THE STUDY OF EVAPORATION FROM SMALL SURFACES BY THE DIRECT MEASUREMENT OF WATER VAPOUR PRESSURE GRADIENTS

BY JOHN MACHIN

Department of Zoology, University of Toronto, Toronto 5, Canada

INTRODUCTION

The evaporation of water from wet surfaces in air is a complex process, largely determined by vapour pressure gradients close to the surface. The nature and magnitude of these gradients depend on many factors including the size, shape and orientation of the surface itself, as well as ambient conditions such as temperature, pressure and speed of air flow. Full analysis of all these factors leading to the formulation of a comprehensive theory of evaporation is still in an early stage. As a result the phenomenon of water loss from many terrestrial plants and animals is still poorly understood.

In studies of evaporative loss from moist-skinned animals, one approach has been the adaptation of equations describing evaporation from flat surfaces or simple three-dimensional forms by empirically determining appropriate constants and functions for the animal under study (Machin, 1964 b). Although this method is fairly successful, it tells us very little about the process of evaporation itself and nothing about the local events which may indicate subtle adaptations for the reduction of water loss.

Since suitably small instruments for the measurement of air flow are readily available and convenient to use, an attempt was made to relate evaporative loss to mechanically defined boundary layers (Machin, 1964 a). It was found that estimations of water vapour gradients from air-velocity profiles were at best questionable. Sometimes air-velocity and humidity profiles were not related at all, particularly when the evaporating surface had dimensions similar to those of most small animals. A more fundamental understanding of evaporation from plants and moist-skinned animals must come from accurate and detailed surveys of conditions immediately adjacent to the surface.

In the literature there are several methods, either already used or potentially available, for the direct measurement of water vapour gradients. These are small evaporators (Ramsay, Butler & Sang, 1938; Weatherley, 1960); radio refractometers (Gates, Vetter & Thompson, 1963) and lithium chloride humidity sensors (Ueda, 1956). These instruments utilize a probe which samples or directly measures the concentration of water vapour close to the evaporating surface. All these methods suffer from one or more defects, the most serious of which is the size of the probe in relation to the gradients being measured.

The present paper describes a new type of probe which is capable of measuring the water-vapour concentration by dew point. The small size of the measuring device and the method of operation permit accurately located humidity determinations to be made

as close as 0·1 mm from the surface. Studies using the probe have led to some un-expected new findings concerning the process of evaporation in slowly moving air.

DEW-POINT PROBE

Design and construction

Plate 1, Text-fig. 1 *a* shows the important features of the probe's construction. The probe consists essentially of a copper rod tapered at one end. The wide end of the rod is cooled by a small thermo-electric cooling module (Frigistors Ltd., Montreal). A 0·43 mm diameter bead of mercury adheres to the pointed end. The temperature of the bead is measured by a copper-constantan thermocouple. The tip of the probe is thermally insulated with beeswax, the remainder by a removable casing of Plexiglas. Overheating of the cooling unit was prevented by circulating water through an aluminium heat-sink in contact with its 'hot' surface. Thermocouple temperatures are measured with a potentiometric microvoltmeter (Medistor, Seattle) against an agitated ice-water reference. The cooling module is powered by a 25 W, 6 V d.c. power supply with less than 2% ripple.

The probe is mounted on a micromanipulator attached to a stereoscopic micro-scope, so that it may be adjusted until the bead coincides with the cross-hairs of an ocular micrometer. The microscope is mounted on a travelling stand, equipped with vertical and horizontal vernier scales reading to 0·05 mm, and oriented so that the vertical probe is viewed from the side.

Maintenance

Dew-point is most readily observed using a perfectly clean mercury bead. It was found that the bead surface deteriorated after a few hours continuous use and had to be replaced with a fresh bead at intervals. The mercury very gradually eroded the copper tip of the probe which needed periodically re-sharpening on a lathe. After this the tip of the probe was re-coated with molten beeswax which was carved away at the tip to re-expose the extreme end of the copper rod. The perfectly clean metal surfaces necessary to make a fresh mercury bead stick to the rod and the thermocouple were obtained by brief immersion in 10% sulphuric acid.

Calibration and performance

Dew-point methods have several practical advantages over methods based on electrical resistance changes. Repeated calibration is unnecessary and dew-point determinations are unaffected by temperature gradients which always occur close to evaporating surfaces. However, dew-point measurement by observation is somewhat subjective and has inherent errors limiting the accuracy of measurement to ± 1 °C (Cambridge Systems Incorporated, 1965).

The dew-point probe was calibrated as far as possible in non-gradient conditions at 20 °C either against saturated salt solutions of known vapour pressure and dew-point (Winston & Bates, 1960) or against a Cambridge Systems Model 990 dew-point hygrometer in slowly moving air (Plate 1, Text-fig. 1 *b*).

Preliminary measurements established that the apparent dew-point temperatures were several degrees below standard. This discrepancy was reduced to less than 1 °C
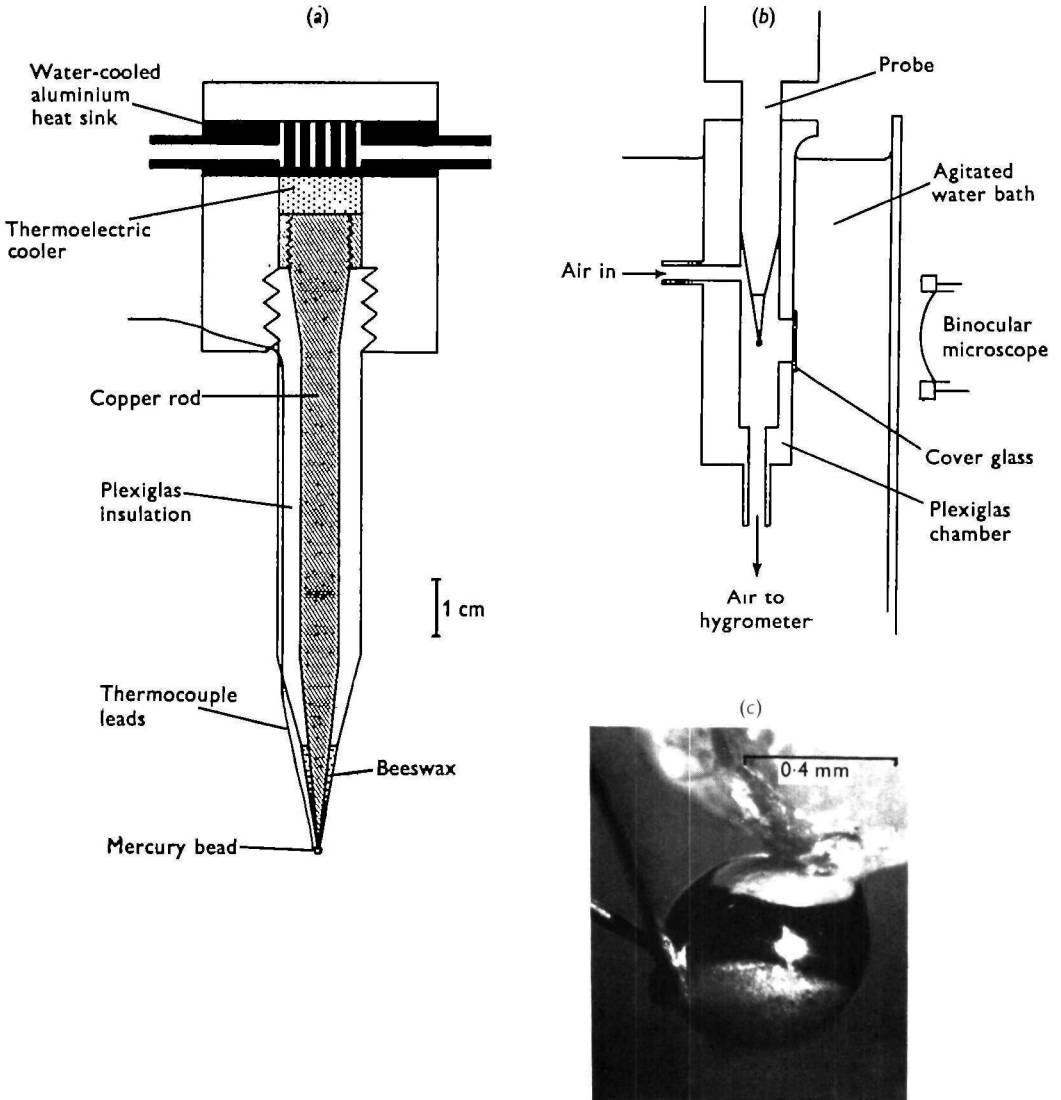
Plate 1/Text-fig. 1 (*a*). Diagrammatic section of dew-point probe showing main features of construction. (*b*) Diagram showing method of calibration against a Cambridge Systems dew-point hygrometer. Before passing through the Plexiglas chamber, air of a given dew-point was obtained by mixing wet and dry streams in known proportions. The combined stream was then equilibrated to bath temperature by passing it through 15 ft of copper tubing. Details of this method of humidity control are given in Machin (1969). (*c*) Photomicrograph of condensed dew formed in gradient conditions. The beeswax insulation on the copper rod, dew on the lower portion of the bead and the thermocouple can all be clearly seen.

by separating the thermocouple leads from the heat-conducting rod at the probe tip. The slopes of regression lines relating standard with observed dew points (Text-fig. 2) differed from the expected values by not more than 0·5%. Calibration by saturated salt solutions consistently underestimated the dew-point. Those values compared with the Cambridge Systems hygrometer underestimated dew-point by 0·25 °C when dew appearance was used and overestimated the value by 0·53 °C using dew disappearance as the end-point. Since dew appearance is also theoretically the more reliable, this end-point was used in subsequent measurements.
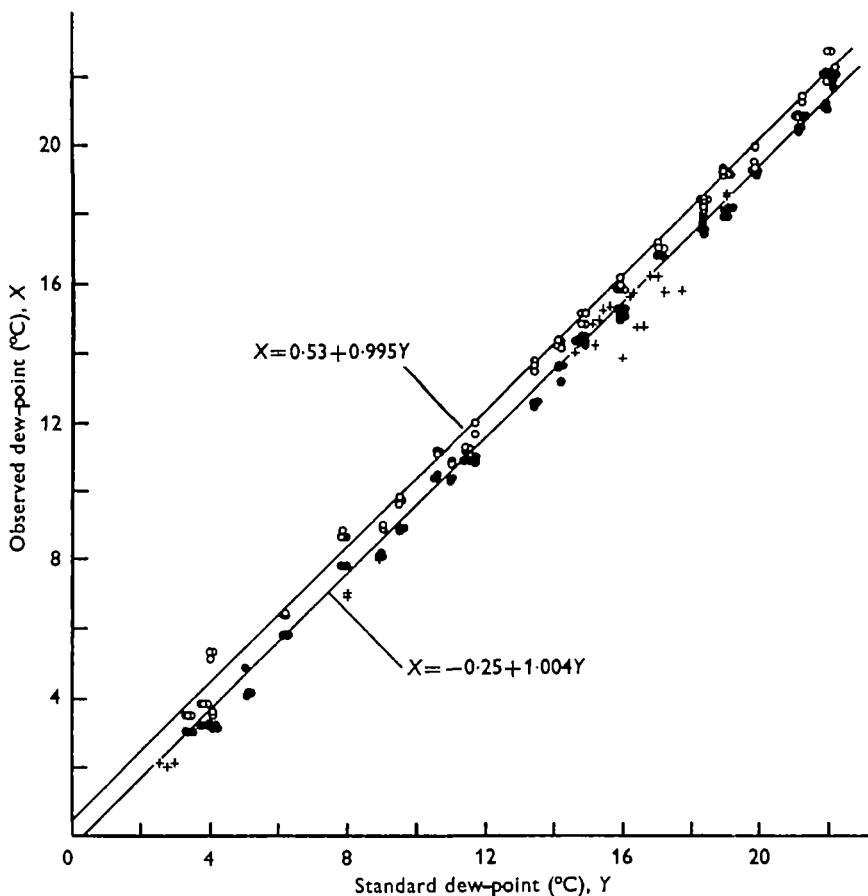
Text-fig. 2. Standard and observed dew-points compared; using the Cambridge Systems hygrometer by dew appearance (●) and by dew disappearance (○); using saturated salt solutions (+) with data from Winston & Bates (1960).

Measurement of vapour-pressure gradients

Vapour pressure gradients were measured above flat dishes or transparent vessels containing distilled water. It was first necessary accurately to locate the position of the water surface with reference to the vertical scale of the microscope stand. The position of the bead, adjusted to coincide with the ocular cross-hairs was known; the position of the water surface was determined by lowering the microscope and probe until the bead and its image, reflected in the water surface, was included within

the field of the microscope. The vertical distance between the bottom of the bead and its image was measured with the calibrated ocular micrometer. Half this gave the distance between the bead and water surface.

For optimum visibility the bead was illuminated by a focused microscope lamp, also mounted on the microscope, and was viewed against a dark background. The dew first appears as a white or silver misting on the bead. In still air this covering appears simultaneously all over the bead. However, in moving air, where vapour pressure gradients are commonly steeper, dew formed only on the lower part of the bead (Plate 1, Text-fig. 1 c).

To make measurements above an evaporating surface, the probe is first positioned a few centrimetres above the water surface. The bead is then brought a few tenths of a °C below ambient, by adjusting the current through the thermo-electric cooler. The probe is then lowered until dew forms at the point corresponding with the microscope cross-hairs. Readings are taken on the microvoltmeter and the vertical vernier scale. Measurements of high dew points could be obtained as close as 0·1 mm from the evaporating surface. Measurements could be conveniently confirmed or repeated by raising the probe slightly until the dew evaporated and then lowering it again to dew-point. It was usually not possible or necessary to keep the probe temperature absolutely constant. Adjusting the probe to slightly different temperatures enabled a complete dew-point profile to be constructed.

A series of measurements was made from still air up to wind speeds of approximately 100 cm/s in a small transparent-walled wind tunnel. A typical vapour-pressure profile, obtained in still air, is shown in Text-fig. 3. The profile consists of a more or less linear section close to the surface, which gives way to curved transitional zone gradually approaching ambient conditions. This shape is similar to that obtained by other direct methods (Ueda, 1956).

At wind speeds in excess of about 20 cm/s the normally horizontal edge of the dew-covered area became tilted, making the trailing edge higher than the lending edge. This suggests that the bead deflects the air flow around it significantly. Diagrams in Text-fig. 4 illustrate a number of possible ways in which this may affect the measurement of D. The most likely result is a downward deflexion of air of a given dew-point by the lower leading surface of the bead and an upward deflexion at its rear (b, c). Since it is most unlikely once dew forms that the bead causes an upward deflexion alone (a) dew-point cannot be lower than the lowermost point of the bead. Similarly, this height cannot exceed the mid-point of the bead because air striking the bead above this point is deflected upwards (d) and results in dew formation over the entire bead. Height measurements based on dew formations midway between the centre and bottom of the bead may therefore be subject to a maximum error equivalent to half the radius of the mercury bead (±0·1 mm).

Vapour-pressure surveys were also made by keeping the bead temperature constant and measuring the height at which dew-point occurred at different points over the surface. Under these conditions it was sometimes possible to increase the sensitivity of the microvoltmeter until dew formation could be observed as a momentary increase in bead temperature as condensation began.
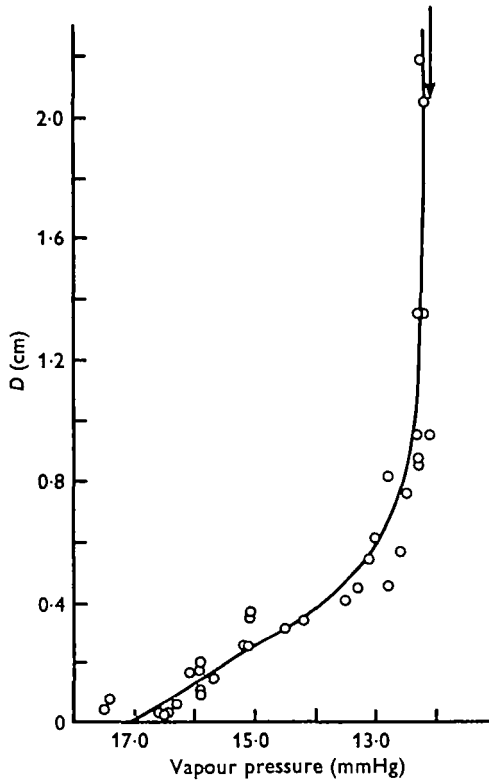
Text-fig. 3. Typical vapour-pressure profile obtained in still air, showing upper curved and lower linear regions. The arrow indicates ambient v.p.
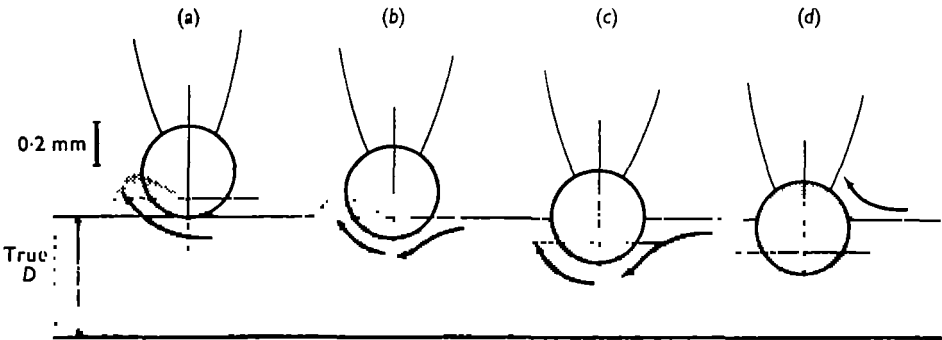
Text-fig. 4. Diagrams of the possible effects of air-flow distortion (arrows) by the probe in relation to the measurement of D. Air at or above a given dew-point is indicated by the stippled area. The ocular cross-hairs in their normal position relative to the bead are shown.

Comparison with other techniques for gradient measurement

Vapour-pressure gradients were also measured using the technique of other workers. A lithium chloride electrical resistance hygrometer, similar to that used extensively by Ueda (1956; and personal communication), was constructed. The

hygrometer probe was prepared by removing the surface of a small epoxy resin disk to expose parallel lengths of two platinum wires embedded within. The area between the wires was then coated with a 5 % solution of LiCl and allowed to dry. A thermistor, connected to a Wheatstone bridge circuit, was also mounted on the probe. Overall dimensions of the measuring part of the probe were 10 × 2 × 2 mm.

The hygrometer required calibrating after every measurement of vapour-pressure profile. This was done over saturated salt solutions. Since lithium chloride hygrometers are temperature-sensitive, calibrations were performed at temperatures of 21, 20 and 18 °C. The lithium chloride hygrometer was mounted in place of the dew-point probe and used in the same way to measure gradients. Measurements were not practicable closer than 0·5 mm to the water surface.

A number of profile measurements were also made by extracting air from a particular position in the gradient, after the method of Gates et al. (1963). Air was drawn through a 0·5 mm diameter tube connected to the Cambridge Systems hygrometer. Several pumping rates were used down to a practical minimum of 50 ml/min. Calculated coefficients of diffusion were all considerably greater than the theoretical, and highly dependent on the rate of pumping, and are not therefore considered valid.

Determination of diffusion coefficients

Diffusion coefficients (k) were determined by means of the following equation

$$E = k\frac{(p_0 - p_d)}{D}. \tag{1}$$

Where E is the rate of evaporation in mg $H_2O/cm^2/h$, p_0 is the apparent vapour pressure (mmHg) at the water surfaces obtained by extrapolating the linear portion of the vapour pressure profile, p_d is the vapour pressure some distance along the linear profile and D is perpendicular distance separating them in cm.

Experimental determinations were made at a temperature of 20 ± 2 °C over an ambient vapour-pressure range of 10–15 mm Hg. Experimental wind speeds varied between 0 and 94 cm/s, as measured by a constant-current hot-wire anemometer (Disa Elektronik, Copenhagen), calibrated by rotating the instrument at known speeds through still air.

Measurements of evaporation rate were made by weighing a shallow Plexiglas trough (8·8 cm long and 6·3 cm wide) filled with distilled water and mounted in the working section of the wind tunnel. The trough was closely surrounded by a second water-filled trough occupying the whole width of the tunnel and projecting 12 cm up and downstream from the experimental surface. Measurements indicated that the second trough considerably reduced the variation in vapour pressure above the experimental surface. For example, the mean vapour pressure measured at 18 different points 0·14 cm above the experimental surface was $18·3 \pm 0·1$ mmHg (Text-fig. 5). Measurement of the complete vapour-pressure profile perpendicularly above the centre of the experimental surface was therefore considered representative of the whole surface.

Text-fig. 6 shows a series of vapour-pressure profiles and demonstrates that the gradients become steeper as wind speed increases. Calculated values for k from still-air profiles showed substantial agreement with the coefficients of diffusion obtained

by other workers (Table 1). Since moving air brought about measurable changes in the vapour-pressure profiles, it was expected that evaporative water loss varied directly with these new gradients. Results presented in Text-fig. 7 show this not to be true; evaporation rate per unit gradient (*k*) is not constant in moving air. Results obtained by the dew-point probe indicate that *k* decreases significantly with wind speed up to about 67 cm/s and then increases. The relationship between *k* and wind speed between 0 and 67 cm/s was computer-analysed in terms of six curve formulae.
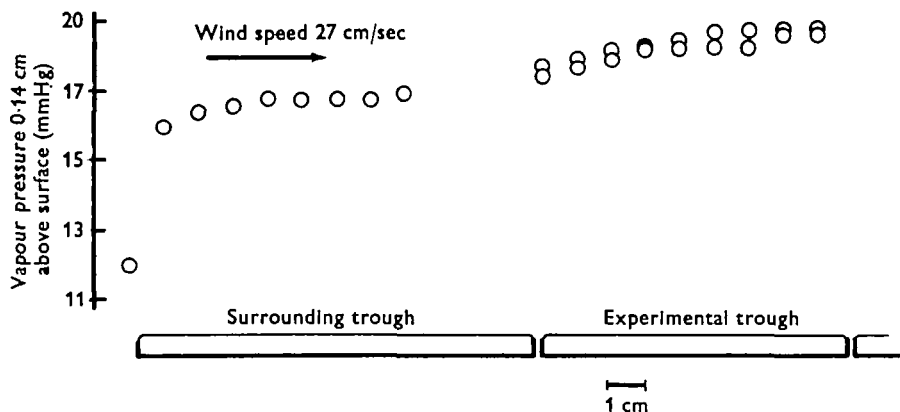
Text-fig. 5. Diagram to show the distribution of water vapour as measured 0·14 above the evaporative surface. At a wind speed of 27 cm/s, measurements fall within the linear portion of the vapour-pressure profile.

Table 1. *Theoretical and experimentally determined coefficients of diffusion of water vapour in air at approximately 1 atmosphere pressure*

Diffusion coeff. *k* (cm²/s*)	Temperature (°C)	Theoretical or experimental	Reference
0·207	10	Theor.	Mason & Monchick, 1965
0·221	20		
0·236	30		
0·258	25·9	Exptl.	Gilliland, 1934
0·235	14·4	Exptl.	Ueda, 1956
0·220±0·012†	20±2	Exptl.	Present study

* Units of *k* are (cm²/s), i.e. moles/cm²/s when there is a concentration gradient of 1 mole/cm³/cm. In practice it is more convenient to use units which are more readily applicable to direct measurement, i.e. mgH₂O/cm²/h/mmHg/cm (Leighly, 1937). Leighly's coefficient at 20 °C was converted to the coefficient given here by multiplying by 0·282.
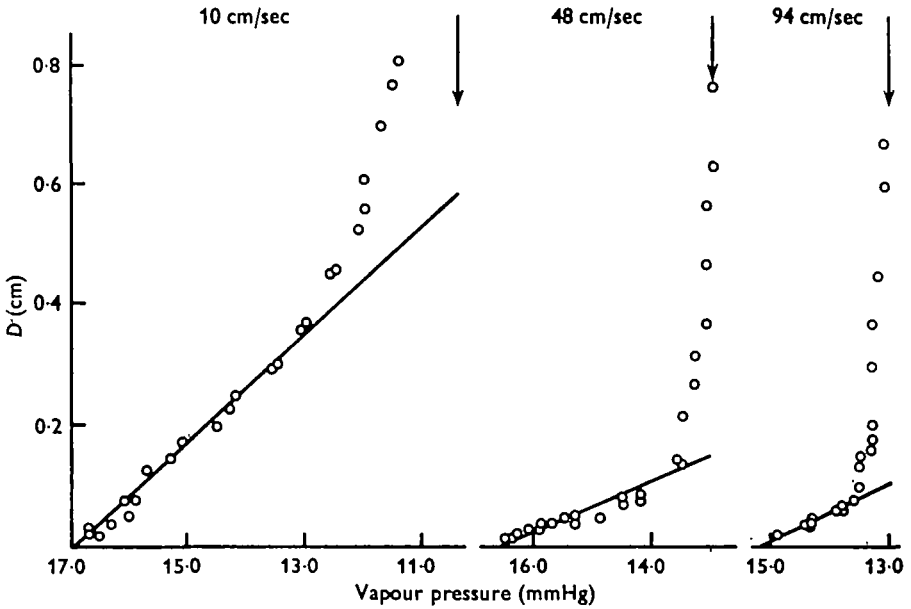
† Standard error of the mean.

The best fit was obtained with the following hyperbolic function using the least squares method in its linear transformation

$$k = 1/(5·2 \pm 0·09\, v), \tag{2}$$

where *v* is the wind speed in cm/s.

Results obtained with the lithium chloride probe show similar though less marked inconsistencies in the apparent values of *k*.

Text-fig. 6. Typical vapour-pressure profiles at three different wind speeds. Slopes of the linear portion of the curves were calculated by the least squares method, using the lowermost points. Arrows indicate ambient vapour pressures. It can be seen that extrapolated surface vapour pressures decrease with wind speed. Higher rates of evaporation at more rapid wind speeds produce greater surface cooling.
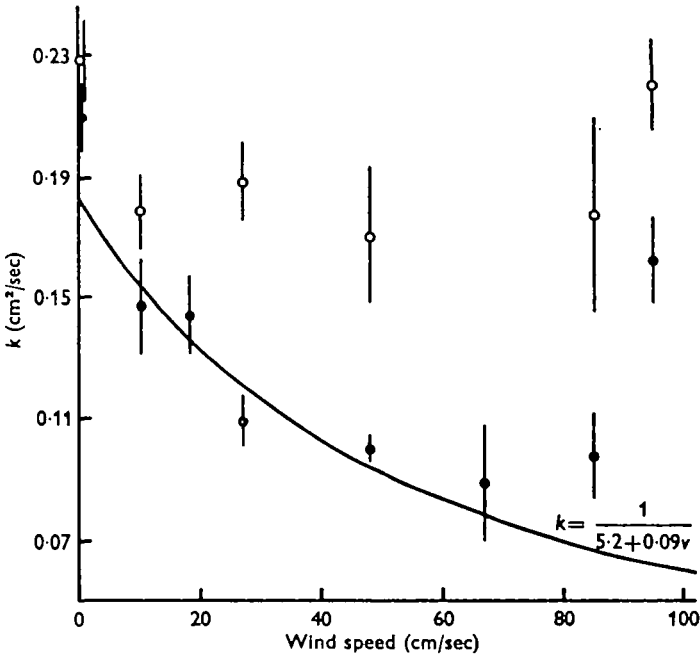
Text-fig. 7. Relationship between k and windspeed (v) as determined by the dew-point probe (closed circles), lithium chloride hygrometer (open circles). Vertical bars indicate $\pm$s.e.

DISCUSSION

This paper has described the design and construction of a new hygrometer suitable for the detailed study of evaporation from various moist surfaces. The hygrometer was first tested and calibrated against known uniform humidities and shown to be reliable. Confirmation that the instrument performs equally well under gradient conditions is more difficult. However, the fact that calculated coefficients of diffusion agreed fairly well with theoretical values strongly suggest that the probe is reliable at least in still air.

In moving air an instrument probe, no matter how small, may interfere with the normal pattern of air flow, as previously described. The interference may give rise to an error of 0·1 mm, which is equivalent to 14% of the maximum D value used to calculate vapour-pressure gradients at the highest wind speeds used in this study (Text-fig. 6). Since k in moving air can differ from its value in still air by as much as 50%, (Text-fig. 7) measuring error cannot account for this discrepancy. Calculated values for k in moving air between 10 and 67 cm/s are significantly less than values obtained in still air, and are related inversely to some function of the wind speed.

A possible explanation of low k values is as follows. In still air the average path taken by diffusing water molecules is perpendicular to the open water surface, and parallel to the axis along which dew-points are measured. It is suggested this is no longer true in moving air flowing from a particular direction. The average path must be the resultant of perpendicular diffusion and convection forces and a horizontal force due to the wind. The effective gradient along the path of the escaping water molecules must therefore be considerably less steep than that measured perpendicularly to the surface by the dew-point probe. This discrepancy between effective and measured values for D could lead to an apparent reduction in k in moving air. This finding has not been reported by previous workers, who have either been concerned with diffusion in still air or with evaporation at higher wind speeds than those used in this study. Little was known about water-vapour transfer in the transition between still and slowly moving air, in spite of its importance to the study of evaporation from plants and small animals.

Measurements made at wind speeds greater than 67 cm/s indicate that apparent values for k increase (Text-fig .7). The most obvious explanation of this is that above certain critical wind speeds, evaporation depends predominantly not on diffusion gradients but on air turbulence. In a study which did not involve the determination of diffusion coefficients Ueda (1960) has concluded that forced convection becomes a predominant factor at wind speeds from 30 to 50 cm/s. The results in Text-fig. 7 also show that k values obtained with the lithium chloride probe are significantly higher than those determined by dew-point, particularly at intermediate wind speeds. This suggests that air turbulence may affect the gradient measurement at wind speeds lower than 67 cm/s when relatively bulky measuring devices are used. Error produced by the mechanical presence of a probe must be considered in the design of such instruments; it is important to keep the measuring part of the probe as streamlined as possible and small in relation to the boundary layer being studied.

It was hoped that the use of the dew-point probe described here would considerably simplify the detailed analysis of evaporative water loss from small three-dimensional

objects, living and non-living. It is possible that the small size and stability of the dew-point probe still make it the most convenient and reliable instrument of its type to date, in still air conditions. Unfortunately, evaporation in slowly moving air appears to be more complex than at first realized. Evaporation rates cannot necessarily be calculated from vapour pressure gradients measured perpendicularly above the surface. It is possible that studies of local evaporative loss could be successfully made by incorporating a hot-wire anemometer into the dew-point probe. This, however, would tned to compromise one of the more attractive features of the dew-point probe; its simplicity of calibration and operation.

SUMMARY

1. The construction, maintenance and calibration of a sensitive instrument capable of making numerous vapour-pressure measurements within humidity gradients by the dew-point method is described.

2. Coefficients of diffusion of water vapour in air, calculated from observed vapour-pressure gradients and measured rates of evaporation agree with theoretical and other experimental values in still air.

3. Apparent coefficients in wind speeds between 10 and 100 cm/s were significantly lower than those in still air.

4. This finding, together with the performance of the dew-point probe, is discussed in relation to its possible use in the study of evaporation from animals and plants.

REFERENCES

CAMBRIDGE SYSTEMS INCORPORATED (1965). Analysis of errors for the thermoelectric dew point hygrometers. *Engineering Application Notes*, 992 N 2.

GATES, D. M., VETTER, M. J. & THOMPSON, M. C. (1963). Measurement of moisture boundary layers and leaf transpiration with a microwave refractometer. *Nature, Lond.* **197**, 1070–2.

GILLILAND, E. R. (1934). Diffusion coefficients in gaseous systems. *Ind. Engng. Chem.* **26**, 681–5.

LEIGHLY, J. (1937). A note on evaporation. *Ecology* **18**, 180–98.

MACHIN, J. (1964a). The evaporation of water from *Helix aspersa*. II. Measurement of air flow and the diffusion of water vapour. *J. exp. Biol.* **41**, 771–81.

MACHIN, J. (1964b). The evaporation of water from *Helix aspersa*. III. The application of evaporation formulae. *J. exp. Biol.* **41**, 783–92.

MACHIN, J. (1969). Passive water movements through skin of the toad *Bufo marinus* in air and in water. *Am. J. Physiol.* **216**, 1562–8.

MASON, E. A. & MONCHICK, L. (1965). Survey of the equation of state and transport properties of moist gases. *Humidity and Moisture* **3**, 257–72. New York: Reinhold.

RAMSAY, J. A., BUTLER, C. G. & SANG, J. H. (1938). The humidity gradient at the surface of a transpiring leaf. *J. exp. Biol.* **15**, 255–65.

UEDA, M. (1956). Measurements of the gradient of water-vapour pressure and the diffusion coefficient. *J. appl. Phys. Japan* **25**, 144–9.

UEDA, M. (1960). Rate of evaporation of water by forced air convection. *J. appl. Phys. Japan* **29**, 443–51.

WEATHERLEY, P. E. (1960). A new micro-osmometer. *J. exp. Bot.* **11**, 258–68.

WINSTON, P. W. & BATES, D. H. (1960). Saturated solutions for the control of humidity in biological research. *Ecology* **41**, 232–7.