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Brief Note

A simple mixture of gases is a mixture of ideal gases

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If the thermodynamics of fluid mixture has a classical form, then the simple fluid mixture (Müller [1, 2]) has the special form of the state equation (see Eq. (3.5)). Moreover, if such mixture is gaseous, then it is equivalent to the mixture of ideal gases.

1. Introduction

Truesdell's theory of mixtures [3, 4] is based on the partial quantities (which characterize properties of each constituent of mixture) taken as primitives. To obtain the classical thermodynamic results, the mixture of fluids (e.g. model with linear transport) must be *nonsimple*, i.e. the starting constitutive equations must depend (among others) not only on partial densities but also on density gradients [1, 2, 6, 5, 9]. Less usual results are noted in Sec. 2; details are described in [6, 5, 9]. Namely, it may be shown, by the so-called *mixture invariance* [5, 6], that an uncertainity of partial thermodynamic quantities may be removed and they may be identified with those used in classical thermodynamics of mixtures [7, 8]. Then, for fluid mixtures, such partial quantities may be calculated explicitly from the dependence of (obtainable) properties of mixture on the composition (see Eqs. (2.2), (2.3)).

In Sec. 3 we restrict this model to the *simple* fluid mixture (where dependence on density gradients is removed). Constitutive equations for free energies are then simplified to (3.1) (Müller [1, 2], cf. [6] § 25)[1]. Here we show that the classical thermodynamic structure leads in a simple fluid mixture to the special form of state equation (3.5). If such simple mixture is gaseous, it is not only sufficient but also necessary that this should be the mixture of ideal gases (for this we use the approaching to ideal gas behaviour at decreasing density, cf. postulate (3.6)).

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[1] Note that the simple mixture is generally different from *ideal mixture* [7, 8] but in mixture of ideal gases both definitions coincide, see [6] § 25.

2. Mixture of fluids

The rational thermodynamic theory of mixtures of fluids (i.e. gases or liquids) [1, 2, 3, 4] containing n constituents ($\alpha = 1, 2, ..., n$) achieves ([6] Ch.IV, [5] § 8, [9]Ch.IV) the classical form with the specific partial thermodynamic quantities y_α (internal energy u_α, entropy s_α, volume v_α, enthalpy h_α, free energy f_α, Gibbs energy g_α (chemical potential)). They are functions of temperature T and all partial densities ρ_γ or temperature T, pressure P and independent mass fractions w_β (denoted by hat or tilde respectively)

$$y_\alpha = \hat{y}_\alpha(T, \rho_1, \rho_2, .., \rho_n) = \hat{y}_\alpha(T, \rho_\gamma) = \tilde{y}_\alpha(T, P, w_1, w_2, .., w_{n-1}) = \tilde{y}_\alpha(T, P, w_\beta), \qquad \alpha, \gamma = 1, 2, .., n; \qquad \beta = 1, 2, ..., n-1, \tag{2.1}$$

(note the shortened writing of independent variables). Corresponding specific thermodynamic quantities for the mixture y (denoted by u, s, v, h, f, g) are defined by $y = \sum_{\alpha=1}^{n} w_\alpha y_\alpha = \hat{y}(T, \rho_\gamma) = \tilde{y}(T, P, w_\beta)$. We prefer specific quantities, namely, mass fractions instead of molar ones [7, 8], because of their possible application to nonequilibrium processes. Therefore the usual relations $\sum_{\alpha=1}^{n} w_\alpha = 1, w_\alpha = \rho_\alpha/\rho$ with density of mixture $\rho = \sum_{\alpha=1}^{n} \rho_\alpha$ are valid.

Mixture (or *form*) *invariance* [5, 6, 9] permits to calculate all partial quantities y_α from the mixture quantities y and their dependence on the mass fractions by (e.g. v_α from density $\rho = 1/v$, cf. Eqs. (5), (6) in [10])

$$y_n = y - \sum_{\beta=1}^{n-1} w_\beta \frac{\partial \tilde{y}}{\partial w_\beta}, \tag{2.2}$$

$$y_\beta = y_n + \frac{\partial \tilde{y}}{\partial w_\beta}, \qquad \beta = 1, 2, ..., n-1, \tag{2.3}$$

which may be identified with those in classical texts [7, 8] in molar units. Here the special case of uniform (homogeneous) mixture is usually treated; then, instead of (2.2), (2.3) simpler relations are used, e.g. Eq. (8.41) in [5].

Thermodynamic quantities are related by the usual relations like

$$f_\alpha = u_\alpha - T s_\alpha, \qquad h_\alpha = u_\alpha + P v_\alpha, \qquad g_\alpha = f_\alpha + P v_\alpha, \tag{2.4}$$

by analogous relations for thermodynamic quantities of mixture, Gibbs and Gibbs-Duhem relations, etc. Less usual is the expression for chemical potential

$$g_\alpha = \frac{\partial \rho \hat{f}}{\partial \rho_\alpha}, \qquad \alpha = 1, 2, ..., n. \tag{2.5}$$

Because of (2.4) the *generalized* partial pressures P_α and Dalton law may be introduced [6, 9, 5]

$$P_\alpha = \rho_\alpha v_\alpha P, \qquad \alpha = 1, 2, ..., n, \tag{2.6}$$

$$\sum_{\alpha=1}^{n} P_\alpha = P = \hat{P}(T, \rho_\gamma). \tag{2.7}$$

Equations (2.1), (2.7), (2.4) and other classical relations (like $\partial\tilde{g}_\alpha/\partial T = -s_\alpha$, $\partial\tilde{g}_\alpha/\partial P = v_\alpha$) then gives (cf. [5]§8, [6] §23, [9] §45)

$$P_\alpha = \sum_{\gamma=1}^{n} \rho_\alpha \rho_\gamma \frac{\partial \hat{f}_\gamma}{\partial \rho_\alpha}, \tag{2.8}$$

$$-s_\alpha = \frac{\partial \hat{f}_\alpha}{\partial T} + P\frac{\partial \hat{v}_\alpha}{\partial T}, \tag{2.9}$$

$$\rho\frac{\partial \hat{g}_\alpha}{\partial \rho_\gamma} = \rho v_\alpha \frac{\partial \hat{P}}{\partial \rho_\gamma} + \sum_{\beta=1}^{n-1} \frac{\partial \tilde{g}_\alpha}{\partial w_\beta}\left(\delta_{\beta\gamma} - w_\beta\right) \tag{2.10}$$

($\delta_{\beta\gamma}$ is Kronecker's delta, $\delta_{\beta n} \equiv 0$, $\alpha, \gamma = 1, 2, .., n; \beta = 1, 2, ..., n-1$).

From (2.5) we have $\partial\hat{g}_\eta/\partial\rho_n = \partial\hat{g}_n/\partial\rho_\eta$ which gives (by (2.10), (2.6), Gibbs and Gibbs–Duhem equations

$$\frac{\rho_\eta}{P_\eta}\frac{\partial \hat{P}}{\partial \rho_\eta} = \frac{\rho_n}{P_n}\frac{\partial \hat{P}}{\partial \rho_n}, \qquad \eta = 1, 2, ..., n-1. \tag{2.11}$$

3. Simple fluid mixture

Fluid mixture of Sec. 2 we now restrict to the *simple* fluid mixture possessing the essential simplification (proven by MÜLLER [1, 2], cf. [6] §25): partial free energy of constituent α depends (besides T) on the density ρ_α of this constituent α only

$$f_\alpha = \hat{f}_\alpha(T, \rho_\alpha) \tag{3.1}$$

(cf. difference from the general $f_\alpha = \hat{f}_\alpha(T, \rho_\gamma)$ in (2.1)). Then from (2.8), (2.5), (2.4) the same property follows for partial pressures and chemical potentials (and also for Pv_α)

$$P_\alpha = \rho_\alpha^2 \frac{\partial \hat{f}_\alpha}{\partial \rho_\alpha} = \hat{P}_\alpha(T, \rho_\alpha), \tag{3.2}$$

$$g_\alpha = \hat{g}_\alpha(T, \rho_\alpha). \tag{3.3}$$

We show, that such a simple fluid mixture has the special form of “state equation” (3.2).

Indeed, using (3.2) in (2.7) we have $\partial\hat{P}/\partial\rho_\alpha = \partial\hat{P}_\alpha/\partial\rho_\alpha$ depending, as well as P_α, on temperature and only on one density of the respective constituent α. Therefore from (2.11), we obtain a universal C (possibly a function of temperature)

$$\frac{\rho_\alpha}{P_\alpha}\frac{\partial\hat{P}_\alpha}{\partial\rho_\alpha} = C = C(T), \qquad \alpha = 1, 2, ..., n. \tag{3.4}$$

By integration we obtain the following general form of dependence of the partial pressures on densities in a simple fluid mixture (state equation)

$$P_\alpha = K_\alpha(\rho_\alpha)^C, \qquad \alpha = 1, 2, ..., n, \tag{3.5}$$

where $K_\alpha = K_\alpha(T)$ as well as $C(T)$ are some functions of temperature T.

At last we restrict this simple fluid mixture to the mixture of gases and we show that this *simple gas* mixture is equivalent to the mixture of ideal gases.

We use the Denbigh’s definition of mixture of ideal gases ([8] Eq. (3.18), cf. Eq. (3.15)) having the state equation of ideal gas mixture for partial volumes or classical partial pressures (cf. (3.9), (3.8)). Then this definition of ideal gas mixture gives (3.3), (3.1) (see (2.4)), which prove the sufficiency of the assertion made above (cf. [1], [2] §6.4): ideal gas mixture is the simple gas mixture.

To prove the necessity we postulate the general property of any gas and gas mixture, including the simple one:

If, at any given temperature, the density of gas (or all densities in a gas mixture) tends to zero, their properties approach the ideal gas behaviour. Specifically, for partial volumes the following limits of state equations are valid for all $\alpha = 1, 2, .., n$ (in the last expression we use (2.6))

$$\lim_{\rho_\alpha\to+0} Pv_\alpha = \frac{RT}{M_\alpha} = \lim_{\rho_\alpha\to+0}\frac{P_\alpha}{\rho_\alpha}, \tag{3.6}$$

where R is the gas constant and M_α is the molar mass of constituent α.

Inserting (3.5) into (3.6) we obtain for a simple mixture (and chosen α)

$$\lim_{\rho_\alpha\to+0}(\rho_\alpha)^a = b, \tag{3.7}$$

where $a \equiv C - 1,\ b \equiv \mathrm{R}T/(K_\alpha\, M_\alpha)$.

But (3.7) is valid if and only if $a = 0,\quad b = 1$ (limits for $a > 0$ or $a < 0$ are 0 or $+\infty$ respectively, without physical sense; densities are only positive).

Therefore $C = 1$, $K_\alpha = \mathrm{R}T/M_\alpha$ and "state equation" (3.5) of the simple gas is an ideal one

$$P_\alpha = \rho_\alpha \frac{\mathrm{R}T}{M_\alpha} \tag{3.8}$$

valid at any density and pressure (and not only in the limit (3.6)).

Moreover, for such a simple gas mixture it follows by (2.6), (2.7), (3.8) that molar partial volumes of all constituents are the same

$$v_\alpha M_\alpha = \frac{\mathrm{R}T}{P} = \left(\sum_{\gamma=1}^{n} \frac{\rho_\gamma}{M_\gamma} \right)^{-1} , \qquad \alpha = 1, 2, ..., n. \tag{3.9}$$

From this it may be seen that $\rho_\alpha v_\alpha$ in the simple gas mixture is the molar fraction and (2.6), (2.7) are the *classical* partial pressures and the Dalton law. It also follows that $v_\alpha = \hat{v}_\alpha(\rho_\gamma)$ and by (2.9)

$$-\frac{\partial \hat{f}_\alpha}{\partial T} = s_\alpha = \hat{s}_\alpha(T, \rho_\alpha)\,. \tag{3.10}$$

Further, partial internal energies and enthalpies are functions only of temperature in such a simple gas mixture

$$u_\alpha = \hat{u}_\alpha(T)\,, \tag{3.11}$$

$$h_\alpha = \hat{h}_\alpha(T)\,. \tag{3.12}$$

Equation (3.11) follows from (2.4) and from (3.10) by the differentiation with respect to ρ_α. Namely $\partial \hat{u}_\alpha / \partial \rho_\alpha \equiv 0$, because it follows from (3.2) and (3.8) that

$$\frac{\partial \hat{f}_\alpha}{\partial \rho_\alpha} = \frac{P_\alpha}{\rho_\alpha^2} = \frac{RT}{M_\alpha \rho_\alpha}\,. \tag{3.13}$$

Equation (3.12) then follows from (3.11) , (3.9).

All these results for a simple gas mixture are the properties of the mixture of ideal gases. Also the logarithmic dependence of $f_\alpha, s_\alpha, g_\alpha$ on densities (and therefore on classical partial pressures as a consequence of (3.8)) is valid. E.g., by integration of (3.13) and by (3.8), (2.4), (2.6)

$$f_\alpha = \hat{f}_\alpha^0(T) + \frac{RT}{M_\alpha} \ln \rho_\alpha, \tag{3.14}$$

$$g_\alpha = \hat{g}_\alpha^0(T) + \frac{RT}{M_\alpha} \ln P_\alpha. \tag{3.15}$$

The last one is the Denbigh's definition of the mixture of ideal gases, [8] Chap. 3.

Therefore a simple gas mixture is necessary and therefore equivalent to the mixture of ideal gases.

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References

1. I. Müller, *A thermodynamic theory of mixtures of fluids*, Arch. Rational Mech. Anal., **28**, 1–39, 1968.
2. I. Müller, *Thermodynamics*, Pitman, Boston 1985.
3. C. Truesdell, R. Toupin, *The classical field theories*, Handbuch der Physik III/1, (S. Flügge) [Ed.], Springer, Berlin 1960.
4. C. Truesdell, *Rational thermodynamic* (2nd Ed.), Springer, New York 1984.
5. I. Samohýl, M. Šilhavý, *Mixture invariance and its applications*, Arch. Rational Mech. Anal., **109**, 299–321, 1990.
6. I. Samohýl, *Thermodynamics of irreversible processes in fluid mixture*, Teubner, Leipzig 1987.
7. R. Haase, *Thermodynamik der Mischphasen*, Springer, Berlin 1956.
8. K. Denbigh, *The principles of chemical equilibrium*, Cambridge University Press, 1961.
9. I. Samohýl, *Rational thermodynamics of chemically reacting mixtures* [in Czech], Academia, Prague 1982.
10. P. Hrma, *Empirical models and thermodynamic constitutive functions for high-level waste glass properties*, Ceram. Trans., **87**, 245–252, 1998.

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