DYNAMIC* PROCESSES WHICH ACCOMPANY MASS **TRANSFER**

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Аннотация-Рассматриваются особеиности теплоемкости в процессах с массообменом, вводится массовое воздействие и видоизменение понятия относительной влажности IIIPHMEHHTEJIBHO К Таким процессам. Приводятся основные результаты исследования частных процессов : расчетные выражения для производных от основных параметров состояния и для теплоемкостей. Излагается метод исследования процессов в общем случае, основанный на результатах исследования частных процессов.

ture in processes without

[kcal/kg of dry gas $°C$];

NOMENCLATURE

* Processes bound up with the transformation of mechanical energy.

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A, heat equivalent of 1 kg m of mechanical work [kcal/kg m];
\n
$$
\psi = \frac{Ap_s(v'' - v') \text{ fraction of heat of evaporation}}{r} \text{,} \text{tion used in expansion work};
$$

$$
\sigma = \frac{R_g}{R_{va}} + d_{va};
$$
\n
$$
R_g, \qquad \qquad \text{gas constant for gas component of mixture [kg m/kg}^{\circ}\text{C};
$$

$$
R_{va} = \frac{p_{va}v_{va}}{T} [\mathrm{kg/kg} \text{ }^{\circ}\mathrm{C}];
$$

$$
R = R_g + d_{va}R_{va};
$$

IN VARIOUS fields of engineering dynamic processes are encountered which result from internal energy transformations bound up with the external mass transfer. There are, for example, processes occurring when water is injected into a high temperature gas flow to study the thermal aerodynamic effect, processes of gas outflow with condensation of vapour in it, etc. Sometimes internal transformations are accompanied by the external energy exchange as in processes of gas compression in a compressor cooled by fluid injection or expansion of gas with vapour condensation in it.

A mixture of gas and vapour is the working medium and is considered as a single thermodynamic system possessing certain specific properties.

The laws of such processes in vapour-gas mixtures are notable for the great complexity involved in calculation and study. One of the peculiarities of such processes is that the character of relations connecting the parameters and energy properties change considerably when transforming from one state to the other. This made it necessary to make use of differential relations. Since the state of a vapour-gas mixture is defined in the general case by three independent variables, the expression for the perfect differential and derivative of any state function has three partial derivatives. **The** problem is to find for them such calculation expressions that would allow the quantitative dependence of partial derivatives on the rate of mass transfer to be observed. To obtain such

expressions particular processes should be studied.

The particular thermodynamic processes of vapour-gas mixture may have two independent parameters. If the process is limited by the adiabatic condition one of the parameters remains constant in this case as well. The number of such processes depends on the number (n) of the state parameters or process properties, which have to be used. If they are given in pairs of any combination of constant values, different processes will be obtained. There can be many such processes namely $(n!/2(n-2)!)$, but not all of them are of the same interest. It is advisable to consider only those processes, which are either themselves encountered in engineering practice or yield the derivatives found in investigations.

For these reasons, to reveal the processes to be studied, the three thermal parameters (p, V, T) , vapour concentration K , relative humidity ρ and the adiabatic condition of the process were considered. Six properties yield fifteen combinations, i.e. fifteen particular processes, which have been studied.

As a matter of convenience they were classified on two different bases: (1) the nature of the change in humidity and (2) the way the surroundings affect them. According to the nature of change in humidity they are divided into three groups :

I—at $K = \text{const}$ (5 processes) II—at $K = \text{var}, \varphi = \text{const.}$ (4 processes) III-at $K = \text{var}, \varphi = \text{var}.$ (6 processes).

The processes of the first group take place without mass transfer, they are therefore not discussed in the present paper. Processes II and III are given in Table 1.

Classification according to the way the surroundings affected the processes is shown by the diagram Fig. I. Each pair of letters designating a definite particular process shows which of the parameters are kept constant in the process. According to this classification of the particuIar processes they are divided into four groups: A , isochoric; B , adiabatic; C , processes at constant concentration; D , processes effected by the surroundings in all three ways.

When studying thermodynamic processes

Notation

SV, adiabatic process at constant volume; *Sp* adiabatic process at constant pressure; ST, adiabatic process at constant temperature; S_{φ} , adiabatic process with constant relative humidity; Sk, adiabatic process with constant concentration; *pK,* adiabatic process with constant concentration and relative humidity; *TK,* isothermal process with constant concentration; *pK,* isobaric process with constant concentration; *VK* isochoric process with constant concentration; $V\varphi$ isochoric process with constant relative humidity; *VT,* isothermal process at constant volume; *Vp,* isochoric process at constant pressure; *pT,* isothermal process at constant pressure; $p\varphi$ isobaric process with constant humidity; T_{φ} , isothermal process with constant relative humidity.

bound up with internal energy transformation and external heat transfer, it is advisable and even necessary to introduce the third effect, mass effect, besides the two energy exchanges (mechanical action and heating effect).

Mass effect should be understood as the introduction or removal of fluid by such an amount as corresponds with the conditions of complete phase transformation in an infinitesimally small region of the process under consideration. Mass effect is positive $(dd_{va}>0)$ with evaporation and negative $(dd_{va}<0$) with condensation, where *dva* is vapour content in kg/kg of dry gas. Mass effect may exert its influence both together with energy exchange and independently of it. Whether independent or isolated, the mass effect is the effect on an energetically isolated system. The ability of mass

effect to change the thermodynamic state of an energetically isolated system allows this effect to be considered as a special kind of external effect on the thermodynamic system.

To produce independent mass effect it is not enough to exclude heating effect and mechanical action of the surroundings. It is also a requirement that the energy of the fluid introduced and removed be zero. Thus, the fluid should be introduced (removed) in such a state (p, T) that the sum of its internal energy and potential energy of pressure is assumed to be zero. Otherwise (as actually occurs) the fluid energy should be recorded separately or summed up with corresponding components of energy exchange.

The kinetics of the phenomena bound up with mass transfer is not taken into account in thermodynamic studies and is not considered in the present paper. It is convenient to assume the value dd_{va}/dT to be the basic intensity criterion for mass effect.

For the convenience of studying dynamic processes, it is necessary to alter the notion of the relative humidity. The relative humidity is the ratio of the specific weight of vapour at its partial pressure and temperature of mixture to the specific weight of dry saturated vapour at the same temperature irrespective of the pressure in the mixture

$$
\varphi=\frac{\gamma_{va}}{\gamma''}
$$

Usually in literature the relative humidity is defined in the same way but, at a first with the small difference: it is advisable to define the value of the specific weight of dry saturated vapour in denominator not only by the temperature but also by the pressure in the mixture.

The latter circumstance restricts unjustifiably both the region over which this parameter applies and the limits over which it can change. It can be used in this case only at such temperatures which do not exceed the temperature of saturated vapour corresponding to the pressure of the mixture. Thus, for example, the application of the parameter φ at a temperature equal to 1 atm abs. is restricted by a temperature of 99.1° C. Further temperature rise with constant pressure and concentration no longer alters the value φ (shown in Fig. 2).

This figure represents the dependence of the relative humidity on the temperature of the vapour-air mixture with different weight fractions of the vapour. The figure shows that with the weight fraction of the vapour equal to 0.5 the relative humidity changes from 1 only to a value of 0.6. With further temperature rise shown by dotted line the relative humidity hardly alters. If the recommended definition of this parameter is used, it will then change smoothly as well (solid line), and the application region for vapour will extend up to the critical point.

When studying the process, the gas component of the mixture is assumed to be the state of an ideal gas, in most cases the real properties of water vapour being taken into account. For the mixture the state equation is used

$$
pV = RT
$$
 (a)

where V is the volume of the mixture per kg of dry gas; $R = R_g + d_{va}R_{va}$ is the variable dependent on the concentration of vapour and its properties in the present state. From (a) we get

 $dd_{va} = \sigma \left(\frac{dp}{p} + \frac{dV}{V} - \frac{dT}{T} \right)$

where

$$
\sigma = \frac{R_g}{R_{va}} + d_{va}
$$

is always positive.

FIG. 2. Dependence of relative humidity on temperature with different weight fractions of vapour g_n in vapour-air mixture.

Heat capacity per kg of dry gas was taken as the basic energy property of the thermodynamic process. In processes without mass effect heat capacity is determined by the ordinary thermodynamic formulae for a gas mixture

$$
C_V = c_{vg} + d_{va} c_{vva} \tag{1}
$$

$$
C_p = c_{pg} + d_{va} c_{pva} \tag{2}
$$

When mass effect appears heat capacity changes sharply and it becomes necessary to consider the thermal effect of phase transformation. In strict conformity with the first law of thermodynamics in this case we can obtain two equivalent expressions for heat capacity per kg of dry gas

$$
C_{yz} = C_V + u_{va} \left(\frac{\partial d_{va}}{\partial T}\right)_{yz} + Ap \left(\frac{\partial V}{\partial T}\right)_{yz} \quad (3)
$$

$$
C_{yz} = C_p + i_{va} \left(\frac{\partial d_{va}}{\partial T} \right)_{yz} - AV \left(\frac{\partial p}{\partial T} \right)_{yz} \tag{4}
$$

where heat capacities C_V and C_p are determined by formulae (1) and (2); u_{va} and i_{va} are the internal energy and enthalpy of the vapour; V is the volume of the mixture per kg of dry gas; y and z are the arbitrary parameters which in the process remain constant.

If equation (3) is applied to the particular case of the isochoric process, when $y = V = \text{const.}$ and $z =$ const., the last component becomes zero. Therefore for the true heat capacity of a vapour-gas mixture at constant volume per kg of dry gas, we obtain the following expression

$$
C_{Vz}=C_V+u_{va}\left(\frac{\partial d_{va}}{\partial T}\right)_{Vz} \qquad \qquad (5)
$$

Similarly, using equation (4) for the isobaric process, we obtain

$$
C_{pz} = C_p + i_{va} \left(\frac{\partial d_{va}}{\partial T}\right)_{pz} \tag{6}
$$

The intensity of mass effect $(\partial d_{va}/\partial T)_{Vz}$ and $(\partial d_{va}/\partial T)_{pz}$ depends not only on the condition $V =$ const. or $p =$ const., but also on that, what second parameter z remains constant. In the general case, therefore, both heat capacity at constant volume and that at constant pressure are the functions of the process and they take values from 0 (heat capacity at constant volume in the adiabatic isochoric process and heat capacity at constant pressure in the adiabatic isobaric process) to ∞ (in isothermal processes).

Hence it follows as well that in the general case the values C_{Vz} and C_{pz} do not represent the amount of heat that goes to change the internal energy and enthalpy. Also, the increment of these functions depends on the mechanical action and the internal energy exchange, i.e. mass effect. This circumstance makes it necessary to introduce special temperature coefficients of internal energy and enthalpy.

By analogy with relation (3) given for heat capacity, we can obtain the expression for the temperature coefficient of the internal energy. Thus, we have

$$
(C_{U})_{yz} = \left(\frac{\partial U}{\partial T}\right)_{pz} = C_{V} + u_{va} \left(\frac{\partial d_{va}}{\partial T}\right)_{pz}
$$

$$
\left[\frac{\text{kcal}}{\text{kg of dry gas }^{\circ}\text{C}}\right] \qquad (7)
$$

and for the particular case of an isochoric process

$$
(C_{\it U})_{\it pz}=C_{\it Vz}
$$

Similarly, the expression for the temperature coefficient of the enthalpy is

$$
(C_I)_{pz} = \left(\frac{\partial I}{\partial T}\right)_{yz} = C_p + i_{va} \left(\frac{\partial d_{va}}{\partial T}\right)_{yz}
$$

$$
\left[\frac{k \text{cal}}{\text{kg of dry gas }^\circ \text{C}}\right] \qquad (8)
$$

in particular case of an isobaric process

$$
(C_I)_{yz}=C_{pz}
$$

From (7) and (8) it is easy to find an expression similar to the Meier formula

$$
(C_I - C_U)_{yz} = AR + Ap_{va} v_{va} \left(\frac{\partial d_{va}}{\partial T} \right)_{yz}
$$

The apparatus thus prepared enables us to reveal peculiarities in the particular equilibrium thermodynamic processes and to obtain and study the expressions for particular derivatives, temperature coefficients C_U and C_I and heat capacity of the process. The results obtained for **ZK**

all the investigated processes with mass effect are presented in Table 1.

The following notation is adopted in the Table:

- *Pt* pressure of mixture $\left[\frac{\text{kg}}{\text{m}^2}\right]$;
- p_s , saturated pressure at temperature of mixture $\lceil \frac{kg}{m^2} \rceil$;
- specific volume of fluid and saturated *U', v",*

Uva, ha,

 $\rho, r,$

$$
\psi = \frac{Ap_s v^{\prime\prime} - v^{\prime}}{r} = 1 - \frac{\rho}{r}
$$

T, \boldsymbol{A}

 $k = \frac{C_p}{C_v}.$

heat of evaporation at mixture temperature [kcal/kg]; fraction of heat of evaporation required for expansion work; absolute temperature $[°K];$ heat equivalent of

vapour $[m^3/kg]$; internal energy and enthalpy of vapour under conditions of mixture $[kcal/kg]$; internal and total

unit of work [kcal/ kgml;

The notation of the processes is given in captions for Fig. 1.

The expressions listed in the Tabie for each particular process characterize it at any given point determined by the known parameters. Integrating these expressions from the initial to the final state, we can determine the change in the parameters and the average values of heat capacity and temperature coefficients C_U and Cr throughout the process. The latter *allows* calculation of the change in the internal energy and enthalpy in the process by the ordinary thermodynamic formulae.

However this does not exhaust the significance of the expressions obtained. A number of other processes, as mentioned above, can be studied with their help. The processes which go on without heat exchange with the surroundings but with mechanical action (pure dynamic

processes) are of the greatest interest, In Fig. 1 the particular cases of the adiabatic processes are presented by group B . Besides the particular processes, however, there exist a number of other adiabatic processes, notable for intensity of mass effect. Such processes are the most common in engineering. Consider the method of their investigation.

In the general case for the differentials of pressure, the volume per kg of dry gas and vapour content, can be written:

$$
\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_{S d_{va}} \mathrm{d}T + \left(\frac{\partial p}{\partial d_{va}}\right)_{ST} \mathrm{d}d_{va} + \left(\frac{\partial p}{\partial S}\right)_{T d_{va}} \mathrm{d}S \quad (9)
$$

$$
dp = \left(\frac{\partial p}{\partial V}\right)_{S d_{vu}} dV + \left(\frac{\partial p}{\partial d_{va}}\right)_{SV} dd_{va} + \left(\frac{\partial p}{dS}\right)_{V d_{vu}} dS \quad (10)
$$

$$
dV = \left(\frac{\partial V}{\partial T}\right)_{S d_{vu}} dT + \left(\frac{\partial V}{\partial d_{va}}\right)_{ST} dd_{va} + \left(\frac{\partial V}{\partial S}\right)_{Td_{va}} (11)
$$

$$
dd_{va} = \left(\frac{\partial d_{va}}{\partial T}\right)_{Sp} dT + \left(\frac{\partial d_{va}}{\partial p}\right)_{ST} dd_{va} + \left(\frac{\partial d_{va}}{\partial S}\right)_{Tp} dS. (12)
$$

If thermodynamic irreversibility of mass effect is neglected and it is supposed that the adiabatic process is mechanically reversible, then the entropy S per kg of dry gas will remain constant $(dS' = 0)$ and the last term in equations (9)-(12) will vanish. The following relations for derivatives can be written:

$$
\frac{\mathrm{d}p}{\mathrm{d}T} = \left(\frac{\partial p}{\partial T}\right)_{S_{d_{va}}} + \left(\frac{\partial p}{\partial d_{va}}\right)_{ST} \frac{\mathrm{d}d_{va}}{\mathrm{d}T} \tag{13}
$$

$$
\frac{\mathrm{d}p}{\mathrm{d}V} = \left(\frac{\partial p}{\partial V}\right)_{Sd_{va}} + \left(\frac{\partial p}{\partial d_{va}}\right)_{SV} \frac{\mathrm{d}d_{va}}{\mathrm{d}V} \tag{14}
$$

$$
\frac{\mathrm{d}V}{\mathrm{d}T} = \left(\frac{\partial V}{\partial T}\right)_{S d_{va}} + \left(\frac{\partial V}{\partial d_{va}}\right)_{ST} \frac{\mathrm{d}d_{va}}{\mathrm{d}T} \tag{15}
$$

$$
\frac{\mathrm{d}d_{va}}{\mathrm{d}T} = \left(\frac{\partial d_{va}}{\partial T}\right)_{Sp} + \left(\frac{\partial d_{va}}{\partial T}\right)_{ST}\frac{\mathrm{d}p}{\mathrm{d}T} \tag{16}
$$

$$
\frac{\mathrm{d}d_{va}}{\mathrm{d}p} = \left(\frac{\partial d_{va}}{\partial p}\right)_{ST} + \left(\frac{\partial d_{va}}{\partial T}\right)_{Sp}\frac{\mathrm{d}T}{\mathrm{d}p} \tag{17}
$$

Substituting the expressions for partial derivatives from Table l* with constant *ST, SY* and Sp, and the known relations

$$
\begin{aligned}\n\left(\frac{\partial p}{\partial T}\right)_{S d_{va}} &= \frac{k}{k-1} \frac{p}{T};\\
\left(\frac{\partial V}{\partial T}\right)_{S d_{va}} &= -\frac{1}{k-1} \frac{V}{T}; \ \left(\frac{\partial p}{\partial V}\right)_{S d_{va}} &= -k \frac{p}{V},\n\end{aligned}
$$

with constant Sd_{va} (adiabatic process at constant concentration), we obtain

$$
\frac{dp}{dT} = \frac{k}{k-1} \frac{p}{T} + \frac{i_{va}}{AV} \frac{dd_{va}}{dT}
$$
\n
$$
= \frac{1}{AV} \left(C_p + i_{va} \frac{dd_{va}}{dT} \right) \quad (18)
$$

$$
\frac{\mathrm{d}V}{\mathrm{d}p} = -k\frac{p}{V} - \frac{u_{va}}{C_V}\frac{p}{T}\frac{1}{k-1}\left(k - \frac{i_{va}}{u_{va}}\right)\frac{\mathrm{d}d_{va}}{\mathrm{d}V}\left(19\right)
$$

$$
\frac{dV}{dT} = -\frac{1}{k-1} \frac{V}{T} - \frac{u_{va}}{Ap} \frac{dd_{va}}{dT}
$$

$$
= -\frac{1}{AP} \left(C_V + u_{va} \frac{dd_{va}}{dT} \right) \quad (20)
$$

$$
\frac{\mathrm{d}d_{va}}{\mathrm{d}T} = -\frac{Cp}{i_{va}} + \frac{AV}{i_{va}}\frac{\mathrm{d}p}{\mathrm{d}T} \tag{21}
$$

$$
\frac{\mathrm{d}d_{va}}{\mathrm{d}p} = \frac{AV}{i_{va}} - \frac{Cp}{i_{va}} \frac{\mathrm{d}T}{\mathrm{d}p}.\tag{22}
$$

From equations (18)-(22) the derivatives considered can be plotted versus the degree of change in pressure and mass effect intensity for the whole range of adiabatic processes.

Depending on the character of the adiabatic process the derivatives under consideration change their sign as well as (over a wide range} their value. They assume values from 0 to ∞ , have the points of discontinuity, inflexion points, extremal points and each curve, representing the change of some derivative, has one or two asymptotes.

^{*} In Table 1 instead of the derivative $(\partial p/\partial V)$ its inverse value is given.

Being now in possession of relations (18)-(22) or graphs plotted by them, we can study every possible process of vapour-gas mixtures with mass transfer including such complicated processes as those of near-sonic and supersonic gas flows. The relations given allow the "sound" adiabatic exponent and local speed of sound to be determined, the influence of mass transfer upon the flow rate and the shape of nozzle to be established, some crisis phenomena in the flow to be found, the factors and conditions that caused them to be revealed, and so on.

Thus, for example, the speed of a sound for the vapour-gas mixture is

$$
a = \sqrt{\left(k_{Sn} \, gp \frac{V}{1 + d_{va}}\right)}\tag{23}
$$

where k_{Sn} is the adiabatic exponent for the calculation of the speed of sound.

If the gas is not saturated or the vapour-gas mixture is of a high temperature, and may be considered as a perfect gas, then using equations (18) and (20) we obtain

$$
k_{Sn} = -\frac{V}{p} \frac{\frac{dp}{dT}}{\frac{dV}{dT}} = \frac{C_p + i_{va} \frac{dd_{va}}{dT}}{C_V + u_{va} \frac{dd_{va}}{dT}}
$$
 (24)

If the gas is saturated, we find, using Table 1

$$
k_{Sn} = -\frac{V}{p} \left(\frac{\partial p}{\partial V}\right)_{S\varphi}
$$

=
$$
\frac{C_p v'' - d_{va} i_{va} \frac{dv''}{dT} + \frac{C_p u_{va} - C_v i_{va}}{Ap}}{C_V v'' - d_{va} u_{va} \frac{dv''}{dT}}
$$
(25)

Another example follows. From the Bernoulli's equation for a mixture containing 1 kg of dry gas

$$
V dp + d \left[(1 + d_{va}) \frac{w^2}{2g} \right] = 0 \qquad (26)
$$

we can obtain

$$
\frac{\mathrm{d}w}{\mathrm{d}p} = -\frac{1}{\rho_c w} \left[1 + \frac{\rho_c w^2}{2\left(1 + d_{va}\right)} \frac{\mathrm{d}d_{va}}{\mathrm{d}p} \right] \tag{27}
$$

where ρ_c and w are the density and velocity of the vapour-gas mixture.

Since in any adiabatic process of unsaturated gas $dd_{va} > 0$, the sign of the derivative dd_{va}/dp is the same as that of dp. Hence, the absolute value dw/dp (from 24) increases with $dp > 0$ and decreases with $dp < 0$, i.e. mass effect influences the velocities in these two cases in different ways. When the equality

$$
\frac{\rho_c w^2}{2(1+d_{va})}\frac{dd_{va}}{dp}-1
$$

is satisfied in processes which take place with pressure drop, the derivative passes through zero value and with further increase in the left part of this equality reverses sign. From reiations (21) and (22) we can find the conditions under which the sign reversal of dw/dp will occur.

As in the case of equation (27) we can obtain the expression for dw/dT , whose value under certain conditions passes through zero as well. It can shown that the flow rate equal to the local speed of sound is reached (at high temperatures) both in a nozzie and in a diffuser after the narrow cross section had been passed through.

CONCLUSIONS

1. A vapour-gas mixture should be considered as a single thermodynamic system possessing specific properties. The latter are mainly determined by thermal effect of the phase transformation and by external mass transfer.

2. When studying thermodynamic processes of vapour-gas mixtures with phase transformations of the moisture it is advisable to consider the third, namely the mass effect, in addition to the two others.

3. It is convenient to classify particular processes of vapour-gas mixtures, which occur with two constant parameters, according to the two features: the nature of the change in humidity (it is used when studying particular processes) and the way the surroundings affect them (used in studying processes on a larger scale).

is advisable to introduce the temperature 4. Heat capacity at constant volume and that at constant pressure are functions of a process and in the general case do not determine the increment of the internal energy and enthalpy. To define the increments of these functions it coefficients of the internal energy C_U and enthalpy C_I .

5. The specific properties of the mixture which are manifest in the processes with mass effect predetermine the necessity of their study with partial differential operators. Expressions for the derivitives of the basic state functions for ten partial processes with mass effect are obtained.

6. The particular derivatives obtained constitute an effective means of studying every possible process with mass transfer. The method of investigation is demonstrated by considering some of the laws of energy transformations in a flow.

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Abstract-Heat capacity properties in processes with mass transfer are considered, and mass effect and change in relative humidity concepts are introduced in conformity with such processes. The main results of a study of particular **processes** are given, these are in the form of calculation expressions for derivatives of basic state parameters and for heat capacities. A method for studying general processes is given. This is based on the results of investigations of particular processes.

Zusammenfassung-Der Einfluss der Wärmekapazität auf Prozesse mit Stofftransport wird untersucht, wobei Masseneffekt und Änderung der relativen Feuchtigkeit einbezogen werden. Die Hauptergebnisse eines Studiums der Teilvorgänge sind angegeben, und zwar in Form berechneter Ausdrücke für die Ableitungen der Grundparameter und der Wärmekapazitäten. Eine Methode zur Untersuchung allgemeiner Vorgänge wird mitgeteilt. Sie beruht auf den Ergebnissen des Studiums der Teilvorgänge.