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Book Reviews

Moist Gases: Thermodynamic Properties. By V. A. Rabinovich and V. G. Beketov. Begell House, Inc., New York. 1995. 176 pp. $117.50. ISBN 1-56700-033-9.

This new book has a great deal of valuable information on the thermodynamic properties of mixtures of water vapor with a number of “dry gases”; the latter include air, nitrogen, oxygen, methane, hydrogen, helium, neon, argon, krypton, xenon, carbon dioxide, and ethane. At each temperature and pressure, the specific volume, enthalpy, entropy, isobaric heat capacity, partial pressure of water vapor, moisture content by weight, absolute moisture content, and average molecular weight are provided from 200 to 400 K and pressures to 10 MPa at relative moisture contents of 0.2, 0.4, 0.6, 0.8, and unity. However, the book relies heavily on previous correlations, many about 20 years old, for many properties, including pure and cross virial coefficients, many of which have been measured or remeasured since that time. There are also basic problems with definitions such as partial pressure, so one must use the tabular values with caution and understand exactly which equation has been used for their calculation, as next discussed in detail.

We are dealing with binary gas mixtures of some *dry gas* (1) with water vapor (2). We cannot expect a saturated CO_2/H_2O mixture at 400 K and 10 MPa, for example, to be an ideal solution (IS), let alone a perfect gas mixture (pgm). If we ignore the solubility of the gas in the aqueous liquid, as done by the authors, the partial pressure of water vapor is

$$Py_2 = P_2^{\sigma}(\mathrm{PC})_2/\Phi_2^{\sigma} \qquad (1)$$

where P_2^{σ} is the vapor pressure of water and $(\mathrm{PC})_2$ is the Poynting correction for the fugacity of pure liquid water from the vapor pressure to system pressure. As we are well below the critical temperature of water (647 K), this correction is a maximum of 1.0579 at 10 MPa and 400 K. Φ_2^{σ} is the combined fugacity coefficient ($\hat{\phi}_2^{\sigma}/\phi_2^{\sigma}$), where the first coefficient is for the *gas mixture* and the second is for pure steam at its vapor pressure. Assuming a second virial gas mixture (SVGM),

$$\ln(\Phi_2^{\sigma}) = [(P - P_2^{\sigma})B_{22}/RT] + (P{y_1}^2\delta_{12}/RT) \qquad (2)$$

where $\delta_{12} = 2B_{12} - B_{11} - B_{22}$. The authors have included some, but not all, of the terms for a *third virial gas mixture*; the simplified SVGM equations here are sufficient to show some of the problems in the book. First, after correctly defining the partial pressure as in eq 1, the authors calculate it in their eq 4.19 as (n_2z_2RT/V), where n_2 is moles of water vapor in the total volume V and z_2 is the compressibility factor for pure water vapor at the same temperature and pressure as that of the gas mixture. This term is then $y_2z_2(nRT/V)$ and the total pressure P, being *always* the sum of partial pressures, is $P = (y_1z_1 + y_2z_2)\cdot(nRT/V)$, a familiar result for the ideal solution assumption. It is this partial pressure that is tabulated throughout the tables as $\bar{p}_2$, but it cannot equal Py_2 except upon approaching zero pressure or when the high-pressure mixture is truly an ideal solution ($\delta_{12} = 0$). In our example of a saturated CO_2/H_2O mixture at 400 K and 10 MPa, the two terms on the right-hand side of eq 2 are −1.0383 and +0.6977 (δ_{12} = 250.2 cm^3/mol), respectively, from the reviewer’s laboratory (Patel; et al. Thermophysical Properties of Gaseous Carbon Dioxide-Water Mixtures. *Fluid Phase Equilibria* **1987**, *36*, 279−299). Then $\Phi_2^{\sigma} = 0.7113$ and $Py_2 = 365$ kPa from eq 1. Then y_2 is 0.0365 in rough agreement with the authors’ saturation value of 0.0370 corresponding to the value of $c_{\mathrm{eq}} = 0.0155$, the fractional content of water in the vapor on a mass basis, from their Table XXI. The ~1.4% difference is expected as I am not using third virial coefficient corrections and am using a different value of B_{12} (and hence δ_{12}), as discussed below. However, what is very different is the authors’ value of the partial pressure of 430.8 kPa calculated from $\bar{p}_2 = y_2z_2(nRT/V) = (y_2RT/v)[1 + (y_2B_{22}/v)]$, where v is the molar (not molal) specific volume of the gas mixture. Although the authors have used the correct saturation value of 0.0370 for y_2 to calculate $\bar{p}_2$, they are then left with the dilemma that their correct original definition of partial pressure as Py_2 (see eq 1.29) now yields y_2 = (430.8 kPa/10 MPa) = 0.043 08 or an inconsistency of about 16.5%! This discrepancy will be less for gas mixtures at lower total pressure as we approach a pgm, which is a special case of an ideal solution (all $B_{ij} = 0$). At higher pressures deviations from pgm also mean deviations from IS, as δ_{12} is strongly positive. Thus, this inconsistency between the *equilibrium molar faction of water vapor*, the first table given for each gas, and the thermodynamic properties, the second table given for each gas, is found to some degree in all of the tables in the appendix of the book. To correct the second table: (1) ignore values of $\bar{p}_2$ given therein, (2) calculate y_2(sat.) from c_{eq} of the first table at the same total pressure and temperature as noted above, (3) when $\varphi \equiv [y_2/y_2(\mathrm{sat.})]$ is not unity calculate the water vapor y_2 as φy_2(sat.), and (4) multiply by the total pressure to get the correct partial pressure.

A separate but minor problem with the second table is that M is the average molecular weight of the gas mixture but its units are given as *kg/mol* but this is obviously per kg mol not per g mol. Also v is described in the text as the molar volume but printed in the tables as 10^{-3} m^3/kg or volume per unit mass. The Mv product from the tables is the molar volume but as 10^{-3} m^3/(kg mol) or cm^3/(g mol).

Several problems with fundamentals appear in Chapter 1. First, eq 1.15 is a special form of the Gibbs−Duhem equation at constant pressure and temperature. Second, at the start of section 1.2, there is a misunderstanding of what is Dalton’s law. It is *not* that the partial pressures sum to the total pressure as this is true for any solution, liquid, or gas, where the partial pressure is correctly defined, as done here by the authors. Rather Dalton found that the pressure of a mixture in a fixed-volume container was the sum of the pressures for each pure component occupying that same container at the same temperature. He was working with mostly atmospheric gases at low pressures and near ambient temperatures, so they formed nearly pgm. There is thus a one-to-one correspondence between Dalton’s law and pgm (all B_{ij} = 0) and also between Amagat’s law and IS (δ_{ij} = 0, for gases) with a pgm being a special case of an IS. Both lead to $z_{\mathrm{m}} = \sum z_ix_i$ but with the important difference that the pure-component z_i is evaluated at the mixture pressure under Amagat’s law but at the partial pressure Px_i under Dalton’s law. For this reason, in practice, Dalton’s law never works unless the z_i’s are all unity, whereas Amagat’s law works for many hydrocarbon gas mixtures to high pressures and also hydrocarbon liquid mixtures. However, moist gas mixtures at high pressures will obey neither law although that of Amagat will be closer than that of Dalton. The authors have later used Amagat's law to calculate their $\bar{p}_2$, as noted previously.

A final problem, as noted above, is that while the pure-component second and third virial coefficients appear reasonable in comparison with more recent measurements for water vapor, CO_2, ethane, and other dry gases, the interaction or cross coefficients, B_{12}, C_{112}, and C_{122}, do not always agree even approximately. For our example above, $B_{12} = -81.7$ cm^3/(g mol) as measured by Patel et al. but the authors show -96.2 at 400 K in Table 3.11.7 as estimated from a Lennard-Jones intermolecular potential model. It is well-known that this potential fails where highly polar components are involved.

In summary, this book is very valuable for its extensive tables of the thermodynamic properties of common moist gases but must be used by experts with care. All values in the tables must be checked back with the text as to their definition and units and, most importantly, the equation from which they have been calculated.

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Thermodynamic Properties of Butane. By V. V. Sychev, A. A. Vasserman, A. D. Kozlov, and V. A. Tsymarny. Begell House, Inc., New York. 1995. 265 pp. $117.50. ISBN 1-56700-049-5.

This volume continues the series of monographs that started with nitrogen and has included methane, ethane, and propane. This series has been published in both Russia and the United States. This volume on normal butane is the first of that series to be published first in the United States.

This volume provides a comprehensive correlation and set of tables of the thermodynamic properties for normal butane at temperatures from 135 to 700 K over the pressure range of 0.01 to 100 MPa. The tables include properties for the saturation curve and along isobars. The bulk of the book consists of these isobaric tables of properties such as compressibilities, enthalpies, entropies, isobaric and isochoric heat capacities, sound speeds, Joule–Thomson coefficients, and fugacities. All numerical data are presented in SI units.

The chapter on experimental data presents a comprehensive compilation of the major sources of thermodynamic property data for normal butane. It also includes useful descriptions of experimental techniques suggesting careful analysis and critical evaluation of the experimental data. A list of 80 references is included that covers sources of experimental data, other correlations, and other relevant work.

A brief description of the equation of state is presented with references given to earlier volumes in the series that provide more detail. Also presented are the formulas for calculating the thermodynamic properties.

Extensive comparisons with experimental data are presented. Also presented are comparisons with the results from previous comparable correlations. This new equation extends to slightly higher pressures and temperatures than the previous correlations. It also includes tabulation of more properties than the earlier correlations.

In summary, this book presents a useful correlation and set of tables for the thermodynamic properties of normal butane, especially of interest to practicing engineers in the oil and gas industry.

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