

A new diagram for air + water vapor mixtures¹

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Water vapor may be considered a perfect gas in the practical applications of air-water vapor mixtures. The fundamentals of calculation are therefore very simple. A new diagram and its application to drying and water cooling processes are presented.

C_{DA}	Specific thermal capacity of dry air, $[kcal \cdot kg^{-1} \cdot ^\circ C^{-1}]$
C_ℓ	Specific thermal capacity of liquid water, $[kcal \cdot kg^{-1} \cdot ^\circ C^{-1}]$
C_w	Specific thermal capacity of water vapor, $[kcal \cdot kg^{-1} \cdot ^\circ C^{-1}]$
i	Specific enthalpy, $[kcal \cdot kg^{-1}]$
M	Mass, $[kg]$
m	Mass flow rate, $[kg \cdot h^{-1}]$
p	Barometric pressure, $[mm \text{ Hg}]$
p_w	Partial pressure of water vapor in the air, $[mm \text{ Hg}]$
p_{ws}	Saturation pressure of water vapor in the air, $[mm \text{ Hg}]$
Q	Heat rate, $[kcal \cdot h^{-1}]$
q	Specific heat rate, $[kcal \cdot kg^{-1} \cdot h^{-1}]$
T	Temperature (Absolute), $[K]$
t	Temperature (Celsius), $[^\circ C]$
V	Volume, $[m^3]$
x	Humidity ratio, $[-]$ (kg water vapor per kg dry air)
ϕ	Relative humidity, $[-]$ (usually expressed in %)
τ_w	Volume fraction of water vapor in the air, $[-]$

Dalton's law constitutes the basis of all calculations for air+water vapor mixtures (moist air) as well as for other gas mixtures. It is exactly valid only for mixtures of ideal gases, i.e. for gases that obey the equation of state $p v = R T$, and for which the energy and the enthalpy depend exclusively upon their temperature.

Air obeys accurately the ideal gas law. On the other hand, as is well known, water vapor deviates markedly from that law, the deviation increasing with pressure and decreasing with temperature. Would we have to deal with air+water vapor mixtures with a partial pressure of

¹ Translation of the original (in German) published in Zeitschrift des Vereins deutscher Ingenieure, 67(36), 869-872, 1923.

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The translation is offered *in memoriam* of Professor Richard Mollier on the 70th anniversary of his death.

water vapor of several atmospheres, exact calculations would be much more complex, since instead of Dalton's law and simple expressions for energy and enthalpy, we would have to deal with complex laws not yet well known. Usually, only air+water vapor mixtures with water vapor partial pressures below one atmosphere, are important for technical applications. At these low partial pressures, water vapor may be considered as a perfect gas with perfectly satisfactory accuracy. Thereby all calculations are extraordinarily simple.

Frequently an alternate process is used: The Dalton's law is used for air, however, data from steam tables are used for water vapor, instead of the ideal gas law, when the water vapor is saturated. Yet, since a consistent consideration of the unsaturated (superheated) water vapor leads to rather complex calculations, one returns here to the ideal gas law, by calculating the density of the water vapor as proportional to the partial pressure, at a given temperature, and by assuming the enthalpy as independent of the pressure. This method is time consuming, involved, and full of internal contradictions. If air+water vapor mixtures of vapor partial pressures so high that the simple ideal gas law fails, ever gain technical importance, it will be necessary to critically reassess the complete basis of the calculation procedures.

Gases can in general mix in any proportion. We express the composition in volume fractions (mole fractions). The volume fractions also express the partial pressure fractions of the total pressure. Yet, water vapor may only mix with air in limited quantities, since its partial pressure can never be higher than the water saturation pressure, p_{ws} , at the current temperature. We shall express all pressures in *mm Hg*. The partial pressure of water vapor, p_w , may take any value smaller than the saturation pressure. It is common, and convenient, to express the partial pressure as a fraction of the saturation pressure $p_w = \varphi p_{ws}$. We see immediately how far from saturation the air still is. According to the ideal gas law, φ represents the ratio of the amount of water vapor in a given volume, to the maximum amount that such volume may contain. φ is called the *relative humidity*, or the *degree of saturation*² of the air.

If a space with a volume of $V \text{ m}^3$ is filled with an air+water vapor mixture of total pressure p , and is at the absolute temperature $T = 273 + t$, we may apply the perfect gas law to both the total amount and its two constituent parts. For air we have

$$V(p - \varphi p_{ws}) = 2.153 M_{DA} T \quad [1]$$

where $p - \varphi p_{ws} = p_a$ is the partial pressure in *mm Hg*, and M_{DA} the mass, in *kg*, of dry air. For the water vapor it is

$$V \varphi p_{ws} = 3.46 M_w T \quad [2]$$

For the mixture we have

$$V p = M_M R T; \quad R = \frac{2.153}{1 - 0.378 \frac{\varphi p_{ws}}{p}} \quad [3]$$

² NT: This is the original expression of the author. In today's nomenclature these concepts are not equivalent: While in the current nomenclature the *Relative Humidity* definition agrees with that of the author, that for the *Degree of Saturation* refers to the ratio of the actual humidity ratio to that at saturation at the same temperature and pressure.

and

$$M_M = M_{DA} + M_W = \frac{0.465 p - 0.176 \varphi p_{ws}}{T} V \quad [4]$$

One m^3 of moist air contains therefore $0.289 \frac{\varphi p_{ws}}{T}$ kg of water vapor.

Since by the changes of state of air+water vapor mixtures the amount of dry air remains mostly constant, while the amount of water vapor increases through evaporation, or diminishes through condensation, it is convenient and usual to refer to a mixture containing 1 kg of dry air with variable amounts of water vapor. We represent by x this amount of vapor contained in 1 kg of dry air:

$$x = \frac{M_W}{M_{DA}} = \frac{2.153}{3.460} \frac{\varphi p_{ws}}{p - \varphi p_{ws}} = 0.622 \frac{\varphi p_{ws}}{p - \varphi p_{ws}} \quad [5]$$

and the total amount of mixture is $M_M = 1 + x$. The volume one such mixture is

$$V = \frac{2.153 T}{p - \varphi p_{ws}} \quad [6]$$

the volume fraction of the water vapor is then

$$\tau_W = \frac{\varphi p_{ws}}{p} = \frac{x}{0.622 + x} \quad [7]$$

Besides the relationships among pressure, temperature and volume, we need to know, above all, the enthalpy i for technical calculations of air+water vapor mixtures. For the narrow range of temperatures that are usually considered, we may assume a constant specific thermal capacity,

$$i = C_{DA} t + K \quad [8]$$

where K is an arbitrary constant. We set $K = 0$ for dry air, by referring the enthalpy of the mixture to air at 0 °C. $C_{DA} = 0.24 \text{ kcal} \cdot \text{kg}^{-1} \cdot \text{°C}^{-1}$.

For water vapor $C_W = 0.46 \text{ kcal} \cdot \text{kg}^{-1} \cdot \text{°C}^{-1}$ in the relevant range of temperatures. We do not want to refer the enthalpy of the water vapor to vapor at 0 °C, but to liquid water at 0 °C. The constant K is then $K = 595 \text{ kcal} \cdot \text{kg}^{-1}$ at 0 °C, that is $i_{DA} = 0.24 t$, and $i_W = 595 + 0.46 t$, and for the enthalpy of a mixture with 1 kg dry air we have

$$i = i_{DA} + i_W = 0.24t + x(595 + 0.46t)$$

$$i = 0.24t + 0.622 \frac{\varphi p_{ws}}{p - \varphi p_{ws}} (595 + 0.46t)$$

$$i = 0.24t + \frac{\varphi p_{ws}}{p - \varphi p_{ws}} (370 + 0.286t)$$

[9]

It is important for many applications to note that this equation represents as well the enthalpy of a mixture of 1 kg air + x kg water vapor + an arbitrary amount of water at 0 °C.

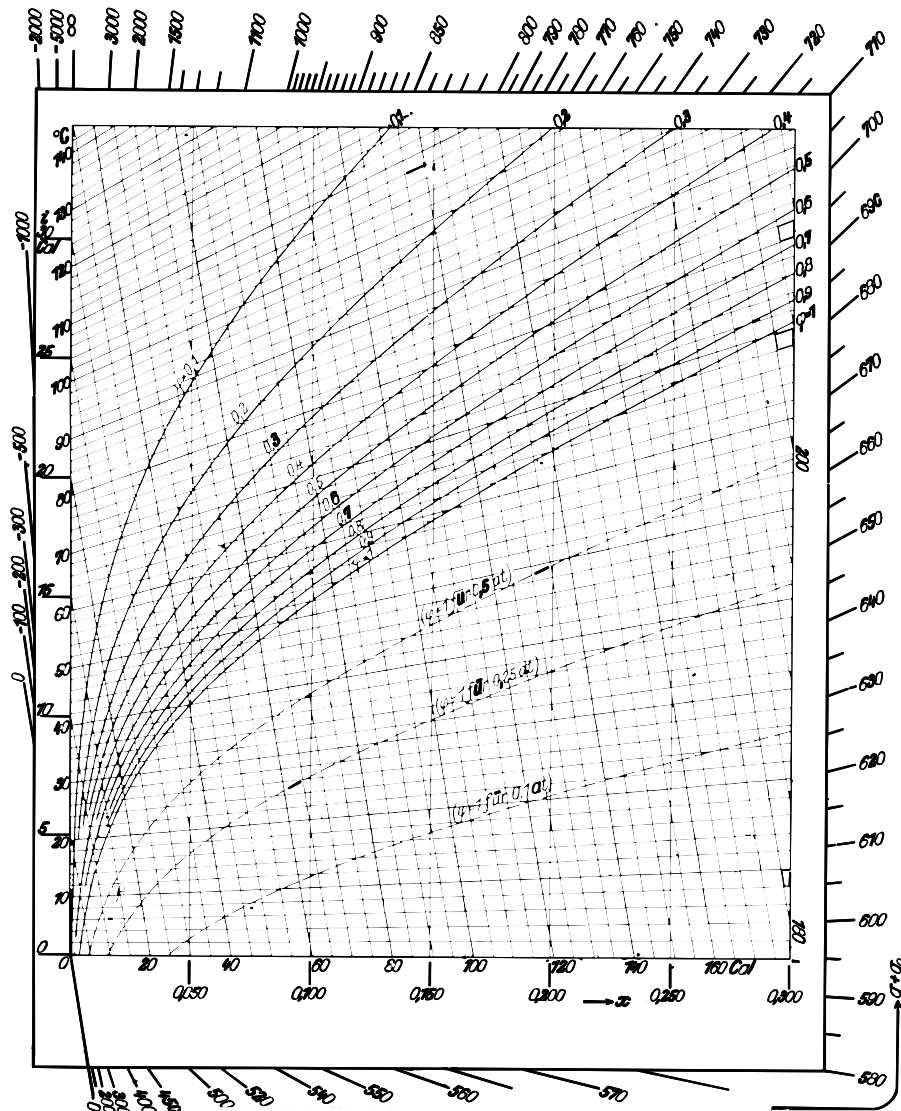


Fig. 1 - Diagram for air+water vapor mixtures.

In practice we have most often to deal with changes of state that take place at constant pressure, and this pressure is also mostly the pressure of atmospheric air. In such cases, the solution of practical problems may be significantly simplified through a graphical representation. At a constant total pressure p , the state of an air+water vapor mixture, referred to 1 kg air, is defined by just two of the four variables t , i , x , φ . It is thus obvious to take two of these magnitudes as coordinates, and represent in a diagram families of curves for constant values

of the other two. Following the proposition of O. H. Mueller³, one takes in general t and i as coordinates and represents lines of constant x and constant φ in the diagram. Lines of constant x are straight lines.

I shall recommend another diagram, Fig. 1: If one chooses as coordinates i and x , the resulting representation, not only permits an easy solution of the problems that may be solved with the i, t -diagram, but is also suitable for the solution of many others. It is advantageous to use oblique coordinates to obtain a clear picture. Good proportions are obtained by taking the 0°C isotherm as horizontal (following to equation [8] isotherms are straight lines).

The diagram is developed clearly as follows: We write eq.[9] in the following form:

$$i = (0.24 + 0.46x)t + 595x \quad [10]$$

the first term, $i' = (0.24 + 0.46x)t$, represents the enthalpy of the mixture, referred to air and water vapor at 0°C , and the second, $595x$, is the vaporization enthalpy of the water vapor part x , at 0°C . We set, to begin with, x as abscissa and i' as ordinate in an orthogonal system.

The isotherms are straight lines that divide the ordinates into equal parts. The line $t = 0$ coincides with the abscissa axis. The lines for constant relative humidity are easily plotted following eq.[5]. Both families of lines remain unchanged, when we now move to an oblique coordinate system, with i as ordinate, as we draw a line shifted by $595x$ from the current abscissa axis. The straight line thus obtained is the final abscissa axis, and defines the direction of the isenthalps.

The diagram in Fig. 1 is for a total pressure of $735.5 \text{ mm Hg}(= 1 \text{ atm}^*)^4$, (276 m above sea level) it may as well be used however, for other, not much different air total pressures, without significative error. The isotherms will not change when the diagram is plotted for another total pressure. The layout of the curves of constant relative humidity results from eq.[5] that we may re-write

$$x = 0.622 \frac{p_{ws} \left(\varphi \frac{735.5}{p} \right)}{735.5 - p_{ws} \left(\varphi \frac{735.5}{p} \right)} = 0.622 \frac{p_{ws} \frac{\varphi}{P}}{735.5 - p_{ws} \frac{\varphi}{P}} \quad [11]$$

where p is in mm Hg , and P represents the new total pressure in atm^* .

³ Mueller, Zeitschrift des VDI 49(1905), pp. 10.
Schuele, Zeitschrift des VDI 63(1919), pp. 682.
Hoehn, Zeitschrift des VDI 63(1919), pp. 821.

⁴ NT: The author equals the pressure of 735.5 mm Hg to one atm^* . This is, obviously, not in agreement with the definition of the standard atmosphere, which corresponds to 760 mm Hg at 0°C . Eq. [11] has been left as in the original for the purpose of illustration. The dependence of the relative humidity iso-lines upon the total pressure may better be determined from $\varphi = \frac{p}{p_{ws}} \frac{x}{0.622 + x}$ where the units of p and p_{ws} must be the same.

From this equation we observe that the family of φ -lines does not change as well, only the value of φ , corresponding to a given line, changes with the total pressure. A line representing the value φ at 735,5 mm Hg, or at 1 atm*, represents at p mm Hg, or P atm*, the relative humidity $\varphi \frac{P}{735.5}$, or φP . The diagram of Fig. 1 shows some saturation lines at other P values.

The diagram may be applied to changes of state at constant humidity content, to begin with. In such changes of state, x remains constant. They are thus represented by lines parallel to the ordinate axis. In this respect, the new diagram has the advantage, in comparison with the i, t -diagram, that the change of enthalpy is simply represented by the line segment joining the start and end state points. To determine the dew-point, one has simply to draw a line parallel to the ordinate axis until it crosses the saturation, $\varphi = 1$, line and read the temperature at this point.

In general, in a change of state of an air+water vapor mixture, the water vapor content x changes as well. Besides the change of vapor content, we have now also to do with an amount of liquid water that, either shows up through condensation, or disappears through evaporation, and that, for a change of state 1-2, is given by $x_2 - x_1$ for 1 kg of dry air. The change of the enthalpy $i_2 - i_1$, obtained from the diagram, or calculated with eq.[9], does not represent any more the energy that is supplied, or extracted, but an enthalpy that is smaller, or larger, by $(x_1 - x_2) C_\ell t_0$, where t_0 is the evaporation, or condensation temperature of the water and C_ℓ is the specific thermal capacity of the liquid water⁵. This follows from the fact, mentioned earlier, that both our diagram and eq.[9] represent as well the enthalpy of an air-water mixture with 1 kg air + an arbitrary amount of liquid water at 0 °C. It is then $Q_{1,2} = i_2 - i_1 - (x_2 - x_1) C_\ell t_0$.

Use of the Diagram

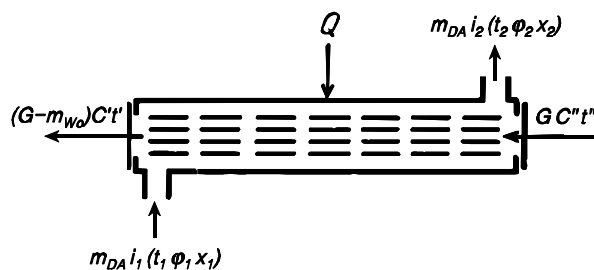


Fig. 2

Energy balance of a dryer⁶: Fig. 2 depicts schematically a dryer in continuous operation. G kg/h of wet material enter the dryer at the temperature t'' , and $G - m_{w0}$ kg/h of dried material leave the dryer at the temperature t' . m_{w0} is the amount of water lost by the material per unit of time. Let C' be the specific thermal capacity of the material at the end of the process. We may include into G and C' any transportation devices used. m_{DA} kg/h of dry air enter the dryer at the temperature t_1 , with the

vapor content x_1 , the relative humidity φ_1 , and the enthalpy i_1 . m_{DA} kg/h of dry air at t_2 , φ_2 , x_2 and i_2 leave the dryer. Furthermore, Q kcal/h are supplied to the dryer, either with the air or by heaters inside the dryer, or even directly to the material to dry. Finally, the dryer also loses Q_L kcal/h to the ambient. The following explanation applies as well to dryers with air recirculation.

⁵ NT: The author does not include the specific thermal capacity of liquid water explicitly in the original. He considers it unity (1 kcal·kg⁻¹·°C⁻¹). It is included in the translation for the sake of consistency.

⁶ Merkel, F., Beitrag zur Thermodynamik des Trocknens, Zeitschrift des VDI, 67(4), 81-84, 67(5), 106-108 1923.

The energy balance of the dryer is then given as

$$Q = m_{DA} (i_2 - i_1) + (G - m_{wo}) C'' (t' - t'') - m_{wo} C'' t'' + Q_L \quad [12]$$

Let us relate every term to 1 kg of the water lost by the material, and represent $\frac{Q}{m_{wo}}$ by q and $\frac{m_{DA}}{m_{wo}}$ by a , so that we have

$$q = a (i_2 - i_1) - \left[C'' t'' - \left(\frac{G}{m_{wo}} - 1 \right) C'' (t' - t'') - \frac{Q_L}{m_{wo}} \right] \quad [13]$$

The expression in the square brackets shall be represented as q_0 . Its value is negligible in many cases, in comparison to $a (i_2 - i_1)$, so that it may be ignored when establishing general expressions. q_0 may take large negative values when, as for example in the drying of cereals, $\frac{G}{m_{wo}}$ is particularly large.

The water lost by the material, m_{wo} , leaves the dryer as vapor mixed with the dry air, thereby increasing its vapor content from x_1 to x_2 . It is then

$$m_{wo} = m_{DA} (x_2 - x_1) \quad \text{or} \quad a (x_2 - x_1) = 1 \quad [14]$$

combining eq.[13] and [14] we obtain

$$q + q_0 = \frac{i_2 - i_1}{x_2 - x_1} \quad [15]$$

For numeric calculations we may replace eq.[9] into eq.[15], which results in:

$$q + q_0 = 595 + (0.24 + 0.46 x_1) \frac{t_2 - t_1}{x_2 - x_1} + 0.46 t_2 \quad [16]$$

and

$$q + q_0 = 595 + \frac{0.386 + 0.46 \frac{\varphi_1 P_{ws,1}}{p - \varphi_1 P_{ws,1}}}{\frac{\varphi_2 P_{ws,2}}{p - \varphi_2 P_{ws,2}} - \frac{\varphi_1 P_{ws,1}}{p - \varphi_1 P_{ws,1}}} (t_2 - t_1) + 0.46 t_2 \quad [17]$$

This last equation gives the energy required by a dryer as function of the temperatures and relative humidity of the air at inlet and outlet. The overview and calculation of the required energy is extremely simplified by the use of the ix -diagram. We start from the simple eq.[15], which shows that $q + q_0$ is given by the slope of the line joining points 1 and 2, that are defined by the temperatures t_1 and t_2 and the relative humidities φ_1 and φ_2 .

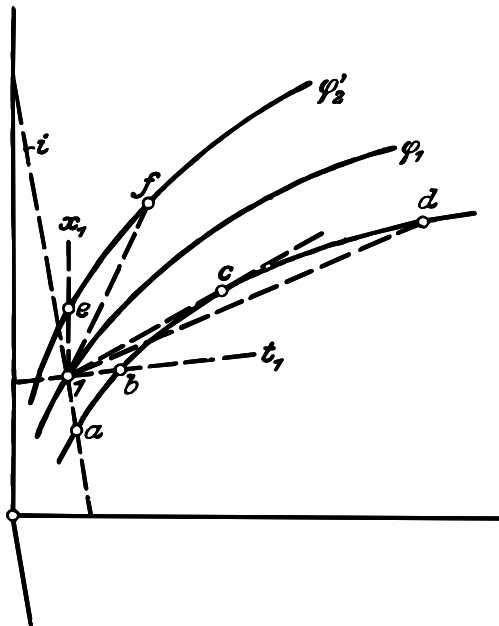


Fig. 3

Drying is only possible when $x_2 > x_1$. If we do not supply any external energy, $q = 0$, then we have natural drying. It must be $\varphi_1 < \varphi_2$. If $q_0 = 0$, then $i_1 = i_2$, and $t_2 < t_1$, which implies a large air requirement. This case is illustrated in Fig. 3 by $l - a$. If we maintain the initial state of the air and φ_2 constant, and suppose t_2 increases substantially, then the energy required will increase while the required air rate will decrease.

For $t_2 = t_1$, $l - b$, we get $q + q_0 = 595 + 0.46 t_1$, that is the enthalpy of the water vapor at t_1 . q increases, but is limited to a maximum that is attained when the process line, $l - c$, through the initial state, becomes tangent to the φ_2 line. A further increase of t_2 leads to a reduction of $q + q_0$, $l - d$, until for $a = 0$, $x_2 = \infty$, which is the case of pure vaporization when

$$q + q_0 = 595 + 0.46 t_2 = 640 \text{ is attained.}$$

If $\varphi_1 > \varphi_2$, drying may only begin at a temperature $t_2 > t_1$, $l - e$ in Fig. 3, with $a = \infty$, and $q = \infty$. q will decrease continuously with the increase of t_2 , $l - f$, and the limiting maximum value has disappeared.

Drying with pre-heated air, Fig. 4: The pre-heating is represented by the line $l - l'$, parallel to the ordinate axis. The length of this line segment gives the enthalpy change during pre-heating. Point l' represents now the air state at the dryer inlet. Since no other energy is supplied to the air,

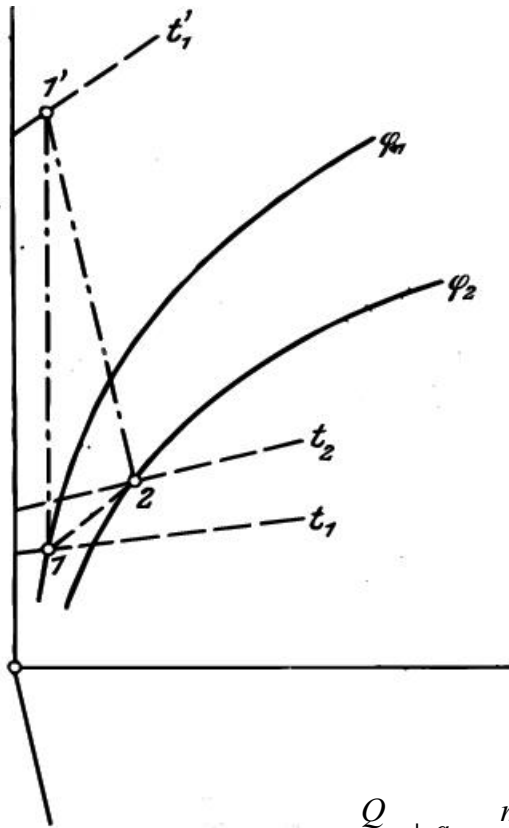
it is now $q_0 = \frac{i_2 - i_1}{x_2 - x_1}$, and further changes of state of the air follow the line through l' and

parallel to a line through the origin crossing the edge scale at the value q_0 . The direction of this line is in general undistinguishable from that of the isenthalps, so that one may set $i_2 = i_1$. We see

The diagram in Fig. 1 shows as well an edge scale for the values of $\frac{i}{x}$, that further simplifies the calculation of q . One has simply to draw a line parallel to $l-2$ through the origin, which defines the value $q + q_0$ at its intersection with the edge scale. Since q is always of the order of magnitude of the enthalpy of vaporization, q_0 is often negligible.

The amount of air required per kg H₂O removed is given as $a = \frac{1}{x_2 - x_1}$ by eq.[14], that is, by the reciprocal of the horizontal distance between points 1 and 2. This distance represents the amount of water that has to be 'dried out' by a kg of air.

that for a given pre-heating temperature t_1 , the energy required becomes smaller as the outlet temperature t_2 is reduced, since φ_2 gets higher and $q + q_0$ continues to be given by the line joining 1 - 2.



The minimum practical limit of the specific energy required by a dryer is represented by the pure vaporization at 640 kcal/kg . Below this limit, the air rate required increases rapidly to unpracticable values. We shall therefore still question whether there is some other plausible arrangement that might reduce the energy required, without an unacceptable increase of the required air rate? This possibility exists in effect, if we relax the pre-imposed condition that the water removed from the material to dry leaves the dryer as vapor. If we accept that one part may leave the dryer as liquid, there is then the possibility of driving the first stages of the drying process with moist air from the last stages, from which part of the vapor is condensed. Such concepts have been often proposed, and built in some cases.

If m_{wc} is the amount of condensate leaving the dryer at t_c , the new energy balance is given as:

Fig. 4
$$\frac{Q}{m_{wo}} + q_0 = \frac{m_{DA}}{m_{wo}} (i_2 - i_1) + t_c C_\ell \frac{m_{wc}}{m_{wo}} \quad [18]$$

and to calculate the air rate we have

$$m_{wo} = m_{DA} (x_2 - x_1) + m_{wc} \quad \text{or} \quad \frac{m_{DA}}{m_{wo}} = \frac{1 - \frac{m_{wc}}{m_{wo}}}{x_2 - x_1} \quad [19]$$

which gives, combining both equations:

$$q + q_0 = \left(1 - \frac{m_{wc}}{m_{wo}}\right) \frac{i_2 - i_1}{x_2 - x_1} + t_c C_\ell \frac{m_{wc}}{m_{wo}} \quad [20]$$

from where we conclude that, compared with the earlier cases, the air rate is now only the fraction $1 - \frac{m_{wc}}{m_{wo}}$, and the energy required is proportionally reduced.

Energy balance of a cooling tower⁷: m_{DA} kg/h of air flow through the tower, Fig. 5, driven either by natural or forced draft. A water rate of m_W kg/h enter the tower at the temperature t'' °C, and leaves at the tower outlet reduced by the evaporated amount m_{Wo} kg/h at t' °C. Make-up water at the temperature t_o °C replaces the evaporated water. The circulating water extracts Q kcal/h from a condenser of a steam engine, or any other device. We have then the simple energy balance

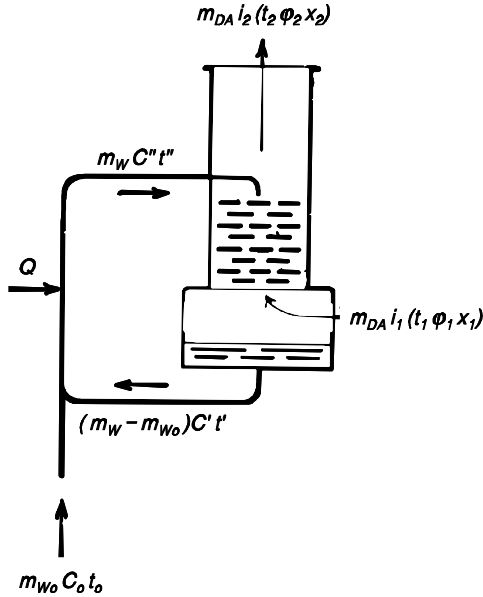


Fig. 5

$$Q + m_{Wo} C_o t_o = m_{DA} (i_2 - i_1) \quad [21]$$

on the other hand the mass balance is

$$m_{Wo} = m_{DA} (x_2 - x_1) \quad [22]$$

and hence

$$\frac{Q}{m_{DA}} + (x_2 - x_1) C_o t_o = i_2 - i_1 \quad [23]$$

Eq.[21], where $m_{Wo}C_o t_o$ is always smaller than Q , permits the calculation of the enthalpy i_2 of the air leaving the tower, when the energy to dissipate Q and the initial state of air are known. The outlet temperature of the air remains undetermined, as in the case of the dryers, if no assumption can be made regarding its relative humidity ϕ_2 . If it is possible to make one such assumption, then one may calculate the air rate $\frac{m_{DA}}{Q}$ that must flow through the tower in order to attain the outlet temperature t_2 . This all is extremely simplified by the use of the ix -diagram. The magnitude $\frac{Q}{m_{Wo}}$, that was so important, as the specific energy required in a drier, is not as important in a cooling tower. Its reciprocal value, that represents the required water make-up for a given thermal power, may be determined immediately using the edge scale on the diagram.

The controlling magnitudes of a cooling tower are the water temperatures t' and t'' . They may be easily introduced in our energy balance through the relation

$$Q = m_W C''(t''-t') + m_{Wo} C'(t'-t_o) \quad [24]$$

The cooling of the water is practically determined by the value of $t'' - t'$, since $m_{Wo} C'(t'-t_o)$ represents only a few percent of Q . The energy balance, that we now write as

$$m_W C''(t''-t') + m_{Wo} C' t' = m_{DA} (i_2 - i) \quad [25]$$

⁷ K. Neumann, Die Beurteilung von Kaminkühlern, Zeitschrift des VDI, 65(41), 1070-1074, 1921.

does not say anything regarding the temperatures of the water. These temperatures, like those of the drying material, the temperature t_2 , or the relative humidity φ_2 of the exhaust air of dryers and cooling towers, are determined by the laws of the heat and mass transfer processes taking place between the air, and the drying material, or the circulating water.

The theoretical treatment, which is at present almost inexistent, must go hand in hand with the experimental investigation of dryers and cooling towers in suitable setups, for the explanation of these processes. Experimental data on dryers are extremely scanty. Regarding experimental work on cooling towers I shall mention in particular the work of Geibel⁸ and a summary of American work by Robinson⁹.

⁸ Geibel, C., Ueber die Wasserrückkühlung mit selbstventilierendem Turmkühler, VDI Forschungsheft 242, 1921.

⁹ Robinson, C. S., The Design of Cooling Towers, Mechanical Engineering, 45(2), 99-102, 1923.