

Pointyng Correction in Phase Equilibrium Thermodynamics of Non Polar Gases and Brines: A Review

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Abstract: The development of an equation for Poynting correction, is of paramount importance in the field of modeling and interpretation of phase equilibrium thermodynamics in a wide range of temperatures and pressures /densities for practical applications in chemistry, physical chemistry, geochemistry and industrial technology. The unique previous existing equation for Poynting correction is a simple expression, represented by a product of a constant volume by a pressure difference between which the correction is applied. [1] proposed an equation based on a semitheoretical expression for the partial molar volume at infinite dilution of volatile aqueous non-electrolyte solute (V_2^0) that considers as variables the density and isothermal compressibility of the solvent, as well as the second cross solvent-solute virial coefficient (β_{12}) and the second virial coefficient of pure solvent (β_{11}). The mathematical equation is applicable to solutes whose β_{12} is known or can be estimated, in a temperature range of 273.16 K to 647 K, values of pressure up to 2 kbar and brines with ionic strength equal to 6 m NaCl. The expression provides excellent correlation with experimental data as shown for the H₂S-H₂O-NaCl system (with maximum deviation of 7%), through a thermodynamic model that uses this formula proposal coupled with the Law of Henry and the Soave- Redlich-Kwong equation of state for modeling the liquid-vapor phase equilibria.

Keywords: Thermodynamic modeling, Poynting correction.

INTRODUCTION

The development of an equation for determining the isothermal pressure increment of the standard (infinite dilution) Gibbs free energy (or chemical potential) of a volatile solute on the basis of its partial molar volume at infinite dilution applicable to subcritical temperatures, based on parameters with available experimental data in the literature or easily estimated, as used in this work (the partial molar volume at infinite dilution of the volatile aqueous nonelectrolyte solute, the density and isothermal compressibility of solvent and the second virial coefficients) is of paramount importance in the field of modeling and interpretation of phase equilibrium thermodynamics in a wide range of temperatures and pressures /densities for practical applications in chemistry, physical chemistry, geochemistry and industrial technology [2-4]. In this paper we use the semitheoretical expression for the partial molar volume at infinite dilution for an aqueous non-electrolyte solute (V_2^0) developed by Plyasunov *et al.* (2000a and b) based on the fluctuation solution theory [5] as well as in the fluctuation theory of statistical mechanics of a solution [6-8]. the equation contains the aforementioned density (ρ) and the isothermal compressibility of solvent (κ), as well as the second

solvent-solute cross virial coefficient (β_{12}) and the second virial coefficient of pure solvent (β_{11}), so it can be used in a wide range of temperature and pressure. The equation used [1, 9] is the next:

$$V_2^0 = NV_1^0 + \kappa_{PT}RT(1 - N) + \dots$$

$$2\kappa_{PT}RT\rho_{P,T}\Omega(\beta_{12} - N\beta_{11})e^{-C_1\rho_{P,T}} + \dots$$

$$\left(\frac{a}{T^5} + b\right)(e^{C_2\rho_{P,T}} - 1) \quad (1)$$

ANALYTICAL INTEGRATION OF V_2^0

To obtain the equation for determining the isothermal change of the standard (infinite dilution) Gibbs free energy (or chemical potential) of the volatile solute, is integrated analytically with respect to pressure the expression of the partial molar volume at infinite dilution of the volatile aqueous non-electrolyte solute according to the expression [9]:

$$\Delta G_2^0 = \int_{p_{sat}}^P V_2^0 dP \quad (2)$$

To integrate the equation of the partial molar volume at infinite dilution for volatile aqueous non-electrolyte solutes respect to the pressure, some auxiliary correlations were used [4, 10-12], finally obtaining the equation:

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$$\int_{P_{sat}}^P V_2^\infty dP = \int_{P_{sat}}^P \left[\begin{array}{l} NV_1^0 + \kappa_{PT}RT(1-N) + \dots \\ 2\kappa_{PT}RT\rho_{PT}\Omega \dots \\ (\beta_{12} - N\beta_{11})e^{-C_1\rho_{PT}} \\ + \left(\frac{a}{T^5} + b\right)(e^{C_1\rho_{PT}} - 1) \end{array} \right] dp \quad (3)$$

$$\Delta G_2^0 \int_{P_{sat}}^P V_2^0 dp = \Delta G_2^0(A) + \Delta G_2^0(B) + \Delta G_2^0(C) + \Delta G_2^0(D) \quad (4)$$

$$\Delta G_2^0(A) = \int_{P_{sat}}^P NV_1^0 dp = \frac{V_0(P_{sat} + B)^A}{1-A} \dots \left[\frac{1}{(P+B)^{A-1}} - \frac{1}{(P_{sat}+B)^{A-1}} \right] \quad (4A)$$

$$\Delta G_2^0(B) = \int_{P_{sat}}^P \kappa_{PT}RT(1-N)dp = RT(1-N) \ln \left[\frac{P+B}{P_{sat}+B} \right]^A \quad (4B)$$

$$\Delta G_2^0(C) = \int_{P_{sat}}^P 2\kappa_{PT}RT\rho_{PT}\Omega \dots (\beta_{12} - N\beta_{11})e^{-C_1\rho_{PT}} dp$$

$$\Delta G_2^0(C) = 2RT\Omega(\beta_{12} - N\beta_{11}) \dots \left\{ \left(\frac{1}{C_1}\right) \left[\exp\left[-\frac{C_1}{v_0}\right] - \exp[-C_1\rho_{PT}] \right] \right\} \quad (4C)$$

$$\Delta G_2^0(D) = \int_{P_{sat}}^P \left(\frac{a}{T^5} + b\right) \dots (e^{-C_2\rho_{PT}} - 1) dp$$

$$\Delta G_2^0(D) = \left(\frac{a}{T^5} + b\right) \dots$$

$$\left\{ \begin{array}{l} \frac{C_2}{v_0(P_{sat} + B)^A} \left[\frac{(P+B)^{A+1}}{-(P_{sat} + B)^{A+1}} \right] + \dots \\ \frac{C_2^2}{2v_0^2(P_{sat} + B)^{2A}(2A+1)} \dots \\ \left[\frac{(P+B)^{2A+1}}{-(P_{sat} + B)^{2A+1}} \right] \dots \\ + \frac{C_2^3}{6v_0^3(P_{sat} + B)^{3A}(3A+1)} \dots \\ \left[\frac{(P+B)^{3A+1}}{-(P_{sat} + B)^{3A+1}} \right] \dots \end{array} \right\} \quad (4D)$$

EXAMPLE OF APPLICATION IN THE H₂S-H₂O-NACL SYSTEM

This mathematical tool is applicable below the critical temperature of pure water (674°K), pressures

up to 2 Kbars and molalities equal to 6m for NaCl solutions, in the field of modeling and interpretation of phase equilibrium thermodynamics, where the standard partial molar Gibbs energy of hydration for the non-electrolyte solute is the most important thermodynamic property [9], because with this thermodynamic property is applied the Poynting correction in phase equilibrium thermodynamic modeling [13]. The equation is restricted to solutes for which are known or can be estimated their β₁₂ (second virial cross solvent-solute coefficient). The expression provides excellent correlation with experimental data [14] as shown for the H₂S-H₂O-NaCl system, using a thermodynamic model [3, 4] that uses this mathematical tool developed coupled with the Henry's Law and the Soave–Redlich–Kwong equation of state [14] to reproduce experimental data in the aqueous liquid and vapor region [3, 4], as can be observed in the following Figure 1:

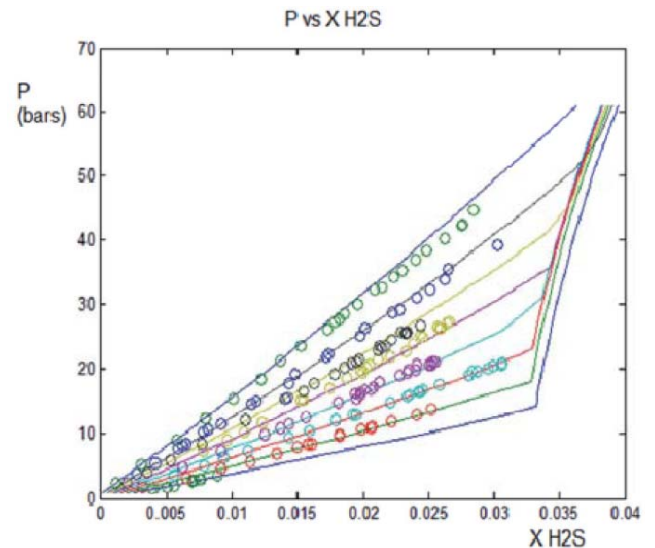


Figure 1: The solid line is the calculation of the thermodynamic model with analytical integration for V₂⁰ and the symbols are the experimental data by Lee and Mather (1977) [14].

CONCLUSIONS

In this work we developed a mathematical expression for the isothermal pressure increment of the standard (infinite dilution) Gibbs free energy (or chemical potential) of the volatile non-electrolyte solute, applicable below the critical temperature of pure water (674°K), pressures up to 2 Kbars and molalities equal to 6m for NaCl, analytically integrating respect to the pressure the semitheoretical expression for the partial molar volume at infinite dilution for an aqueous non-electrolyte volatile solute, applicable for the Poynting correction in thermodynamic modeling. The

mathematical expression developed provides excellent correlation with experimental data.

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