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THERMODYNAMICS OF A MULTICOMPONENT GASEOUS PHASE AS VIEWED BY THE BALANCE THEORY

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The article presents some formalised definitions of volume density of the molar number of a mixture and a mixture component. With the help of the above definitions, the molar concentration of a mixture component has been determined. An analysis has also been made to define partial volume density. The mass density of a substance component production has been defined and the notion of the referential density of the stream exchange of a substance component has been applied to analyse the movement of substance components in the mixture, whereby defining the notion of a diffusion stream density. Next, with the help of the referential balance equation of a substance component, an analysis has been made of the balance of substance components leading to the definition of an equation of diffusion continuity which in turn, under the accepted constraints, leads to the so-called second Fick's law.

1. VOLUME DENSITY OF THE MOLE NUMBER IN THE MIXTURE

For the sake of the definition of the volume density of the mole number in mixture ρ_n, we will mark molecules in volume V by current index ν. Each indexed molecule marked by symbol „cz_ν" will be assigned the numerical value of one

$$cz_\nu = 1 \tag{1.1}$$

for $\nu = 1, 2, ..., k$.

Summing up the number of molecules in volume V and relating the sum to Avogardo's number N_A, we will obtain the number of molecules in volume V,

$$n = \sum_{\nu=1}^{k} \frac{cz_\nu}{N_A}, \tag{1.2}$$

Thus the volume density of the mole number in the mixture is defined by the following relationship:

(1.3)
$$\rho_n = \lim_{V\to\delta^3 V} \frac{\sum\limits_{v=1}^{k} \frac{cz_v}{N_A}}{V} = \lim f\frac{n}{V} = \frac{d^3 n}{d^3 V}\,.$$

2. VOLUME DENSITY OF THE MOLE NUMBER OF A MIXTURE COMPONENT

The components of a mixture are of the same volume as the mixture of gases as a whole.

We will mark the component of a gas mixture by current index "i", where "i" assumes the value of numeric set $i = 1, 2, ..., l$, where "l" is the number defining the quantity of mixture components. We assign the numerical value of 1 to the molecule of a mixture component cz_{iv} the same way we used to define the volume density of the mole number in the mixture

(2.1)
$$cz_{iv} = 1$$

for $i = 1, 2, ..., l$ and for $\nu = 1, 2, ..., k_i$.

The number of moles of a mixture component will be defined by the relationship

(2.2)
$$n_i = \sum_{v=1}^{k_i} \frac{cz_{i\nu}}{N_A}$$

while the volume density of the mole number in a mixture component will be expressed by the relationship

(2.3)
$$\rho_{n_i} = \lim_{V\to\delta^3 V} \frac{\sum\limits_{\nu=1}^{k_i} \frac{cz_{i\nu}}{N_A}}{V} = \lim f\frac{n_i}{V} = \frac{d^3 n_i}{d^3 V}\,.$$

3. MOLE CONCENTRATION OF A MIXTURE COMPONENT

The mole concentration of a mixture component is defined in a similar way as the concentration of a mixture component

(3.1)
$$c_{n_i} = \frac{\rho_{n_i}}{\rho_n}\,.$$

The sum of all volume densities of the moles of mixture components is equal to the volume density of moles in the mixture

(3.2)
$$\rho_n = \sum_{i=1}^{l} \rho_{n_i}\,.$$

Thus the sum of all mole concentrations of mixture components equals 1,

$$\sum_{i=1}^{l} c_{n_i} = 1\,. \tag{3.3}$$

4. Partial density of volume

The volume of a multicomponent gaseous phase can be analytically described as a function of two state parameters, e.g. pressure and temperature, and the number of moles of mixture components,

$$V = V(p, T, n_1, n_2, \ldots, n_k). \tag{4.1}$$

Figure 1 shows volume V taken up by the gas mixture whose pressure is p and temperature T, and which consists of "k" components. Two states have been distinguished. In the case of the first one, the mixture components are separated in volume V (before mixing). Each component has pressure p and temperature T and occupies partial volume V_i, and it also has number n_i of moles, where $i = 1, 2, \ldots, k$. In the case of the second state, the mixture components are mixed and are all of the same volume V, and the gas mixture as a whole has pressure p and temperature T, while mixture components have partial pressure p_i, temperature T and volume densities of moles – ρ_{ni}. An elementary increase of volume dV can be obtained, under the above conditions, only when elementary quantities of moles of mixture components dn_i having temperature T and pressure p are added to the gas mixture.

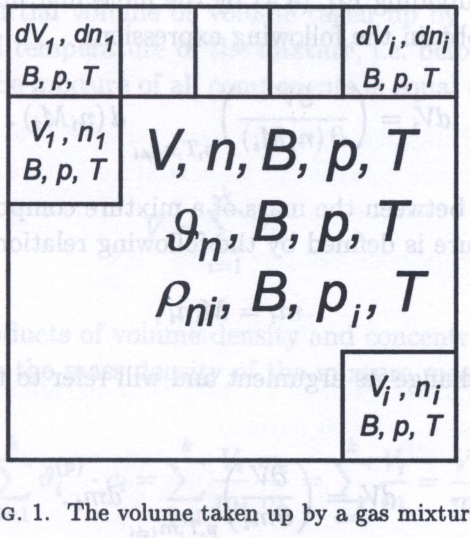

FIG. 1. The volume taken up by a gas mixture.

In compliance with relationship (4.1) describing the volume of a gas mixture, we can express an elementary volume increase by calculating the total differential of the volume. So we have

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_{j\neq 1}} dn_1 + \ldots + \left(\frac{\partial V}{\partial n_n}\right)_{p,T,n_{j\neq k}} dn_k\,, \tag{4.2}$$

or

$$dV = \sum_{i,j=1}^{k} \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{j\neq i}} dn_i\,. \tag{4.3}$$

An elementary increase of partial volume caused by the addition of an elementary number of moles of i-component to the mixture is defined, in compliance with relationships (4.2) or (4.3), by the following relation

$$dV_i = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{j\neq i}} dn_i. \tag{4.4}$$

Taking account of relation (4.4) in Eq. (4.3), we will obtain the equation which shows that an elementary increase in the mixture volume equals the sum of elementary increments of partial volumes of mixture components,

$$dV = \sum_{i=1}^{k} dV_i\,. \tag{4.5}$$

Multiplying and dividing Eq. (4.4) by the molecular mass of a mixture component M_i, we will obtain the following expression:

$$dV_i = \left(\frac{\partial V}{\partial (n_i M_i)}\right)_{p,T,n_{j\neq i}} d\left(n_i M_i\right). \tag{4.6}$$

Because the relation between the mass of a mixture component and the number of moles in the mixture is defined by the following relationship

$$m_i = M_i n_i\,, \tag{4.7}$$

Equation (4.3) will change its argument and will refer to the mass of a mixture component

$$dV_i = \left(\frac{\partial V}{\partial m_i}\right)_{p,T,m_{j\neq i}} dm_i\,. \tag{4.8}$$

Dividing the last relation by the elementary mass increase of a mixture component, we will obtain an equation defining partial volume density marked by symbol $\vartheta_i^{(p)}$

$$\vartheta_i^{(p)} = \left(\frac{\partial V}{\partial m_i}\right)_{p,T,m_{j\neq i}} . \tag{4.9}$$

When the fields of partial volume densities of mixture components are homogenous (non-gradient) or when

$$\overline{\mathrm{grad}}\,\vartheta_i^{(p)} = \overline{0} , \tag{4.10}$$

we can separate variables in Eq. (4.9) and integrate them within limits

$$\int_0^{V_i} dV_i = \vartheta_i^{(p)} \int_0^{m_i} dm_i . \tag{4.11}$$

After integrating Eq. (4.11) and transforming it, with condition (4.10) taken into account, we will obtain the relation describing the partial density of volume

$$\vartheta_i^{(p)} = \frac{V_i}{m_i} , \tag{4.12}$$

where V_i stands for partial volume or volume taken up by mixture component "i" at the pressure and temperature of the mixture, i.e. before mixing. The sum of partial volumes of the mixture of all components is equal to the volume taken up by the mixture

$$V = \sum_{i=1}^{k} V_i . \tag{4.13}$$

The sum of partial products of volume density and concentration of all mixture components is equal to the mass density of the mixture mass

$$\vartheta = \sum_{i=1}^{k} \vartheta_i^{(p)} \cdot c_i = \sum_{i=1}^{k} \frac{V_i}{m_i}\frac{m_i}{m} = \sum_{i=1}^{k} \frac{V_i}{m} = \frac{V}{m} . \tag{4.14}$$

5. Density of a diffusion stream

At the beginning, we will define the notion of production mass density of a substance component.

$$\left.\begin{array}{l}\text{production}\\ \text{mass density}\\ \text{of a substance}\\ \text{component}\end{array}\right\} = \lim f \frac{\text{Production of a substance component mass}}{\text{time, substancemass}} = \xi_i \left[\frac{1}{\text{s}}\right]. \tag{5.1}$$

Due to the principle of conservation of joint substance mass, the sum of mass densities of mass production of all substance components equals zero.

$$\sum_{i=1}^{n} \xi_i = 0 \left[\frac{1}{\text{s}}\right]. \tag{5.2}$$

The sum of volume densities of mass production of all substance components also equals zero.

$$\sum_{i=1}^{n} \rho\xi_i = 0 \left[\frac{\text{k}g}{\text{m}^3\text{s}}\right]. \tag{5.3}$$

Relating the quantities in question to generalised motion, i.e. referential velocity $\bar{w}$, we can write, according to [1], that the density of the exchange stream of substance component mass through the referential surface is expressed by the following relation:

$$\underset{\to \overline{w}}{\overline{j}_i} = \rho_i (\overline{u}_i - \overline{w}) \left[\frac{\text{k}g}{\text{m}^3\text{s}}\right] \tag{5.4}$$

where $\overline{u}_i$ stands for component velocity (the velocity of a substance component). The mass of a substance component travels at velocity $\overline{u}_i$, which is at the same time the velocity of component surface $\underset{\to \overline{u}_i}{A}$. Thus, identifying the referential velocity with the component velocity in Eq. (5.4)

$$\overline{w} = \overline{u}_i \left[\frac{\text{m}}{\text{s}}\right] \tag{5.5}$$

we will obtain the density value of the exchange stream of substance component mass through the componential surface

$$\underset{\to \overline{u}_i}{\overline{j}_i} = \overline{0} \left[\frac{\text{k}g}{\text{m}^2\text{s}}\right], \tag{5.6}$$

from which it follows that componential surface $\underset{\to \overline{u}_i}{A}$ is a nonpervious surface for the flow of the mass of a substance component.

However, if we compare the referential velocity to zero

$$\overline{w} = \overline{0}. \tag{5.7}$$

then we will obtain, from equation (5.4), the relation describing the exchange stream density of substance component mass through a stationary surface

$$\underset{\to \overline{0}}{\overline{j}_i} = \overline{j}_i = \rho_i \overline{u}_i \left[\frac{kg}{\mathrm{m^2 s}}\right]. \tag{5.8}$$

By analogy with Eq. (5.4) describing the stream density of the mass exchange of a substance component through a referential surface, we will define the stream density of the mass exchange of all substance through a referential surface by the following relation:

$$\underset{\to \overline{w}}{\overline{j}_i} = \rho(\overline{u} - \overline{w}) \left[\frac{kg}{\mathrm{m^3 s}}\right] \tag{5.9}$$

where is $\overline{u}$ substantial velocity.

If we compare, in this case, the value of referential velocity to zero

$$\overline{w} = \overline{0} \tag{5.10}$$

then we will obtain the relation describing the stream density of a substance mass exchange through a stationary surface

$$\underset{\to \overline{0}}{\overline{j}_i} = \overline{j} = \rho\, \overline{u} \left[\frac{kg}{\mathrm{m^2 s}}\right]. \tag{5.11}$$

The flow of substance mass through a stationary surface equals the sum of the mass of substance components constituting it.

Thus taking (5.8) and (5.11) into account, we will obtain

$$\sum_{i=1}^{n} \overline{j}_i = \overline{j} \left[\frac{kg}{\mathrm{m^2 s}}\right], \tag{5.12}$$

or

$$\sum_{i=1}^{n} \rho_i\, \overline{u}_i = \rho\, \overline{u}. \tag{5.13}$$

Taking relation (3.1) into account, we can define the value of substantial velocity from the last relationship

$$\overline{u} = \sum_{i=1}^{n} c_i \overline{u}_i = 0. \tag{5.14}$$

The motion of a substance component in relation to a substantial point is called diffusion motion and the exchange stream density of the mass of a substance component through a substantial surface is called the stream density of diffusion.

Thus comparing the referential velocity to the substantial velocity in Eq. (5.4)

$$\overline{w} = \overline{u}. \tag{5.15}$$

we will obtain an expression describing the stream density of diffusion

$$\overline{j}_{di} = \underset{\to\overline{u}}{\overline{j}_i} = \rho_i(\overline{u}_i - \overline{u}) \left[\frac{\mathrm{kg}}{\mathrm{m}^2\mathrm{s}}\right]. \tag{5.16}$$

It follows from relation (5.12) and (3.3) that the sum of stream densities of diffusion of substance components equals zero

$$\sum_{i=1}^{n} \overline{j}_{di} = 0. \tag{5.17}$$

It follows from equation (5.16) describing the density of a diffusion stream that the stream density of the mass exchange of a substance component through a stationary surface equals the sum of an individual stream density of the mass exchange of a substance component taking part in the joint mass exchange and the stream density of diffusion.

If the substance consisting of components does not move as a whole, then the following condition is fulfilled for the stationary mixture:

$$\overline{u} = 0 \tag{5.18}$$

which implies the relation

$$\overline{j}_i = \rho_i \overline{u}_i = \overline{j}_{di}. \tag{5.19}$$

In this case, for small concentration gradients of substance components c_i, for binary diffusion in a incompressible mixture,

$$\rho = \mathrm{const}$$

the vector of diffusion stream density is described by Fick's law expressed by the relationship

(5.20)
$$\overline{j}_{di} = -\rho\, D\, \overline{\operatorname{grad}}\, c_i \left[\frac{\mathrm{kg}}{\mathrm{m}^2\mathrm{s}}\right].$$

where $D = \text{const} \left[\frac{\mathrm{m}^2}{\mathrm{s}}\right]$ is called the diffusion coefficient.

6. Equation of diffusion continuity

According to [1], the referential derivative of a scalar which is, e.g. the storage volume density of the mass of a substance component, is described by the following relation:

(6.1)
$$\underset{dt}{\overset{d\rho_i}{\longrightarrow}}{}_{\overline{w}} = \frac{\partial \rho_i}{\partial t} + (\overline{w}\cdot \overline{\operatorname{grad}}\, \rho_i) \left[\frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{s}}\right]$$

and then, according to [1], the referential balance equation of the mass of a substance component can be expressed by the relation

(6.2)
$$\underset{dt}{\overset{d\rho_i}{\longrightarrow}}{}_{\overline{w}} + \rho_i \operatorname{div} \overline{w} = \rho \xi_i - \operatorname{div}((\overline{u}_i - \overline{w})\rho_i).$$

The above equation in a stationary point, i.e. when referential velocity is as follows:

(6.3)
$$\overline{w} = \overline{0}$$

will be reduced to the form given below

(6.4)
$$\frac{\partial \rho_i}{\partial t} + \operatorname{div}(\rho_i\, \overline{u}_i) = \rho \xi_i \left[\frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{s}}\right].$$

However, when the referential velocity is identified with substantial velocity

(6.5)
$$\overline{w} = \overline{u}$$

the referential balance equation of the mass of a substance component (6.2) will be transformed into a substantial balance equation of the mass of a substance component which will be written down as follows:

(6.6)
$$\underset{dt}{\overset{d\rho c_i}{\longrightarrow}}{}_{\overline{u}} + \rho\, c_i \operatorname{div} \overline{u} = \rho \xi_i - \mathit{div}\, \overline{j}_{di} \left[\frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{s}}\right].$$

Expanding the substantial derivative of product ρc_i, putting the terms on the right-hand side of the equation in order and at the same time, taking account of the continuity equation for the substance as a whole

(6.7) $$\frac{d\rho}{dt}_{\rightarrow\overline{u}} + \rho \operatorname{div} \overline{u} = \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \overline{u}) = 0 \left[\frac{\mathrm{kg}}{\mathrm{m^3 s}}\right],$$

we will obtain a substantial balance equation of the mass of a substance component which is called the equation of diffusion continuity

(6.8) $$\rho \frac{dc_i}{dt}_{\rightarrow\overline{u}} = \rho \xi_i - \operatorname{div} \overline{j}_{di} \left[\frac{\mathrm{kg}}{\mathrm{m^3 s}}\right].$$

However, if referential velocity is equal to component velocity

(6.9) $$\overline{w} = \overline{u}_i$$

then the component balance equation of the mass of a substance component will be expressed by the relation

(6.10) $$\frac{d\rho_i}{dt}_{\rightarrow\overline{u}_i} + \rho_i \operatorname{div} \overline{u}_i = \rho \xi_i \left[\frac{\mathrm{kg}}{\mathrm{m^3 s}}\right].$$

The above equation indicates the missing element of the mass exchange of a substance component through a component surface.

It follows that in this case, the mass exchange of a substance component in a component area can only be the result of mass production, that is, of a chemical reaction.

In the case of a free binary diffusion occurring in a stationary mixture

(6.11) $$\overline{u} = \overline{0}$$

without any chemical reaction

(6.12) $$\overline{\xi_i} = 0,$$

the diffusion continuity equation (6.8) will be reduced to the following form:

(6.13) $$\rho \frac{\partial c_i}{\partial t} = -\operatorname{div} \overline{j}_{di} \left[\frac{\mathrm{kg}}{\mathrm{m^3 s}}\right].$$

Taking account of Fick's law (5.20) in the above equation, describing the vector of a diffusion stream for the binary diffusion in an incompressible stationary mixture

$$\rho = \mathrm{const},$$

we will obtain the so-called Fick's second law which is, in fact, a substantial balance equation of the mass of a substance component, under conditions (6.11) and (6.12) still holding.

$$\frac{\partial c_i}{\partial t} = D \operatorname{div} \overline{\operatorname{grad}} \, c_i \left[\frac{1}{\mathrm{s}}\right]. \tag{6.14}$$

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