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GENERALIZATION OF THE ENTROPY OF MIXING I.

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In order to give a theoretical treatment of the mixing process, the formula describing the increase in entropy of the mixing of ideal gases has been generalized and the properties of the quantity thus obtained are dealt with. The entropy of mixing seems to be adequate to serve as a quantitative indication of the degree of permixing.

The second part of this paper reviews the practical application on a simplified fluid mechanical model.

INTRODUCTION

Numerous problems were encountered in the Research Institute for Technical Chemistry of the Hungarian Academy of Sciences in which mixing was an important or even central problem. In the surveyed literature it was found that the papers can be devided into two groups. In one group, mixing is of central interest, but entropy is not mentioned at all. The remainder of the papers include those which deal with entropy, but without mentioning its application in connection with the question of mixing [1]. It also became apparent during these studies that two types of state parameters are necessary for the description of the mixing process:

1. a quantity showing how intensive the mixing process is, and how fast it is, etc. This is a state parameter of intensive type;
2. a quantity showing what changes occur during the mixing operation, i.e. the degree of permixing. This is a state parameter of extensive type.

Undoubtedly a certain degree of arbitrariness cannot be avoided in selecting the quantities of the two types; however, qualitative properties can be stated in connection with both types of state parameters. Such qualitative properties, in the case of the quantity mentioned under 1. are the following:

a) In a domain being mixed, the rate of mixing is certainly different in the various space elements, and consequently, this type of state parameter must be one of the local type.

b) If the rate of mixing is the same everywhere (homogenous space), the state parameter should be greater if the material is mixed faster and smaller if the mixing is slower.

The qualitative properties of the state parameter described under 2. are the following:

a) The degree of permixing is characteristic of a whole domain and is an extensive measure.

b) The degree of permixing should be higher if the material distribution is more uniform and lower if the material is more inhomogeneous.

For example, a quantity of type 1. may be the current density vector of the material to be homogenized or mixed.

A quantity of type 2. may be some quantity that is a monotonic function of the deviation from the uniform concentration.

In the author's thesis, a quantity has been proposed for the characterization of the degree of permixing. This is a quantity defined by an integral formula obtained by the generalization of the entropy of mixing of ideal gases, if the domain to be mixed is a set of single connection and measurable. The density of the substance to be mixed is taken as $\rho'(\bar{r},t)$. In this case, if the total mass present in the domain is denoted by M, the quantity: $\frac{\rho'}{M} = \rho(\bar{r},t)$ represents the probability density of an individual particle, selected at random, of the substance. On the basis of the latter function, the quantity can be defined:

$$s = -\int_{(V)} \rho \ln (\rho\Delta V)dV; \quad s_k = \frac{\int\rho \ln \Delta V\rho dV}{\ln \frac{\Delta V}{V}} \tag{1}$$

γ is the density of the substance being permixed, and[1]:

$$\Delta V = \frac{\gamma}{M}$$

ΔV is, according to its meaning, the minimum volume in which the substance to be permixed is present.

As to s, it can be shown that:

1. $$0 < s < s_m$$

   where s_m is the value of maximum entropy:

   $$s_m = -\ln \frac{\Delta V}{V}$$

2. If the distribution is uniform, then:

   $$s = s_m$$

   if the distribution is such that the substance to be permixed and the carrier substance are perfectly separated from each other, thus:

   $$s = 0$$

These properties offer a reason for using the quantity s for the measurement of the degree of permixing. It would have been

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[1] The introduction of ΔV is not only a question of the selection of dimension and zero point, but also that of choice of scale; cf. [2].

preferable to show that s is in a monotonic connection with the uniformity of distribution. However, this was shown only for a special case, numerically, i.e. for the case of a normal distribution. It was found that in such a case there is a monotonic connection between s and the scattering of the distribution:

$$\frac{ds}{d\sigma} > 0$$

1. GENERALIZATION OF THE ENTROPY OF MIXING IN THE CASE OF MORE THAN ONE SUBSTANCE BEING MIXED

Formula (1) can also be generalized if it is not one single substance whose degree of permixing is to be determined. Let us suppose that a number n of substances to be mixed are present in a domain V, each of them in a certain distribution, and let the density of the i^{th} mixed substance be $\rho_i'(r,t)$ $i = 1, 2, \ldots, n$; in this case if M_i is the total mass of the i^{th} substance in the domain, the formula:

$$\frac{\rho_i'}{M_i} = \rho_i(\bar{r},t)$$

is the probability density distribution of an individual particle of the i^{th} substance, selected at random.

The following generalization of Formula (1) will now be considered:

$$S = -\underbrace{\int_{(V)} \int_{(V)} \ldots \int_{(V)}}_{(n)} (\rho_1 \rho_2 \ldots \rho_n) \ln (\Delta V_1 \rho_1 \Delta V_2 \rho_2 .. \Delta V_n \rho_n) dV_1 dV_2 \ldots dV_n \quad (2)$$

Equation (2) can be transformed by the known functional equation of logarithm:

$$\ln (\Delta V_1 \rho_1 \ldots \Delta \rho_n V_n) = \sum_{i=1}^{n} \ln \Delta V_i \rho_i \quad (3)$$

By substituting Eq. (3) into Eq. (2) we obtain:

$$S = -\int_{(V)}\int_{(V)}\cdots\int_{(V)} (\rho_1\rho_2\ldots\rho_n)\ \ln\ (\Delta V_1\rho_1\ldots\Delta V_n\rho_n)\ dV_1dV_2\ldots dV_n =$$

$$= -\int_{(V)}\int_{(V)}\cdots\int_{(V)} \sum_{i=1}^{n} (\rho_1\rho_2\ldots\rho_n)\ \ln\ (\Delta V_i\rho_i)dV_1dV_2\ \ldots\ dV_n =$$

$$= -\sum_{i=1}^{n} \int_{(V)}\int_{(V)}\cdots\int_{(V)} (\rho_1\rho_2\ldots\rho_n)\ \ln\ (\Delta V_i\rho_i)dV_1dV_2\ \ldots\ dV_n \qquad (4)$$

The integrals under the sign Σ can now be solved by transformation to multiple integrals, since the factors, which do not contain V_i, can be factored out of the integral according to V_i:

$$S=-\sum_{i=1}^{n} \int_{(V)}\int_{(V)}\cdots\int_{(V)}\int_{(V)} [\int(\rho_1\rho_2\ldots\rho_n)\ln(\Delta V_i\rho_i)dV_i]dV_1dV_2..dV_{i-1}dV_{i+1}..dV_n=$$

$$= -\underset{(n-1)}{\int_{(V)}\int_{(V)}\cdots\int_{(V)}} [\rho_1\rho_2\ldots\rho_{i-1}\rho_{i+1}\ldots\rho_n \sum_{i=1}^{n} \int_{(V)} \rho_i\ \ln(\Delta V_i\rho_i)dV_i]\cdot$$

$$\cdot\ dV_1dV_2\ \ldots\ dV_{i-1}dV_{i+1}\ \ldots\ dV_n \qquad (5)$$

As a result of these transformations, the quantity s_i is gained in an explicit form:

$$s_i = -\int_{(V)} (\rho_i\ \ln\ (\Delta V_i\rho_i))\ dV_i \qquad (6)$$

s_i is independent on the other variables, and can be factored out from under the integrals. Accordingly, calculation (5) can be continued:

$$S = -\sum_{i=1}^{n} s_i \underset{(n-1)}{\int_{(V)}\int_{(V)}\cdots\int_{(V)}} (\rho_1\rho_2\ldots\rho_{i-1}\rho_{i+1}\ldots\rho_n)\ \cdot$$

$$\cdot\ dV_1dV_2\ \ldots\ dV_{i-1}dV_{i+1}\ \ldots\ dV_n$$

The integral can again be resolved to a multiple integral:

$$S = -\sum_{i=1}^{n} s_i \int_{(V)} \rho_1 dV_1 \int_{(V)} \rho_2 dV_2 \ldots \int_{(V)} \rho_{i-1} dV_{i-1} \int_{(V)} \rho_{i+1} dV_{i+1} \ldots \int_{(V)} \rho_n dV_n \tag{7}$$

The values of the individual volume integrals are all unity, since the densities are normalized:

$$\int_{(V)} \rho_i dV_1 = 1 \tag{8}$$

and as a result we obtain:

$$S = \sum_{i=1}^{n} s_i \tag{9}$$

that is to say, if S - as defined by Equation (2) - is regarded as the degree of permixing when a number of substances are simultaneously mixed, the additivity theorem is valid: the degree of permixing, when mixing a number of substances, is the algebraic sum of the various degrees of permixing.

It can be seen by a short calculation that the maximum property shown for s in 1. also holds for S, i.e. S is the functional of the functions $\rho_1, \rho_2, \ldots \rho_n$:

$$S = S\,[\rho_1, \rho_2, \ldots \rho_n] \tag{10}$$

However, on the basis of formula (9):

$$S\,[\rho_1 \rho_2 \ldots \rho_n] = \sum_{i=1}^{n} s_i[\rho_i] \tag{11}$$

Consequently, if S is varied according to the variables of ρ_i, and the condition of the extreme value is found, we arrive at:

$$\delta S = 0 \tag{12}$$

If the supplementary condition is included into the method of variation, the following equation is obtained:

$$\sum_{i=1}^{n} \delta s_i[\rho_i] = 0 \tag{13}$$

The ρ_i functions can be varied independently, and consequently:

$$\sum_{i=1}^{n} \delta s_i[\rho_i] = 0 \rightarrow \delta s_i[\rho_i] = 0 \tag{14}$$

However, the second Equation in (14) involves uniform distribution as a condition. It is apparent that the maximum value of S according to (9) is not unity. If S is divided with maximal values of the sum of s_i-s S will be normalized to unity.

In order to comprehend this, let us consider the quantity:

$$s_i = - \int_{(V)} \rho_i \ln (\Delta V \rho_i) \, dV \tag{15}$$

Since: $\rho_i \geq 0$

and

$$\rho_i \leq \frac{1}{\Delta V}$$

consequently:

$$\ln (\Delta V \rho_i) \leq 0$$

and thus:

$$s_i \geq 0$$

The maximum value of (15), with the complementary condition:

$$\int_{(V)} \rho_i dV = 1 \tag{16}$$

can be determined by variation calculus. The task is to determine the extreme value of:

$$\phi = \int [- \rho_i \ln (\Delta V \rho_i) + \alpha \rho_i] \, dV$$

The Euler-equation is:

$$\frac{\partial \varphi}{\partial \rho} = 0$$

where

$$\varphi = -\rho_i \ln (\Delta V \rho_i) + \alpha \rho_i \tag{18}$$

With the substitution of (18), (17) becomes:

$$- \ln \Delta V - (\ln \rho_i + 1) + \alpha = 0$$

$$\rho_i = e^{-(\ln \Delta V - 1 - \alpha)} \tag{19}$$

i.e. we have a uniform distribution which is independent of the space co-ordinates.

The extreme value condition (16) determines α:

$$V\ e^{-(\ln \Delta V - 1 - \alpha)} = 1$$

$$\alpha = - \ln V$$

$$(\ln \Delta V - 1 - \alpha) = \ln V$$

$$\alpha = \ln \frac{\Delta V}{V} - 1$$

Substituting back into (19):

$$\rho_i = \frac{1}{V}$$

(15) becomes:

$$s_i = - \frac{1}{V} \int \ln \frac{\Delta V}{V}\, dV = - \ln \frac{\Delta V}{V} \tag{20}$$

The property mentioned under (1) has hereby been proven. At the same time, it has also been shown on the basis of (14) that S has its maximum at:

$$\rho_i = \frac{1}{V} \qquad i = 1, 2, \ldots, n$$

whose value is:

$$S_M = - \sum_{i=1}^{n} \ln \frac{\Delta V_i}{V}$$

Accordingly, S is not normalized to 1 and its maximum value is S_M.

$$0 \le S \le S_M$$

2. CALCULATION OF THE ENTROPY OF MIXING IN A GENERAL CASE

It is sufficient to show the entropy determination for a single mixed component; if there are more components, the same differential equation is valid on the basis of the same consideration for all of the components as in the case of a single component.

The system of equations, valid for the process of mixing, is the following:

1. The equation of the conservation of mass:

$$\frac{\partial \rho}{\partial t} + \mathrm{div}\,(\rho \bar{v} - D_1 \,\mathrm{grad}\, \rho) = 0 \tag{21}$$

where

$\bar{v}$ is the velocity distribution of substance (metre.second^{-1})

D_1 is the effective diffusion constant (sq.metre·second^{-1})

ρ is the density of the mixed component (kilogram/cu.metre)

In a general case:

$$\begin{aligned} \rho &= \rho(\bar{r},t) \\ \bar{v} &= \bar{v}(\bar{r},t) \end{aligned} \tag{22}$$

where $\bar{r}$ is the position vector.

2. The flow equation pertaining to the rate space, in the usual form of the law of the conservation of impulse:

$$\frac{\partial \rho \bar{v}}{dt} + \mathrm{Div}\,(P + \rho \bar{v} \circ \bar{v}) = \rho \bar{f} \tag{23}$$

where

Div is tensor-divergence (metre^{-1})

P is the stress-tensor (kilogram·metre^{-1}·second^{-2})

$\bar{f}$ is the vector of mass force (metre·second^{-2})

It is necessary to formulate an assumption in connection with the stress terms and mass forces which give a more exact definition of the nature of the carrier medium. As it is known, such assumptions are the model of the ideal fluid or that of Newtonian fluid, but it may also be any other model [3].

The form of Equation (23) is not identical to that of the Navier-Stokes equation, since the divergence of the first term of (23) and of the diadic tensor of the convective stream **cannot be** eliminated by Equation (21),**only in such cases where the diffusion can be neglected**. This assumption is justified in the case of common diffusion; however, if mixing is described by a diffusion-type model, **essentially** it cannot be neglected. In the following, a flow equation **that also takes mixing into consideration** will be quoted. The mass forces and the stress-tensor will not be specified, the generalization will still be sustained. The left side of Equation (23) is modified:

$$\frac{\partial \rho \bar{v}}{\partial t} + \mathrm{Div}\,(P + \rho\bar{v} \circ \bar{v}) =$$

$$= \bar{v}\,\frac{\partial \rho}{\partial t} + \rho\,\frac{\partial \bar{v}}{\partial t} + \mathrm{Div}\,P + \mathrm{Div}\,\rho\bar{v} \circ \bar{v} \qquad (24)$$

but:

$$\mathrm{Div}(\rho\bar{v} \circ \bar{v}) = \bar{v}\,\mathrm{div}\,\rho\bar{v} + \rho(\bar{v},\nabla \circ \bar{v}) \qquad (25)$$

By substituting Equations (24) and (25) back into Equation (23), the multiplicator of $\bar{v}$ van be collected:

$$\bar{v}\,\left(\frac{\partial \rho}{\partial t} + \mathrm{div}\,\rho\bar{v}\right) + \rho\,\frac{d\bar{v}}{ft} + \rho(\bar{v},\nabla \circ \bar{v}) + \mathrm{Div}\,P = \rho\bar{f} \qquad (26)$$

The first term of Equation (26) is equal to zero, if the term originating from the diffusion stream can be neglected in Equation (21):

$$\frac{\partial\rho}{\partial t} + \operatorname{div} \rho\bar{v} = D_1\Delta\rho \qquad 0 \tag{27}$$

Should this not be the case, the simplification of Equation (2) can be carried out only by writing Equation (27):

$$\bar{v}D_1\Delta\rho + \rho\frac{d\bar{v}}{dt} + \rho(\bar{v},\nabla\circ\bar{v}) + \operatorname{Div} P = \rho\bar{f} \tag{28}$$

Accordingly, the Navier-Stokes equation will be supplemented with the first term of Equation (28).* It can be added that the Navier-Stokes equation is also different from Equation (28) inasmuch as the medium to be mixed is not incompressible, and consequently:

$$\operatorname{div} \bar{v} \neq 0 \tag{29}$$

since the component being mixed is not present alone in the space of streaming, but together with the carrier. With a view to a more exact formulation, it should also be taken into consideration that the velocity of the molecules of the component to be mixed is not the same as that of those of the carrier medium and accordingly the law of viscosity ought to be taken into account. The system of simultaneous equations thus grows further. Two Navier-Stokes equations are valid for the two velocity spaces, and a conservation law of the type (21) for both substances, one of these (that pertaining to the component to be mixed) also containing a diffusion term. In the two equations of streaming, e.g. the Stokes law of viscosity has to be taken into consideration as a mass force. The friction force has a greater influence upon the mixed component than upon the carrier,and consequently it is sufficient to account for it only in one case:

$$\rho\bar{f} = -6\,\pi\eta r(\bar{v} - \bar{v}')\rho \tag{30}$$

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*The attenation of the author was drawn to this fact by Dr.I.Fényes, for which the author expresses his thanks.

where

η is the viscosity of the carrier medium (kilogram·second/sq.metre)

r is the radius of a particle (molecule) of the mixed component (metre)

$\bar{v},\bar{v}'$ is the rate of the mixed component and of the carrier (metre/second)

Furthermore, if the carrier medium is present at a high density of the incompressibility condition is justified (as against the case of the component being mixed):

$$\operatorname{div} \bar{v}' = 0$$

The equation of streaming becomes simpler. However, it is most reasonable to accept Equations (21) and (28) as basic equations of satisfactory accuracy, which are, at the same time, theoretically accurate.

Summing up, Equations (21) and (28), or (23) are four differential equations for the functions ρ, v_1, v_2, v_3.

The pressure p (stress tensor) is to be regarded as known data of the problem, furthermore the $\bar{f}$ mass force and the initial and boundary conditions. However, if the problem has been solved, by means of these, the value of ρ' and the ρ density function will also be obtained. In this case, Equation (1) gives the degree of permixing by calculation of the integral.

In conclusion it should mentioned that the normal differential equation, describing the changes of the entropy of mixing in time cannot be deduced it has no universal form. This can be explained in the following manner. The entropy of mixing has been regarded as the degree of mixing, whether the task is to mix materials or internal energy. (Equation (1) can be generalized for the simultaneous mixing of both material and internal energy.) Accordingly, the II. law of thermodynamics can be applied, but not the theorems of irreversible thermodynamics describing processes in time. The equations of thermodynamics, describing process in time, always refer to **spontaneous** - although complex - equalization processes [4]. **Mixing is doubtlessly an equalization process, but not a spontaneous one.** Therefore a mechanical mixing process cannot be described as a spontaneous equalizing process where the gradient of an intensive quantity is the driving force. E.g. a mixing which produces eddy currents the velocity field has not potential function [1]. If the equalization process was brought about by generalized thermodynamical forces (the gradients of the intensity parameters within the system), the irreversible entropy production brought about in the process (i.e. the entropy of mixing) could be calculated from the equations describing the changes in time, formulated to a continuum [4]. It is outside the scope of this paper, but nevertheless it can be mentioned that mixing could perhaps be described as the tendency of a generally fictive and as yet unknown intensity parameter for equalization. The theoretical foundation seems, on the basis of the foregoing, to be doubtful, but in order to reach only a given aim, not impossible. Only a comparison with practice can tell whether it is successful or not. Consequently, the expansion of the theory in this direction will not be dealt with. (The differential equation of the change in time, which is founded on an empyrical basis and can be checked asymptotically, has been elaborated together with Dr. T. BLICKLE [5].)

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РЕЗЮМЕ

Для теоретического описания смешивания автор обобщает выражение приращения энтропии при перемешивании идеальных газов, рассматривает свойства величины, получаемой таким путем. Энтропия смешивания оказывается пригодной для количественного охарактеризования перемешивания.

В следующей части сообщения автор представит практическое применение метода на упрощенной гидродинамической модели.