

Latent Heat of Vaporization in Thermal Physiology

THE evaporation of water from the skin and the respiratory tract is an important mechanism of heat loss in homeotherms, and man's ability to sweat is essential for his survival when the temperature of the environment approaches or exceeds body temperature. The transfer of latent heat from an animal to its environment is often estimated by multiplying the loss in weight attributable to evaporation by the latent heat of vaporization of water, λ , which decreases from 2,501 J/g at 0° C to 2,406 J/g at 40° C.

In physiological problems, the temperature of the evaporating water (T_1) is usually higher than the temperature (T_2) of the surrounding air. The net amount of heat needed to convert 1 g of water at T_1 to 1 g of water vapour at T_2 is then $[\lambda - c_p (T_1 - T_2)]$ where c_p is the specific heat of water vapour at constant pressure. The change in heat capacity is usually small enough to be neglected in practice. For example, if skin at 33° C is surrounded by air at 20° C, $\lambda = 2,423$ J/g, $c_p = 1.9$ J g⁻¹ degrees K⁻¹, and the heat needed to vaporize 1 g of water is $2,423 - (1.9 \times 13) = 2,398$ J.

Several textbooks of thermal physiology^{1,2} refer to a much larger adjustment to the heat of vaporization, which was introduced by Hardy³. He assumed that the evaporation of sweat from the skin and of saliva from the respiratory tract is accompanied by an expansion of water vapour as a result of the decrease in vapour pressure from e_s , the value for saturated air in contact with the wet surface, to e_a in the ambient air. The work done during this expansion was calculated as $RT \ln (e_s/e_a)$ where the gas constant $R = 8.31$ J mol⁻¹ deg K⁻¹, and T is air temperature (K). For example, when water at 33° C evaporates into air at 27° C and 20% relative humidity, $e_s = 50.3$ mbar and $e_a = 7.1$ mbar. The term $RT \ln (e_s/e_a)$ is 270 J/g and on this basis the net heat needed to vaporize 1 g of water is $2,433 - (1.9 \times 6) + 271 = 2,683$ J. Hardy cited experimental evidence to support this value of λ but it is manifestly incorrect. If the latent heat of vaporization were a function of relative humidity, the conventional psychrometer equation could not be used to calculate vapour pressure from dry- and wet-bulb temperatures because the three parameters would not be uniquely related. Furthermore, an infinite amount of heat would be needed to evaporate a finite amount of water into completely dry air.

The expansion term introduced by Hardy is appropriate for a closed system containing water vapour and no air—the cylinder of a steam engine, for example. The term is not appropriate in the free atmosphere because the total atmospheric pressure exerted on a surface from which water is evaporating must be the same as the total pressure in the surrounding air. Differences in the partial pressure of water vapour near the evaporating surface are compensated by equal and opposite differences in the partial pressure of air. In the example above, the true value for the net heat of vaporization is 2,412 J/g, about 10% less than the value given by Hardy's approach. Discrepancies of similar size may be concealed in a number of publications describing the heat balance of farm animals and humans.

When the first draft of this note was sent to Dr Hardy for comment, he kindly drew my attention to an article⁴ in which Dr C. B. Wenger reaches a similar conclusion by more rigorous argument. Controversy still exists, however. Mitchell and his colleagues^{5,6} recently made a series of very careful determinations of λ for the evaporation of sweat from men in a calorimeter. They concluded that although λ was independent of air temperature and humidity, its mean value was $2,595 \pm 84$ J/g, about 7% greater than the value for pure water. This discrepancy cannot be an artefact of the experimental system because, when pure water was evaporated in the calorimeter, λ was 2,460 J/g, close to the conventional value.

The anomalously large values of λ derived from these and other sets of observations imply a depression in the free energy of water of about 170 J/g but this is at least two orders of

magnitude too large to be accounted for by the action of dissolved salts or of surface tension within the ducts of the sweat glands. When a sample of water has a free energy of G , the vapour pressure e of air in equilibrium with the water is given by $G = -RT \ln (e_s/e)$ J/mole or $138 \ln (e_s/e)$ J/g at $T = 306$ K. A value of $\lambda = 2,595$ J/g implies $G = -170$ J/g and an equilibrium relative humidity $(e/e_s) = 0.31$. In this state, sweat with a temperature of 33° C would not evaporate into air with a vapour pressure exceeding 16 mbar—an absurd conclusion. As fresh sweat is a very dilute solution of sodium chloride and other salts, the vapour pressure of air in contact with sweating skin will usually be within 1% of the saturation vapour pressure of water at the appropriate temperature.

In the absence of any rational physical explanation for an excess component of latent heat, the analysis of heat balance for people exposed to thermal stress must include at least one undetected and systematic source of error. Wenger suggests that Mitchell and other workers have failed to make proper allowance for a storage of heat when the body temperature of their subjects rose in response to heat stress or exercise.

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