A Theory of the Ventilated Psychrometer Based on the Thermodynamics of Irreversible Processes

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Abstract

It is shown that the thermodynamics of irreversible processes as developed by PRIGOGINE (1947) and DE GROOT (1951) offer the possibility of deriving the psychrometric equation without using pseudothermostatic reasoning.

1. The traditional theory

As a specimen of the theory of the ventilated psychrometer one may quote MONTGOMERY (1948). In this paper the argument runs literally (except for some slight modifications in notation):

"It follows from the definition of wet-bulb temperature that a mass M of dry air and a mass Mx of water vapor are imagined to cool from T to T_w and a mass $M(x_w - x)$ of water to evaporate at the temperature T_w. The enthalpy of the dry air decreases by $Mc_{p_1}(T - T_w)$ and that of water vapor decreases by $Mxc_{p_2}(T - T_w)$. The enthalpy of the added water increases by $ML_w(x_w - x)$. Since the process is adiabatic and isobaric, the total change in enthalpy is zero. Hence

$$(c_{p_1} + xc_{p_2})(T - T_w) = L_w(x_w - x) \qquad (1)$$

the basic and complete form of the *psychrometric formula* (for a ventilated psychrometer)."

Others have given derivations of (1) which differ only in minor points from that of MONTGOMERY, their main difference being the substitution of the word *heat* for *enthalpy* which illustrates the loose use often found in meteorological literature of these words which, however, denote quite different thermodynamical concepts.

At first sight there is nothing wrong with arguments of this kind. But a little reflection shows that the whole way of reasoning is at variance with the basic postulates of thermodynamics. For it is known that classical thermodynamics are only valid under very stringent restrictions. Indeed the application of thermodynamics is limited to:

a) closed systems
b) equilibrium conditions
c) quasi-static processes
d) reversible processes

Ad *a*. The system under consideration is clearly not closed. Therefore MONTGOMERY's remark "the total change in enthalpy is zero" is not valid in this form. For

one never knows how much enthalpy is added to the system by the ventilation.

Ad *b*. The system under consideration lacks the most essential condition of equilibrium *viz*. the uniformity of temperature through the system. Even the final state is not an equilibrium but a stationary state. But classical thermodynamics offer no tools to treat stationary states.

Ad *c*. The process which occurs in a ventilated psychrometer cannot be considered as a quasi-static process, since it is known that it is impossible to ventilate infinitesimally slowly. In fact the ventilation should preferably exceed 3 or 4 m sec.$^{-1}$

Ad. *d*. As it is impossible to apply a reversed ventilation the process cannot be considered as reversible.

Of course there is nothing to say against MONTGOMERY's reasoning if it is interpreted not as a theory of the ventilated psychrometer but as a theory of the concept of *wet-bulb temperature* as a property of the air. The real problem is to prove the identity of a theoretically defined *wet-bulb temperature* with the temperature of the *wet-bulb thermometer*.

Some authors have given treatments in which they try to avoid one of the above mentioned four defects. The most important paper on this subject is one by VAN MIEGHEM (1941), who used the thermodynamics of open systems. But a theory in which the four defects are avoided simultaneously has as far as the present author knows never been given. The main purpose of this paper is to offer such a treatment with the aid of the recently developed thermodynamics of irreversible processes. A short summary of this new theory will be given in the next section. For details the reader should consult the books of PRIGOGINE (1947) and DE GROOT (1951), where the subject is dealt with in full detail.

2. Introductory remarks on the thermodynamics of irreversible processes

In the thermodynamics of open systems the differential $d\Omega$ of any quantity Ω is split up in two parts, the exterior part $d_e\Omega$ and the interior part $d_i\Omega$.

$$d\Omega = d_e\Omega + d_i\Omega \tag{2}$$

The exterior part is defined as the change in Ω as far as it is a consequence of the exchange of matter with the surroundings, the interior part is defined by equation (2). By definition a pseudo-adiabatic process is a process for which

$$d_iQ = 0 \tag{3}$$

The last equation might be interpreted as follows: except for what happens as a consequence of exchange of matter with the surroundings, the system under consideration exchanges no heat with the surroundings.

Strictly speaking there is no first law for open systems. The often quoted formula*

$$dQ = dE + PdV - hdM = dH - VdP - hdM \tag{4}$$

is not a generalisation of the first law for closed systems to open systems, but is to be considered as a definition of dQ, a quantity which for open systems is often not measurable. In fact other definitions may be used *e.g.* the definition proposed by TOLHOEK and DE GROOT (1952)

$$dQ^\star = dE + PdV - \sum_k h_k d_e M_k \tag{5}$$

Comparing (4) with (5) one infers that the ambiguity in the definition of dQ has no consequences for the equation of the pseudo-adiabatic process, which reads in both cases

$$d_iQ = d_iQ^\star = d_iE + Pd_iV = 0 \tag{6}$$

The second law for open systems offers no difficulties and has already been given by GIBBS (1875—'78)

$$TdS = dE + PdV - \sum_k \mu_k dM_k = dH - VdP - \sum_k \mu_k dM_k \tag{7}$$

As far the *entropyproduction* σ, defined by

$$\sigma \equiv \frac{d_iS}{dt} \tag{8}$$

* List of symbols in section 5.

classical thermodynamics can only assert

$$\sigma \geqq 0 \tag{9}$$

but according to the new theory σ can always be written as

$$\sigma = \sum_A J_A X_A \tag{10}$$

The quantities J_A, which must be time-derivatives of some function of state, are called *flows* or *fluxes*. It appears that they are flows of matter, electrical currents, flows of heat, etc. The quantities X_A are called *conjugated forces* or *conjugated affinities*. Apart from some factor they are temperature gradients, electrical potential gradients, concentration gradients, etc. In the case of the presence of chemical reactions one of the X_A is the affinity as it is extensively used by the Belgian thermodynamicists of the school of DE DONDER.

For a large class of problems one may assume linear relations between fluxes and forces, called *phenomenological relations:*

$$J_A = \sum_B L_{AB} X_B \tag{11}$$

The coefficients L_{AB} are called *phenomenological coefficients;* in most cases the only way to compute them is by kinetic reasoning. They appear to be of the same kind as *e.g.* diffusion coefficients.

In 1931 ONSAGER proved with the tools of statistical mechanics his famous reciprocity law

$$L_{AB} = L_{BA} \tag{12}$$

which later on (1945) was discussed by CASIMIR.

At first sight this formalism does not seem to be of much use. But PRIGOGINE (1947) and DE GROOT (1951) have shown in their books that the reciprocity law (12) is a mighty weapon which in many cases enables one to arrive at far-reaching conclusions without the knowledge of the exact values of the coefficients L_{AB}.

3. The ventilated psychrometer

The psychrometer is a polythermal system, consisting of two phases, a gaseous phase and a liquid phase, having different temperatures. The following convention will be used: quantities referring to the gaseous phase are denoted by symbols with one accent, quantitie referring to the liquid phase by symbols witl two accents, whereas quantities referring to the whole system are denoted by symbols without accents. With the subscripts *1*, *2* and *3* the components dry air, water vapor and liquid water are indicated, thus *e.g.* M_2' stands for the mass of water vapor in the gaseous phase.

Furthermore the abbreviation

$$J_2 \equiv \frac{d_i M_2'}{dt} = -\frac{d_i M_3''}{dt} \tag{13}$$

is used. Equation (13) expresses the conservation of matter.

As for the distinction between exterior and interior changes, it should be kept in mind that this distinction refers always to the whole system even in an equation which is set up for a part of the system.

Now apply the first "law" (4) first to the whole system and afterwards to the two subsystems formed by the gaseous and the liquid phase. Since the process is pseudo-adiabatic and isobaric, one gets

$$\frac{d_i Q}{dt} = \frac{d_i H}{dt} = 0 \tag{14}$$

$$\frac{d_i Q''}{dt} = \frac{d_i H'}{dt} - h' \frac{d_i M'}{dt} = \frac{d_i H'}{dt} - h' J_2 \tag{15}$$

$$\frac{d_i Q'}{dt} = \frac{d_i H''}{dt} - h'' \frac{d_i M''}{dt} = \frac{d_i H''}{dt} + h'' J_2 \tag{16}$$

Equation (14) may be considered as the exact formulation of MONTGOMERY's statement "the total enthalpy does not change". One observes that this is only valid as far as exterior changes are left out of consideration. Adding (15) and (16) together one gets

$$\frac{d_i Q'}{dt} + \frac{d_i Q''}{dt} = \frac{d_i H'}{dt} + \frac{d_i H''}{dt} + (h'' - h') J_2$$

from which together with (14) and

$$H = H' + H''$$

it follows that

$$\frac{d_i Q'}{dt} + \frac{d_i Q''}{dt} = (h'' - h') J_2 \tag{17}$$

an equation which is often called PRIGOGINE's equation since PRIGOGINE discussed it extensively in his book (PRIGOGINE, 1951). As a consequence of (17) one gets

$$d_iQ' + d_iQ'' \neq d_iQ \tag{18}$$

an inequality which is one of the often unexpected freaks of the thermodynamics of open systems.

Now apply the second law (7) to both subsystems

$$\left.\begin{aligned} T'\frac{d_iS'}{dt} &= \frac{d_iH'}{dt} - \mu_2' J_2 \\ T''\frac{d_iS''}{dt} &= \frac{d_iH''}{dt} + \mu_3'' J_2 \\ \sigma = \frac{d_iS}{dt} &= \frac{d_iS'}{dt} + \frac{d_iS''}{dt} = \frac{1}{T'}\frac{d_iH'}{dt} + \frac{1}{T''}\frac{d_iH''}{dt} + \\ &+ \left(\frac{\mu_3''}{T''} - \frac{\mu_2'}{T'}\right) J_2 \end{aligned}\right\} \tag{19}$$

Using (14) and the abbreviations

$$J_1 \equiv \frac{d_iH'}{dt} \quad (20); \qquad X_1 \equiv \frac{1}{T'} - \frac{1}{T''} \quad (21);$$

$$X_2 \equiv \frac{\mu_3''}{T''} - \frac{\mu_2'}{T'} \tag{22}$$

the entropyproduction σ may be written as

$$\sigma = J_1X_1 + J_2X_2 \tag{23}$$

which has the form (10).

It is interesting to remark that VAN MIEGHEM and DUFOUR (1948) in their joint paper derived an equation (VIII, 42) which is substantially equivalent to (19). But since they did not use the ONSAGER theorem (12) but only the inequality (9) they failed to produce the psychrometric equation and could only prove

$$T_d \leqq T'' \leqq T' \tag{24}$$

in which T_d denotes the dewpoint. The fertility of the reciprocity law (12) is thus clearly demonstrated by the fact that on account of (12) we shall now proceed to deduce the said equation.

The phenomenological equations (11) are

$$\left.\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned}\right\} \tag{25}$$

and the reciprocity law (12) yields

$$L_{12} = L_{21} \tag{26}$$

Therefore

$$\sigma = L_{11}X_1^2 + 2\,L_{12}X_1X_2 + L_{22}X_2^2 \tag{27}$$

It is a well known theorem in classical thermodynamics, that the state of equilibrium corresponds with maximum entropy. In the thermodynamics of irreversible processes there is an analogeous theorem which states that the stationary state corresponds with minimum entropy production. Since T' is given by the exterior circumstances and T'' is sought, the stationary state is given by

$$\frac{\partial\sigma}{\partial T''} = 0 \tag{28}$$

Application to (27) gives, making use of (25) and (26)

$$\frac{\partial\sigma}{\partial T''} = (2\,L_{11}X_1 + 2\,L_{12}X_2)\frac{\partial X_1}{\partial T''} +$$

$$+ (2\,L_{12}X_1 + 2L_{22}X_2)\frac{\partial X_2}{\partial T''} = 2\,J_1\frac{\partial X_1}{\partial T''} +$$

$$+ 2\,J_2\frac{\partial X_2}{\partial T''} = \frac{2}{T''^2}\{J_1 - h_3''J_2\} = 0$$

or

$$J_1 = h_3''J_2 \tag{29}$$

(Here use is made of the well known formula

$$\ldots\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) = -\frac{h}{T^2}\right)$$

Going back to the definitions (13) and (20) one gets from (29)

$$\frac{d_iH'}{dt} = h_3''\frac{d_iM_2'}{dt} \tag{30}$$

Now H' is a function of T' and the masses M_1' and M_2' of the gaseous phase. Therefore

$$\frac{d_iH'}{dt} = \frac{\partial H'}{\partial T'}\cdot\frac{d_iT'}{dt} + \frac{\partial H'}{\partial M_1'}\cdot\frac{d_iM_1'}{dt} + \frac{\partial H'}{\partial M_2'}\cdot\frac{d_iM_2'}{dt} \tag{31}$$

By definition

$$\frac{\partial H'}{\partial M_2'} = h_2' \quad (32) \qquad \text{and} \qquad \frac{\partial T'}{\partial H'} = C_p' \quad (33)$$

whereas

$$\frac{d_i M_1'}{dt} = 0 \quad (34)$$

Substituting (31, 32, 33, 34) in (30) the last equation becomes

$$C_p' \frac{d_i T'}{dt} = (h_3'' - h_2') \frac{d_i M_2'}{dt} \quad (35)$$

Now the temperatures T' and T'' are sufficiently close to each other to substitute in (35)

$$h_3'' - h_2' = h_3''(T'') - h_2'(T') = -L \quad (36)$$

L being the latent heat of evaporation at some suitable intermediate temperature. Furthermore

$$C_p' = -M' c_p \quad (37)$$

and

$$\frac{d_i M_2'}{dt} = M' \frac{d_i x'}{dt} \quad (38)$$

Substitution of (36), (37) and (38) in (35) yields:

$$c_p' \frac{d_i T'}{dt} = -L \frac{d_i x'}{dt} \quad (39)$$

Now one may integrate the last equation over a time τ in which a quantum of air is in thermal contact with the wet surface of the psychrometer. During this time τ the air would in absence of exchange of matter with the surroundings cool from T' to T'' and increase its water content from x' to x_m''. Thus one arrives at the psychrometric equation

$$c_p'(T' - T'') = L(x_m'' - x') \quad (40)$$

which is equivalent to (1).

4. Concluding remarks

A. MONTGOMERY (1948) thinks it is very important that in the psychrometric equation (1) or (40) one should take the latent heat of evaporation at the wet-bulb temperature. The present theory shows that this is not the case. This was already known to VAN MIEGHEM (1941) who in his paper clearly demonstrated the approximations involved in equation (40) even if it is interpreted as an equation for the theoretically defined "wet-bulb temperature". This paper was apparently known to but not fully appreciated by MONTGOMERY.

B. The general theory of irreversible processes shows that the theories criticized in par. 1 in many cases may give the correct results. But no general rule can be given which enables one to decide *apriori* in which circumstances the pseudo-thermostatic theories, as they are called nowadays, give correct results. Thus one is never *apriori* certain that one may use pseudo-thermostatic reasoning unpenalized. The present paper shows that the formalism developed by PRIGOGINE and DE GROOT makes the use of pseudo-thermostatic methods unnecessary and provides very powerful tools, which are easy to handle as well as a sound basis for theoretical reasoning.

5. List of symbols

NB.: *Specific* means always: per unit of mass.

C_p' = heat capacity of total mass in gaseous phase at constant pressure.
E = internal energy
J = flow or flux
L_{AB} = phenomenological coefficients
L = latent heat of evaporation
M' = total mass gaseous phase
M_1' = mass of dry air
M_2' = mass of water vapor
M_3'' = mass of liquid water
P = pressure (overall pressure)
dQ = absorbed heat
S = entropy
T = absolute temperature
T_d = dewpoint
V = volume
X = force or affinity
c_p' = specific heat of gaseous phase at constant pressure
d_e = exterior change
d_i = interior change

h = mean specific enthalpy
h_2' = specific partial enthalpy of water vapor
h_3'' = specific enthalpy of liquid water
t = time
x' = specific humidity
x_m'' = maximum specific humidity at wet-bulb temperature
μ_2', μ_3'' = chemical potential (specific partial thermodynamic potential, specific partial GIBBS function, specific partial free enthalpy) for water vapor and liquid water respectively.
σ = entropyproduction
Ω = any quantity

One accent = gaseous phase
Two accents = liquid phase
Subscript 1 = dry air
2 = water vapor
3 = liquid water

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