

Tools for determination of humid air state for experimental and numerical investigation of equilibrium physical processes

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Abstract. The presented article deals with the solution of processes in humid air involving the particular elimination of moisture contained in the air. In the case that all of the moisture in the humid air is in the gaseous state, it is a homogeneous mixture. In the case that a part of the moisture in the humid air is in the state of liquid or solid, it is a heterogeneous mixture. In the presented paper processes, where the partial elimination of moisture from humid air (either as a liquid or as a solid phase) can appear, are studied. They are the processes, where the moist air mixture becomes heterogeneous. Based on the theory of ideal mixtures the computational methods enabling determination of the thermodynamic state of the beginning of the elimination of moisture are developed. The thermodynamic properties of dry air and water are applied. Subsequently there are designed diagrams that can be used as an aid to identify interfaces of homogeneous and heterogeneous humid air.

1 Introduction

Moist air is a mixture of dry air and moisture. To simplify the physical description of humid air which occurs in nature or participates in technical processes, it is possible to consider only those of its constituents. The presence of other substances in the air (such as various gaseous impurities, a liquid component of substances from different technologies, solid dust) will not be considered.

If all of the moisture in the humid air is in the state of gas, it is homogeneous mixture. Moist air as the heterogeneous mixture contains moisture

- partially in the vapour state and partially in the liquid state, or
- partially in the vapour state and partially in the solid state, or
- partially as a vapour state, partially in the liquid state and partially in the solid state.

Moisture in the atmospheric air is present in relatively small amounts, but it is of great importance.

A very common problem is the determination of the parameters of the state when moist air as a homogeneous mixture becomes heterogeneous mixtures, i.e. a state in which a moist air begins to secrete moisture. This condition is usually at isobaric conditions, referred to as dew point. This paper focuses on the theoretical tools to determine the equilibrium conditions on the border of homogeneous and heterogeneous mixtures.

2 Components of moist air

Dry air can be considered as an ideal gas in the wider area around the atmospheric conditions. For the needs of aviation, the composition of dry air was adopted according to Table 1 by the international convention [1]. It is the standard used as a reference, especially for instrument calibration.

Table 1. Composition of dry air.

Gas	chemical symbol	volume fraction [%]
Nitrogen	N_2	78
Oxygen	O_2	21
other gases		1

Basic physical and thermodynamic properties of dry air as the ideal gas:

- average molecular weight: $M = 28.9583 \frac{\text{kg}}{\text{kmol}}$
- specific gas constant: $r = 287.12 \frac{\text{J}}{\text{kg} \cdot \text{K}}$
- isobaric specific heat capacity: $c_p = 1005.9 \frac{\text{J}}{\text{kg} \cdot \text{K}}$
- isochoric specific heat capacity: $c_v = 718.8 \frac{\text{J}}{\text{kg} \cdot \text{K}}$

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- Poisson ratio: $\kappa=1.399$

A theoretical model of an ideal gas for dry air near atmospheric conditions is sufficient for working calculations. For the purposes of exact solutions, especially for scientific applications, it is appropriate to apply the theoretical model of semi-ideal or real gas for dry air. For cases of high pressure dry air (pressure above 1 MPa) and dry air at a higher temperature (the temperature above 250 °C) it is necessary to use the model of a real gas, for example NIST (National Institute for Standards and Technology, USA) [2].

Water is thermodynamically relatively complex matter. It is most widely used and best available medium for energy transfer. Therefore, extensive research concentrates and focused at her. For work of professionals are gradually approved documents by the International Association for the Properties of Steam (IAPWS) as a reference for determining the values of thermodynamic and thermophysical properties of water and steam. Important documents are:

- 1995 (Revision 2014) - Formulation of thermodynamic properties of ordinary water substance for general and scientific use (abbreviated IAPWS-95)
 - 1997 - New international formulation of the thermodynamic properties of water and steam for industrial purposes (abbreviated IAPWS IF-97).
- The equation of state for water and steam under those two documents are substantially distant ideal gas.

Basic physical properties of water and water vapour, according to [3]:

- molar weight: $M=18.015 \frac{kg}{kmol}$

- specific gas constant: $r=461.26 \frac{J}{kg \cdot K}$

- triple point:

the temperature of the triple point:

$$t_{tr}=0.01^{\circ}C, T_{tr}=273.16K$$

the pressure at the triple point:

$$p_{tr}=611.657 Pa$$

- critical point:

the temperature of the critical point:

$$t_{cr}=373.946^{\circ}C, T_{cr}=647.096K$$

the pressure at the critical point:

$$p_{cr}=22.064 MPa$$

Thermodynamic behaviour of moisture occurring in a homogeneous moist air (it is water vapour) may be at normal atmospheric conditions described by the model of an ideal gas.

Basic thermodynamic properties of steam as an ideal gas:

- isobaric specific heat capacity: $c_p=1898.56 \frac{J}{kg \cdot K}$

- isochoric specific heat capacity: $c_v=1398.56 \frac{J}{kg \cdot K}$

- Poisson ratio: $\kappa=1.33$

In field of conditions, when the moist air becomes a heterogeneous mixture, it is, when it begins to eliminate of moisture from the moist air in the form of liquid or solid phase, it is necessary to take into account the real properties (behaviour) of H_2O when describing the properties of moisture.

For the thermodynamics of moist air it is very important determination of thermodynamic properties of water vapour at saturation limits.

The dependence of the pressure of saturated steam at a temperature function on the saturation limit vapour-liquid from the triple point to the critical point determines the scientific formulation (IAPWS 95) [4]

$$p'' = p_{cr} \cdot \exp \left[\frac{1}{1 - \tau} \left(a_1 \cdot \tau + a_2 \cdot \tau^{1.5} + a_3 \cdot \tau^3 + a_4 \cdot \tau^{3.5} + a_5 \cdot \tau^4 + a_6 \cdot \tau^{7.5} \right) \right], \quad (1)$$

where:

$$\tau = 1 - \frac{T}{T_{cr}} \quad (2)$$

is the temperature function,

T is the temperature [K],

$T_{cr}=647,096 K$ is the critical temperature of water vapour,

$p_{cr}=22,064 MPa$ is the critical pressure of water vapour,

the constants in equation (1) are listed in Table 2.

Table 2. The constants in equation (1).

a_1	a_2	a_3
-7.5951783	1.84408259	-11.7866497
a_4	a_5	a_6
22.6807411	-15.9618719	1.80122502

Pressure depending on the temperature from 50 K to the triple point on the saturation limit between the solid and gas phase H_2O , it is for sublimation and desublimation, is solved according to equation [5]

$$p'' = p_{tr} \cdot \exp \left(\theta^{-1} \cdot \sum_{i=1}^3 a_i \cdot \theta^{b_i} \right), \quad (3)$$

where:

$$\theta = \frac{T}{T_{tr}} \quad (4)$$

is the temperature function

T is the temperature [K],

$T_{tr}=273.16 K$ is the temperature of triple point of water,

$p_{tr}=611.657 Pa$ is the pressure of triple point of water,

the constants in equation (3) are shown in Table 3.

Table 3. The constants in equation (3).

a_1	-21.2144006
a_2	27.3203819
a_3	-6.1059813
b_1	0.00333333333
b_2	1.20666667
b_3	1.70333333

3 Moist air

Moist air as a thermodynamic system is a mixture of dry air and water substance. Moisture (water) contained in the moist air is always in the form of steam, but also (in the case of a heterogeneous mixture) may be part of the moisture in the moist air also in a state of liquid or solid.

The object of this paper is to find a boundary at which ends the existence of moisture in the air only in the form of steam.

The temperature of the moist air $t_{MA} [^{\circ}C]$ is equal to the temperatures of its components

$$t_{MA} = t_{DA} = t_V = t. \quad (5)$$

The pressure of the moist air $p_{MA} [Pa]$ according to Dalton's law is equal to the sum of the partial pressures of dry air and water vapour

$$p_{MA} = p_{DA} + p_V. \quad (6)$$

The weight of the moist air $m_{MA} [kg]$ is

$$m_{MA} = m_{DA} + m_{H_2O}. \quad (7)$$

The density of the moist air $\rho_{MA} \left[\frac{kg}{m^3} \right]$ is a ratio of weight of moist air to its volume, it is assuming that the moisture in humid air only as vapour

$$\rho_{MA} = \rho_{DA} + \rho_V. \quad (8)$$

The pressure of saturated steam $p_V'' [Pa]$ is for moist air a significant magnitude determining the limit among of moisture in the air for the existence of a homogeneous mixture:

- if $p_V < p_V''$, the humid air is unsaturated and the mixture is homogenous,
- if $p_V = p_V''$, the humid air is saturated and the mixture is homogenous,
- if $p_V > p_V''$, the humid air is supersaturated and the mixture is heterogeneous.

The pressure of saturated steam is an unequivocal function of temperature

$$p_V'' = p_V''(t), \quad (9)$$

(see equations (1), (3))

Dew point temperature $t_{DP} [^{\circ}C]$ is the temperature of moist air, in which the humid air reaches the saturation state after isobaric cooling

$$p_V(t) = p_V''(t_{DP}), \quad (10)$$

it is when all water as vapour, which is contained therein, is in a state of saturated steam.

Absolute humidity of moist air $a \left[\frac{kg}{m^3} \right]$ is the mass of vapour contained in a unit volume of air. It is the density of vapour ρ_V at a pressure of vapour p_V and at the temperature t . Absolute humidity is defined only for a homogeneous mixture, and can be at a given temperature at the range $\langle 0; \rho_V''(t) \rangle$.

Relative humidity of moist air $\varphi [-]$ is the ratio of the absolute humidity to the absolute humidity of saturated air at a given temperature

$$\varphi = \frac{a}{a''}. \quad (11)$$

Relative humidity is defined only for a homogeneous mixture and can at the range $\langle 0; 1 \rangle$. Assuming that the water vapour containing in the humid air can be described by the model of an ideal gas

$$\varphi = \frac{p_V}{p_V''}. \quad (12)$$

Specific humidity $x \left[\frac{kg_V}{kg_{DA}} \right]$ is the ratio of the mass of water to the weight amount of dry air

$$x = \frac{m_{H_2O}}{m_{DA}}. \quad (13)$$

In the case of a homogeneous mixture the contained moisture is in vapour form and

$$x = \frac{m_V}{m_{DA}} = \frac{\rho_V}{\rho_{DA}}. \quad (14)$$

In the supersaturated air, it is heterogeneous mixture, a part of moisture is as saturated steam and the remaining moisture will be excluded. For $t > 0^{\circ}C$ will be portion of the moisture

$$x' = x - x'' \quad (15)$$

excluded as a liquid. For $t < 0^{\circ}C$, a portion of the moisture

$$x''' = x - x'' \quad (16)$$

will be excluded as solid phase. For $t = 0^{\circ}C$ may be part of the moisture excluded as a liquid phase and a part as a solid phase

$$x''' + x' = x - x''. \quad (17)$$

If the moist air forms a homogeneous mixture and its components (dry air and steam) can be described by the model of an ideal gas, it is possible to derive the relationship between the specific and the relative humidity

$$x = \frac{\rho_V}{\rho_{DA}} = 0,622 \cdot \frac{\varphi p_V''}{p_{MA} - \varphi p_V''}. \quad (18)$$

For specific humidity of saturated homogeneous mixture ($\varphi=1$)

$$x'' = 0,622 \cdot \frac{p_V''(t)}{p_{MA} - p_V''(t)} = x''(t). \quad (19)$$

4 Equilibrium $p - t$ and $t - x$ diagrams for moist air

For a given value of specific humidity of moist air it is possible to solve the dependence of the pressure of saturated moist air on the temperature from equations (19) and (1) respectively (3), it means the curve at steady $p - t$ diagram (with parameter specific humidity x) at which there occur the elimination of moisture from humid air, see Figure 1. In the diagram there is marked the triple point for the dry air - tr_{DA} , the critical point for the dry air - cr_{DA} , the saturation line of the vapour with the triple point for the vapour - tr_V and the critical point for the vapour - cr_V and curves of pressure of saturated moist air on the temperature for selected values of specific humidity x . Figure 2 is a detail of $p - t$ diagram which is thus a tool for displaying the state of moist air and the equilibrium processes in moist air, and for distinguishing whether the moist air is a homogeneous or heterogeneous mixture.

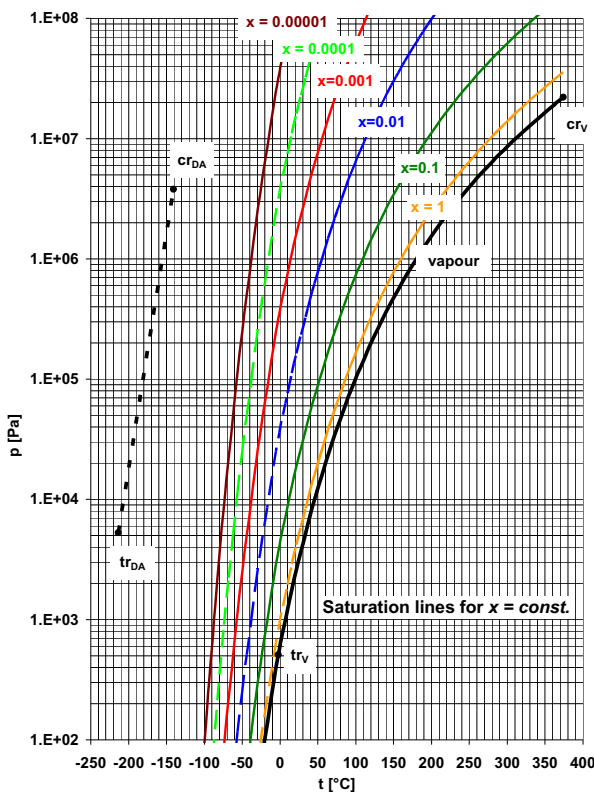


Fig 1. Curves of saturated moist air for different values of specific humidity $x [kg_V/kg_{DA}]$ in $p - t$ diagram.

For a given value of the pressure of moist air it is possible to solve the dependence of the temperature of saturated moist air on specific humidity from equation (19), it means the curve in the $t - x$ diagram (with parameter total pressure p_{MA}) at which there occur the elimination of moisture from humid air, see Figure 3. Such a diagram is a tool for displaying the state of moist air and the equilibrium processes in humid air, and for distinguishing whether the humid air is a homogeneous or heterogeneous mixture.

It should be noted that for the pressures and temperatures greatly differing from normal atmospheric conditions is no longer possible to describe the components of the moist air by a model of ideal gas and the shape of the curves of saturation would deviated in $p - t$ and $t - x$ diagram from the ideal shapes counted on the basis of these simplifying assumptions in paragraph 2.

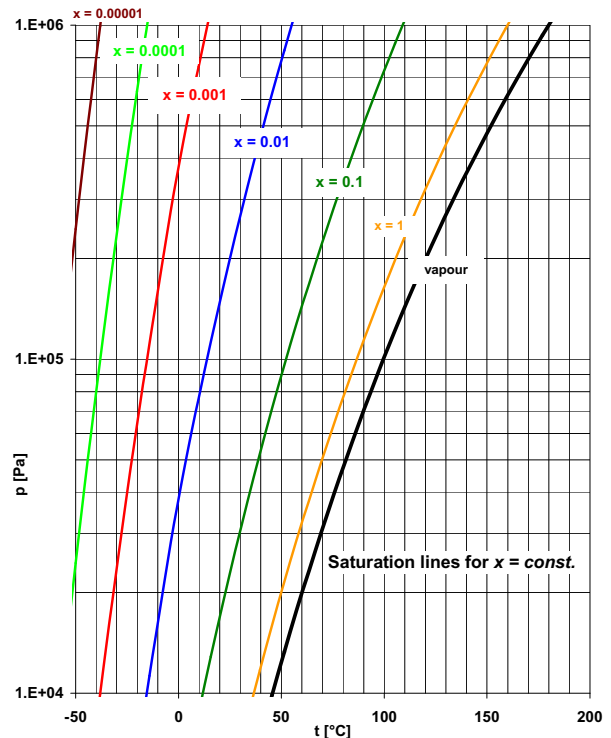


Fig. 2. Curves of saturated moist air for different values of specific humidity $x [kg_V/kg_{DA}]$ in $p - t$ diagram (detail).

5 Basic reversible processes in unsaturated moist air of unchanging composition

In moist air different thermodynamic processes can run. Under certain conditions the originally unsaturated - homogeneous - moist air can get on the border between homogeneous and heterogeneous mixtures during thermodynamic process, it is to the state of saturated moist air. The above-mentioned diagrams can be used for finding those conditions advantageously.

To the equilibrium $p - t$ diagram can be drawn isochoric network, it is lines of constant specific volume of moist air (dashed curves in Figure 4), respectively isentropic network, it is lines of constant entropy moist air (dotted curves in Figure 4).

If the isobaric process carried in the unsaturated moist air, it can be displayed in the $p - t$ diagrams in Figure 1, Figure 2 and Figure 4, as a horizontal line ($p = const.$). If it is an isobaric heating, the process runs in diagrams "to the right", it is to the higher temperature values, conversely, isobaric cooling runs in diagrams "to the left". In $t - x$ diagram on Figure 3, each action occurring in the moist air at constant composition can be

displayed as vertical line, whose position is determined by the value of its specific humidity. When isobaric heating (temperature increase), the amount of moisture which may contain a homogenous moist air, increases, the saturation therefore can not occur. Conversely, when cooling, the quantity of moisture which may contain homogeneous moist air decreases, i.e. when a certain temperature value is achieved, the moist air becomes saturated. The value of this temperature can be easily detected from any of the diagrams.

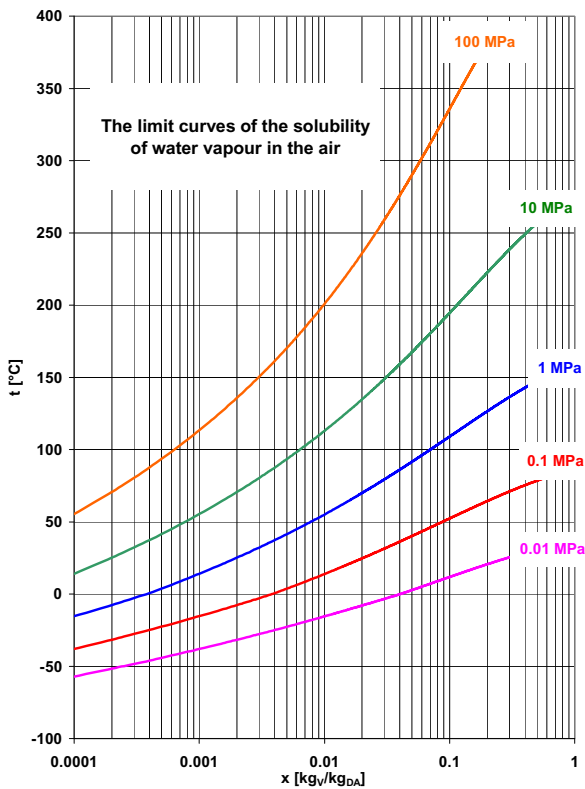


Fig. 3. The curves of saturated moist air for different values of the total pressure p_{MA} in the $t - x$ diagram.

If the isothermal process carried in the unsaturated moist air, it can be displayed in the $p - t$ diagrams in Figure 1, Figure 2 and Figure 4, as a vertical line ($t = const.$). If it is an isothermal expansion, the process runs in diagrams toward "down", it is to the lower pressure values, conversely, isothermal compression toward "up". In $t - x$ diagram on Figure 3 is each isothermal process displayed as a single point, given by the temperature and composition. When isothermal expansion (pressure reduction), the amount of moisture which may contains homogeneous moist air, increases, saturation can not occur. Conversely, when isothermal compression (pressure increase), the quantity of moisture which may contain homogeneous moist air decreases, it is when a certain pressure value is achieved, the moist air becomes saturated. The value of this pressure can be easily detected from any of the diagrams.

Isochoric processes occurring in the unsaturated moist air are shown in Figure 4 as a set of dashed lines - isochors ($v = const.$). If it is an isochoric heating, the process runs in diagrams "to the right and up", it is to the higher temperature values and higher pressure values,

conversely, isochoric cooling runs in diagrams "to the left and down". When isochoric heating (temperature increase), the amount of moisture which may contain a homogenous moist air, increases, the saturation therefore can not occur. Conversely, when cooling, the quantity of moisture which may contain homogeneous moist air decreases, it is when a certain temperature value is achieved, and the moist air becomes saturated. The value of this temperature can be easily detected from diagrams in Figure 4.

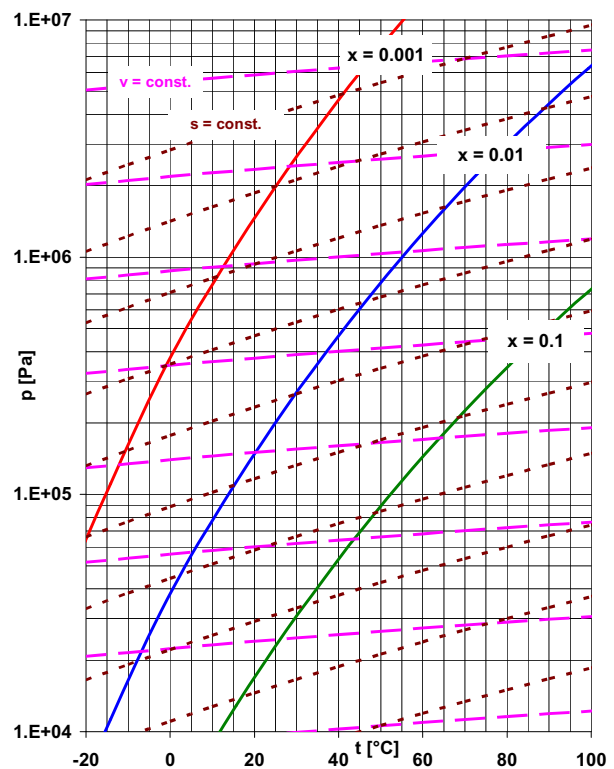


Fig. 4. The curves of saturated moist air for different values of specific humidity $x [kgv/kg_{DA}]$ in the $p - t$ diagram supplemented with network of isentropic lines (dotted curves) and isochoric lines (dashed curves).

Isentropic processes occurring the unsaturated moist air are shown in Figure 4 shows a set of dotted lines - isentropic lines ($s = const.$). If it is an isentropic compression, the process runs in diagrams toward "up and right", it is to the higher pressure values and higher temperature values, conversely, isentropic expansion toward "down and left". When isentropic compression (pressure increase), the amount of moisture which may contains homogeneous moist air, increases, saturation can not occur. Conversely, when isentropic expansion (pressure reduction), the quantity of moisture which may contain homogeneous moist air decreases, it is when a certain pressure value is achieved, the moist air becomes saturated. The value of this pressure can be easily detected from diagrams in Figure 4.

For illustration, the particular processes are compared in $p - t$ diagram in Figure 5: It is assumed unsaturated moist air at $50\text{ }^{\circ}\text{C}$, 100 kPa and a specific humidity 0.01 kgv/kg_{DA} . When the isobaric cooling the saturation is reached at about $14\text{ }^{\circ}\text{C}$. When isochoric cooling, the

saturation is achieved at about $12\text{ }^{\circ}\text{C}$, the pressure is about 90 kPa . If the isentropic process proceeds in this moist air, the state of saturation is reached by air expansion to a pressure of 55 kPa and a temperature of $5\text{ }^{\circ}\text{C}$. If the isothermal process proceeds in this moist air, the state of saturation is reached by air compression to a pressure of 600 kPa .

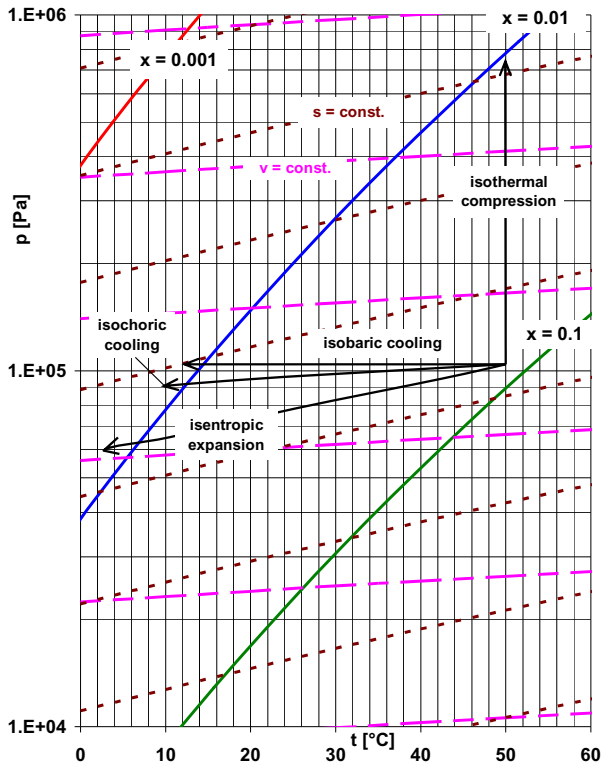


Fig. 5. The curves of saturated moist air for different values of the total pressure p_{MA} in the $p - t$ diagram supplemented with network of isentropic lines (dotted curves) and isochoric lines (dashed curves). (Detail with illustrative examples) (Specific humidity x [$\text{kg}_v/\text{kg}_{DA}$]).

Conclusions

Assuming ideal behaviour of the gaseous components of moist air (dry air and water vapour) there were constructed diagrams (equilibrium $p - t$ diagram and $t - x$ diagram) allowing for experimental and numerical investigation of the processes in the humid air easily to find a boundary at which the existence of moisture air only as vapour ends. Upon reaching this limit (it is upon reaching the states lying on curves of saturation in the diagrams), the moisture begins exclude from the moist air, it is moist air becomes the heterogeneous mixture, which is illustrated in the cases of the isobaric cooling, isothermal compression, isochoric cooling and isentropic expansion for $x = \text{const.}$ in unsaturated moist air.

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