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Effect of Impurities upon Pure Component Thermophysical Properties

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This article first derives thermodynamic relations between the dew-point/bubble-point gap, the infinite dilution activity coefficient (γ_2^∞), and Henry's constant (H_{21}) for binary mixtures where the first component is the pure (solvent) component and the second component is the impurity (solute). Equations for prediction of these quantities from a one-fluid van der Waals (VdW-1) model give poor results. Both relative volatility and chemical nature of the two species are shown to affect significantly the dew-/bubble-point gap. We recommend the UNIFAC method for prediction of infinite dilution activity coefficients. A priori prediction of the dew-/bubble-point gap with impurity level follows, allowing the experimentalist to confirm his measurements when (1) the impurities are known by prior analysis or (2) the impurities have been formed by decomposition of the pure component. Five example cases are presented, including the effect of decomposition on the vapor pressure curve of "pure" hydrogen sulfide.

1. Introduction

When a trace impurity (solute 2) is present in an otherwise pure liquid (solvent 1), the dew-/bubble-point gap of pressure of parts a and b of Figure 1 (constant temperature) is often taken as an indication of the level of impurity. A narrow dew-/bubble-point gap is seen to be a *necessary but not sufficient* condition for sample purity and for $\bar{P}_1^\sigma = (P_{BP} + P_{DP})/2$ to be a close approximation of the true pure solvent vapor pressure, P_1^σ . An azeotrope, for example, has no dew-/bubble-point gap. If the gaps of Figure 1 are narrow, laboratory I with a volatile impurity (Figure 1a) will report a vapor pressure $P_{II}^\sigma > P_1^\sigma$ but laboratory II with a nonvolatile impurity (Figure 1b) reports $P_{II}^\sigma < P_1^\sigma$. Both laboratories maintain that their sample is pure and theirs is the correct value of P_1^σ because in both cases $(P_{BP} - P_{DP})$ may be only a few kilopascals or, perhaps, $[(P_{BP} - P_{DP})/P_1^\sigma] < 10^{-3}$.

An allied problem of equal importance is the erroneous fixation of a temperature scale due to trace impurities (Ancsin, 1973, 1974). For example, the normal boiling point of oxygen is assigned the temperature 90.188 K on the International Practical Temperature Scale of 1968 (IPTS-68). Suppose the "pure" oxygen of the Bureau of Standards of nation X has a trace volatile (with respect to O_2) impurity as shown in Figure 1c (constant pressure; here 1 atm); nation X will calibrate all of its resistance thermometers at $T_1 = 90.188$ K but actually the temperature is lower. That is, they will assign temperatures that are *high*. Likewise, the "pure" oxygen of the Bureau of Standards of nation Y has a trace nonvolatile impurity as shown in Figure 1d, causing that bureau to calibrate all thermometers *low*. Laboratory I in nation X measures the vapor pressure of another pure compound in the vicinity of 90 K and publishes an erroneously low vapor pressure, whereas laboratory II in nation Y publishes a high vapor pressure. The disagreement between laboratories I and II, due to their respective erroneous temperature scales, would be aggravated if the pure compound of lab I contains a nonvolatile impurity, whereas the sample of lab II contains a volatile impurity; compensation would occur, possibly yielding perfect agreement of the measured vapor pressures, if the lab I sample contained a volatile impurity and lab II the nonvolatile impurity.

The objectives for this article are (1) to provide an improved physical understanding of the effects of impurities on the dew-point and bubble-point curves and (2) to generate reasonably accurate ($\pm 5\%$) a priori prediction

methods for these curves. Satisfaction of the second objective allows experimentalists to estimate errors in measured vapor pressures (and temperature scale calibration errors) from chemical analysis of their sample.

2. Theoretical Equations

Three predictive models are applied to estimate dew-/bubble-point gaps: (1) the well-known ideal solution model, (2) the simple PCS (principle of corresponding states) method based upon the one-fluid van der Waals model (VdW-1) and using a particular cubic EOS (equation of state), and (3) a dilute solution model using either Henry's constants or infinite dilution activity coefficients based upon either literature experimental data or prediction schemes.

2.1. General Equations. On Figure 1, the infinite dilution equilibrium constant of the solute (impurity) is

$$K_2^\infty = \lim_{x_2 \rightarrow 0} (y_2/x_2)_T = \lim_{x_2 \rightarrow 0} (\partial y_2/\partial x_2)_T = (\partial P/\partial x_2)_T^\infty / (\partial P/\partial y_2)_T^\infty \quad (1)$$

These limiting slopes provide linear estimates of the bubble-point and dew-point curves of Figure 1 nearing infinite dilution:

$$\begin{aligned} P_{BP} &= P_1^\sigma + (\partial P/\partial x_2)_T^\infty x_2 \\ P_{DP} &= P_1^\sigma + (\partial P/\partial y_2)_T^\infty y_2 \end{aligned} \quad (2)$$

An impurity mole fraction $z_2 (=x_2 = y_2)$ then provides a dew-/bubble-point gap of

$$B_{DP}P = P_{BP} - P_{DP} = (\partial P/\partial y_2)_T^\infty (K_2^\infty - 1)z_2 \quad (3)$$

where

$$K_2^\infty = f_2^\infty \gamma_2^\infty / P_1^\sigma \hat{\phi}_2^{v,\infty} = H_{21} / P_1^\sigma \hat{\phi}_2^{v,\infty} \quad (4)$$

where x_2 is the mole fraction of solute in the liquid phase, y_2 the corresponding mole fraction in the vapor phase, z_2 the overall mole fraction, f_2^∞ the fugacity of pure liquid solute at (P_1^σ, T) , γ_2^∞ the infinite dilution activity coefficient, $\hat{\phi}_2^{v,\infty}$ the infinite dilution fugacity coefficient of the solute in the vapor phase, and H_{21} the Henry's constant.

The vapor mixture is characterized adequately by a Leiden second virial gas:

$$P = \rho_m RT [1 + B_m \rho_m] \quad (5)$$

and

$$B_m = y_1 B_{11}^2 + y_2 B_{22}^2 + 2y_1 y_2 B_{12} \quad (6)$$

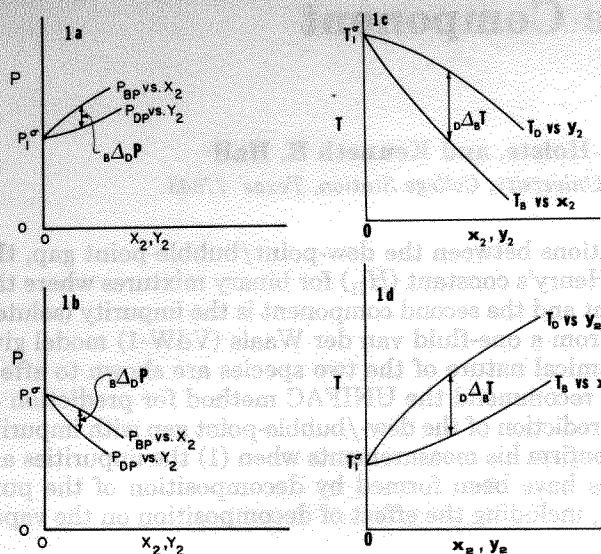


Figure 1. General pressure-composition diagram showing the effect of a small impurity (2) upon the vapor pressure of compound 1. (a) indicates a volatile impurity whereas (b) indicates a nonvolatile impurity. (c) and (d) are the corresponding temperature-composition diagrams to illustrate the effect of impurities upon a temperature scale fixed at a normal boiling point.

where ρ_m is the mixture molar density and B is the second virial coefficient of the mixture (m), pure solvent (11), pure solute (22), and the unlike interaction (12). For such a gas mixture, the Gibbs-Duhem equation provides the dew-point slope at infinite dilution as

$$(\partial P / \partial y_2)_T^{\infty} = RT(K_2^{\infty} - 1)P_1^s / K_2^{\infty}(RT + B_{11}P_1^s) \quad (7)$$

so that eq 3 becomes

$${}_B\Delta_D P = RT(K_2^{\infty} - 1)^2 P_1^s z_2 / K_2^{\infty}(RT + B_{11}P_1^s) \quad (8)$$

our general working equation for the dew-/bubble-point gap of the pressure at constant temperature. When working with measurements at constant pressure, the dew-/bubble-point gap of the temperature is most easily calculated from

$${}_D\Delta_B T = T_{DP} - T_{BP} = {}_B\Delta_D P / (dP_1^s / dT) \quad (9)$$

where the last equality applies only for low values of z_2 .

2.2. Ideal Solution Model. Assuming an ideal solution to exist in both the liquid and vapor phases allows simple evaluation of K_2^{∞} of eq 8. While the liquid-phase, infinite dilution activity coefficient γ_2^{∞} of eq 4 is now unity, it remains for us to evaluate f_2^s and ϕ_2^s for a Leiden second virial gas:

$$\ln \phi_2^s = \rho_2^s B_{22} \quad (10)$$

where $\phi_2^s = f_2^s / P_2^s$ is the fugacity coefficient at the vapor pressure of pure 2, $f_2^s = \hat{f}_2^s$ (neglect of the Poynting correction), and ρ_i^s is the molar density of saturated vapor of pure i or

$$\rho_i^s = [-1 + (1 + (4B_{ii}P_i^s / RT))^{1/2}] / 2B_{ii} \quad (11)$$

from eq 5. The mixture fugacity coefficient is

$$\ln \hat{\phi}_2^s = \rho_1^s (B_{22} + \delta_{12}) \quad (12)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (13)$$

is zero for a vaporous ideal solution. Our ideal solution model thus yields

$$K_2^{\infty} = (P_2^s / P_1^s) \exp[B_{22}(\rho_2^s - \rho_1^s)] \quad (14)$$

for use in conjunction with eq 8.

This model thus provides a priori prediction of ${}_B\Delta_D P$ as a function of the impurity level z_2 (or ${}_D\Delta_B T$ as a function of z_2) when (1) the approximate vapor pressures P_1^s and P_2^s are available and (2) the second virial coefficients B_{11} and B_{22} are known from either experiment or an independent prediction method. The vapor pressure of the solvent, P_1^s , is not a problem since the experimentalist already has a rough measure as discussed in the first sentence of section 1. Likewise, the vapor pressure of the solute, P_2^s , can usually be estimated—when it exists. Two basic instances when P_2^s fails to exist are (a) the volatile solute is supercritical at the temperature (T) where we seek to measure P_1^s or (b) the nonvolatile solute is below its triple point at T . The pure component second virial coefficients are preferably found from the experimental literature (Dymond and Smith, 1980), but when not available may be estimated from one of several accurate correlations (Tsonopoulos, 1974; Hayden and O'Connell, 1975).

The above equations are further simplified when the vapor is assumed to be a perfect gas mixture, where $B_{ii} = 0$, so that

$$K_2^{\infty} = P_2^s / P_1^s \quad (15)$$

and

$${}_B\Delta_D P = (P_2^s - P_1^s)^2 z_2 / P_2^s \quad (16)$$

2.3. Simple PCS Model. The derivation of dew- and bubble-point loci, infinite dilution activity coefficients (γ_2^{∞}), and Henry's constants (H_{21}) for a one-fluid van der Waals model has been given by Kim (1984). The principal results of the simple PCS model are

$$\ln K_2^{\infty} = -(\alpha\eta_1^s - \beta)\Delta Z_1 \quad (17)$$

where $\eta_1^s = (T/P_1^s)(dP_1^s/dT)$, $\Delta Z_1 = P_1^s(\Delta v_1)/RT$, and Δv_1 is the saturated vapor molar volume less that of the liquid for pure solvent. Equation 17 allows estimation of the dew-/bubble-point gaps when used with eq 8 and 9. Neither η_1^s nor ΔZ_1 is difficult to evaluate because both are pure solvent properties. The constants α and β describe the limiting slope of the mixture critical locus at the solvent critical point (T_{c1} , P_{c1} , v_{c1}) and are characteristic of the pure-impurity interaction:

$$T_{cm} = T_{c1}(1 + \alpha z_2) \quad (18)$$

$$P_{cm} = P_{c1}(1 + \beta z_2) \quad (19)$$

$$v_{cm} = v_{c1}[1 + (\alpha - \beta)z_2] \quad (20)$$

where m indicates the mixture. The constants α and β are evaluated from the critical temperature and critical pressure of pure 1 and 2 upon assuming (a) a cubic equation of state (EOS) and (b) a set of mixture combining rules (MCR).

The Henry's constant (H_{21}) and the infinite dilution activity coefficient (γ_2^{∞}) of the solute are closely related by $H_{21} = f_2^s \gamma_2^{\infty}$, and they are further related to K_2^{∞} via eq 4. When the fugacity coefficients are evaluated by eq 10 and 12,

$$K_2^{\infty} = (P_2^s / P_1^s) \gamma_2^{\infty} \exp[B_{22}(\rho_2^s - \rho_1^s) - \rho_1^s \delta_{12}] \quad (21)$$

and

$$K_2^{\infty} = (H_{21} / P_1^s) \exp[-\rho_1^s (B_{22} + \delta_{12})] \quad (22)$$

Four EOS were used in this study (VdW = van der Waals, RK = Redlich/Kwong, SRK = Soave/Redlich/

Kwong, and PR = Peng/Robinson) with two sets of MCR. We have estimated H_{21} and γ_2^∞ by using eq 17, 21, and 22 for the PCS model with these various EOS/MCR for solvent/solute pairs where experimental values have been reported in the literature. The ability of the PCS model to estimate H_{21} and γ_2^∞ is indicative of its ability to predict $B_{\Delta D}P$ —percent deviations in K_2^∞ , H_{21} , and γ_2^∞ are identical but must be multiplied by $|(K_2^\infty + 1)/(K_2^\infty - 1)|$ to obtain the absolute percent deviation of $B_{\Delta D}P$. Kim (1984) has classified the solvent/solute pairs as (a) nonpolar 1/nonpolar 2, (b) nonpolar 1/polar 2, (c) polar 1/nonpolar 2, and (d) the general case of supercritical solutes. She presents a detailed study of PCS model predictions of H_{21} and γ_2^∞ for the eight EOS/MCR combinations and compares these values to both experiment and to rival prediction methods for H_{21} and γ_2^∞ . The results are very poor, indicating that the PCS method should not be used to predict impurity errors. PCS model predictions vs. experiment show average absolute differences of roughly 100% for H_{21} and 50% for γ_2^∞ , omitting several extreme examples where the differences are as high as 80 000%!

3. Dilute Solution Model

The general equations of section 2.1 form the basis for this model which unlike the ideal solution and PCS models requires a mixture property (e.g., H_{21} or γ_2^∞) as input to estimate $B_{\Delta D}P$ or $D_{\Delta B}T$. Combination of eq 4, 8, and 12 provides the direct relation between H_{21} and $B_{\Delta D}P$:

$$B_{\Delta D}P = \frac{\{H_{21} - P_1^\sigma \exp[\rho_1^\sigma(B_{22} + \delta_{12})]\}^2 z_2}{H_{21}[1 + (B_{11}P_1^\sigma/RT)] \exp[\rho_1^\sigma(B_{22} + \delta_{12})]} \quad (23)$$

To relate γ_2^∞ to $B_{\Delta D}P$, use eq 23 and

$$H_{21} = f_2^\infty \gamma_2^\infty = P_2^\sigma \gamma_2^\infty \exp(\rho_2^\sigma B_{22}) \quad (24)$$

Estimates for $B_{\Delta D}P$ of good accuracy ($\pm 5\%$) can be expected when experimental values of H_{21} or γ_2^∞ are available for the solvent/solute pair at the desired temperature. Both H_{21} and γ_2^∞ are but weak functions of pressure, except near the critical temperature of the solvent, so their pressure dependency is a minor concern.

Lugo (1982) has made an uncritical compilation of experimental Henry's constants appearing in the literature from 1970 to 1980. A complete, critical compilation of all experimental H_{21} and γ_2^∞ values needs to be performed and published in book form similar to Dymond and Smith (1980) for second virial coefficients.

The Appendix section contains our recommended procedure for estimation of $B_{\Delta D}P$, $(P_{BP} - P_1^\sigma)$, and $(P_{DP} - P_1^\sigma)$ through use of H_{21} or γ_2^∞ with eq 23 and 24. When experimental values of H_{21} and γ_2^∞ are not available for a solvent/solute pair, this study has shown that prediction by the PCS model is not trustworthy. Nonpolar mixtures of similar molecular size and shape may be assumed to be ideal solutions ($\gamma_2^\infty = 1$); otherwise, the modified UNIFAC procedure (Fredenslund et al., 1975, 1977), a group contribution method, is recommended for a priori prediction of γ_2^∞ , leading to $B_{\Delta D}P$ (or $D_{\Delta B}T$) through eq 23 and 24. This approach fails when T falls outside the liquid range of pure solute. In this event, the equation of Antunes and Tassios (1983) in the Appendix is used to estimate f_2^∞ . When an experimental Henry's constant is available at a temperature different from that desired, the procedure of Joffe (1977) allows estimation. The prediction methods listed above are not exhaustive. New methods are continually under development, and the reader should feel free to use his favorite methods. For example, the correlation and prediction methods for H_{21} of Jonah (1983) are well

based on statistical mechanics and hold considerable promise.

4. Impurity Errors in Molar Volumes and Virial Coefficients

The general expression for the fractional error in the molar volume of the solvent due to the presence of a single solute is

$$(\delta V_m/V_1) = [(\bar{V}_2^\infty/V_1) - 1]z_2 \quad (25)$$

where \bar{V}_2^∞ is the partial molar volume of the solute at infinite dilution in the solvent. \bar{V}_2^∞ diverges to negative infinity at the critical point of the solvent, and the critical exponent of the divergence is path dependent (Chang et al., 1984). These recent findings agree with mixture measurements in the critical region of the solvent and with the long-recognized notion that pure component critical region measurements are highly sensitive to impurities.

Outside the critical region of the solvent, Kim (1984) has shown that the PCS model predicts poorly \bar{V}_2^∞ except for near ideal solutions when $\bar{V}_2^\infty = V_2$ (same P , T). When the liquid solution is nonideal and especially in the case of supercritical solutes, the prediction method of Lyckman et al. (1965) was found to give reasonable if not highly accurate values of \bar{V}_2^∞ .

The general expressions for the fractional error in the Leiden second and third virial coefficients due to the presence of a single solute are

$$(\delta B_m/B_{11}) = 2[(B_{12}/B_{11}) - 1]z_2 \quad (26)$$

and

$$(\delta C_m/C_{111}) = 3[(C_{112}/C_{111}) - 1]z_2 \quad (27)$$

When not available from experiment, accurate estimation of B_{12} is available from Tsonopoulos (1974) even for polar-nonpolar mixtures (Eubank et al., 1985) and many polar-polar mixtures. The prediction of Orbey and Vera (1983) for C_{ijk} is recommended for nonpolar systems.

5. Examples

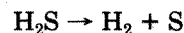
5.1. Calculation of $B_{\Delta D}P$ for a Nonpolar System.

Statement. TMP (1)/heptane (2) at 313.15 K with 500 ppm heptane ($z_2 = 0.0005$), $\gamma_2^\infty = 0.98$ (exptl). $P_1^\sigma = 7.335$ kPa, $P_2^\sigma = 12.36$ kPa, or $r = P_2^\sigma/P_1^\sigma = 1.686$. Find $B_{\Delta D}P$ and $(P_{BP} - P_1^\sigma)$.

Results. $f_2^\infty = P_2^\sigma$, $H_{21} = f_2^\infty \gamma_2^\infty = (12.36)(0.98) = 12.12$ kPa. $B_{\Delta D}P = (P_1^\sigma - H_{21})^2 z_2 / (z_1 H_{21} + z_2 P_1^\sigma) = 0.9342$ Pa or $B_{\Delta D}P/P_1^\sigma = 1.285 \times 10^{-4}$. $(\partial P/\partial x_2)_{x_2=0} = \gamma_2^\infty P_2^\sigma - P_1^\sigma = 4.78$ kPa or $P_{BP} - P_1^\sigma = (0.0005)(4.78) = 2.39 \times 10^{-3}$ kPa. $(P_{BP} - P_1^\sigma)/P_1^\sigma = 3.258 \times 10^{-4}$.

5.2. Sensitivity of H_2S Vapor Pressures to Decomposition.

Statement. A 69.0-kPa gap is observed experimentally for "pure" H_2S at 25 °C. The decomposition reaction



is suspected with H_2 dissolving into the liquid H_2S . At 25 °C (298.15 K), H_{21} is estimated to be 1500 MPa (through UNIFAC). What is the value of z_2 (or extent of the reaction)?

Results. $P_1^\sigma = 1.974$ MPa and $B_{\Delta D}P = 69.0/1000 = (1.974 - 1500)^2 z_2 / 1500$ or $z_2 = 4.61 \times 10^{-5}$ or 46 ppm.

For this supercritical impurity, $(\partial P/\partial x_2)_{x_2=0} \approx H_{21} - P_1^\sigma = 1500 - 1.974 = 1498$ MPa or $P_{BP} - P_1^\sigma = (1498)(4.61 \times 10^{-5}) = 69.06$ kPa. Since $B_{\Delta D}P = 69.0$, $P_{DP} - P_1^\sigma = 0.06$ kPa. Also, $(P_{BP} - P_1^\sigma)/P_1^\sigma = 3.40 \times 10^{-2} = B_{\Delta D}P/P_1^\sigma$.

5.3. Relative Volatility Reversal for a Polar/Polar System.

Statement. Alcohols are highly hygroscopic. A sample of ethanol (1) has water (2) as an impurity with $z_2 = 0.01$. At 100 °C, $\gamma_2^\infty = 3.0$ (exptl). Find ${}_B\Delta_D P$ and $P_{BP} - P_1^\sigma$.

Results. $P_1^\sigma = 226.1$ kPa, $P_2^\sigma = 101.3$ kPa. $f_2^\sigma = P_2^\sigma \phi_2^\sigma = 99.30$ kPa. $H_{21} = \gamma_2^\infty \cdot f_2^\sigma = 298.1$ kPa. ${}_B\Delta_D P = 0.172$ kPa, ${}_B\Delta_D P/P_1^\sigma = 7.64 \times 10^{-4}$, $(\partial P/\partial x_2)_{x_2=0} = \gamma_2^\infty P_2^\sigma - P_1^\sigma = 77.9$ kPa, $P_{BP} - P_1^\sigma = 0.779$ kPa, $P_{BP} - P_1^\sigma = 0.607$, $(P_{BP} - P_1^\sigma)/P_1^\sigma = 3.45 \times 10^{-3}$.

Note. Water has a lower vapor pressure than does ethanol, but traces of water in ethanol result in the qualitative behavior of Figure 1a not Figure 1b. Higher water concentrations would result in a positive azeotrope. Use of the ideal solution model ($H_{21} = P_2^\sigma$, $\gamma_2^\infty = 1$) would predict $P_{DP} < P_{BP} < P_1^\sigma$ and ${}_B\Delta_D P/P_1^\sigma = 1.52 \times 10^{-2}$.

5.4. A Nonpolar Solvent with a Heavy Polar Impurity.

Statement. Methane (1) at 123.15 K shows a ${}_B\Delta_D P = 30$ kPa with $P_1^\sigma = 0.239$ MPa. Dissolved H_2S (2) is suspected. Find z_2 , the impurity level, and $P_1^\sigma - P_{DP}$.

Results. $H_{21} = 6.788$ kPa from estimation (through UNIFAC). Note that $T_{TP} = 187.6$ K for H_2S ; 30 kPa = $[(239 - 6.788)^2 z_2 / (6.788 + 239 z_2)]$ or $z_2 = 0.00436$ or 4360 ppm (check solubility). $(\partial P/\partial x_2)_{x_2=0} = H_{21} - P_1^\sigma = 6.788 - 239 = -232.2$ kPa or $P_{BP} - P_1^\sigma = (-232.2)(0.00436) = -1.012$ kPa. Therefore, $P_1^\sigma - P_{BP} = 1.012$ kPa and $P_1^\sigma - P_{DP} = 31.01$ kPa.

Note that $[(P_1^\sigma - P_{DP})/P_1^\sigma] = 0.130$, whereas $z_2 = 0.00436$. Ideal solubility = 0.06 for z_2 —thus impurity level is possible.

5.5. Errors in Molar Volumes and Virial Coefficients.

Statement. Benzene (1) at 298.15 K contains a principal impurity of 0.05% N_2 (2). For the liquid mixture at 101.3 kPa, find the fraction error in molar volume. For the gaseous mixture, estimate the fractional error in the second virial coefficient, the third virial coefficient, and the molar volume at 10 kPa.

Results. For the liquid solution at 101.3 kPa, \bar{V}_2^∞ is 53.0 $cm^3/g\text{-mol}$ (exptl), 43.9 (estimated from Lyckman et al. (1965)), and 119.1 (estimated by PCS model). By use of the experimental value of \bar{V}_2^∞ , eq 25, and $V_1 = 88.1$ $cm^3/g\text{-mol}$, the value of $\delta V_m/V_1$ is -0.0199%.

With the gaseous mixture, $B_{11} = -1468$ $cm^3/g\text{-mol}$ and $B_{12} = -109$ (experimental values from Dymond and Smith (1980)). By eq 26, $\delta B_m/B_{11} = -0.0926\%$. Likewise, $C_{111} = -2.382 \times 10^6$ ($cm^3/g\text{-mol}$)² and $C_{112} = -1.585 \times 10^6$, both from the prediction method of Orbey and Vera (1983). From eq 27, $\delta C_m/C_{111} = -0.0502\%$. To find the fractional error in the molar volume at 10 kPa, we note that

$$-(\delta V_m/V_m) = \delta \rho_m/\rho_m = -\rho_m[\delta B_m + \rho_m(\delta C_m)]/[1 + 2B_m\rho_m + 3C_m\rho_m^2] \quad (28)$$

With $\rho_m = \rho_1 = 4.058 \times 10^{-6}$ $g\text{-mol}/cm^3$, $\delta V_m/V_1 = 0.0056\%$. The fractional error in the molar volume is low due to the fact that the gas is nearly perfect at this low pressure.

6. Conclusions

We have provided the general equations for calculation of dew-/bubble-point gaps from Henry's constants and infinite dilution activity coefficients. In the absence of experimental values, either H_{21} or γ_2^∞ can be estimated to reasonable accuracy by methods cited in the literature. In some cases, the liquid solution may be assumed ideal. Extensive calculations have shown that the PCS model (one-fluid van der Waals model) is not a trustworthy method regardless of the equation of state and mixture combining rules assumed. General equations have also

been provided for impurity errors in the molar volume of a single-phase fluid, in the second virial coefficient, and in the third virial coefficient.

The sample problems given in the last section demonstrate that the fractional error in a measured thermophysical property may be several orders of magnitude more or less than the impurity fraction, z_2 . In azeotropic systems, the direction of the error may be opposite physically to that supposed by the ratio of volatility of the pure components. In other examples, erroneous estimation of an infinite dilution property (H_{21} , γ_2^∞ , or \bar{V}_2^∞) may lead to forecasting the impurity error in the wrong direction—a frequent occurrence with PCS model predictions. Because we are estimating hopefully small errors in experimental measurements, high accuracy is not required—only the correct sign and approximate magnitude.

Acknowledgment

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Appendix: Specific Recommendations for Estimation of Impurity Effects

The following procedure allows estimation of ${}_B\Delta_D P$ (or ${}_B\Delta_B T$) through H_{21} or γ_2^∞ and is given in order of preference. When a portion of the procedure is unchanged, it is not repeated in the paragraphs that follow. The examples of section 5 follow this procedure.

1. When an experimental value of H_{21} exists for your solute/solvent pair at the desired temperature, use it directly in eq 23. Take B_{11} , B_{22} , and B_{12} from Dymond and Smith (1980), an experimental compilation, or, when not available, estimate from Tsionopoulos (1974).

2. If $H_{21}(T)$ is not experimentally available, search the literature for a measured value of $\gamma_2^\infty(T)$. To calculate H_{21} from γ_2^∞ , (a) use P_2^σ in eq 24 when P_2^σ exists, or (b) otherwise estimate f_2^σ from the equation of Antunes and Tassios (1983):

$$\ln(f_2^\sigma/P_{c2}) = A_0 + A_1 T_{r2}^{-1} + A_2 T_{r2} + A_3 T_{r2}^2 + A_4 T_{r2}^3$$

where $T_{r2} = (T/T_{c2})$ plus $A_0 (=3.54811)$, $A_1 (= -4.74547)$, $A_2 (=1.60151)$, $A_3 (= -0.87466)$, and $A_4 (=0.10971)$. T_{r2} should not exceed 3.0. In either case, H_{21} is found from eq 24 followed by ${}_B\Delta_D P$ from eq 23.

3. Nonpolar mixtures of similar molecular size and shape may be assumed ideal ($\gamma_2^\infty = 1$). Ideal solutions are often assumed for hydrocarbon mixtures, inert gas mixtures, and N_2/O_2 mixtures. Sufficient accuracy is obtained for impurity estimates when γ_2^∞ is actually 1 ± 0.05 . Because we have assumed the liquid phase to be an ideal solution, the gas phase should also be an ideal solution (or $\delta_{12} = 0$).

4. For mixtures containing a polar component, either solvent or solute or both, and for which no experimental values of H_{21} nor γ_2^∞ are available, estimate γ_2^∞ from UNIFAC (Fredenslund et al., 1975, 1977). Then use P_2^σ or f_2^σ as above to estimate H_{21} by eq 24. This procedure should also be followed for nonpolar/nonpolar mixtures, where it is questionable that the conditions of 3 (above) are met. Examples are hydrocarbon pairs of much different size and/or shape particularly when both components are not in the same subgroup: alkane, cycloalkane, aromatic, alkene, etc.

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