Chapter 8

THERMODYNAMIC EVALUATION OF THE DUAL-FUEL PDE CONCEPT

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Three approximate approaches to determine the total pressure and gas-phase composition in water – hydrogen peroxide (HP) two-phase systems depending on solution composition and temperature are presented. Chemical composition is assumed to vary (e.g., due to HP decomposition) slowly as compared with the rate of physical relaxation processes. Although the approaches are based on different prerequisites, all of them are in good agreement with each other in terms of predictions of total pressure, activity coefficients, and equilibrium gas-phase composition. The approaches have been generalized on three- and four-component systems containing low-volatility (nonsolvable jet propulsion fuel (JPF)) and high-volatility (air) components. The results are discussed in view of the dual-fuel concept of pulse detonation engine (PDE) for advanced propulsion.

8.1 INTRODUCTION

The operational ability of an air-breathing liquid-fueled PDE is dependent on the fuel used. In authors' previous publications, a concept of a dual-fuel PDE has been suggested and substantiated [1–3]. The concept particularly implies the use of two liquid energetic materials: conventional JPF and HP*. In terms of the critical initiation energy, the gas-phase JPF–air mixtures with 5% and 20% of HP vapor were shown to be equivalent to stoichiometric ethylene–air and hydrogen–air mixtures, respectively [3]. As the dual-fuel air-breathing PDE [1–3] implies

*Contrary to other PDE concepts utilizing one fuel and two oxidizers (air and oxygen), this concept applies two liquid fuels (JPF and HP) and one oxydizer — air. The use of HP increases the energy density of the burning material and the detonation sensitivity of the JPF–HP blend. (*Editor's remark.*)

the use of liquid sprays of JPF and HP, it is important to know thermodynamic properties (activity coefficients, gas-phase composition, etc.) of the multiphase multicomponent mixture containing JPF, aqueous solution of HP, and air at high temperature and pressure. There is no general approximation that would be readily applicable to such two-phase systems [4–6].

This paper suggests three approximate analytical approaches for calculating total pressure $P(x,T)$ and activity coefficients of the H_2O_2–H_2O two-phase systems. The effect of JPF and air on the total pressure is also considered.

8.2 LIQUID–VAPOR PHASE EQUILIBRIUM CURVES FOR INDIVIDUAL COMPONENTS

For individual components, a two-parameter approximation [7–9] of pressure vs. temperature dependence along the phase equilibrium curve is used:

$$P(T) = \left[\left(\frac{T}{\alpha}\right)^{1/8} - A\right]^8 \tag{8.1}$$

where T is temperature in K, P is pressure in atm, α and A are parameters. Equation (8.1) provides very accurate results at relatively high pressure, including the critical point. Parameters α and A are determined by using experimental data for saturated vapor pressure vs. temperature. Equation (8.1) differs from other available approximations of the $P(T)$-curve by its simplicity and a possibility to resolve it in terms of a simple temperature vs. pressure dependence:

$$T(P) = \alpha[Z + A]^8\,, \quad Z \equiv \left(\frac{P}{P_0}\right)^{1/8}, \quad P_0 = 1 \text{ atm} \tag{8.2}$$

For water, HP, and n-tetradecane (to simulate JPF), the liquid–vapor phase equilibrium curves have the following explicit formulae:

$$P_w(T) = \left[\left(2.8836 \cdot 10^6 T\right)^{1/8} - 12.4575\right]^8 \tag{8.3}$$

$$P_{\mathrm{HP}}(T) = \left[\left(2.6566 \cdot 10^6 T\right)^{1/8} - 12.5302\right]^8 \tag{8.4}$$

$$P_{\mathrm{JPF}}(T) = \left[\left(7.5324 \cdot 10^5 T\right)^{1/8} - 10.8801\right]^8 \tag{8.5}$$

Parameters α and A for water and n-tetradecane were determined by using tables of thermodynamic data [11, 10]; for HP they were calculated by using nonlinear regression and 8 points on a 4-parameter $P(T)$-curve approximation [11]:

$$\log P_{HP}(\text{mm Hg}) = C_0 + \frac{C_1}{T} + C_2 \log T + C_3 T \tag{8.6}$$

Table 8.1 Comparison between liquid–vapor phase equilibrium curves (Eqs. (8.3) to (8.5)) and experimental data [10, 12] for water and n-teradecane, and with the approximation of experimental data [13] by Eq. (8.6) for HP. $\Delta P/P$ is the error of approximation. Last lines of each block correspond to the critical points

	Water		
T (K)	P (kgf/cm^2) [14]	P (kgf/cm^2), Eq. (8.3)	$\lvert\Delta P/P\rvert$, %
73.15	1.0332	1.0364	0.31
423.15	4.854	4.8616	0.16
473.15	15.857	15.76 0	0.62
523.15	40.56	40.326	0.58
573.15	87.61	87.641	0.03
623.15	168.63	169.15	0.31
633.15	190.42	190.72	0.16
638.15	202.21	202.25	0.02
643.15	214.68	214.31	0.17
647.30	225.65	224.72	0.41
	Hydrogen peroxide		
T (K)	P (atm), Eq. (8.6)	P (atm), Eq. (8.4)	$\lvert\Delta P/P\rvert$, %
423.15	0.994	1.012	1.8
473.15	4.004	4.069	1.6
523.15	11.99	12.06	0.6
573.15	29.19	29.19	0
623.15	61.23	61.17	0.1
673.15	115.2	115.2	0
723.15	199.9	199.8	0.03
730.15	214	214.66	0.3
	n-tetradecane		
T (K)	P (mm Hg) [15]	P (mm Hg), Eq. (8.5)	$\lvert\Delta P/P\rvert$, %
423.15	34.57	34.386	0.5
433.15	50.73	50.714	0.03
453.15	102.28	102.55	0.2
473.15	190.99	191.32	0.7
493.15	334.34	334.33	0
513.15	553.9	553.49	0.07
533.15	875.52	875.69	0.02
695.15	$\sim$ 16 atm	16.6 atm	—

$$C_0 = 44.5760; \quad C_1 = -4025.3; \quad C_2 = -12.996; \quad C_3 = 0.0046055$$

Table 8.1 shows the accuracy of Eqs. (8.3) to (8.5) as compared to the experimental data (for water and n-tetradecane) and to Eq. (8.6) (for HP). The error of the approximations at pressure 0.003 atm $\leq P \leq P_c$ (P_c is the critical pressure) is typically a fraction of percent*.

*It would be interesting to apply Eq. (8.1) or determining the phase-equilibrium curve for JP-10. (*Editor's remark.*)

Considering HP as an individual substance and a component of solution, the authors digress from considering the kinetic issues of its stability in terms of decomposition and other chemical transformation. This is acceptable if the local characteristic time of attaining the conditional thermodynamic equilibrium (at "frozen" chemical composition of the solution) is less than the characteristic times of chemical relaxation. The probability of violation of this condition increases with temperature. Here, quantitative criteria for the existence of this type of conditional equilibrium are not formulated.

8.3 CALCULATION OF THE TOTAL PRESSURE OF TWO-PHASE SYSTEM AT ISOTHERMS

8.3.1 Correlation Based on Redlich–Kister Method

To provide the correlation for the total pressure $p(x,T)$, the authors [13] use the formula:

$$P(x,T) = \gamma_{\mathrm{HP}} P_{\mathrm{HP}}(T)x + \gamma_w P_w(T)X \tag{8.7}$$

where x and $X = 1 - x$ are the molar fractions of HP and water, respectively, γ_{HP} and γ_w are the corresponding activity coefficients. To calculate γ_{HP} and γ_w, the following relationships [14] are used:

$$\gamma_w = \exp\left\{\left(\frac{x^2}{RT}\right)[B_0 + B_1(1-4X) + B_2(1-2X)(1-6X)]\right\} \tag{8.8}$$

$$\gamma_{\mathrm{HP}} = \exp\left\{\left(\frac{X^2}{RT}\right)[B_0 + B_1(3-4X) + B_2(1-2X)(5-6X)]\right\} \tag{8.9}$$

Parameters B_0, B_1, and B_2 in Eqs. (8.8) and (8.9) were determined by fitting the results provided by Eq. (8.7) with the experimental data. For this purpose, total pressure of aqueous solutions of HP at several values of x, at 5 isotherms (T = 317.65 K, 333.15, 348.15, 363.15, and 378.15 K) was measured [13]. The data for phase equilibrium curves $P_{\mathrm{HP}}(T)$ and $P_w(T)$ have been taken from literature. As a result, the following expressions for B_0, B_1, and B_2 have been obtained (dimension in cal/mol):

$$B_0 = -1017 + 0.97T\,, \quad B_1 = 85\,, \quad B_2 = 13 \tag{8.10}$$

When substituting Eqs. (8.8) and (8.9) for γ_w and γ_{HP} and Eqs. (8.3) and (8.4) for $P_w(T)$ and $P_{\mathrm{HP}}(T)$ into Eq. (8.7) and using Eqs. (8.10), one obtains the explicit analytical dependence $P(x,T)$. Application of Eqs. (8.8) and (8.9), that are based on low-temperature data ($T \leq 378$ K) to high temperatures can be considered as extrapolation. Its accuracy can be estimated by comparing the results obtained by different methods (see below).

8.3.2 Correlation Based on Similarity of Component Properties

For systems containing components with similar thermodynamic properties, the values of α and A in Eq. (8.1) appear close (e.g., for water and HP they differ by 8.5% and 0.6%, respectively). It is reasonable to assume that for such systems, Eq. (8.1) can be used for estimating $P(x,T)$. In this case, parameters α and A in Eq. (8.1) can be approximated as linear combinations:

$$\alpha(x) = \alpha_1(1-x) + \alpha_2 x\,, \quad A(x) = A_1(1-x) + A_2 x \tag{8.11}$$

with indices 1 and 2 corresponding to components of a binary solution, and $1-x$ and x representing their molar fractions. Within this approximation, Eqs. (8.1) and (8.2) provide isothermal dependence of pressure and isobaric dependence of temperature on solution composition, respectively. Application of Eqs. (8.1) and (8.11) to aqueous solutions of HP results in the following approximation for $P(x,T)$:

$$\begin{aligned} P(x,T) &= \left[\left(\frac{T}{\alpha(x)}\right)^{1/8} - A(x)\right]^8 \\ \alpha(x) &= 3.4679 \cdot 10^{-7}(1-x) + 3.7642 \cdot 10^{-7} x \\ A(x) &= 12.4575(1-x) + 12.5302x \end{aligned} \tag{8.12}$$

8.3.3 Correlation Based on Boiling Temperature of Binary Solution

The other approach for estimating $P(x,T)$ is based on Eq. (8.2). If one knows the dependence $T_b(x,P)$ of the solution boiling temperature T_b on solution composition at $P = const$, then the procedure of determining $P(x,T)$ is straightforward.

Figures 8.1*a* and 8.1*b* show the measured dependences of T_b on HP concentration in aqueous solutions [16] at total pressure $P = 0.04$ atm (Fig. 8.1*a*) and $P = 1$ atm (Fig. 8.1*b*). It follows from Fig. 8.1 that function $T_b(x,P)$ at $P = const$ is almost linear, at least within the range $P = 0.04$–1 atm. This finding allows one to assume that the isobaric function $T_b(x,P)$ remains approximately linear for higher pressures. Although this assumption is insufficiently substantiated due to the lack of available experimental data, a general trend of balancing the thermodynamic properties of liquids and dense gases with temperature can serve as the indirect indication of its validity. With this in mind, function $T_b(x,P)$ is represented as a linear combination:

$$T_b(x,P) = T_w(P)(1-x) + T_{\mathrm{HP}}(P)x \tag{8.13}$$

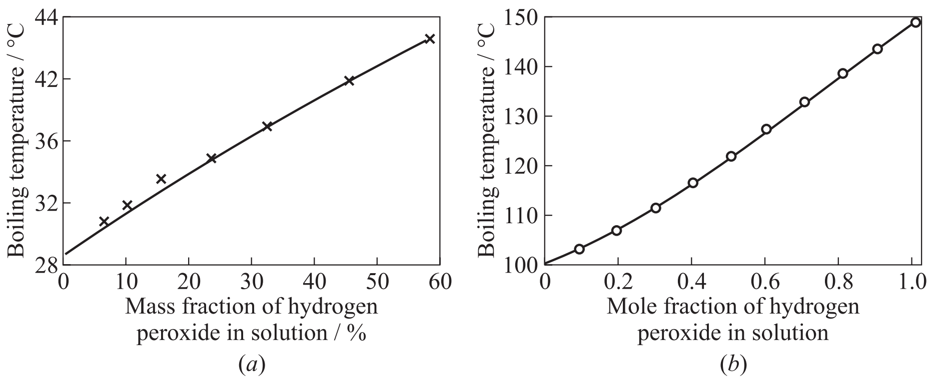

Figure 8.1 Experimental dependencies of the boiling temperature on the mass and mole fraction of HP in aqueous solution at $P = 0.04$ atm (a), and $P = 1$ atm (b) Experiments [15]

where $T_w(P)$ and $T_{\rm HP}(P)$ are given by (see Eq. (8.2)):

$$\begin{aligned} T_w(P) &= 3.4679 \cdot 10^{-7}[Z + 12.4575]^8 \\ T_{\rm HP} &= 3.7642 \cdot 10^{-7}[Z + 12.5302]^8 \\ Z &\equiv \left(\frac{P}{P_0}\right)^{1/8}, \quad P_0 = 1 \text{ atm} \end{aligned} \tag{8.14}$$

Substituting Eqs. (8.14) into Eq. (8.13) results in an equation relating T_b, P, and x. Thus, for a given $T = T_b$ one obtains the equation determining $P(x, T)$ implicitly:

$$T = 3.4679 \cdot 10^{-7}[Z + 12.4575]^8(1 - x) + 3.7642 \cdot 10^{-7}[Z + 12.5302]^8 x \tag{8.15}$$

8.4 RESULTS OF TOTAL PRESSURE CALCULATIONS

Figure 8.2 shows the example of total pressure calculations at isotherm $T = 573$ K for aqueous solutions of HP. The curves are marked with abbreviations corresponding to various approximations: RK stands for Redlich–Kister approach (Eqs. (8.7) to (8.10)); CS for "Component Similarity" approach (Eqs. (8.12), and BT for "Boiling Temperature" approach (Eq. (8.15)). To distinguish between curves CS and BT, the CS curve is plotted as dashed curve. In addition, "Ideal

Solution" — IS curve is plotted in Fig. 8.2. Within the ideal solution approximation, the total pressure is determined by Eq. (8.7) with $\gamma_w = \gamma_{\mathrm{HP}} = 1$, i.e.,

$$P(x,T) = P_{\mathrm{HP}}(T)x + P_w(T)X \tag{8.16}$$

The difference between the calculated results for nonideal solutions attains a maximum value at $x \approx 0.3$–0.4 for all isotherms within the temperature range $373 \le T \le 623$ K. The maximum difference in the total pressure predicted by the approaches of Sections 8.3.1 to 8.3.3 is 13% at $T = 373$ K, 8% at $T = 423$ K, 5% at $T = 573$ K, 3.5% at $T = 523$ K, 3% at $T = 573$ K, and 2.6% at $T = 623$ K. The remarkable feature of the comparison is that a good agreement between the predicted values of total pressure exists even at 573 and 623 K, i.e., in the domain where the gas-phase density is high and interaction between molecules in the gas phase becomes significant. Equations (8.12) and (8.15) provide almost identical dependencies $P(x,T)$. The maximum difference of less than 2% is attained in the vicinity of $x = 0.3$.

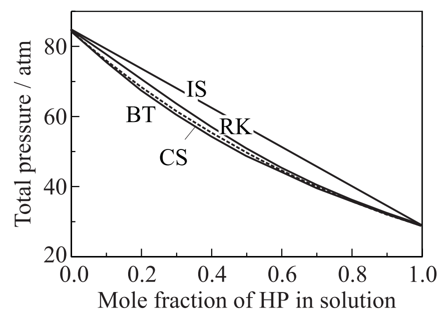

Figure 8.2 Predicted dependencies of total pressure on the mole fraction of HP in aqueous solution at $T = 573$ K

The value of total pressure predicted by the ideal-solution relationship (8.16) differs considerably from the values provided by other approaches.

8.5 CALCULATION OF ACTIVITY COEFFICIENTS AND GAS-PHASE COMPOSITION

Parameters B_0, B_1, and B_2 entering Eqs. (8.8) and (8.9) for the activity coefficients were obtained [13] based on the limited set of low-temperature ($T \le 378$ K) experimental data on the total pressure of binary water–HP system for several values (x,T). As Sections 8.3.2 and 8.3.3 provide the approximate expressions for $P(x,T)$ that are applicable at temperatures ranging from 330–370 K to $T \le T_c$, it becomes possible to determine B_0, B_1, and B_2 more precisely for the extended temperature range. For this purpose, Eq. (8.7) combined with Eqs. (8.3) and (8.4) was applied to determine B_0, B_1, and B_2 by attaining the best least square fit with the $P(x,T)$-dependence of Eq. (8.12). Two approximations were used: in the first (referred to as II-parameter approximation), parameter B_2 in Eqs. (8.8) and (8.9) was taken zero; in the second (III-parameter approximation), all three parameters B_0, B_1, and B_2 were determined. It was found that the dependencies of B_0, B_1, and B_2 on T are very regular. The following exponential interpolations were obtained for the II-parameter approximation:

$$
\begin{aligned}
B_0^{(II)} &= -431.31 - 225 \exp \frac{423.15 - T}{125.54} \\
B_1^{(II)} &= 201.0 + 247.1 \exp \frac{423.15 - T}{121.3} \\
B_2^{(II)} &= 0
\end{aligned}
\tag{8.17}
$$

and for the III-parameter approximation:

$$
\begin{aligned}
B_0^{(III)} &= -376.69 - 197.41 \exp \frac{438.39 - T}{112.81} \\
B_1^{(III)} &= 99.21 + 110.77 \exp \frac{445.66 - T}{140.69} \\
B_2^{(III)} &= -106.62 - 189.07 \exp \frac{438.58 - T}{111.79}
\end{aligned}
\tag{8.18}
$$

Maximum interpolation errors are 0.2% for $B_0^{(II)}$ and 0.7% for $B_1^{(II)}$ (Eqs. (8.17)), and 0.2% for $B_o^{(III)}$, 0.2% for $B_1^{(III)}$ and 0.8% for $B_2^{(III)}$ (Eqs. (8.18)).

Equations (8.8) and (8.9) in combination with Eqs. (8.17) or (8.18) can be used for calculating γ_{HP} and γ_w. Then, one can determine the equilibrium composition of gas phase in the water–HP system by applying the following formulae:

$$
Y = \frac{\gamma_w P_w(T) X}{P(x,T)} \tag{8.19}
$$

$$
y = \frac{\gamma_{\mathrm{HP}} P_{\mathrm{HP}}(T) x}{P(x,T)} \tag{8.20}
$$

where Y and y are the molar fractions of water and HP vapor, respectively.

Alternatively, for gas phase obeying the Dalton's law, y can be obtained directly (i.e., without calculating γ_{HP} and γ_w) using the Duhem's equation [6]:

$$
\left(\frac{\partial \ln P}{\partial y} \right)_T = \frac{y - x}{y(1-y)} \tag{8.21}
$$

If the total pressure P is known as a function of y (along the isotherm) then Eq. (8.21) provides algebraic or transcendental dependence $y(x)$ at a given T. Usually, total pressure is known as a function of solution composition, x. By changing variables from y to x in Eq. (8.21), one can arrive at the differential equation for water concentrations in the two-phase water–HP system:

$$\frac{dY}{dX} = \frac{Y(1-Y)}{Y-X} Z(X,T)\,, \quad Z(X,T) = \left(\frac{\partial \ln P}{\partial X}\right)_T \tag{8.22}$$

To find a unique integral curve of Eq. (8.22), it is necessary to specify a point on the curve. For this purpose, one can choose a singular point at the edge of interval $0 \leq X \leq 1$, where the molar fraction of one component in solution and in gas phase is zero. It can be shown that the singular point $X = 0$, $Y = 0$ is of saddle type and Eq. (8.22) should be integrated from this point.

Thus, the gas-phase composition in the water–HP system can be determined by using Eqs. (8.19) and (8.20) or by direct integration of Eq. (8.22). It is instructive to compare the results provided by the both approaches. Although the latter approach does not require evaluation of γ_w and $\gamma_{\rm HP}$, the calculated dependencies $Y(X)$ or $y(x)$ can be used to calculate γ_w and $\gamma_{\rm HP}$ by using Eqs. (8.19) and (8.20). The activity coefficients thus obtained are compared in Fig. 8.3 for $T = 523$ K. Both II- and III-parameter approximations of Eqs. (8.17) and (8.18) for B_0, B_1, and B_2 were applied. The discrepancy in γ_w values obtained by direct integration of Eq. (8.22) and using Eqs. (8.8) and (8.9) with II- and III-parameter approximations for B_0, B_1, and B_2 does not exceed 4% within interval $0 \leq x \leq 0.9$. However, at $0.9 \leq x \leq 1$, i.e., at the interval where water concentration in solution is small ($X \ll 1$), the discrepancy is getting higher and it is both quantitative and qualitative (see dotted line in Fig. 8.3 depicting the result relevant to II-parameter approximation). The use of the III-parameter approximation does not diminish the discrepancy (see dashed line in Fig. 8.3). However, discrepancies relevant to II- and III-parameter approximations exhibit different sign within wide range of x. In view of it, one can naturally suggest a better approximation for the activity coefficients that is based on the arithmetic means:

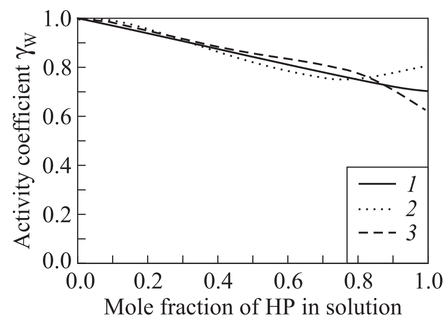

Figure 8.3 Predicted dependencies of water activity coefficient γ_w on the mole fraction of HP in aqueous solution at $T = 523$ K: *1* — integration of Duhem's equation; *2* — II-parameter approximation; and *3* — III-parameter approximation

$$\gamma_w = \frac{\gamma_w^{(II)} + \gamma_w^{(III)}}{2}\,, \quad \gamma_{\rm HP} = \frac{\gamma_{\rm HP}^{(II)} + \gamma_{\rm HP}^{(III)}}{2} \tag{8.23}$$

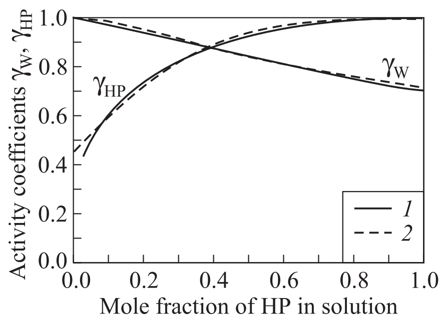

Figure 8.4 Predicted dependencies of activity coefficients γ_{HP} and γ_w on the mole fraction of HP in aqueous solution at $T = 523$ K; *1* — integration of Duhem's equation; and *2* — approximation given by (Eqs. 8.23)

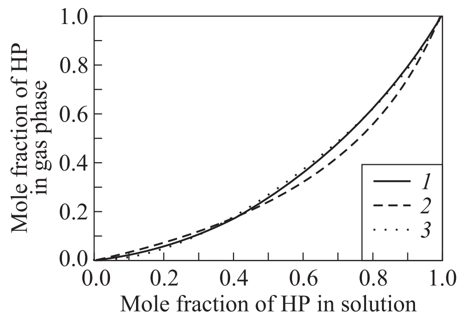

Figure 8.5 Predicted dependencies of HP mole fractions in gas phase on the HP mole fraction aqueous solution at $T = 523$ K: *1* — integration of Duhem's equation; *2* — ideal solution approximation; and *3* — approximation given by Eqs. (8.23)

where indices II and III correspond to II- and III-parameter approximations, respectively.

The accuracy of approximation given by Eqs. (8.23) in relation to the numerical solution of Eq. (8.22) is illustrated in Figs. 8.4 and 8.5. Solid curves in Fig. 8.4 show the results of calculations of γ_w and $\gamma_{\rm HP}$ based on function $Y(X)$ obtained by direct integration of Eq. (8.22) along isotherm $T = 523$ K. Dashed curves in Fig. 8.4 correspond to approximation given by Eqs. (8.23). Solid curve in Fig. 8.5 shows the results of direct integration of Eq. (8.22). Dotted curve in Fig. 8.5 corresponds to approximation given by Eqs. (8.23); dashed curve corresponds to ideal solution approximation.

It follows from Fig. 8.4 that at $x > 0.02$, mean and maximum discrepancies $|\Delta\gamma_i|/\gamma_i$ are, respectively, fractions of percent and 4%–6%. However, gas-phase HP concentrations determined by Eqs. (8.20) and (8.23) differ from those obtained by direct integration of Eq. (8.22) no more than by 0.011 at $T = 423$ K and 0.006 at $T = 523$ K at all $0 \leq x \leq 1$ (see Fig. 8.5). Such accuracy allows one to apply Eqs. (8.20) and (8.23) for practical calculations of gas-phase composition at given x and T rather than directly integrate the Duhem's equation (8.22).

8.6 IDEAL SOLUTION APPROXIMATION

The fact that coefficients γ_w and $\gamma_{\rm HP}$ can be considerably less than unity (see Figs. 8.3 and 8.4) indicates that aqueous solutions of HP do not obey the ideal solution laws, in particular, at small x or X. Nonideality of the solutions has a relatively insignificant effect on the total pressure. Nevertheless, it results in a considerable variation of the deficient gas-phase component, i.e., the component that can be considered as a small additive in the gas phase. With increasing temperature, the activity coefficients tend to unity. The accuracy of formulae used for evaluation of γ_w and γ_{HP} decreases with the gas-phase density and, correspondingly, with the degree of gas phase departing from the ideal gas law. However, as the gas-phase density approaches the liquid density along the phase equilibrium curve one can expect that realistic activity coefficients are closer to unity than the estimated values.

8.7 TERNARY SYSTEM WATER – HYDROGEN PEROXIDE – AIR

Consider the effect of air on the phase equilibrium of aqueous solutions of HP. When the volume V_G occupied by a three-component gas phase is large as compared to the volume V_L occupied by the liquid solution, and air pressure P_A is not too high (e.g., $V_G > V_L$ and $P_A < 10$ atm), the fraction of air solved in the solution is negligibly small as compared to both the mole fraction of air in the gas phase and to mole fractions of other components. Due to low compressibility of liquid, variation of gaseous pressure caused by the presence of air does not affect significantly the thermodynamic state of solution and, in particular, the chemical potentials of main solution components. Chemical potentials of main components in the gas phase remain also unaffected if the molar fraction of air is small or if the total pressure does not exceed several dozens of atmospheres. If the chemical potentials of main components in the solution and in the gas phase are independent of the air partial pressure, all above formulae and equations determining $P(x,T)$ and binary system composition remain valid (with the original normalization: $x + X = 1$, $y + Y = 1$). The total pressure of the three-component system (denoted as $\Pi(x,T,\rho_A)$) within the ideal gas approximation will be given as a sum:

$$\Pi(x,T,\rho_A) = P(x,T) + P_A\,, \quad P_A = \frac{\rho_A RT}{\mu_A}$$

where ρ is the density, μ is the molecular mass, and subscript A denotes properties of air.

8.8 TERNARY SYSTEM WATER–HYDROGEN PEROXIDE–JET PROPULSION FUEL

Herein, JPF is modeled by n-tetradecane (NTD). NTD differs from water and HP by low volatility. For example, at temperature $T = 423$ K the saturated vapor pressure of NTD is 34.6 mm Hg, that is 103 times less than the corresponding water vapor pressure and 22 times less than HP vapor pressure. NTD is not soluble in aqueous solutions of HP and may form emulsions similar to water-in-oil emulsions. In such emulsions, NTD affects thermodynamics of the water–HP binary subsystem through the gas-phase pressure (with the accuracy of the order of inter-phase surface effects in emulsion), as the partial pressure of NTD vapor contributes to the total pressure. However, taking into account the above examples for the vapor pressure of individual components, this contribution is insignificant and the effect of NTD on the equilibrium composition of the water–HP subsystem is negligible. As for the effect of water and HP vapors on the phase equilibrium of NTD itself, it is also insignificant, at least at $T \leq 523$ K. At $T = 523$ K, the density of gas phase in the water–HP system is approximately two orders of magnitude less than the liquid density, and the Dalton's law relating the partial pressures of components is still valid. However, at higher temperatures and, correspondingly, higher densities of the gas phase, the chemical potential of NTD vapor changes considerably (increases) due to intermolecular interaction (with domination of repulsive forces). As a result, phase equilibrium of NTD is shifted towards lower vapor pressure. Quantitative description of these effects is beyond the scope of this paper.

8.9 CONCLUDING REMARKS

Approximate approaches to estimate the total pressure in water–HP system are presented. Chemical composition of the system is assumed to be either "frozen" or varying slowly as compared with the rate of physical relaxation processes. Although the approaches are based on different prerequisites, they are in a good agreement with each other in terms of predictions of total pressure, activity coefficients, and equilibrium gas-phase composition. In the approach of Section 8.3.1, total pressure was calculated as a sum of partial pressures of water and HP vapors. In Sections 8.3.2 and 8.3.3, the concept of partial pressure was not used at all. The expression for the total pressure derived in Section 8.3.2 does not incorporate the ideal gas approximation and is applicable within the entire temperature range where each of the solution components exists in both liquid and gas phases. It is hardly possible that a good agreement (within a wide temperature range including the critical temperature of water) between the predictions is occasional. More preferably, all the approaches give realistic approximations for $P(x,T)$. The extended validity of the approach of Section 8.3.1 (based on the ideal gas law) for calculating $P(x,T)$ is most probably caused by compensation of errors in the approximations for the binary system under consideration.

The activity coefficients and the equilibrium gas-phase composition have been calculated by using relationships based on the Dalton's law. This also applies to the Duhem's equation in the form of Eq. (8.22). For water–HP system this approach is approximately valid at $T \leq 520$ K. Comparison of activity coefficients and gas-phase composition obtained within the Redlich–Kister approximations and by numerical integration of Eq. (8.22) indicates that the modified approach of Eq. (8.23) agrees well with the solution of Eq. (8.22). With this modification, Eqs. (8.8), (8.9), (8.17), (8.18), and (8.23) provide the explicit and fairly accurate dependencies of activity coefficients on solution composition and temperature. Based on the activity coefficients, gas-phase composition can be readily obtained by using the approximations for the total pressure and Eqs. (8.3) and (8.4). Application of these formulae for estimating activity coefficients and gas-phase concentrations at higher temperatures ($T > 520$ K) should be considered as extrapolation. The accuracy of this extrapolation can be worse as compared to total pressure calculations.

The approaches for calculating equilibrium gas-phase composition in a two-phase system containing aqueous solution of HP, air, and JPF are also suggested. The further step in evaluating the performance of the dual-fuel air-breathing PDE [1–3] is to incorporate chemical kinetics of HP decomposition and JPF oxidation. Preliminary results on simulation of JPF (or HP) liquid drop ignition and combustion in air with HP (or JPF) vapor have been reported [16].

ACKNOWLEDGMENTS

The work was performed under ONR contract.

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