

Partial Pressures in Thermodynamics of Classical Fluid Mixtures

Vít Samohýl, Ivan Samohýl, Petr Voňka

Department of Physical Chemistry, Institute of Chemical Technology, Prague,
Technická 5, 166 28 Prague 6, Czech Republic
ivan.samohyl@vscht.cz, petr.vonka@vscht.cz (corresponding author)

Abstract: In the rational thermodynamics of most usual nonequilibrium “classical” fluid mixtures it has been proposed the “thermodynamic” partial pressure which generalize traditional definitions and merge together in an ideal gas mixture. In this paper, these thermodynamic partial pressures are calculated for a (real) gas mixture of methane-ethane-carbon dioxide and a liquid mixture of lithium hydroxide in water. The results are compared with those obtained using the classical formulations of partial pressures calculated in these mixtures as well.

Key words: Gas mixture, Irreversible thermodynamics, Liquid mixture, Partial pressure, Rational thermodynamics, Thermodynamics of mixtures

Introduction

In the classical thermodynamics of mixtures composed of n constituents (components of mixture) $\alpha = 1, \dots, n$ partial pressures are rarely used. However when they are used, the following two classical formulations are typically applied to gas mixtures, even chemically reacting ones:

- A. (Partington 1949) p. 609: Partial pressure P_α^A of any gas α is the pressure this gas would exert if it alone occupied the total volume of the mixture at the same temperature.
- B. (Prausnitz et al. 1999) p. 584: Partial pressure P_α^B of constituent α in an n -constituent mixture is

$$P_\alpha^B = x_\alpha P, \alpha = 1, \dots, n \quad (1)$$

where x_α is the *molar fraction* of α in the considered mixture at the (total) pressure P .

While both of these definitions are used for mixtures of real gases, they generally do not give the same results. For example, in case A the sum of the partial pressures ($\sum_{\alpha=1}^n P_\alpha^A$) need not be equal to the total pressure of the mixture P , i.e. Dalton’s law is generally invalid (see Tables and Figures below for examples). However in the case of ideal gas mixtures both definitions do give the same result, i.e. Dalton’s law is valid. For this reason the partial pressures are most often used in a mixture of (at least approximately) ideal gases (Samohýl and Voňka 2006). In principle, these definitions may also be used for liquid mixtures, but the application of definition A is limited by either the low compressibility or nonexistence of constituents as pure liquids (cf. below).

Apart from classical thermodynamics, partial pressures, or, more generally, partial stress tensors, have

also been used in nonequilibrium thermodynamics (de Groot and Mazur 1962), (Truesdell and Toupin 1960), particularly in the theory of rational thermodynamics (Truesdell 1984, 1968), (Müller 1968, 1985). Using this theory, (Samohýl 1982, 1987, 1975a, 1975b) already proposed a concept for partial pressures, termed *thermodynamic* partial pressure (see Eq. (5)). This can be applied to common fluid mixtures, the “classical” ones, by which we mean the most used fluid mixture with linear transport relations (newtonian with Fourier and Fick laws) possibly chemically reacting, with local equilibrium (i.e. usual thermodynamic relations are valid). In special cases (e.g. low pressure) this concept gives the same results as the formulations for classical partial pressures. In the following Section we briefly describe this conception, together with the reasons for it, and in next Section we demonstrate the application of thermodynamic partial pressures to selected gas and liquid mixtures.

Partial Pressures in Rational Thermodynamics

In recent decades, continuum thermodynamics of mixtures has developed to also encompass irreversible processes (de Groot and Mazur 1962), (Truesdell 1984). Continuum thermodynamics uses some *partial* properties (i.e. properties concerning mixture constituents; because of the use of momentum balances we prefer specific quantities rather than molar ones) that generally form *fields*, i.e. functions of position and time. Such fields include partial *densities* ρ_α (in chemistry termed *mass concentrations* – mass of constituent $\alpha = 1, \dots, n$ per unit volume of a mixture composed of n constituents). Partial densities enable us to define the *density of a mixture* ρ and to express its composition using the *mass fraction* w_α :

$$\rho \equiv \sum_{\alpha=1}^n \rho_{\alpha}, \quad w_{\alpha} \equiv \rho_{\alpha} / \rho, \quad (2)$$

$$\alpha = 1, \dots, n, \quad \sum_{\alpha=1}^n w_{\alpha} = 1$$

Theories of this type can be applied to rational thermodynamics (Truesdell and Toupin 1960), (Truesdell 1984, 1968), (Müller 1968, 1985), (Samohýl 1982, 1987), in which some partial properties can be used a priori as primitive concepts. Such properties include not only *partial specific internal energies* u_{α} and *entropies* s_{α} , but also *partial stress tensors* \mathbf{T}_{α} , which were introduced (Truesdell and Toupin 1960) Sect. 215 to describe the surface forces in the momentum balance of each constituent α . Rational thermodynamics describes the continuum thermomechanics of different constitutive (or material) models of pure solids, fluids, etc. and their mixtures (Truesdell 1984), (Müller 1985), (Samohýl 1982). Primarily it is applied to mixtures of *fluids* (i.e. gases or liquids) because, under certain limited conditions, it encompasses the classical thermodynamics of mixtures (primarily equilibrium and uniform (homogeneous) theories). The classical thermodynamic structure (i.e. “local equilibrium”) is valid even when transport phenomena (e.g. viscosity, heat conduction, diffusion) and chemical kinetics are in progress (Müller 1968, 1985), (Samohýl 1982, 1987, 1975a, 1975b). In fluid mixtures partial stress tensors take the typical form, see, e.g. (Samohýl 1987) Eq. 27.1.

$$\mathbf{T}_{\alpha} = -P_{\alpha} \mathbf{1} + (\text{nonequilibrium stress})_{\alpha}, \quad \alpha = 1, \dots, n \quad (3)$$

where P_{α} is the *partial pressure* of a constituent α and $\mathbf{1}$ is the unit tensor. To stress the difference from the classical definitions A and B above, we hereinafter denote P_{α} as *thermodynamic partial pressures*. The partial nonequilibrium stresses in (3) primarily result from viscosity, but may additionally be influenced by chemical reactions, see (Samohýl 1987) Sect. 22, for details.

In the commonly used model of fluid mixtures with linear transport properties (e.g. Fourier, Fick and Newtonian laws are valid), and even with nonlinear chemical kinetics (Samohýl 1982, 1987, 1975a), thermodynamic partial pressures only depend on the (absolute) *temperature* T and the densities ρ_{γ} , $P_{\alpha} = \hat{P}_{\alpha}(T, \rho_1, \dots, \rho_n) = \hat{P}_{\alpha}(T, \rho_{\gamma})$, $\alpha, \gamma = 1, \dots, n$. (We use this shorter notation in the following, i.e. P_{α} depends on all partial densities ρ_{γ} , $\gamma = 1, \dots, n$. Similarly, e.g. in (6), the specific volume v depends not only on T and P , but also on all independent mass fractions w_{β} , $\beta = 1, \dots, n - 1$. Note also that the use of an overhead symbol, e.g. \hat{P}_{α} , \tilde{v} , \hat{v}_{α} , means functions with corresponding values P_{α} , v , v_{α} , cf. Eqs. (6), (7).)

Moreover, the *thermodynamic mixture pressure* P defined as

$$P = \hat{P}(T, \rho_{\gamma}) \equiv \sum_{\alpha=1}^n P_{\alpha} \quad (4)$$

is the same as that appearing in the structure of classical thermodynamics (local equilibrium, implying e.g. Gibbs equations, is proved in this model). The structure of rational thermodynamics also permits the definition of the following (specific) quantities: partial free energies $f_{\alpha} = u_{\alpha} - Ts_{\alpha}$, free energy of a mixture

$$f = \sum_{\alpha=1}^n w_{\alpha} f_{\alpha} = \hat{f}(T, \rho_{\gamma})$$

and chemical potentials $g_{\alpha} = \partial \rho \hat{f} / \partial \rho_{\alpha}$. These quantities depend on temperature and densities (such as \hat{f} , \hat{P} above), see (Samohýl 1982, 1987, 1975a, 1975b), (Samohýl and Šilhavý 1990) for details. In non-reacting mixtures the thermodynamic pressure P is equal to the actual (measured) pressure, but need not be the same in chemical kinetics (cf. discussion of (3)). It can be also proved, see (Samohýl 1987) Eqs 22.39, 23.1, (Samohýl 1975) Eq. 52, (Samohýl 1975b) Eq. 1, that $g_{\alpha} = f_{\alpha} + P_{\alpha} / \rho_{\alpha}$. The classical counterpart of this expression provides the motivation for the following relation between thermodynamic partial pressures P_{α} and thermodynamic mixture pressure P

$$P_{\alpha} = \rho_{\alpha} v_{\alpha} P, \quad \alpha = 1, \dots, n \quad (5)$$

which may be understood as the definition of the *partial specific volume* v_{α} of a constituent α . Indeed, from (4), in accordance with the expected properties, we obtain the *specific volume* v of a mixture

$$v = 1 / \rho = \sum_{\alpha=1}^n w_{\alpha} v_{\alpha} = \tilde{v}(T, P, w_{\beta}), \quad \beta = 1, \dots, n - 1 \quad (6)$$

By the inversion of (4) and with (2), the independent variables T , P , w_{β} may be used (Samohýl 1982, 1987), (Samohýl and Šilhavý 1990) instead of T, ρ_{γ} , and therefore, for example, we can obtain

$$v_{\alpha} = \hat{v}_{\alpha}(T, \rho_{\gamma}) = \tilde{v}_{\alpha}(T, P, w_{\beta}), \quad \alpha = 1, \dots, n \quad (7)$$

All of these relations are valid for the fields of this model, even when it is out of equilibrium but the partial quantities are not unique (except in the case of g_{α} and mixture properties, such as f , v), see (Samohýl 1982, 1987, 1975a, 1975b). However, using a basic property of all mixture balances (mass, momentum and their moment, energy and entropy inequality) called *mixture* (or *form*) *invariance* (Samohýl 1982, 1987, 1975b), (Samohýl and Šilhavý 1990), this non-uniqueness may be removed, and, for example, partial specific volumes may be calculated from specific mixture volume (6) as follows

$$v_n = v - \sum_{\beta=1}^{n-1} w_\beta (\partial \tilde{v} / \partial w_\beta) \quad (8)$$

$$v_\beta = v_n + \partial \tilde{v} / \partial w_\beta, \quad \beta = 1, \dots, n-1 \quad (9)$$

In a uniform (homogeneous) fluid mixture the formulas (8), (9) are equivalent to v_α expressed as derivatives of the extensive volume of the mixture according to the mass of each constituent $\alpha = 1, \dots, n$ at a constant T, P , see, e.g. (Samohýl and Šilhavý 1990) Eq. 8.41 or (Samohýl 1987) Eq. 23.62.

In fact, if we use molar quantities instead of specific ones, these formulas become, in effect, the classical ones. Namely, the counterparts of $\rho_\alpha, \rho, w_\alpha$ are *molar concentrations* c_α , *molar density* c and *molar fractions* x_α as given by:

$$c_\alpha = \rho_\alpha / M_\alpha, \quad c \equiv \sum_{\alpha=1}^n c_\alpha, \quad x \equiv c_\alpha / c, \quad \sum_{\alpha=1}^n x_\alpha = 1 \quad (10)$$

where M_α is the *molar mass* of the corresponding constituent $\alpha = 1, \dots, n$. The classical *partial molar volumes* V_α are given by (cf. Rem. 2)

$$V_\alpha = v_\alpha M_\alpha = \bar{V}_\alpha(T, P, x_\beta), \quad \alpha = 1, \dots, n, \quad \beta = 1, \dots, n-1 \quad (11)$$

and the *molar volume* V of a mixture is given by

$$1/c = V = \sum_{\alpha=1}^n x_\alpha V_\alpha = \bar{V}(T, P, x_\beta) = Mv \quad (12)$$

The (classical) independent variables T, P, x_α here follow from

$$w_\alpha = x_\alpha M_\alpha / M, \quad M \equiv \sum_{\alpha=1}^n x_\alpha M_\alpha \quad (13)$$

where M is the *average molar mass* (depending on composition). Note also that (Samohýl 1987) Sect. 23

$$\rho_\alpha v_\alpha = c_\alpha V_\alpha, \quad \alpha = 1, \dots, n \quad (14)$$

From the derivative of (12), we obtain the molar counterparts of (8), (9)

$$V_n = V - \sum_{\beta=1}^{n-1} x_\beta (\partial \bar{V} / \partial x_\beta) \quad (15)$$

$$V_\beta = V_n + \partial \bar{V} / \partial x_\beta, \quad \beta = 1, \dots, n-1 \quad (16)$$

Again, in a uniform (homogeneous) mixture formulas (15), (16) are equivalent to the classical thermodynamic definitions of partial molar volumes (i.e. to derivatives of extensive volume, with respect to the moles of each constituent at a constant T, P (Prausnitz et al. 1999).

For a mixture of ideal gases, it holds that (Samohýl and Voňka 2006).

$$\rho_\alpha v_\alpha = c_\alpha V_\alpha = x_\alpha, \quad \alpha = 1, \dots, n \quad (17)$$

and, therefore (in gases), it follows that, in the case

of low pressure limit, all definitions of partial pressures are the same, $P_\alpha = P_\alpha^A = P_\alpha^B$.

From these formulas it can be seen that by knowing the state equations of a mixture in molar or mass units, i.e. $V = \bar{V}(T, P, x_\beta)$ or $v = \tilde{v}(T, P, w_\beta)$, we can calculate either the partial molar or specific volumes (at a given pressure P and composition) using (15), (16) or (8), (9) respectively. The corresponding thermodynamic partial pressures can then be calculated using (5) and (14). The necessary partial densities or concentrations follow from (2) or (10) respectively.

Partial Pressures in Gas and Liquid Mixtures

In this Section we demonstrate the calculation of thermodynamic partial pressures for selected gas and liquid systems, and compare them with the classical definitions A and B.

For the calculation of thermodynamic partial pressures in gas mixtures we used a ternary mixture of methane, ethane and carbon dioxide at 320 K and at pressures up to 10 MPa. The state equation of this mixture, determined by (Hou et al. 1996), permits the calculation of thermodynamic partial pressures, as well as of the classical partial pressures of types A and B.

For the calculation of thermodynamic partial pressures in liquid mixtures we used a water solution of lithium hydroxide, for which densities as a function of mass fractions were given by (Söhnel and Novotný 1983) at 20 °C and atmospheric pressure. We compared the calculated partial pressures with classical partial pressures of type B (as was already noted, model A cannot be applied in this case).

All results are presented in Tables 1-4 and Figures 1 and 2 below. For the ternary gas mixture CH₄(1)-C₂H₆(2)-CO₂(3), the state equation (Hou et al. 1996) takes the form of the following virial equation for pressure P as a function of molar volume V :

$$P = RT/V + BRT/V^2 + CRT/V^3 = P(T, V, x_\beta) \quad (18)$$

where R is the gas constant, and B and C are the second and third virial coefficients. These coefficients depend not only on temperature T (which is fixed and not stated in the following), but also on the molar fractions $x_\beta = x_1, x_2$ ($x_3 = 1 - x_1 - x_2$) as follows (upper indices represent powers)

$$B = B_{11}x_1^2 + B_{22}x_2^2 + B_{33}x_3^2 + 2B_{12}x_1x_2 + 2B_{13}x_1x_3 + 2B_{23}x_2x_3 \quad (19)$$

$$C = C_{111}x_1^3 + C_{222}x_2^3 + C_{333}x_3^3 + 3C_{112}x_1^2x_2 + 3C_{113}x_1^2x_3 + 3C_{223}x_2^2x_3 + 3C_{122}x_1x_2^2 + 3C_{133}x_1x_3^2 + 3C_{233}x_2x_3^2 + 6C_{123}x_1x_2x_3 \quad (20)$$

Tab. 1. Pressure $P = 5$ MPa, temperature $T = 320$ K, molar volume $V = 440.1$ cm³/mol, compressibility factor $PV/RT = 0.82702$, virial coefficients $B = -86.37$ cm³/mol, $C = 4510$ cm⁶/mol², pressures in MPa, *sum* = sum of pressures.

Constituents	CH ₄ (1)	C ₂ H ₆ (2)	CO ₂ (3)	<i>sum</i>
molar fractions x_α	0.3000	0.3000	0.4000	-----
partial molar volumes V_α cm ³ /mol	522.3	374.1	428.0	-----
thermodynamic partial pressures P_α	1.780	1.274	1.946	5.000
A partial pressures P_α^A	1.772	1.625	2.197	5.594
B partial pressures P_α^B	1.500	1.500	2.000	5.000

Tab. 2. Pressure $P = 10$ MPa, temperature $T = 320$ K, molar volume $V = 173.4$ cm³/mol, compressibility factor $PV/RT = 0.65195$, virial coefficients $B = -86.37$ cm³/mol, $C = 4510$ cm⁶/mol², pressures in MPa, *sum* = sum of pressures.

Constituents	CH ₄ (1)	C ₂ H ₆ (2)	CO ₂ (3)	<i>sum</i>
molar fractions x_α	0.3000	0.3000	0.4000	-----
partial molar volumes V_α cm ³ /mol	273.4	102.9	151.3	-----
thermodynamic partial pressures P_α	4.734	1.780	3.486	10.000
A partial pressures P_α^A	4.352	3.466	4.800	12.419
B partial pressures P_α^B	3.000	3.000	4.000	10.000

This state equation can also describe pure substances (e.g. CH₄(1) when $x_1 = 1$ and $x_2 = x_3 = 0$, see (23) below) and binary mixtures (e.g. CH₄(1)-CO₂(3), see (25), (26), (27) below).

The values of the second and third virial coefficients B (cm³/mol) and C (cm⁶ mol⁻²) used for our mixture at 320 K are (Hou et al. 1996)

$$B_{11} = -35.17, B_{22} = -159.42, B_{33} = -104.54, \quad (21)$$

$$B_{12} = -76.71, B_{13} = -54.02, B_{23} = -105.65$$

$$C_{111} = 2229, C_{222} = 9692, C_{333} = 4411,$$

$$C_{112} = 3594, C_{113} = 2641, C_{122} = 5902, \quad (22)$$

$$C_{133} = 3195, C_{223} = 6963, C_{233} = 5075,$$

$$C_{123} = 4204$$

Firstly, using (18), we calculated the molar volume V for each given pressure P and composition (given by x_1, x_2). The state equation (18) implicitly contains $V = \bar{V}(T, P, x_\beta)$, and therefore it holds that the derivatives are given by $\partial \bar{V} / \partial x_\beta = -(\partial P / \partial x_\beta) / (\partial P / \partial V)$, $\beta = 1, 2$. Then, using (15), (16) for $n = 3$, we calculated partial molar volumes V_α ($\alpha = 1, 2, 3$) for each given (total) pressure and composition. Next, (10), (12) were used to calculate c_α . Finally, using (5), (14), the thermodynamic partial pressures P_α were calculated at total pressure P . The results are displayed in Table 1. For comparison purposes, we also calculated the classical partial pressures (see also Table 1):

To obtain classical partial pressures A, denoted P_α^A , we considered 1 mol of a mixture, i.e. the molar vol-

ume V at a given temperature ($T = 320$ K), pressure P and composition x_1, x_2 (molar fraction of CH₄(1), C₂H₆ (2); for CO₂(3) is $x_3 = 1 - x_1 - x_2$). According to definition A, the classical partial pressure P_α^A of CH₄(1) is equal to the pressure of pure CH₄ given by (18) (where $B = B_{11}$, $C = C_{111}$ because here $x_1 = 1$, $x_2 = x_3 = 0$), so that the molar volume equals V/x_1 . The same applies for other pure constituents. Therefore it holds:

$$P_\alpha^A = RT/(V/x_\alpha) + B_{\alpha\alpha}RT/(V/x_\alpha)^2 + \quad (23)$$

$$+ C_{\alpha\alpha\alpha}RT/(V/x_\alpha)^3, \quad \alpha = 1, 2, 3$$

It also holds that classical partial pressures B, denoted P_α^B , can be obtained from (1)

$$P_\alpha^B = x_\alpha P, \quad \alpha = 1, 2, 3 \quad (24)$$

Tables 1 and 2 present the thermodynamic partial pressures P_α and the classical partial pressures P_α^A, P_α^B calculated, as explained above, for ternary mixture CH₄(1)-C₂H₆(2)-CO₂(3) at temperature $T = 320$ K, composition $x_1 = 0.3, x_2 = 0.3, x_3 = 0.4$ and two (total) pressures, $P = 5$ MPa and $P = 10$ MPa.

Because at low pressures state equation (18) converges to an ideal gas mixture (cf. (17)), all partial pressures converge to ideal gas pressure B, e.g. calculation of the same system at $P = 0.1$ MPa gave relations $P_1 = P_1^A = P_1^B = P_2 = P_2^A = P_2^B = 0.030$ MPa, $P_3 = P_3^A = P_3^B = 0.040$ MPa (with the precision of data shown in Tables 1 and 2).

In addition to a ternary gas mixture, we used a binary equimolar mixture of methane (1) and carbon

Tab. 3. Pressure $P = 10$ MPa, temperature $T = 320$ K, molar volume $V = 204.7$ cm³/mol, compressibility factor $PV/RT = 0.76947$, virial coefficients $B = -61.94$ cm³/mol, $C = 3018$ cm⁶/mol², pressures in MPa, *sum* = sum of pressures.

Constituents	CH ₄ (1)	CO ₂ (3)	<i>sum</i>
molar fractions x_α	0.5000	0.5000	-----
partial molar volumes V_α cm ³ /mol	253.4	156.0	-----
thermodynamic partial pressures P_α	6.186	3.814	10.000
A partial pressures P_α^A	6.026	5.010	11.036
B partial pressures P_α^B	5.000	5.000	10.000

Tab. 4. System LiOH(1)-H₂O(2) at 20 °C and atmospheric pressure $P = 101325$ Pa. The dimensions cm³/g for specific volumes, g/cm³ for densities, and Pa for pressures are used.

w_1	ρ	ν	$-\partial\tilde{v}/\partial w_1$	ν_1	ν_2	P_1	P_2	P_1^B	P_2^B
0	0.9982	1.0018	1.2903	-0.2885	1.0018	0	101325	0	101325
0.01	1.0103	0.9898	1.1488	-0.1475	1.0013	-151	101476	764	100561
0.02	1.0218	0.9787	1.0884	-0.0880	1.0004	-182	101507	1532	99793
0.04	1.0440	0.9578	0.9999	-0.0020	0.9978	-9	101334	3079	98246
0.06	1.0655	0.9386	0.9289	0.0654	0.9943	423	100901	4642	96683
0.08	1.0862	0.9206	0.8667	0.1232	0.9899	1085	100240	6221	95104
0.10	1.1063	0.9038	0.8101	0.1747	0.9849	1959	99366	7815	93510

dioxide (3) at a constant temperature of $T = 320$ K. In this case the state equation follows from (18), (19), (20) with $x_2 \equiv 0$, $x_3 = 1 - x_1$ expressed as

$$P = RT/V + BRT/V^2 + CRT/V^3 = P(T, V, x_1) \quad (25)$$

where now (with corresponding values (21), (22))

$$B = B_{11}x_1^2 + B_{33}x_3^2 + 2B_{13}x_1x_3 \quad (26)$$

$$C = C_{111}x_1^3 + C_{333}x_3^3 + 3C_{113}x_1^2x_3 + 3C_{133}x_1x_3^2 \quad (27)$$

As for the ternary gas mixture, for each pressure P and composition (given by x_1 ; $x_3 = 1 - x_1$), we calculated the molar volume $V = V(T, P, x_1)$, partial molar volumes V_α , concentrations c_α , and, using (5), (14), the thermodynamic partial pressures P_α ($\alpha = 1, 3$). The results at $T = 320$ K, (total) pressure $P = 10$ MPa, and composition $x_1 = 0.5$ are displayed in Table 3, which, again for comparison purposes, also includes classical partial pressures A and B calculated (for $\alpha = 1, 3$) from (23) and (24) respectively.

The dependence of partial pressures on composition x_1 in the binary system CH₄(1)-CO₂(3) at a temperature of $T = 320$ K and a (total) pressure of $P = 10$ MPa is demonstrated in Fig. 1 (which describes the results for approximately 200 compositions).

Again, in the limit of low pressures we obtained the same partial pressures as for an ideal gas mixture (cf. (17)), e.g. calculation of the same system at $P = 0.1$ MPa gave $P_1 = P_1^A = P_1^B = P_3 = P_3^A = P_3^B = 0.050$ MPa (with the precision of data shown in Table 3). In this limit also both triples of partial

pressures in Fig. 1 converge to lines 7 and 8, thus describing ideal gas with partial pressures P_α^B .

(Zhang et al. 1992) determined the state equation for the binary mixture He(1)-N₂(2) at 25 °C in the pressure range of 200–1000 MPa. From this data, the thermodynamic partial pressures were calculated by similar way (Samohýl V. 2007). For example, for the equimolar mixture at 1000 MPa, $P_1 = 290$ MPa (i.e. $P_2 = 710$ MPa) while $P_1^B = 500$ MPa (due to the limited validity of the state equation at low pressures, partial pressures A could not be calculated).

For the calculation of thermodynamic partial pressures in a liquid mixture we chose the binary system LiOH(1)-H₂O(2) using the known densities (Söhnel and Novotný 1983) of this aqueous solution at 20 °C and atmospheric pressure (we used standard pressure, 101325 Pa) (Almost the same results were obtained by (Samohýl V. 2007) with a rougher estimate of the derivatives (37) using the data from (d'Ans-Lax 1967).). Such a system is interesting because it involves negative partial molar volumes in diluted solutions. In this case, using (5), (14), it is possible to obtain negative thermodynamic partial pressures for LiOH(1) (because the total pressure is positive this negativeness is compensated by the higher thermodynamic partial pressure of water(2), cf. (4)), see Table 4 and Fig. 2.

According to (Söhnel and Novotný 1983) the density ρ (in g/dm³) of a solution of LiOH(1) in water(2) at a constant temperature t (in °C) and pressure $P = 101325$ Pa, depends on the molar concentration c_1 (in mol/dm³) of LiOH(1) as follows (see (Söhnel and Novotný 1983), eqs 45, 20)

(In (Söhnel and Novotný 1983) the dimensions kg/m^3 and kmol/m^3 are used for densities and molar concentrations respectively. The numerical values calculated here and in (Söhnel and Novotný 1983) are identical. Correspondingly, we use molar masses in g/mol .):

$$\rho = \rho_0 + Gc_1 + Hc_1^{3/2} \quad (28)$$

In the following relations, ρ_0 is the density (in g/dm^3) of pure water (2), and the coefficients G, H are dependent on temperature t :

$$\rho_0 = 999.65 + 2.0438t/10 - 6.1744t^{3/2}/100 \quad (29)$$

$$G = \mathcal{A} + \mathcal{B}t + \mathcal{C}t^2, H = \mathcal{D} + \mathcal{E}t + \mathcal{F}t^2 \quad (30)$$

For the LiOH-H₂O system, the constants $\mathcal{A}, \mathcal{B}, \mathcal{C}, \mathcal{D}, \mathcal{E}, \mathcal{F}$ have the following values (Söhnel and Novotný 1983) p. 106:

$$\begin{aligned} \mathcal{A} &= 30.16, \mathcal{B} = 0.04827, \mathcal{C} = -6.976 \times 10^{-4}, \\ \mathcal{D} &= -2.786, \mathcal{E} = -0.04538, \mathcal{F} = 5.916 \times 10^{-4} \end{aligned} \quad (31)$$

Therefore at temperature $t = 20$ °C, the following values are obtained for the density of pure water and the coefficients G, H :

$$\rho_0 = 998,215 \text{ g}/\text{dm}^3 \quad (32)$$

$$\begin{aligned} G &= 30.8464 \text{ g}/\text{mol}, \\ H &= -3.45696 \text{ g} (\text{dm}/\text{mol})^{3/2} \end{aligned} \quad (33)$$

Using (2), (10) we can express $c_1 = w_1\rho/M_1$, where M_1 is the molar mass of LiOH(l). Inserting this into (28) we obtain the function $f(\rho, w_1)$, which must be identical to zero:

$$\begin{aligned} f(\rho, w_1) &\equiv (H/M_1^{3/2})w_1^{3/2}\rho^{3/2} + \\ &+ ((G/M_1)w_1 - 1)\rho + \rho_0 = 0 \end{aligned} \quad (34)$$

Using (32), (33) and $M_1 = 23.950$ g/mol, we can calculate the dependence of ρ on mass fraction w_1 . From (6) we obtain the function $v = \tilde{v}(T, P, w_1)$, from which, using (8), (9), we calculate the partial specific volumes for $n = 2$ as follows:

$$v_1 = v + (1 - w_1)\partial\tilde{v}/\partial w_1 \quad (35)$$

$$v_2 = v - w_1\partial\tilde{v}/\partial w_1 \quad (36)$$

The required derivative follows from functions (34) and (6)

$$\begin{aligned} \partial\tilde{v}/\partial w_1 &= (1/\rho^2)(\partial f/\partial w_1)(\partial f/\partial \rho) \\ &= \left(\frac{3}{2}(H/M_1^{3/2})w_1^{1/2} + \rho^{-1/2} \frac{G}{M_1} \right) / \\ & / \left(\frac{3}{2}(H/M_1^{3/2})\rho w_1^{3/2} + \left(\frac{G}{M_1}w_1 - 1 \right)\rho^{1/2} \right) \end{aligned} \quad (37)$$

For the binary system LiOH(1)-H₂O(2) at a temperature of 20 °C and pressure $P = 101325$ Pa, equations (4) and (5) can be used to calculate the partial thermodynamic pressures P_1 and P_2

$$P_1 = \rho_1 v_1 P \quad (38)$$

$$P_2 = \rho_2 v_2 P = P - P_1 \quad (39)$$

The resulting values are displayed in Table 4. Repeating these calculations for approximately 200 values of w_1 (interval range 0–0.1) we obtained curves 1 and 2 (in Fig. 2) for the thermodynamic partial pressures of this mixture.

While, as explained in the Introduction, it is not possible to obtain classical partial pressures P_α^A of type A for liquid mixtures, classical partial pressures P_α^B can be obtained using for the system LiOH(1)-H₂O(2) (at 20 °C, 101325 Pa). The results are displayed in Table 4 and in Fig. 2. The dependence of P_α^B on w_1 is nonlinear, namely

$$P_1^B = Pw_1M_2/(M_1 + w_1(M_2 - M_1)), P_2^B = P - P_1^B \quad (40)$$

where M_1 is as above and $M_2 = 18.015$ g/mol.

Conclusions

Thermodynamic partial pressures, proposed for common fluid models in rational thermodynamics, were calculated for a (real) gas mixture of methane, ethane and carbon dioxide and for a liquid mixture of lithium hydroxide in water. The results for the gas mixture were compared with those obtained using the classical definitions. All definitions, the classical definitions and the formulation we have proposed in this paper, share the known property that the values of the partial pressures merge to an ideal gas mixture under low pressure. In this paper we have also shown that thermodynamic partial pressures may have negative values in a liquid mixture of lithium hydroxide in water.

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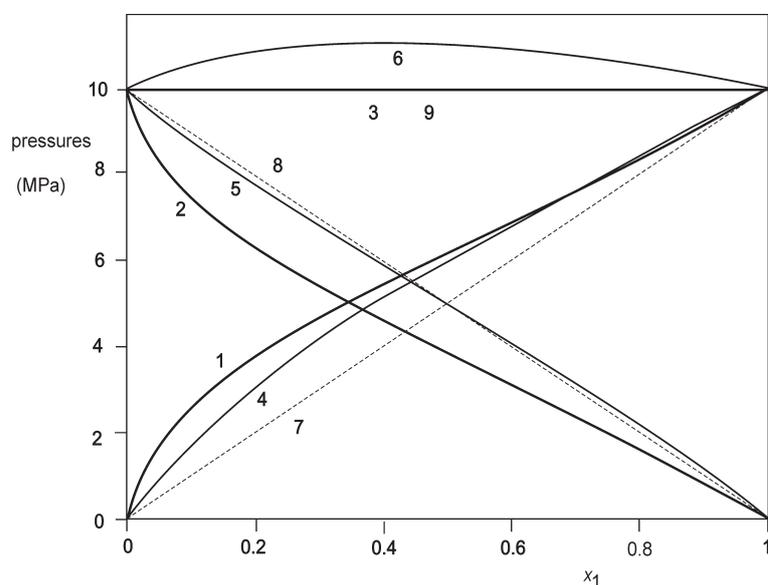


Fig. 1. The dependence of partial pressures (in MPa) on the molar fraction x_1 of methane in the binary gas mixture $\text{CH}_4(1) - \text{CO}_2(3)$ at a temperature of 320 K and total pressure $P = 10$ MPa.

Bold solid lines: 1. thermodynamic partial pressure P_1 of $\text{CH}_4(1)$; 2. thermodynamic partial pressure P_3 of $\text{CO}_2(3)$; 3. thermodynamic pressure P of mixture : sum of both thermodynamic pressures $P_1 + P_3$ (same as line 9). Solid lines: 4. classical partial pressure P_1^A of $\text{CH}_4(1)$; 5. classical partial pressure P_3^A of $\text{CO}_2(3)$; 6. sum of classical partial pressures $P_1^A + P_3^A$. Thin dashed lines: 7. classical partial pressure P_1^B of $\text{CH}_4(1)$; 8. classical partial pressure P_3^B of $\text{CO}_2(3)$; 9. sum of classical partial pressures $P_1^B + P_3^B$ (the same as the line 3.).

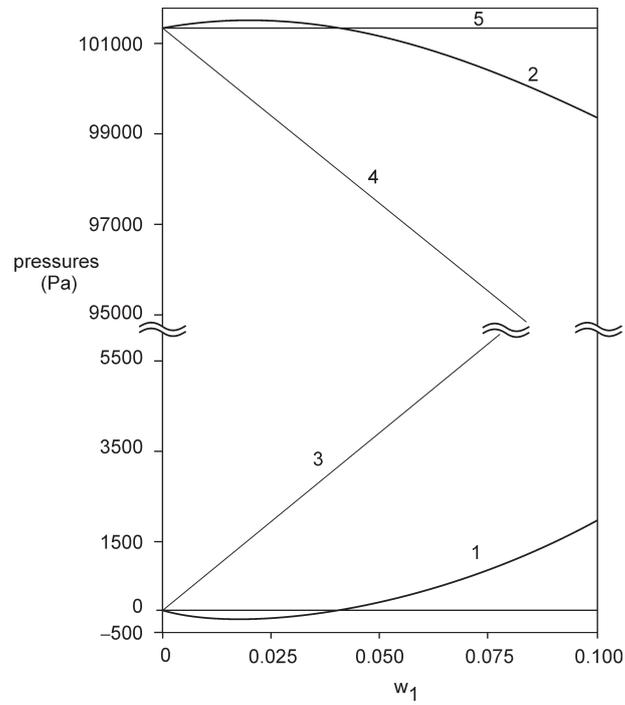


Fig. 2. The dependence of partial pressures (in Pa) on the mass fraction w_1 of LiOH in the binary liquid mixture LiOH(1) - H₂O(2) at a temperature of 20 °C and total (standard atmospheric) pressure $P = 101325$ Pa. Solid lines: 1. thermodynamic partial pressure P_1 of LiOH(1); 2. thermodynamic partial pressure P_2 of H₂O(2); 5. the sum of partial pressures of both types equals 101325 Pa. Thin solid lines: 3. partial pressure P_1^B of LiOH(1); 4. partial pressure P_2^B of H₂O(2).