Study of heat and mass transfer processes in obtaining fresh water from atmospheric air

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Abstract. The physical processes underlying the perspective method of water extraction in anhydrous arid regions of the Earth are considered in the article. This method is based on the use of a porous, salty material that allows intensive absorption of moisture from the air, followed by evaporation of the formed brine with the help of sunlight and vapor deposition on the inner surface of the transparent solar plant cover. Based on the laws of the molecular-kinetic theory, the authors derive a general expression for the intensity of moisture trapping. Based on the expression obtained, it is concluded that to capture moisture, it is necessary to lower the density of saturated vapor over the porous surface in comparison with the density of the vapor being precipitated. Taking this into account two methods are considered: capillary condensation and salty solution. Considering both ways, their patterns and driving mechanisms, the authors conclude that the most effective way is the second one, and the first one can be considered as an auxiliary method. The article provides a detailed derivation of the conditions necessary to absorb moisture in the form of a brine and its evaporation when obtaining pure water. The material of the article can be useful in the design of solar installations.

1. Introduction
Enhancement of technologies for water obtaining from the air needs further studying of theory and practice of mass and heat transfer on the boundary of moist air and condensed water. In this context, we consider vapor molecules moving toward the surface, which separates the liquid and gaseous phases [1, 2].

Where \( dn = n f(v) dv \) is the number of molecules per volume unit, which have an absolute velocity value in the range from \( v \) to \( v + dv \). In order that a particle, having a velocity in this interval, intersects the surface \( S \) in the solid angle element \( d\Omega \) it has to be in the volume \( dV = v \cos \theta \, S \, dt \), as it is shown on Figure 1. Considering the distribution uniformity by the directions, the number of particles that intersects the surface \( S \) in the solid angle element \( d\Omega \) per unit time are equal

\[
\frac{d^2 N}{dt} = \frac{S}{4\pi} \, dn \int v \cos \theta \, d\Omega, \quad \text{where the integration is over the half-space.}
\]

Considering that

\[
d\Omega = \frac{dS}{R^2} = \frac{R \sin \theta \, \varphi \, d\varphi \, d\theta}{R^2}, \quad \text{find} \quad \frac{d^2 N}{dt \, S} = v \, dn \int_{\varphi=0}^{\pi/2} \int_{\theta=0}^{\pi/2} \sin \theta \cos \theta \, d\varphi = \frac{vdn}{4}.
\]
Integrating over the whole velocity space we find the number of steam molecules coming per space unit in a unit of time, that intersect the surface in one direction:

$$\frac{dN}{dt} = \frac{1}{4} \int vdv = \frac{1}{4} \int n^{\varphi} \langle v \rangle dv = \frac{1}{4} n \langle v \rangle.$$ 

According to the molecular-kinetic theory, the average velocity modulus is equal $$\langle v \rangle = \sqrt{\frac{8RT}{\pi \mu}}$$, where $$\mu$$ - is molar mass of steam, then the flow of molecules moving from the gas phase to the liquid is equal

$$\frac{dN}{dt} = \rho n \sqrt{\frac{RT}{2\pi \mu}}.$$ 

Multiplying the resultant molecular flux by the mass of one molecule and considering that $$m,n = \rho$$ – partial steam density, we get an expression for the condensation intensity:

$$j = \frac{dm}{dt} = j_1 - j_2.$$ 

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In a state of equilibrium between liquid with steam $$j = 0$$, from which we get:

$$j_2 = \sqrt{\frac{RT}{2\pi \mu}} \rho_s,$$

$$j = \sqrt{\frac{R}{2\pi \mu}} \left( \sqrt{T_1} \rho - \sqrt{T_2} \rho_s \right).$$ (1)

where $$\rho_s$$ - saturated steam density at temperature $$T_2$$.

Considering that $$\rho \leq \rho_s$$ and $$\rho_s$$ grows with temperature increase, from the last formula follows that for the final condensation intensity, liquid phase at a lower temperature should be maintained, than gaseous, which leads to the need for cooling and reduces the efficiency of steam trapping. This
can be avoided by using a solution of a non-volatile substance (salt, for example) as a liquid phase. According to Raoult’s laws for ideal solutions, the saturated steam pressure over the solution decreases in proportion to the molar concentration of the solvent:

\[ P_s = (1 - iX_B)P_{0S}, \]  \hspace{1cm} (2)

where \( i \) – the isotonic Van't-Hoff coefficient, which makes it possible to take into account electrolytic dissociation,

\( P_s, P_{0S} \) – partial pressures of saturated steam in the presence and absence of dissolved substance (B),

\[ X_B = \frac{V_B}{V_A + V_B} \] molar part of dissolved substance considering dissociation.

Substituting in (2) the expression of pressure through density \( P = \frac{\rho}{\mu}RT \), we get:

\[ j = \sqrt{\frac{R}{2\pi \mu}} \left( \sqrt{T_1} \rho - \sqrt{T_2} \ (1 - iX_B)\rho_{0S} \right). \] \hspace{1cm} (3)

If we consider that the condensation process proceeds in an isothermal regime, inputting a relative humidity \( \varphi = \frac{\rho_1}{\rho_{0S}} \) we get:

\[ j = \sqrt{\frac{RT}{2\pi \mu}} \rho_{0S} \left( \varphi + iX_B - 1 \right). \] \hspace{1cm} (4)

In the formula (4), the relative humidity of the steam and the molar concentration should be understood locally, at the interface between the two environments. Owing to the finite velocity of the condensation process, the relative humidity of the steam and the molar concentration near the boundary will decrease (the solution is diluted with condensed moisture, and steam is diluted with the air non-penetrating through the surface). As a result of this, formula (4) should be used together with the equations of mass transfer in the liquid and gaseous phases. In each phase, one of the components (dissolved component and air) do not penetrate through the interfacial surface, and the other two (moisture and steam) can freely move from one phase to another, therefore, the mass transfer in a liquid and gas is described in the same way. Shortly, we will call both phases a «solution», the first two components are a «dissolved substance», and the other two are a «permeate» [1].

We consider a solution bounded by a semipermeable (selective) surface \( S \). Let’s consider that this surface completely keeps the dissolved component and pass permeate, which under the action of condensation penetrates through the selective surface.

Density of solution \( \rho = \rho_1 + \rho_2 \), where \( \rho_1 \) and \( \rho_2 \) - partial densities of the solute and permeate, accordingly:

\[ \frac{\partial \rho_i}{\partial t} + \nabla \cdot \left( \rho_i \mathbf{v}_i \right) = 0 \hspace{1cm} (i = 1, 2). \] \hspace{1cm} (5)

Let us determine the velocity of the environment, as the velocity of the mass center of the components:

\[ \mathbf{v} = \frac{\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2}{\rho}, \] \hspace{1cm} (6)
then adding up the equations (5) for \(i=1, 2\), we get the equation of continuity of the environment:

\[
\frac{\partial \rho}{\partial t} + \nabla (\rho \mathbf{v}) = 0 .
\]

(7)

So, instead of two equations (5) \((i=1, 2)\), equation (7) and equation (5) can be considered for \(i=1\).

We input the concentration \(c=\rho_1/\rho\). Assuming that the absolute, convective and conductive velocities of the solute satisfy the Fick's law:

\[
\mathbf{v}_1 = \mathbf{v} - \frac{D}{c} \nabla c,
\]

(8)

we transform equation (5) to the following form:

\[
\rho \left( \frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right) - \nabla \cdot (\rho D \nabla c) = 0 .
\]

(9)

Let us make the assumption of the constancy of the total density, then the equations (3), (5) take the following form:

\[
\nabla \cdot (\rho \mathbf{v}) = 0 ,
\]

(10)

\[
\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c - D \nabla^2 c = 0 .
\]

(11)

We consider the condition on the boundary \(S\). Since the solute does not get through the boundary, then the following equality is valid for it:

\[
\mathbf{v} \big|_{lni} = 0 .
\]

(12)

Using the Fick's law (4), we transform this equation to the following form:

\[
\left[ cv_n - D \frac{\partial c}{\partial n} \right]_{S} = 0
\]

(13)

We choose liquids on the surface that are in contact with moist air, elementary sector with the area \(dS\), as shown in Figure 1. The average number of steam molecules that cross a unit of surface area per unit of time from all directions of the half-space, which is external towards the phase interface:

\[
j = \frac{dN}{dS \, dt} = \frac{1}{4} n(v),
\]

(14)

where \(n\) - is volume concentration of steam molecules,
〈\(v\)〉 = \(\sqrt{\frac{8RT}{\pi \mu}}\) - the average thermal velocity of water molecules.

Multiplying both parts of formula (14) by the mass of one molecule of water \(m_0\) and considering that \(m_0n = \rho(\text{steam density})\) we get an expression for the corresponding mass of water molecules during thermal motion:

\[
\dot{j}_m = \frac{dm}{dS dt} = \frac{1}{4} \rho(\langle v \rangle) = \frac{1}{4} \sqrt{\frac{8RT}{\pi \mu}} \rho.
\]  

(15)

We consider the process of moisture absorption from the moment when the surface of the sorbent is covered with a liquid. On the surface of the liquid the flow of molecules moving from the gas phase side \(j_{m2}\) is added to the counterflow of molecules leaving the liquid phase \(j_{m1}\). Let \(T_1\) be the temperature of the liquid and \(T_2\) - the temperature of gas environment (in the general case it is different from \(T_1\)). Then:

\[
\dot{j}_e = \frac{dm_e}{dS dt} = j_{m2} - j_{m1} = \sqrt{\frac{R}{2\pi \mu}} (\sqrt{T_2 \rho_2} - \sqrt{T_1 \rho_1} ),
\]

where \(\rho_2\) - the partial density of steam molecules moving to the direction of the phase interface surface, \(\rho_1\) - the partial density of steam molecules leaving the liquid environment [2].

In a state of dynamic equilibrium when the steam is saturated, the number of molecules evaporating from the surface is balanced by the number of molecules that condense on it. In this case, the steam density \(\rho_1\) is equal to the saturated steam density at temperature \(T_1 - \rho_{s1}\). Then according to previous formula:

\[
\dot{j}_e = \sqrt{\frac{R}{2\pi \mu}} (\sqrt{T_2 \rho_2} - \sqrt{T_1 \rho_{s1} }).
\]  

(16)

We consider a fluid that is in equilibrium with its steam. A steam molecule that is in close proximity to the surface of the liquid on the outside has an excess potential energy \(A_0\) relative to the molecule inside the liquid. Then, according to the Boltzmann’s distribution, the density of the liquid and the density of saturated steam are related by the Boltzmann’s formula:

\[
\rho_S = \rho_{\infty} \exp \left( -\frac{A_0}{kT} \right) = \rho_{\infty} \exp \left( -\frac{A_0 N_A}{RT} \right).
\]  

(17)

We convert this expression using the table values. For the forming one mole of saturated steam with the temperature \(T\) it is necessary to spend the amount of heat \(Q = q\mu\), where \(q\) is specific heat of vaporization. According to the first law of thermodynamics \(Q = A + \Delta U\), where \(A\) - a work for expanding one mole of saturated steam \(A = RT\), \(\Delta U\) - the change in the internal energy of one mole of substance when it is passing through the surface stratum \(\Delta U = A_0 N_A\). As a result, we get: \(q\mu = RT + A_0 N_A\). Then, expression (17) takes the following form:
\[ \rho_S = \rho_{sc} \exp \left(1 - \frac{q \mu}{RT}\right). \]

We change the form of expression (16). For doing this we leave out the index «2» in it, meaning the gas phase (steam), and substitute the index «1» by «c» (condensate). Then, we put it beyond the brackets \( \rho_S, T \):

\[ j_c = \frac{RT}{2\pi \mu} \rho_s \left( \varphi - \frac{T_c \rho_{sc}}{T \rho_s} \right), \]

where \( \varphi = \frac{\rho}{\rho_s} = P/P_s \) - is the relative moisture of air away from condensate,

\( \rho_{sc} \) - the density of saturated steam in close proximity to the condensate with the condensate temperature \( T_c \). We express the elasticity of saturated steam through its density using the Mendeleev-Clapeyron equation:

\[ P_s = \frac{\rho_s}{\mu} RT. \]

Formula (19) describes the moisture exchange between the gas and liquid phases, which can have different temperatures. Let us analyze formula (19) with respect to condensation possibility. From the formula it follows that in order the moisture condensation could occur \( (j_K > 0) \) it is necessary that:

\[ \frac{\rho_{sc}}{\rho_s} < \varphi \sqrt{\frac{T}{T_c}}, \]

i.e. the saturated steam density over the sorbent should be substantially lower than far from it. It should be noted that steam condensation releases evaporation heat, therefore \( T_c \geq T \), and this fact increases the noted circumstance [3].

This requirement underlies two methods of moisture condensation: 1) capillary condensation by a surface of a substance with a developed capillary-porous structure, 2) condensation on the salt solution surface. We call the last method «solvating». A combination of these methods is also possible. Both of these methods lead to a decrease of \( \rho_{sc} \) towards to the usual, «unperturbed» value of the parameter \( \rho_{sc0} \). This decrease is going to be characterized by the variation coefficient of the saturated steam density:

\[ d = \frac{\rho_{sc}}{\rho_{sc0}}. \]

Using this parameter, we rewrite equation (18) in the following form:

\[ j_c = \frac{RT}{2\pi \mu} \rho_s \left( \varphi - d \sqrt{\frac{T_c \rho_{sc0}}{T \rho_s}} \right). \]

At first, we consider the first method. A necessary condition for capillary condensation is the wettability of the capillaries walls, pores or microcracks of the sorbent with liquid. As a result of
adsorption, the walls are covered with steam molecules and form a thin membrane, which forms a concave meniscus of the surface stratum on the border with the steam. For each molecule of steam that is in close proximity to the concave surface, a larger number of molecules is affected than that from the side of the flat surface, because more molecules of the liquid get in the scope of the molecular forces. As a result of this, an additional attraction force of the steam molecules to the liquid arises, which leads to a decrease of the saturated steam density. This phenomenon is described by the law of Thomson (Kelvin):

$$\ln \frac{P_{s0}}{P_s} = \frac{\mu}{\rho_\infty RT} (P_{s0} - P_s - \sigma K),$$

(24)

where $P_{s0}$ - the pressure of saturated vapor above a flat surface,

$P_s$ - is the pressure of saturated vapor above a curved surface,

$\sigma$ - is the surface tension coefficient,

$K$ - is the curvature of the surface.

For a concave surface, this quantity is considered negative. In general case, $K = \frac{1}{r_1} + \frac{1}{r_2}$, where $r$ are the main radii of curvature. For the cylindrical capillary of radius in the case of complete wetting (non-wetting) $|K| = \frac{2}{r}$. For incomplete wetting with a contact angle $\theta$, $|K| = \frac{2 \cos \theta}{r}$. The ratio $\frac{P_{s0}}{P_s}$ satisfies equation (24).

Let’s consider a typical case of small curvature, when $\sigma |K| \ll P_{s0}$. In this case $P_s$ differs a little from $P_{s0}$: $\left(\frac{P_s}{P_{s0}} \ll 1\right)$ and we can apply an approximate formula $\ln (1 + x) \approx x$, $(|x| \ll 1)$. Then $\ln \left(\frac{P_s}{P_{s0}}\right) = \ln (1 + \frac{P_s - P_{s0}}{P_{s0}}) \approx \frac{P_s - P_{s0}}{P_{s0}}$ whence after transformation of equation (23) we find:

$$P_s - P_{s0} = \frac{\mu P_{s0}}{\rho_\infty RT} (P_s - P_{s0} + \sigma K) = \frac{\rho_{s0}}{\rho_\infty} (P_s - P_{s0} + \sigma K); (P_s - P_{s0}) \left(1 - \frac{\rho_{s0}}{\rho_\infty}\right) = -\frac{\rho_{s0}}{\rho_\infty} \sigma;$$

$$P_s = P_{s0} + \frac{\rho_{s0}}{\rho_\infty} \frac{\rho_\infty}{\rho_{s0}} \sigma K.$$

(25)

Neglecting $\rho_{s0}$ as compared with $\rho_\infty$ in the denominator and passing to the saturated steam with the condensate temperature ($T_c$), we transform the last expression to the following form:

$$\frac{P_{sc}}{P_{sc0}} = 1 + \frac{\rho_{sc} \mu \sigma |K|}{P_{sc0}}.$$

(26)

Expressing the saturated steam pressure through its density, according to the Mendeleev-Clapeyron equation, we get that, taking into account, in the case of wetting ($K < 0$):

$$\frac{\rho_{sc}}{\rho_{sc0}} = 1 - \frac{\rho_{sc} \mu \sigma |K|}{\rho_{sc0} \rho_\infty RT_c}.$$

From this we find the expression for the capillary condensation coefficient $d$ [4]:

$${}$$
Let us consider a simplifying assumption of condenser isothermicity, which is valid for a sufficiently slow process. In this case formula (24) also takes the following form:

$$j_k = \sqrt{\frac{RT}{2\pi \mu}} \rho_s (\varphi - d_{\text{can}}).$$

(28)

Let us give formula (27) a slightly different form:

$$d_{\text{can}} = \frac{1}{1 + \frac{a}{r}},$$

(29)

where $a = \frac{2\mu \sigma}{\rho_{sc}RT}$ is the radius characteristic of the capillary, at which the effect of capillary condensation works. We call it the radius of action of capillary forces. For water, with $T = 283 K$ (10°C), $a = 1.14 \text{nm}$. Using this value, we estimate the possibility of condensation by a capillary-porous environment due to the capillary effect. From the expression (16) follows that for moisture condensation ($j_k > 0$) it is necessary that from which the inequality is coming:

$$r < \frac{a}{\varphi - 1}.$$  

(30)

We graph the dependence of the limiting radius of capillary condensation $r_{\text{max}}$ on the relative moisture $\varphi$ (fig.2):

Figure 2 – The dependence graph of the limiting radius of capillary condensation $r_{\text{max}}$ on the relative moisture $\varphi$
On this graph we can see, that in order to show the effect of condensation on capillaries of micron size, a sufficiently high moisture is needed ($\varphi \geq 99\%$). When the capillaries are filled with water, the concave menisci become flat and the capillary effect ceases. At larger than $r_{\text{max}}$ radii the capillary effect becomes unimportant, because capillary forces cannot provide moisture condensation. However, even in this case, a porous environment with a developed surface can be used for moisture trapping. For this, its temperature should be decreased to the dew point. Since olden times this phenomenon has been used for obtaining water from the air in arid or shallow areas. For this purpose, heaps of rubble, located on a solid waterproof foundation were used. At night or in the morning hours moisture settled on the rubble, flowed down and was led through the potter’s pipes into a special container. This devices existed at the beginning of the last century near Feodosia in the Crimea. The remains of such devices was found in the Sahara, the eastern coast of the Caspian, the Karakum, the mountainous regions of Italy, and others. In fact, the same effect, based on the combination of the precipitation of moisture at night and evaporation during the day, lies at the basis of the following method. The porous or sandy soil is saturated with dew in a natural way during night hours, whereby there is a sufficient amount of moisture in the depth. For its extraction you should dig a hole in daytime, place a bowler on its bottom, then cover a hole by transparent membrane which gives you the appearance of a cone-shaped funnel. The sun's rays are falling onto the bottom and walls of the hole, evaporate the moisture, which turns into saturated steam. Because of transparency of membrane it heats up to much lesser degree than the underlying steam, so that the steam condenses on the membrane and flows down into the bowler in droplets.

It follows from the foregoing, that in the absence of a saturated state of vapor, the method of capillary condensation is ineffective, in contrast to the second method that was mentioned above [5].

The second offered variant of condensation is salvation. This method consists in the fact that moisture from the air settles on a porous substrate saturated with the salt. First, on the surface of the substrate a primary membrane of saturated salt solution is formed as a result of adsorption or another process. This solution has increased hygroscopicity and is able to absorb moisture intensively from the air even in the case of incomplete saturation ($\varphi < 1$).

As known, solutions of non-volatile substances have the following colligative properties:

- Decrease of saturated steam pressure above the solution surface:

$$
\frac{P_{s0} - P_s}{P_{s0}} = \frac{\nu'}{\nu},
$$

where $P_{s0}$ - is saturated steam pressure over a pure solvent,

$P_s$ - is saturated vapor pressure above solution,

$\nu$ - is amount of moles of solvent in the solution volume,

$\nu'$ - moles of solute.

- Increase of the boiling point of the solution:

$$
\frac{T'_{\text{kip}} - T_{\text{kip}}}{T_{\text{kip}}} = \frac{\nu' R}{\nu \mu q_{\text{nap}}},
$$

- Decrease of the freezing point of the solution:
where $T_k$ is the temperature (boiling / crystallization) of pure solvent (water),
$T_k'$ is the temperature (boiling / crystallization) of the solution,
$q_{nap}$ is the specific heat of vaporization,
$q_{kr}$ is the specific heat of crystallization.

Laws (31), (32), (33) are called the laws of Raoul. These laws are a consequence of the Law of Vant-Goff:

$$P_{osm} = \frac{\nu'}{\mu V} RT,$$

which describes the osmotic pressure acting on the semipermeable membrane, which freely passes the solvent and retains the dissolved substance. This pressure leads to the tendency of the solvent to penetrate through the membrane diluting the solution until the pressure inside the vessel with the solvent does not balance the osmotic.

3. Conclusion

The osmotic pressure is numerically equal to the pressure of an ideal gas, with the same concentration of molecules as the solution of the substance retained by the membrane. This effect is explained by the fact that free surface of the solution, like a membrane, retains a non-volatile dissolved substance, which participates in the thermal motion, acts on the surface and, as if it is «stretching» the volume of the liquid, reduces the number of evaporating molecules, shifting the equilibrium towards the pressure decrease of the saturated steam.

Equations (31-33) are given for solutions of nonelectrolytes in which one molecule of a substance before dissolution corresponds to one molecule of a dissolved substance. In solutions of electrolytes, as a result of the processes of dissociation and hydration, there is a set of ions, undissociated molecules and associated aggregates behaving as separate molecules. As a result, the effect described by the laws of Raoul and Vant-Hoff becomes stronger. To take this into account, the isotonic coefficient of Vant-Hoff was amended $i$, showing how many times the amount of non-volatile particles in the solution varies in comparison with the amount of molecules of the solute. Using this coefficient, in equations (31-33) describing the colligative properties of solutions, it is necessary to make a substitution [6]:

$$\nu' = iv_0,$$

$v_0$ is the number of moles of solute.

The value $i$ is usually quite difficult to determine a priori, moreover it can depend on the concentration and temperature of the solution. Therefore, to determine $i$ (or true $\nu'$) it is necessary to use the experimental method with the help of the law (32) (ebullioscopy) or (33) (cryoscopy). With the help of (31) we obtain an expression for the coefficient of variation of the saturated steam density (31) due to solvation:

$$\frac{P_s}{P_{so}} = \frac{P_s}{P_{so}} = 1 - \frac{\nu'}{\nu} = 1 - \frac{iv_0}{\nu}.$$
This expression should be substituted in the formula (11) as \( d \), to obtain the intensity of condensation \( j_K \). Similarly, with (16), we get an expression for the intensity of condensation in the isothermal regime:

\[
    j_K = \frac{RT}{2\pi\mu} \rho_s \left( \varphi - d_{\text{col}} \right),
\]

from which it is easy to get the solvation condensation condition:

\[
    \varphi > 1 - \frac{iv_0}{v}.
\]

As we see, the method of solvation condensation, in contrast to capillary condensation, can be successfully applied with the humidity significantly lower than 100%.

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