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THE COMBINED EFFECTS OF RELATIVE HUMIDITY AND TEMPERATURE ON DIFFUSION  
IN HYDROPHILIC RAINWEAR - WATER VAPOR TRANSFER THROUGH A HYDROPHILIC FIL

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### ABSTRACT

The water vapor diffusion resistance of the hydrophilic component of Gore-Tex™ II is measured at temperatures down to  $-24^{\circ}\text{C}$ . The experiment is designed to simulate diffusion of water vapor through a clothing shell from a coating of ice on its inner surface. The permeability of the samples decreases exponentially with decreasing temperature; this variation is a combined effect of temperature and relative humidity. At subzero temperatures, water vapor transfer through this material is only a few percent of its room temperature value. Other hydrophilic films used in outdoor clothing are likely to be similarly affected.

Even in very cold weather, active people can overheat. The body often has to sweat in order to balance heat loss with heat production at a comfortable body temperature. Unfortunately, evaporative cooling is much less efficient when wearing cold weather clothing. Condensation can occur in the cooler outer layers of clothing or on the inner surface of the shell, whether the shell is highly permeable or not. Sweating must be avoided, or at least minimized, because clothing with

wet insulation is not very good protection from the cold. When vigorous activity ceases and heat production falls, damp clothing can lead to uncomfortable and possibly dangerous cooling.

Premium outdoor clothing often incorporates a breathable waterproof film or coating. The greater cost of such materials is at least partly outweighed by an improvement in comfort. Many of these materials incorporate a hydrophilic film or coating, either as a pri-

mary waterproof layer or as protection for a microporous layer. The water vapor diffusion resistance of this class of materials depends on the relative humidity at which it is measured [7, 8, 10]; it might also depend on the temperature [7].

The series of experiments reported here examines the possibility that these effects are synergistic. The increase in diffusion resistance of a hydrophilic material that is caused by colder temperatures could lower the average relative humidity. This could lead to a further increase in diffusion resistance.

In earlier work, we devised a simple gravimetric procedure [11] to investigate the effect of subfreezing temperatures on the diffusion resistance of clothing materials. We selected the hydrophilic coating used in Gore-Tex™ II for study, because it represents the state of the art in waterproof, water-vapor-permeable rainwear materials.

The temperature of a clothing shell will normally be a few degrees higher than air temperature. The inside surface of the shell will be almost the same temperature as its outer surface, because the thermal resistance of a thin layer of fabric is small. As many dedicated winter joggers know, when it is very cold or cold and windy, the inner surface of a windproof shell can become coated with ice or frost. The experiments reported here attempt to simulate that condition by having one face of a fabric sample in direct contact with ice.

## Experimental

### SAMPLES

The Gore-Tex laminate used in this study comprises two fabrics and a microporous PTFE (Teflon™) film. A hydrophilic coating protects the microporous film from contamination, which might lower its surface tension and cause it to leak. The coating is identified in product advertising as "polyalkylene oxide polyurethane-urea." The layers of the Gore-Tex laminate can be peeled apart, leaving the PTFE film attached to the outer fabric and a continuous film of the hydrophilic coating attached to the light nylon tricot inner fabric [7].

The samples used in this experiment were cut from the inner fabric and were approximately 0.15 mm thick. Most of the thickness was the nylon tricot; the hydrophilic film was probably less than 0.01 mm thick. Samples were conditioned to 65% RH at 20°C before use. Although two samples were sufficient to reveal the general effect of low temperatures on the resistance of this material to water vapor diffusion, we also used a third sample at several subfreezing temperatures.

### TEST CELL

The test cell, shown in Figure 1, had two parts: a Pyrex™ petri dish and a small plastic container (Polytainer Inc. 403A-8, 225 g capacity) with a snap-on lid (Polytainer 403 NL). The plastic container, with a circular cutout in its lid, was used to hold the ice. The petri dish contained the dessiccant. The fabric sample was placed between the ice and the dessiccant, either directly on the surface of the ice for high humidity tests or on the dessiccant bed for low humidity tests.

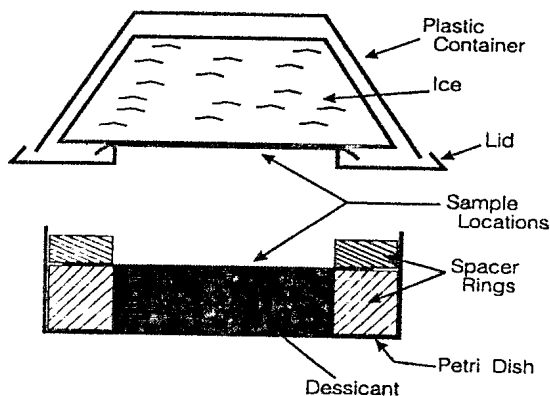


FIGURE 1. The two parts of the test cell, separated for clarity. Samples were normally placed on the surface of the ice.

The upper part of the cell contained approximately 150 ml of ice made from distilled water. The surface of the ice was polished by rubbing it onto a warm metal surface. Diffusion occurred through a circular hole in the lid of the container with an area of  $34 \pm 1 \text{ cm}^2$ .

The film side of the sample was placed against the ice. After each experiment, there was a sharply defined circular depression in the ice where its polished surface had been etched by evaporation. A pattern left by the knitted fabric was often clearly visible on the surface. Evaporation did not change the distance between the ice and the dessiccant by a significant amount. At room temperature, when measured under a load equivalent to the mass of ice, the distance between the ice and the dessiccant was  $9.5 \pm 1 \text{ mm}$ . The cylindrical air space between the dessiccant and the ice had a diameter of 6.6 cm.

The dessiccant was eight-mesh Drierite™ (anhydrous  $\text{CaSO}_4$ ). The upper surface of a compacted bed was made as flat as possible, but small spaces between the grains were unavoidable. Changes in the color of the dessiccant, which is blue when dry and pink when saturated, showed that at first, water vapor was absorbed

only on the upper surface of the desiccant bed. No color changes were detectible deeper in the bed or in the spaces between grains until the color of the exposed surface had become completely pink. This occurred when about 0.25 g of water had been absorbed. Because the rate of diffusion noticeably changed after water vapor began to be absorbed deeper in the desiccant bed, experiments were halted before 0.25 g had been absorbed.

#### PROCEDURE

The cell was assembled, with the sample in place, and left overnight in the environmental chamber at the appropriate temperature. An identical desiccant container was assembled as a conditioning dish. A half-hour before weighings began, the desiccant dish used for conditioning was replaced with the fresh one. At intervals of 2 to 12 hours, depending on the rate of moisture transfer, the parts of the cell were separately removed from the chamber and weighed on an electronic scale with a precision of 0.01 g. The dew or frost that collected during the brief weighing period amounted to less than 10 mg and evaporated in the chamber between weighings. It cancelled out when the net change was calculated, since it was approximately the same at each weighing.

The absolute values of the changes in mass of the two sections of the cell were averaged at each weighing. Linear regression of the mass change against time provided the rate of water vapor transfer. Correlation coefficients were always 0.99 or better.

The total resistance  $R$  to the diffusion of water vapor between the upper and lower parts of the cell ( $\text{m}^2 \text{ Pa s/kg}$ ) was calculated from

$$R = AP_{ice}/M \quad (1)$$

where  $A$  is the area ( $\text{m}^2$ ) of the sample through which diffusion occurs,  $P_{ice}$  is the vapor pressure (Pa) over ice at the temperature of the air in the environmental chamber, and  $M$  is the measured rate of water vapor transfer between the parts of the cell in kg/s. We neglected the vapor pressure over the desiccant surface because it is less than 1 Pa, according to the manufacturer.

#### AIR SPACE

The resistance calculated from Equation 1 includes the resistance of the air space in the cell, which was separately determined by following the same procedure without a sample at a range of air temperatures. The air space resistance varied slightly but regularly with temperature. In a dilute mixture of still air and

water vapor [5], the water vapor diffusion resistivity of air is

$$\rho_{wv} = RT/Dm \quad (2)$$

where  $R$  is the constant in the universal gas law,  $T$  is in Kelvins, and  $m$  is the mass per mole of water vapor.  $D$ , the diffusivity of water vapor in air ( $\text{m}^2/\text{s}$ ) is approximately given [3, 5] by

$$D = 2.5 \times 10^{-5} \times (T/293)^{1.81} \quad (3)$$

At a temperature of  $20^\circ\text{C}$ , the diffusion resistance of a millimeter of standard still air is  $5.4 \times 10^6 \text{ m}^2 \text{ Pa s/kg}$ .

When we accounted for the variation of the water vapor diffusion resistivity with temperature, we found approximately the same thickness of air at all temperatures. The average was  $10.1 \pm 0.5 \text{ mm}$ , which confirmed that there was no appreciable convection in the air space, for convection would have reduced the equivalent thickness relative to the measured distance.

The air space in the apparatus was thicker than the boundary layer of still air on the outer surface of clothing, which is normally equivalent to a still air thickness of between 0 and 5 mm, depending on the wind speed [4]. The greater thickness of air in the cell kept the dry face of the sample from being exposed to an unrealistically low relative humidity, for even in winter, air is never as dry as the air at the surface of the desiccant.

#### ROOM TEMPERATURE RESISTANCE

We measured the water vapor diffusion resistance of four other samples at  $+18^\circ\text{C}$ , using an apparatus of the kind described by van Beest and Wittgen [13]. The samples were placed directly onto the wet surface with the equivalent of a 10 mm air gap between the sample and dry air.

### Results and Discussion

In Figure 2, the water vapor diffusion resistance of the samples is plotted against temperature. Resistance decreased exponentially with temperature, from 26 mm ESSA (millimeters of equivalent standard still air) at  $-24^\circ\text{C}$  to about 3 mm ESSA at  $-3^\circ\text{C}$ . At  $-10^\circ\text{C}$ , the water vapor diffusion resistance of the samples on ice averaged about 5 mm ESSA. At the same temperature, the resistance of two samples tested on the surface of the desiccant was much higher at 61 and 77 mm ESSA.

Diffusion resistance at  $+18^\circ\text{C}$  is also plotted in Figure 2. The average of  $0.9 \pm 0.5 \text{ mm ESSA}$  agrees fairly well with the exponential line that best fits the data obtained at subfreezing temperatures. Between room

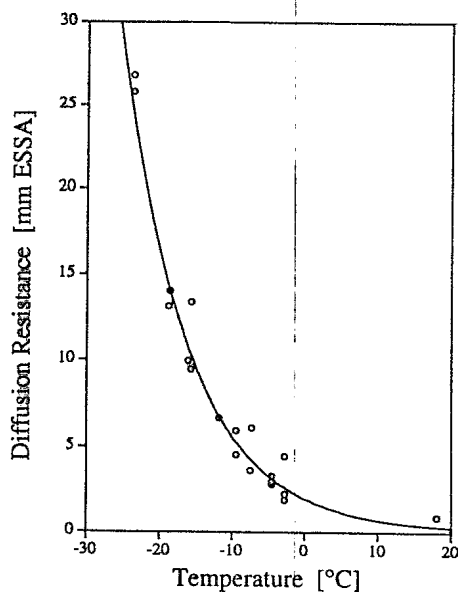


FIGURE 2. Resistance of the hydrophilic component of Gore-Tex™ II to diffusion of water vapor at a range of temperatures. The line is an exponential curve fitted to the subzero data points.

temperature and  $-10^{\circ}\text{C}$ , the diffusion resistance of the samples increased by a factor of at least five.

#### ACTIVATION ENERGY

Diffusion in polymeric materials occurs through the free volume between polymer chains. In order to move through these spaces, water molecules must have more than a certain minimum energy, referred to as the activation energy for diffusion  $\epsilon$ . Diffusion is rapid in a material that has a low activation energy for diffusion. The proportion of water vapor molecules having energies in excess of any given level falls with a decrease in temperature, according to the kinetic theory of gases. Even if the lower temperature does not affect the material, the apparent diffusion resistance should increase with a drop in temperature because fewer molecules of water vapor will have sufficient energy to diffuse.

The line in Figure 2 has the form

$$(1/R) = \text{Constant} \times e^{-\alpha/T} \quad (4)$$

According to Barrer [1], an equation of this form describes the variation of permeability (*i.e.*,  $1/R$ ) with temperature of many materials. In experiments where temperature is the only variable factor,

$$\alpha = \epsilon/R \quad (5)$$

If the change in diffusion resistance had been due solely to the change in temperature, the line in Figure 2 would yield a value of 65 kJ/mole for the activation

energy of this material. This would be high compared to 42–46 kJ/mole for other polyurethane elastomers [2]. Part of the change of permeability with temperature must have been due to a change in relative humidity experienced by the material.

In hydrophilic materials, the activation energy for diffusion is lower at higher regains [9], because adsorbed water vapor tends to plasticize the material and increase the free volume [2]. Keratin, for instance, has an activation energy that ranges from 20 to 31 kJ/mole, depending on regain [9]. At a constant temperature, regain is a function of the concentration of water vapor in the air. Although at cooler temperatures the concentration of water vapor in the air is lower at any value of relative humidity, the regain of materials is usually somewhat higher [12], because a smaller proportion of the water vapor molecules has sufficient energy to escape adsorption. Some textile materials have exhibited lower regains at temperatures below the freezing point [6]. Presumably, they become more crystalline when cold and have fewer or less accessible adsorption sites.

The diffusion resistance of the study material is known to be higher at low relative humidity [7, 8, 10]. This is reflected in the much higher diffusion resistance seen when the samples were placed on the dessicant instead of on the ice.

The diffusion resistance of the samples was higher at lower temperatures. In the cold, more of the total drop of water vapor pressure was across the sample, which caused the surface facing the dessicant to be exposed to a lower relative humidity. Because the mean relative humidity was lower, the diffusion resistance of the sample increased further. The effect of the change in temperature was therefore accentuated by the accompanying change in relative humidity and moisture content of the samples. Figure 3 plots the mean relative humidity in these experiments as a function of temperature.  $\text{RH}_{\text{mean}}$  approaches 100% asymptotically as the temperature increases.

Farnworth *et al.* [7] measured the diffusion resistance of the same material at room temperature, while varying the mean relative humidity. They found that lowering the mean relative humidity increased the diffusion resistance. Their results, recalculated from Figure 3 of their paper, are plotted in Figure 4. The circles in Figure 4 represent the results of our experiments, which we obtained at a range of temperatures. They fall on a curve defined by Equation 6:

$$\text{RH}_{\text{mean}} = 100 \times (R_{\text{air}} + 0.5 \times R_{\text{sample}}) / R_{\text{total}} \quad (6)$$

$R_{\text{air}}$  is the diffusion resistance between the sample and the dry air or dessicant and  $R_{\text{total}}$  is the sum of  $R_{\text{air}}$ ,

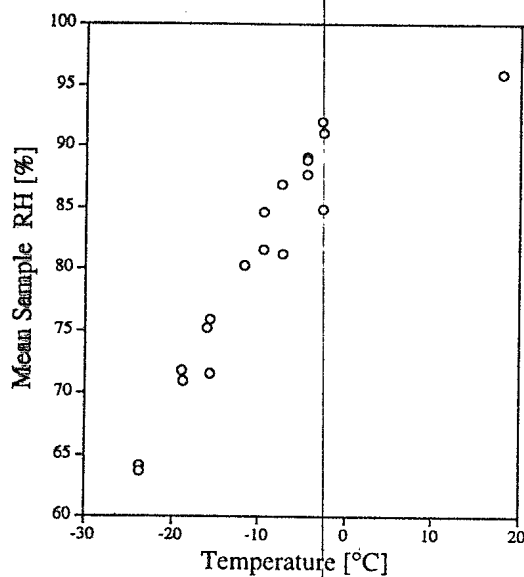


FIGURE 3. Variation of mean sample RH with temperature.

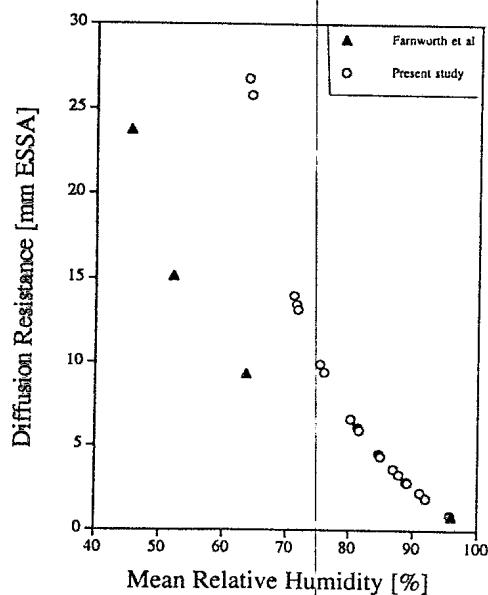


FIGURE 4. Comparison of diffusion resistances measured at a range of temperatures with the room temperature results of Farnworth *et al.* [7]. In general, from left to right, the temperatures of samples in the experiments marked by circles increased from  $-24^{\circ}\text{C}$  to room temperature.

$R_{\text{sample}}$ , and the diffusion resistance of any air layer that might exist between the sample and the water or ice surface of the measuring system.

The circles at lower relative humidities in Figure 4 are the results of measurements at lower temperatures. They differ from Farnworth *et al.*'s results because of

differences in the geometry of the two experiments, as well as the differences in temperature. In our experiments, the sample remained in contact with the ice, while in those of Farnworth *et al.*, the distance between the wet surface and the sample was varied. Their four data points thus fall on four different curves given by Equation 6.

#### WATER VAPOR FLUX

The flux of water vapor through any clothing layer will be greatest if water evaporates from ice or water on the inner surface and diffuses through the material to perfectly dry air on the other side. Because the saturation vapor pressure over water at room temperature is much larger than it is over ice—nine times larger at  $-10^{\circ}\text{C}$ —the maximum diffusion through any material will be much smaller when it is cold.

If the diffusion resistance of the material also increases when it is cold, there will be an even greater reduction in the maximum water vapor flux. For the samples used in this experiment, the diffusion resistance increased by a factor of at least five between room temperature and  $-10^{\circ}\text{C}$ ; thus the maximum possible flux of water vapor through these samples at  $-10^{\circ}\text{C}$  would have been only about 2% of the maximum flux at room temperature.

Maximum flux is rarely attained because there is a boundary layer of still air on the outer surface of clothing that keeps the vapor pressure at outer surface from falling to the ambient vapor pressure. At a wind speed of 8 km/h, the thickness of this boundary layer is equivalent to about 1.7 mm of still air [4]. Thus, the diffusion resistance of the material plus the boundary layer will vary from 2.6 mm at room temperature to about 7 mm at  $-10^{\circ}\text{C}$ , a factor of nearly 3. In these conditions, the diffusive flux of water vapor through the fabric at  $-10^{\circ}\text{C}$  would be approximately 4% of its value at room temperature.

#### Conclusions

Our experiment clearly demonstrates that large increases in the water vapor diffusion resistance of Gore-Tex II can be expected at temperatures below freezing. The same is probably true of any hydrophilic rainwear material. The effects of temperature and humidity are synergistic in these experiments, in that the increase in diffusion resistance caused by a decrease in temperature exposes the material to a lower average relative humidity and further increases diffusion resistance.

The advantage of a "high-tech" vapor permeable waterproof shell over a standard waterproof coating is



less pronounced in subfreezing weather. However, unlike a standard waterproof coating, even in the cold, high-tech waterproof materials should still allow the clothing to dry slowly, provided sweat rates are low. Certainly, in a heated shelter such as a ski lodge or tent, drying would be much faster with a high-tech hydrophilic shell. The diffusion of water vapor through a clothing shell with a hydrophilic film could exceed the steady-state value if the clothing were warmed by bright sunshine or by metabolic heat resulting from a temporary increase in physical activity.

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