{-6}$ g sec^{-1} cm^{-2} (mm Hg)$^{-1}$ for temperatures from -55 to $+40$ °C respectively.

(d) The Theoretical Sensitivity

The sensitivity of the method can be obtained from the vapour-transfer coefficient f and certain physical properties of the saturated solution, namely, its composition, density, and relative vapour pressure and the rate of change of

the relative vapour pressure with temperature. The percentage time rate of change of layer thickness, J, is given by

$$J = (f/db)(\Delta p) \times 100, \quad \ldots \ldots \ldots \ldots \ldots \quad (4)$$

where d is the layer thickness and b, a " thickness factor ", is the mass of liquid water necessary to dissolve the crystal substance per unit volume of solution produced. The quantity b is given in grams per cubic centimetre by

$$b = 100\rho/(100 + x), \quad \ldots \ldots \ldots \ldots \ldots \quad (5)$$

where x is the solubility of the crystal substance in grams per 100 g of water and ρ is the density of the saturated solution in g/cm³. The vapour pressure difference Δp is given in terms of the deviation ΔT of the temperature from the equilibrium value by

$$\Delta p = \frac{\mathrm{d}}{\mathrm{d}T}(S p_w)\Delta T = S p_w \left\{ \frac{1}{p_w} \frac{\mathrm{d}p_w}{\mathrm{d}T} + \frac{1}{S} \frac{\mathrm{d}S}{\mathrm{d}T} \right\} \Delta T. \quad \ldots \ldots \ldots \quad (6)$$

The quantities required for substitution in these equations are given in Table 1 for a number of salts and for temperatures from 40 °C down to the lowest usable values. The specific conductivities of the saturated solutions are also given. The tabulated values of the vapour transfer coefficient f and hence those of the sensitivity J, which is the percentage rate of change of layer thickness (or electrical conductivity) for a temperature deviation of 0·1 °C, relate to the conditions of crystal size and gas flow defined above. The values of J relate to a conducting layer 100 Å thick. The tabulated resistance R, which also relates to a 100 Å layer, is that of a cube-shaped crystal element which conducts on four faces. The table includes the difference between the equilibrium temperature T_e (given in the second column) and the corresponding dew-point T_d. This difference may be plotted against T_e to provide a convenient means of converting observed equilibrium temperatures into a conventional measure of absolute humidity.

The eutectic temperatures, denoted by the subscript E, were determined using salts of analytical reagent purity and are in general higher than values given in reference books. The relative vapour pressure S at the eutectic temperature is simply the ratio of the vapour pressure of ice to that of water. The use of eutectic data in this way has been found to improve, over a wide temperature range, the accuracy with which S is known. S-values given for other temperatures represent an assessment of various published data in conjunction with the eutectic data. Except for sodium chloride, the tabulated specific conductivities are based on measurements made specially for the purpose. Other data given have been taken mainly from the International Critical Tables.

Table 1 gives the electrical resistance at which the crystal element possesses a 100 Å surface layer and the sensitivity to be expected at this layer thickness under the representative conditions defined in Section IV (c) above. The resistance is of a convenient order of magnitude. The sensitivity is seen to be considerable over a wide temperature range and to change with equilibrium temperature roughly in proportion to the vapour pressure of water. In the second paper it will be shown to be in satisfactory agreement with experiment.

TABLE 1

DATA FOR VARIOUS CRYSTALS

(For definitions and units, see footnote on the opposite page)

Crystal Substance	T °C	x	ρ	$\dfrac{100\rho}{(100+x)}$	p_w	S	T_e-T_d	$\dfrac{100}{p_w}\cdot\dfrac{dp_w}{dT}$	$\dfrac{100}{S}\cdot\dfrac{dS}{dT}$	σ	R	$f\times10^6$	J
K₂SO₄ orthorhombic	$-1\cdot48_E$	$7\cdot1_0$	1·06	0·99	4·112	0·986	0·19	7·4	0	0·039	6·4	1·98	6·0
	0	$7\cdot3_7$	1·06	0·99	4·581	0·985	0·21	7·3	0	0·040	6·3	1·99	6·6
	20	11·1	1·08	0·97	17·53	0·976	0·39	6·2	0	0·090	2·8	2·11	23
	40	14·7	1·10	0·96	55·34	0·968	0·69	5·4	0	0·18	1·4	2·25	66
KCl cubic	$-10\cdot65_E$	24·6	1·14	0·91	2·040	0·902	1·30	8·0	−0·2	0·156	1·60	1·94	3·0
	0	28·0	1·15	0·90	4·5812	0·888	1·62	7·3	−0·2	0·208	1·20	1·99	6·4
	1·68	28·5	1·15	0·90	5·1719	0·885	1·69	7·2	−0·2	0·220	1·14	2·00	7·2
	20	34·4	1·17	0·87	17·53	$0\cdot85_8$	$2\cdot4_5$	6·2	−0·2	0·343	0·73	2·11	22
	40	40·3	1·19	0·85	55·34	$0\cdot82_6$	$3\cdot5_4$	5·4	−0·2	0·54	0·46	2·25	62
NaCl cubic	0	35·6	1·21	0·89	4·581	0·76	3·7	7·3	0	0·135	1·85	1·99	5·7
	20	35·8	1·20	0·88	17·53	$0\cdot75_7$	4·4	6·2	0	0·226	1·11	2·11	19
	40	36·3	1·19	0·87	55·34	0·75	5·3	5·4	0	0·35	0·71	2·25	56
Ca(NO₃)₂.4H₂O monoclinic	$-27\cdot9_E$	165	1·42	0·54	0·4644	0·762	2·80	9·3	−0·5	0·013	19	1·85	1·07
	−20	183	1·44	0·51	0·9406	0·731	$3\cdot5_8$	8·6	−0·6	0·017	15	1·89	2·1
	−10	220	1·46	0·46	2·147	0·688	$4\cdot6_4$	7·9	−0·6	0·022	11·4	1·94	4·5
	0	266	1·49	0·41	4·581	$0\cdot64_3$	$5\cdot9_3$	7·3	−0·7	0·029	8·8	1·99	9·3
	20	430	1·56	$0\cdot29_5$	17·53	$0\cdot54_5$	9·4	6·2	−0·9	0·049	5·1	2·11	36
	30	665	1·61	0·21	31·83	0·49	11·8	5·7	−1·1	$0\cdot05_5$	$4\cdot_5$	2·18	74
	40	2020	1·71	0·08	55·34	0·44	14·7	5·4	−1·3	0·06	4	2·25	>300
CaCl₂.6H₂O hexagonal	$-51\cdot5_E$	146	1·32	0·54	0·0510	0·604	4·4	11·6	−0·5	0·04	6	1·76	0·087
	−25	193	1·35	0·46	0·6053	$0\cdot51_5$	7·2	9·0	−0·7	$0\cdot05_9$	$4\cdot_2$	1·87	1·03
	0	279	1·38	0·36	4·581	$0\cdot41_9$	11·5	7·3	−1·0	0·074	3·4	1·99	6·8
	15	414	1·41	0·27	12·78	$0\cdot35_4$	15·4	6·4	−1·3	0·083	3·0	2·08	18
	30	$(\to\infty)$	$1\cdot5_2$	0·00	31·83	0·28	20·5	5·7	−1·7	0·09	$2\cdot_8$	2·18	$(\to\infty)$

The table may be used also to determine the percentage accuracy of the vapour pressure deduced from an equilibrium temperature of given accuracy. The percentage rate of change of derived vapour pressure with equilibrium temperature is simply

$$\frac{100}{p_w}\frac{dp_w}{dT}+\frac{100}{S}\frac{dS}{dT}, \quad \dots\dots\dots\dots\dots\dots (7)$$

evaluated at temperature T_e. The percentage rate of change of vapour pressure with dew-point, on the other hand, is given by just the first term in expression (7), evaluated at temperature T_d. Since the second term in expression (7) is usually negative, and the first term decreases with increasing temperature, the significance of a given error in equilibrium temperature is less than that of an equal error in the corresponding dew-point. For example, for calcium nitrate tetrahydrate and an equilibrium temperature of 20 °C, the sensitivity of vapour pressure to equilibrium temperature is approximately 5·2 per cent. per ° C and to the dew-point is approximately 6·7 per cent. per °C.

(e) The Heat of Formation of the Layer

The heat of formation of the layer, which tends to give rise to a difference in temperature between the crystal and its environment, may be regarded as made up of the heat of condensation of the water vapour taken from the gas and the heat of solution of the corresponding amount of crystal substance. The former preponderates greatly over the latter except in special cases such as that of calcium chloride hexahydrate at a temperature approaching the transformation or melting point at 30 °C. In the more typical case of potassium chloride at 0 °C, 1 g of water vapour condenses with the evolution of approximately 600 cal, dissolving about 0·3 g of salt with the absorption of 15 cal.

While this heat can cause a considerable reduction in the sensitivity if the crystal is suspended in the crystal cavity, surrounded by gas, the effect can be made practically negligible by mounting the crystal in contact with an inner surface of the cavity.

V. The Accuracy and Speed of Response

The accuracy and speed of response obtainable with the method depend essentially on the nature and extent of the deviation in behaviour of the crystal element from ideal behaviour. The observed behaviour will be outlined here

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Definitions and Units of Quantities given in Table 1.—x, The solubility of the crystal substance (g/100 g of water) ; ρ, the density of the saturated solution (g/cm³) ; $100\rho/(100+x)$, the thickness factor (g/cm³) ; p_w, the vapour pressure of water (mm Hg) ; S, the relative vapour pressure of the saturated solution (ratio) ; T_e—T_d, the difference between the equilibrium temperature and the corresponding dew-point (°C) ; $(100/p_w).(dp_w/dT)$, the percentage rate of change of the vapour pressure of water with centigrade temperature ; $(100/S).(dS/dT)$, the percentage rate of change of S with centigrade temperature ; σ, the specific electrical conductivity of the saturated solution $(\Omega \text{ cm})^{-1}$; R, the resistance in MΩ of a cube-shaped crystal element which conducts on four faces and possesses a conducting layer 100 Å thick ; f, the vapour transfer coefficient for the typical conditions defined in the text (g sec⁻¹ cm⁻² (mm Hg)⁻¹) ; J, the sensitivity of the method for a 100 Å layer and the conditions pertaining to tabulated values of f, given as the percentage change in electrical conductance per second per 0·1 °C temperature deviation.

on the basis of experience with elements of potassium chloride, sodium chloride, potassium iodide, sodium thiosulphate pentahydrate, calcium nitrate tetrahydrate, and calcium chloride hexahydrate ; that of potassium chloride elements will be described in greater detail in the second paper.

The behaviour of the crystal element is largely described by the answers to the following three questions :

1. If a crystal element is subjected to a gas stream of constant composition and, by rapid manipulation of the temperature, the resistance is brought to a definite value, how must the temperature subsequently be made to vary with time in order to keep the resistance constant ?

2. How does the ultimate temperature reached in the procedure of question 1 depend on the resistance value chosen ?

3. When the ultimate temperature has been reached at a constant resistance, how does the electrical conductance change if a small deviation of temperature is then imposed on the system ?

For ordinary temperatures and to an accuracy of $0 \cdot 1$ °C very simple answers can be given. Within a range of at least two decades of resistance the answer to question 1 is that the temperature is found to have been brought to a steady value after a matter of seconds. This value is independent of resistance. If a temperature change of the order of $0 \cdot 1$ °C is imposed, the conductance is accurately proportional to the time-integral of the deviation.

At an accuracy of $0 \cdot 01$ °C the answer to question 1 depends on the resistance and the immediate past history of the conducting layer. At ordinary temperatures the temperature becomes constant to $0 \cdot 01$ °C after a time which, depending on the conditions, may be as short as a few seconds or as long as an hour. Over a resistance range of a decade or more the ultimate temperatures are within $0 \cdot 01$ °C of the true equilibrium temperature. Probably the most striking characteristic of the method is revealed by the answer to question 3 : for resistances in a range of a decade or more the integrating property occurs even for the smallest temperature deviations studied (about $0 \cdot 002$ °C).

Except in achieving the initial balance, the answer to question 3 alone decides the sensitivity and speed of response of the hygrometer. Admittedly, in manual operation it may be difficult to vary the temperature in such a manner as to keep the resistance almost constant when the humidity is changing, but in automatic operation this can be achieved while quite rapid humidity changes occur. The resistance range in which the integrating property is followed accurately even for the smallest temperature deviations is the same as that which provides ultimate temperatures differing negligibly from the true equilibrium value.

It follows that an automatic hygrometer operating at ordinary temperatures can measure the equilibrium temperature to $0 \cdot 01$ °C and follow changes in humidity very rapidly. In fact, the instrument can be made to respond with a time-constant of less than 1 sec. As the temperature decreases, the accuracy, expressed in temperature measure, becomes lower, as it does with the conventional condensation hygrometer.

VI. Conclusion

Ionic crystal elements can easily be constructed with which the humidity of a gas can be measured several times more accurately than with a conventional condensation hygrometer. A hygrometer utilizing such an element operates in an analogous way to the condensation hygrometer, can be made at least as rapid in operation, and, if automatic forms are in question, is simpler. The difference in performance is attributable mainly to the difference in structure between the conducting layer in the present hygrometer and the deposit formed in a condensation hygrometer. Very little gas is necessary to obtain a good performance. The possibility of making observations at different resistance values allows an immediate and reliable estimate to be made of any error due to a defect of structure or cleanliness of the crystal element.

On account of its high accuracy, the new method can usefully be applied to a number of investigations which would be difficult otherwise. Not the least of these is the accurate determination of the relative vapour pressures of saturated salt solutions.

To make effective use of the high absolute accuracy of the method some of the definitions and laws involved in hygrometry must be formulated more precisely than is necessary for ordinary purposes. Thus it is no longer adequate to neglect the departure of the gas mixture from ideal-gas behaviour, and the effect of the total pressure on the vapour pressure of a saturated solution must sometimes be taken into consideration. Also, it becomes convenient to define " relative humidity " in terms of the partial thermodynamic potential of water rather than in the way at present gaining acceptance (" Smithsonian Meteorological Tables " (Smithsonian Institution 1951)).

VII. Acknowledgments

VIII. References

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