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IMPLEMENTATION AND DEVELOPING OF A ROUTINE TO DEFINE THE AMMONIA-WATER THERMODYNAMIC PROPERTIES BY USING GIBBS FREE ENERGY DEFINITION

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Abstract. *Computational study of ammonia-water absorption refrigeration cycles requires a proper assessment of thermodynamic properties of the working fluids in subcooled, saturated and superheated states, in order to characterize physical transformation processes that occurs in refrigeration cycle's working fluids. Some of the existing and most accurate thermodynamic libraries have been provided in commercial software such as Engineering Equation Solver (EES), and routines suitable for several programming languages handed over by International Association for the Properties of Water and Steam (IAPWS). On the one hand, EES uses an equation-of-state based on Gibbs free energy developed by Ibrahim and Klein (1993), but on the other hand IAPWS formulation implements Tillner-Roth and Friend (1998) correlations, which are based on Helmholtz free energy. However, IAPWS routines have a limited use due to the limited input parameters allowed (temperature, pressure, and density), and EES requires the acquisition of a license. Therefore, the current study aims to develop an open-source Python thermodynamic library for ammonia-water mixtures by using Ziegler and Trepp (1984) equation-of-state. First of all, a detailed derivation of each property is presented, secondly a comparison within the exposed equations-of-state is carried out, and finally numerical results are compared to experimental data available in open-literature. Such comparisons are performed within 0.2 and 50 bar and from 230 K up to 500 K. It is worth to mention that the implementation of any equation-of-state in a programming language such as python possibilities to approach whatever characterization process in which non-ideal fluid behavior occurs e.g, heat and mass transfer processes and transport phenomena.*

Keywords: *Equation-of-State, Gibbs free energy, Helmholtz free energy, Ammonia-water, Absorption refrigeration cycle*

1. INTRODUCTION

The ammonia-water absorption refrigeration cycle (ARC) has been widely used in different kinds of applications (Narváez-Romo, 2020) such as refrigeration and air-conditioning systems since Ferdinand Carré developed the first absorption refrigeration machine in 1856. The ARC performance is strongly affected by the simultaneous heat and mass transfer processes that occur in both components absorber and generator (Narváez-Romo *et al.*, 2015; Narváez-Romo and Simões-Moreira, 2019; Zavaleta-Aguilar and Simões-Moreira, 2015). The current efforts are not only focused on the study of the simultaneous heat and mass transfer processes (Narváez-Romo *et al.*, 2017, 2020), but also the implementation of the computational methods of programming language more robust by using open-source routines. Computational studies of ammonia-water ARC requires a proper assessment of thermodynamic properties of the working fluids in subcooled, saturated, and superheated states and transport properties (Conde, 2006), in order to characterize physical transformation processes that happen in refrigeration cycle's working fluids.

Thorin *et al.* (1998) studied different correlations for the thermodynamic properties of the ammonia-water mixture focused on Kalina cycle applications. Their review classified these correlations into seven groups; cubic equations of state, virial equations of state, Gibbs excess energy, the law of corresponding states, perturbation theory, group contribution method, and polynomial functions. Also, Ganesh and Srinivas (2011) developed a code to determinate the theromodynamic properties for Kalina cycle. Mirl *et al.* (2020) carried out a comparison of ammonia-water equations of state for absorption systems. Some of the existing and most accurate thermodynamic libraries have been provided in commercial software such as Engineering Equation Solver (EES) or , and routines suitable for several programming languages handed over by International Association for the Properties of Water and Steam (IAPWS).

On the one hand, EES uses an equation-of-state based on Gibbs free energy (same equation as Ziegler and Trepp (1984)) developed by Ibrahim and Klein (1993), but on the other hand IAPWS formulation implements Tillner-Roth and

Friend (1998) correlations, which are based on Helmholtz free energy. The formulation proposed by Tillner-Roth and Friend (1998) achieves excellent agreement between experimental data and numerical model. However, the model implementation is arduous to be applied to the industrial sizing practice (Conde, 2006). Moreover, IAPWS routines have a limited use due to the limited input parameters allowed (temperature, pressure, and density), and EES requires the acquisition of a license. It can be mentioned that the empirical equation-of-state of Ziegler and Trepp (1984) presents an intrinsic consistency and accuracy in the thermodynamic condition range for refrigeration and air-conditioning applications (Rattner and Garimella, 2016). Therefore, the current study aims to develop an open-source Python thermodynamic library for ammonia-water mixtures: specific volume, specific enthalpy, specific entropy, bubble point temperature, and dew point temperature. The model combined the Gibbs excess energy by using Ziegler and Trepp (1984) equation-of-state with the polynomial expressions developed by Johnson *et al.* (2013).

2. THERMODYNAMIC PROPERTIES BY USING GIBBS ENERGY DEFINITION

Gibbs free energy of a phase is composed by the addition of three terms: a) pure components, b) ideal free energy of mixing, and c) free excess energy (Ziegler and Trepp, 1984). The vapor is assumed as an ideal mixture of real gases, and the liquid phase are fixed by using a term determined from the Gibbs excess energy (Thorin *et al.*, 1998).

2.1 Pure substances

Eq. (1) determines the energy contribution for the liquid phase and it's given as a function of the reduced properties, in which the molar heat capacity is given in Eq. (2) (Ziegler and Trepp, 1984).

$$\begin{aligned} g^{\mathrm{l}}_{(R)} &= h^{\mathrm{l}}_{(R_0)} - T_R s^{\mathrm{l}}_{(R_0)} + \int_{T_{Ro}}^{T_R} c^{\mathrm{l}}_{pR} \mathrm{d}T_R - T_R \int_{T_{Ro}}^{T_R} c^{\mathrm{l}}_{pR}/T_R \, \mathrm{d}T_R \\ &+ \left(A_1 + A_3 T_R + A_4 T_R^2\right)\left(p_{\mathrm{R}} - p_{\mathrm{oR}}\right) + A_2\left(p_R^2 - p_{\mathrm{Ro}}^2\right)/2 \end{aligned} \tag{1}$$

$$c^{\mathrm{l}}_{pR} = B_1 + B_2 T_R + B_3 T_R^2 \tag{2}$$

For the gas phase, Eq. (3) is used to compute the Gibbs free energy, and Eq. (4) defines the molar heat capacity (Ziegler and Trepp, 1984).

$$\begin{aligned} g^{\mathrm{g}}_{(R)} &= h^{\mathrm{g}}_{(R_0)} - T_R s^{\mathrm{g}}_{(R_0)} + \int_{T_{Ro}}^{T_R} c^{\mathrm{g}}_{pR} \mathrm{d}T_R - T_R \int_{T_{Ro}}^{T_R} c^{\mathrm{g}}_{pR}/T_R \, \mathrm{d}T_R \\ &+ T_R \ln(p_{\mathrm{R}}/p_{\mathrm{oR}}) + C_1\left(p_{\mathrm{R}} - p_{\mathrm{oR}}\right) \\ &+ C_2\left(p_{\mathrm{R}}/T_{\mathrm{R}}^3 - 4p_{\mathrm{oR}}/T_{\mathrm{oR}}^3 + 3p_{\mathrm{oR}}T_{\mathrm{R}}/T_{\mathrm{oR}}^4\right) \\ &+ C_3\left(p_{\mathrm{R}}/T_{\mathrm{R}}^{11} - 12p_{\mathrm{oR}}/T_{\mathrm{oR}}^{11} + 11p_{\mathrm{oR}}T_{\mathrm{R}}/T_{\mathrm{oR}}^{12}\right) \\ &+ C_4\left(p_{\mathrm{R}}^3/T_{\mathrm{R}}^{11} - 12p_{\mathrm{oR}}^3/T_{\mathrm{oR}}^{11} + 11p_{\mathrm{oR}}^3T_{\mathrm{R}}/T_{\mathrm{oR}}^{12}\right)/3 \end{aligned} \tag{3}$$

$$c^{\mathrm{g}}_{pR} = D_1 + D_2 T_R + D_3 T_R^2 \tag{4}$$

2.2 Ideal energy of mixing

The ideal energy of mixing can be defined by using Eq. (5) (Ziegler and Trepp, 1984),

$$g^{\mathrm{l,g}}_{\mathrm{mix}} = T_{\mathrm{R}}[(1-x)\ln(1-x) + x\ln x] \tag{5}$$

2.3 Free excess energy

Free excess energy definition is given only for the liquid phase. Thus, Eq. (6) determines that contribution (Ziegler and Trepp, 1984).

$$\begin{aligned} g^{\mathrm{l,g}}_{\mathrm{excess}} = x(1-x)\{&E_1 + E_2 p_{\mathrm{R}} + T_{\mathrm{R}}\left(E_3 + E_4 p_{\mathrm{R}}\right) + E_5/T_{\mathrm{R}} + E_6/T_{\mathrm{R}}^2 \\ &+ (2x-1)\left[E_7 + E_8 p_{\mathrm{R}} + T_{\mathrm{R}}\left(E_9 + E_{10} p_{\mathrm{R}}\right) + E_{11}/T_{\mathrm{R}} + E_{12}/T_{\mathrm{R}}^2\right] \\ &+ (2x-1)^2\left[E_{13} + E_{14} p_{\mathrm{R}} + E_{15}/T_{\mathrm{R}} + E_{16}/T_{\mathrm{R}}^2\right]\} \end{aligned} \tag{6}$$

Table 1. Coefficients for the equations for pure components and for the Gibbs excess energy function (Ziegler and Trepp, 1984)

Coeff.	**Ammonia**	**Water**	**Coeff.**	**Ammonia**	**Water**	**Coeff.**		**Coeff.**	
A1	3.971423E-02	2.748796E-02	C1	-1.049377E-02	2.13613E-02	E1	-4.626129E01	E9	-1.475383
A2	-1.790557E-05	-1.016665E-05	C2	-8.288224	-3.169291E01	E2	2.060225E-02	E10	-5.038107E-03
A3	-1.308905E-02	-4.452025E-03	C3	-6.647257E02	-4.634611E04	E3	7.292369	E11	-9.640398E01
A4	3.752836E-03	8.389246E-04	C4	-3.045352E03	0	E4	-1.032613E-02	E12	1.226973E02
B1	1.634519E01	1.214557E01	D1	3.673647	4.019170	E5	8.074824E01	E13	-7.582637
B2	-6.508119	-1.898065	D2	9.989629E-02	-5.175550E-02	E6	-8.461214E01	E14	6.012445E-04
B3	1.448937	2.911966E-01	D3	3.617622E-02	1.951939E-02	E7	2.452882E01	E15	5.487018E01
hl_oR	4.878573	21.821141	sl_oR	1.644773	5.733498	E8	9.598767E-03	E16	-7.667596E01
hg_oR	26.468879	0.965058	sg_oR	8.339026	13.453430				
ToR	3.2252	5.0705	PoR	2.000	3.000				

2.4 Dimensionless free energy for mixture

The equation of state for the liquid mixture based on the non-dimensional free energy is given by Eq. (7) (Ziegler and Trepp, 1984).

$$\begin{aligned} g_{\mathrm{R}}^{\mathrm{l}} &= (1-x)g_{\mathrm{RH_2O}}^{\mathrm{l}} + xg_{\mathrm{RNH_3}}^{\mathrm{l}} + T_{\mathrm{R}}[(1-x)\ln(1-x) + x\ln x] \\ &\quad + x(1-x)\left\{E_1 + E_2 p_{\mathrm{R}} + T_{\mathrm{R}}\left(E_3 + E_4 p_{\mathrm{R}}\right) + E_5/T_{\mathrm{R}} + E_6/T_{\mathrm{R}}^2\right. \\ &\quad + (2x-1)\left[E_7 + E_8 p_{\mathrm{R}} + T_{\mathrm{R}}\left(E_9 + E_{10} p_{\mathrm{R}}\right) + E_{11}/T_{\mathrm{R}} + E_{12}/T_{\mathrm{R}}^2\right] \\ &\quad \left. + (2x-1)^2\left[E_{13} + E_{14} p_{\mathrm{R}} + E_{15}/T_{\mathrm{R}} + E_{16}/T_{\mathrm{R}}^2\right] \right\} \end{aligned} \tag{7}$$

Similarly, the equation of state for gas mixture based on the non-dimensional free energy is given in Eq. (8) (Ziegler and Trepp, 1984):

$$g_{\mathrm{R}}^{\mathrm{g}} = (1-\mathrm{y})g_{\mathrm{RH_2O}}^{\mathrm{g}} + \mathrm{y}g_{\mathrm{RNH_3}}^{\mathrm{g}} + T_{\mathrm{R}}[(1-\mathrm{y})\ln(1-\mathrm{y}) + \mathrm{y}\ln\mathrm{y}] \tag{8}$$

in which the reduced thermodynamic properties are given as Eq. (9), being $T_B = 100K$, $p_B = 10\mathrm{bar}$, and the universal gas constant $\mathrm{R} = 8.314\mathrm{kJ/kmolK}$

$$\begin{aligned} &T_{\mathrm{R}} = T/T_{\mathrm{B}} \\ &p_{\mathrm{r}} = p/p_{\mathrm{B}} \\ &g_{\mathrm{R}} = g/\mathrm{R}T_{\mathrm{B}} \\ &h_{\mathrm{R}} = h/\mathrm{R}T_{\mathrm{B}} \\ &c_{\mathrm{pR}} = c_{\mathrm{p}}/\mathrm{R} \\ &s_{\mathrm{R}} = \mathrm{s}/\mathrm{R} \end{aligned} \tag{9}$$

2.5 Coefficients for the reduced thermodynamic properties

The coefficients of pure substances, reference state values, and for the Gibbs excess energy function are presented in Table (1), whose constants are demanded to compute the thermodynamic properties: specific volume, specific enthalpy, and specific entropy.

3. THERMODYNAMIC PROPERTIES

Next, the thermodynamic properties are defined; volume, enthalpy and entropy for the liquid and gas phase.

3.1 Liquid phase mixture volume

The liquid phase mixture molar volume might be computed by using Eq. (10).

$$v^{\mathrm{l}} = \left(\frac{\partial g_{(T,p,x)}^{\mathrm{l}}}{\partial p}\right)_{T,x} \tag{10}$$

By partial derivation of Eq. (1) for pure substances. The result of the derivative is given by Eq. (11);

$$\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial p}\right)_{T,x} = (1-x)\left(A_1 + A_3T_{\mathrm{R}} + A_4T_{\mathrm{R}}^2 + A_2p_{\mathrm{R}}\right) \tag{11}$$

The partial derivative of the ideal energy of mixing is zero due to that is a function of the reduced temperature. So, the free excess energy derivative is expressed by Eq. (12);

$$\begin{aligned}\left(\frac{\partial g^{\mathrm{l}}_{excess(T,p,x)}}{\partial p}\right)_{T,x} &= x(1-x)[E_2 + E_4T_{\mathrm{R}} + (2x-1)(E_8 + E_{10}T_{\mathrm{R}}) \\ &+ (2x-1)^2E_{14}]\end{aligned} \tag{12}$$

thus, the partial derivation of the free energy equation can be rewritten as is given in Eq. (13);

$$\begin{aligned}\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial p}\right)_{T,x} &= (1-x)\left(A_1 + A_3T_{\mathrm{R}} + A_4T_{\mathrm{R}}^2 + A_2p_{\mathrm{R}}\right)_{\mathrm{H_2O}} \\ &+ (x)\left(A_1 + A_3T_{\mathrm{R}} + A_4T_{\mathrm{R}}^2 + A_2p_{\mathrm{R}}\right)_{\mathrm{NH_3}} \\ &= x(1-x)[E_2 + E_4T_{\mathrm{R}} + (2x-1)(E_8 + E_{10}T_{\mathrm{R}}) \\ &+ (2x-1)^2E_{14}]\end{aligned} \tag{13}$$

Therefore, the liquid specific volume is given by Eq. (14). Here, the molar ammonia-water properties are converted into properties related to the mass.

$$v^l\left[\frac{m^3}{kg}\right] = \frac{\mathrm{RT_B}}{100\mathrm{p_B}}\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial p}\right)_{T,x} \tag{14}$$

3.2 Gas phase mixture volume

Gas phase volume can be defined as given in Eq. (15), in which the energy excess is zero by assuming the gas phase behavior as a ideal gas.

$$v^{\mathrm{g}} = \left(\frac{\partial g^{\mathrm{g}}_{(T,p,x)}}{\partial p}\right)_{T,x} \tag{15}$$

so, the partial derivative of Eq. (3) can define the molar volume for the gas phase of the pure substances as shown in Eq. (16).

$$\left(\frac{\partial g^{\mathrm{g}}_{(T,p,x)}}{\partial p}\right)_{T,x} = \frac{T_{\mathrm{R}}}{p_{\mathrm{R}}} + C_1 + \frac{C_2}{T_{\mathrm{R}}^3} + \frac{C_3}{T_{\mathrm{R}}^{11}} + \frac{C_4}{T_{\mathrm{R}}^{11}} = \mathrm{Factor} \tag{16}$$

$$v^g\left[\frac{m^3}{kg}\right] = \frac{\mathrm{RT_B}}{100\mathrm{p_B}}\left(\frac{1-\mathrm{y}}{M_{\mathrm{H_2O}}}\mathrm{Factor_{H2O}} + \frac{\mathrm{y}}{M_{\mathrm{H_2O}}}\mathrm{Factor_{NH3}}\right) \tag{17}$$

3.3 Liquid phase mixture entropy

Specific entropy is defined as given in Eq. (18),

$$s^{\mathrm{l}} = -\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial T}\right)_{P,x} \tag{18}$$

By derivation of Eq. (1) for pure substances. The result of the derivative is show as follows;

$$\begin{aligned}\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial T}\right)_{P,x} &= -s^{\mathrm{l}}_{Ro} - B_1 \ln\frac{T_{\mathrm{R}}}{T_{\mathrm{Ro}}} - B_2(T_{\mathrm{R}} - T_{\mathrm{Ro}}) - \frac{B_3}{3}(T^2_{\mathrm{R}} - T^2_{\mathrm{Ro}}) \\ &+ (P_{\mathrm{R}} - P_{\mathrm{Ro}})(A_3 + 2A_4 T_{\mathrm{R}})\end{aligned} \tag{19}$$

derivative of mixing energy from Eq. (5);

$$g^{\mathrm{l,g}}_{\mathrm{mix}} = (1-x)\ln(1-x) + x\ln x \tag{20}$$

derivative excess liquid properties from Eq. (6);

$$\begin{aligned}g^{\mathrm{l,g}}_{\mathrm{excess}} &= x(1-x)\left\{E_3 + E_4 p_{\mathrm{R}} - E_5/T^2_{\mathrm{R}} - 2E_6/T^3_{\mathrm{R}}\right. \\ &+ (2x-1)\left[E_9 + E_{10}p_{\mathrm{R}} - E_{11}/T^2_{\mathrm{R}} - 2E_{12}/T^3_{\mathrm{R}}\right] \\ &\left.+ (2x-1)^2\left[-E_{15}/T^2_{\mathrm{R}} - 2E_{16}/T^3_{\mathrm{R}}\right]\ \right\}\end{aligned} \tag{21}$$

so, Eq. (18) can be rewritten as;

$$\begin{aligned}-\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial T}\right)_{P,x} &= -s^{\mathrm{l}}_{Ro} - B_1 \ln\frac{T_{\mathrm{R}}}{T_{\mathrm{Ro}}} - B_2(T_{\mathrm{R}} - T_{\mathrm{Ro}}) - \frac{B_3}{3}(T^2_{\mathrm{R}} - T^2_{\mathrm{Ro}}) \\ &+ (P_{\mathrm{R}} - P_{\mathrm{Ro}})(A_3 + 2A_4 T_{\mathrm{R}}) \\ &+ (1-x)\ln(1-x) + x\ln x \\ &+ = x(1-x)\left\{E_3 + E_4 p_{\mathrm{R}} - E_5/T^2_{\mathrm{R}} - 2E_6/T^3_{\mathrm{R}}\right. \\ &+ (2x-1)\left[E_9 + E_{10}p_{\mathrm{R}} - E_{11}/T^2_{\mathrm{R}} - 2E_{12}/T^3_{\mathrm{R}}\right] \\ &\left.+ (2x-1)^2\left[-E_{15}/T^2_{\mathrm{R}} - 2E_{16}/T^3_{\mathrm{R}}\right]\ \right\}\end{aligned} \tag{22}$$

Entropy in terms of mass might be defined by Eq. (23);

$$s^l\left[\frac{kJ}{kgK}\right] = -\frac{R}{M}\left(\frac{\partial g^{\mathrm{l}}_{(T,p,x)}}{\partial T}\right)_{P,x} \tag{23}$$

3.4 Gas phase mixture entropy

The liquid gas entropy for the ammonia-water mixture can be expressed as given in Eq. (24).

$$s^{\mathrm{g}} = -\left(\frac{\partial g^{\mathrm{g}}_{(T,p,x)}}{\partial T}\right)_{P,x} \tag{24}$$

The derivation result of Eq. (3) for pure substances in the gas phase is given in Eq. (25);

$$\begin{aligned}\left(\frac{\partial g^{\mathrm{g}}_{(T,p,x)}}{\partial T}\right)_{P,x} &= -s^{\mathrm{g}}_{Ro} - D_1 \ln\frac{T_{\mathrm{R}}}{T_{\mathrm{Ro}}} - D_2(T_{\mathrm{R}} - T_{\mathrm{Ro}}) - \frac{D_3}{2}(T^2_{\mathrm{R}} - T^2_{\mathrm{Ro}}) \\ &+ \ln\frac{p_{\mathrm{R}}}{p_{\mathrm{Ro}}} + C_2\left(\frac{-3p_{\mathrm{R}}}{T^4_{\mathrm{R}}} + \frac{3p_{\mathrm{Ro}}}{T^4_{\mathrm{Ro}}}\right) \\ &+ C_3\left(\frac{-11p_{\mathrm{R}}}{T^{12}_{\mathrm{R}}} + \frac{11p_{\mathrm{Ro}}}{T^{12}_{\mathrm{Ro}}}\right) + \frac{C_4}{3}\left(\frac{-11p^3_{\mathrm{R}}}{T^{12}_{\mathrm{R}}} + \frac{11p^3_{\mathrm{Ro}}}{T^{12}_{\mathrm{Ro}}}\right)\end{aligned} \tag{25}$$

By derivative procedure of mixing energy from Eq. (5);

$$g^{\mathrm{g,g}}_{\mathrm{mix}} = (1-\mathrm{y})\ln(1-\mathrm{y}) + \mathrm{y}\ln\mathrm{y} \tag{26}$$

No excess for the gas phase. Thus, gas phase mixture entropy can be computed by using Eq. (27).

$$-\left(\frac{\partial g^{\mathrm{g}}_{(T,p,x)}}{\partial T}\right)_{P,x} = -s^{\mathrm{g}}_{Ro} - D_1 \ln\frac{T_{\mathrm{R}}}{T_{\mathrm{Ro}}} - D_2(T_{\mathrm{R}} - T_{\mathrm{Ro}}) - \frac{D_3}{2}(T_{\mathrm{R}}^2 - T_{\mathrm{Ro}}^2) + \ln\frac{p_{\mathrm{R}}}{p_{\mathrm{Ro}}} + C_2\left(\frac{-3p_{\mathrm{R}}}{T_{\mathrm{R}}^4} + \frac{3p_{\mathrm{Ro}}}{T_{\mathrm{Ro}}^4}\right) + C_3\left(\frac{-11p_{\mathrm{R}}}{T_{\mathrm{R}}^{12}} + \frac{11p_{\mathrm{Ro}}}{T_{\mathrm{Ro}}^{12}}\right) + \frac{C_4}{3}\left(\frac{-11p_{\mathrm{R}}^3}{T_{\mathrm{R}}^{12}} + \frac{11p_{\mathrm{Ro}}^3}{T_{\mathrm{Ro}}^{12}}\right) + (1-\mathrm{y})\ln(1-\mathrm{y}) + \mathrm{y}\ln\mathrm{y} \tag{27}$$

Entropy in terms of mass can be determined as;

$$s^g\left[\frac{kJ}{kgK}\right] = -\frac{R}{M}\left(\frac{\partial g^{\mathrm{g}}_{(T,p,x)}}{\partial T}\right)_{P,x} \tag{28}$$

3.5 Liquid phase mixture enthalpy

Molar enthalpy can be determined by Eq. (29)

$$h^{\mathrm{l}} = -T^2\left(\frac{\partial\left(\frac{g^{\mathrm{l}}_{(T,p,x)}}{T}\right)}{\partial T}\right)_{p.x} \tag{29}$$

Next, the contributions of the pure components, ideal free energy or mixing and free excess energy is given by Eq. (30). The pure contribution is defined by differentiation of Eq. (1).

$$h^{\mathrm{l}}_{(R)} = h^{\mathrm{l}}_{(R_0)} + B_1(T_{\mathrm{R}} - T_{\mathrm{oR}}) + \frac{B_2}{2}(T_{\mathrm{R}}^2 - T_{\mathrm{oR}}^2) + \frac{B_3}{3}(T_{\mathrm{R}}^3 - T_{\mathrm{oR}}^3) - (A_4T_{\mathrm{R}}^2 - A_1)(p_{\mathrm{R}} - p_{\mathrm{oR}}) + \frac{A_2}{2}(p_{\mathrm{R}}^2 - p_{\mathrm{oR}}^2) \tag{30}$$

The mixing energy contribution is equal to zero. So, the excess energy contribution can be determined by Eq. (31).

$$h^{\mathrm{l}}_{\mathrm{R}} = x(1-x)\{E_1 + E_2p_{\mathrm{R}} + 2E_5/T_{\mathrm{R}} + 3E_6/T_{\mathrm{R}}^2 + (2x-1)[E_7 + E_8p_{\mathrm{R}} + 2E_{11}/T_{\mathrm{R}} + 3E_{12}/T_{\mathrm{R}}^2] + (2x-1)^2[E_{13} + E_{14}p_{\mathrm{R}} + 2E_{15}/T_{\mathrm{R}} + 3E_{16}/T_{\mathrm{R}}^2]\} \tag{31}$$

Finally, the enthalpy thermodynamic property for the gas phase can be computed by Eq. (32). The pure substance contribution should be taken into account for each substance; ammonia and water.

$$h^{\mathrm{l}}_{\mathrm{R}} = h^{\mathrm{l}}_{(R_0)} + B_1(T_{\mathrm{R}} - T_{\mathrm{oR}}) + \frac{B_2}{2}(T_{\mathrm{R}}^2 - T_{\mathrm{oR}}^2) + \frac{B_3}{3}(T_{\mathrm{R}}^3 - T_{\mathrm{oR}}^3) - (A_4T_{\mathrm{R}}^2 - A_1)(p_{\mathrm{R}} - p_{\mathrm{oR}}) + \frac{A_2}{2}(p_{\mathrm{R}}^2 - p_{\mathrm{oR}}^2) + x(1-x)\{E_1 + E_2p_{\mathrm{R}} + 2E_5/T_{\mathrm{R}} + 3E_6/T_{\mathrm{R}}^2 + (2x-1)[E_7 + E_8p_{\mathrm{R}} + 2E_{11}/T_{\mathrm{R}} + 3E_{12}/T_{\mathrm{R}}^2] + (2x-1)^2[E_{13} + E_{14}p_{\mathrm{R}} + 2E_{15}/T_{\mathrm{R}} + 3E_{16}/T_{\mathrm{R}}^2]\} \tag{32}$$

Thus, the specific enthalpy is given as follows,

$$h^l\left[\frac{kJ}{kg}\right] = -RT_Bh^{\mathrm{l}}_{\mathrm{R}} \tag{33}$$

3.6 Gas phase mixture enthalpy

Similarly, the molar gas enthalpy is defined as is given in Eq. (34).

$$h^{\mathrm{g}} = -T^2 \left(\frac{\partial \left(\frac{g^{\mathrm{g}}_{(T,p,x)}}{T} \right)}{\partial T} \right)_{p.x} \tag{34}$$

The contributions of mixing energy and excess energy are zero. Thus. the pure components is given by differentiation of Eq. (3).

$$\begin{aligned} h^{\mathrm{g}}_{(R)} = h^{\mathrm{g}}_{(R_0)} &+ D_1 \left(T_{\mathrm{R}} - T_{\mathrm{oR}}\right) + \frac{D_2}{2} \left(T_{\mathrm{R}}^2 - T_{\mathrm{oR}}^2\right) + \frac{D_3}{3} \left(T_{\mathrm{R}}^3 - T_{\mathrm{oR}}^3\right) \\ &+ C_1 \left(p_{\mathrm{R}} - p_{\mathrm{oR}}\right) + 4C_2 \left(p_{\mathrm{R}}/T_{\mathrm{R}}^3 - p_{\mathrm{oR}}/T_{\mathrm{oR}}^3\right) \\ &+ 12C_3 \left(p_{\mathrm{R}}/T_{\mathrm{R}}^{11} - p_{\mathrm{oR}}/T_{\mathrm{oR}}^{11}\right) + 4C_4 \left(p_{\mathrm{R}}^3/T_{\mathrm{R}}^{11} - p_{\mathrm{oR}}^3/T_{\mathrm{oR}}^{11}\right) \end{aligned} \tag{35}$$

The dimensional enthalpy is given as follows,

$$h^g \left[\frac{kJ}{kg} \right] = -R T_B h^{\mathrm{g}}_{\mathrm{R}} \tag{36}$$

4. LIQUID-VAPOR THERMODYNAMIC EQUILIBRIUM

The liquid-vapor equilibrium properties of ammonia-water mixture can be determined by using the chemical potential μ definition, in which the mixtures' equilibrium statements given by Eq. (37) are required. The chemical potential of the component in each phase must be equal, meaning no mass migration between the phases. Moreover, Johnson *et al.* (2013) proposed two purely empirical polynomial correlations to define the bubble and dew curve, whose functions were improved of the study developed by Patek and Klomfar (1995). q_i, r_i, s_i, and , a_i are the exponents and coefficients of Eq. (38). $T_0 = 100$ K, $P_0 = 2$ MPa. It is worthwhile to mention that those polynomial correlations present adequate accurate for the absorption refrigeration systems for pressure ranged between 0.5 and 20 bar. Therefore, the current program employed the polynomial correlation proposed by Johnson *et al.* (2013) as given in Eq. (38).

$$\begin{aligned} T^l &= T^g \\ p^l &= p^g \\ \mu^l_{\mathrm{H2O}} &= \mu^g_{\mathrm{H2O}} \\ \mu^l_{\mathrm{NH3}} &= \mu^g_{\mathrm{NH3}} \end{aligned} \tag{37}$$

$$\begin{aligned} T(P,x)_{\text{bubble}} &= T_0 \sum_{i=0}^{15} a_i x^{q_i} (1-x)^{r_i} \left[\ln\left(\frac{P_0}{P}\right) \right]^{s_i} \\ T(P,x)_{\text{dew}} &= T_0 \sum_{i=0}^{18} a_i y^{q_i/4} (1-y)^{r_i/4} \left[\ln\left(\frac{P_0}{P}\right) \right]^{s_i} \end{aligned} \tag{38}$$

5. COMPARISON WITH OTHER EQUATION-OF-STATE

Results were compared from de equation-of-state of Ibrahim and Klein (1993) by using the external function "NH3H2O" implemented in the *Engineering Equation Solver* - EES routine. The liquid thermodynamic properties were defined for the following conditions; $T = 333.15$ K, $p = 30$ bar. Similarly, the vapor phase thermodynamic properties were fixed for $T = 523.15$ K and $p = 5$ bar. Fig. (1) shows the specific volume for the liquid (left side) and vapor phase (right side) as a function of the ammonia-water molar concentration. As previously mentioned, the vapor curve follows the ideal behavior as a result of the ideal gas approximation. Results of the volume thermodynamic property obtained from the current study show agreements with the EES routine. A 0.60% maximum difference between the Python and EES routines was achieved.

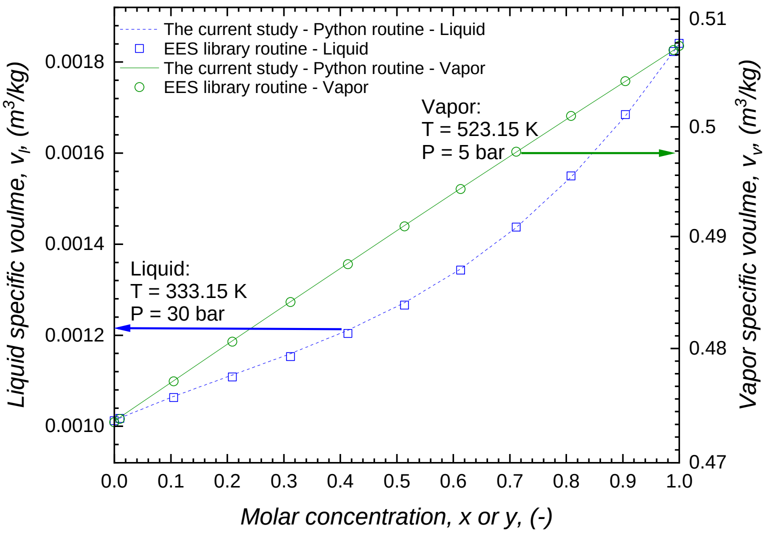

Figure 1. Liquid and vapor specific volume comparison between EES library routine and the current Python routine as a function of the molar concentration

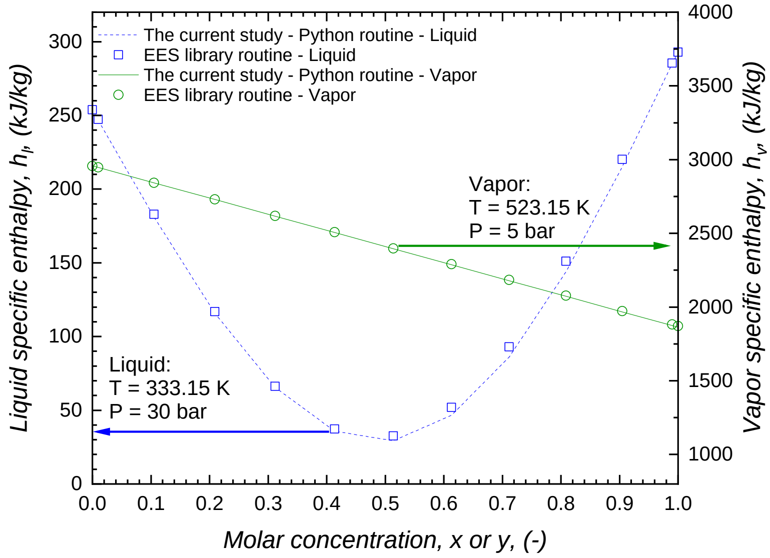

Figure 2. Liquid and vapor specific enthalpy comparison between EES library routine and the current Python routine as a function of the molar concentration

According to the specific enthalpy and specific entropy, Figs. (2) and (3) show the results of the present study. The specific enthalpy for the liquid and vapor phase depict agreement with the equation of state of Ibrahim and Klein (1993). A 11.3 % maximum difference between the Python and EES routines was achieved for the liquid phase, and a 0.38% for the vapor phase. Finally, results of the specific entropy is displayed in Fig. (3). It can be noted that the liquid phase entropy shows differences from the EES routine, achieving a 4% of difference between each one. A 0.43 % maximum difference is obtained for the gas phase. In a general way, results obtained by using the current Python routine show that the gas phase present lower difference value as compared with the EES routine (no more than 0.43 % of relative difference). For the liquid phase, that difference might achieve to 11.3 %, for all thermodynamic properties. It its worthwhile to mention that the equation of state of Ibrahim and Klein (1993) use the same equations as Ziegler and Trepp (1984), adopting new constant values in the function for the Gibbs free energy.

Finally, Fig. (4) depict the results of liquid-vapor thermodynamic equilibrium, in which the bubble curve and the dew curve temperature are defined. These curves were obtained by using the polynomial correlation proposed by Johnson *et al.* (2013). Three different pressure values are defined to compare the results with the EES routine: $P = 0.5$, $P = 10$ and $P = 20$ bar. Results of the Python routine are defined as follows: the bubble curve and dew curve temperature are defined in blue dashed line and green solid line, respectively. As can be noted, the present study reproduces the ammonia-water properties obtained from the EES routine: green circles and blue squares.

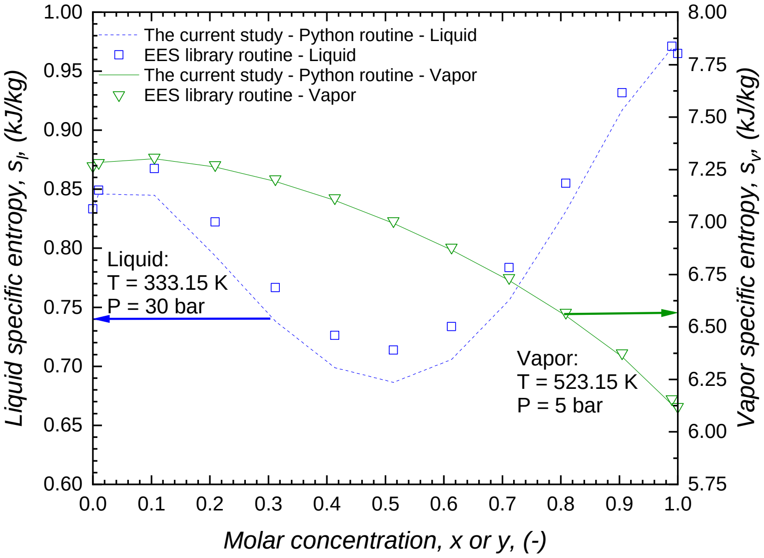

Figure 3. Liquid and vapor specific entropy comparison between EES library routine and the current Python routine as a function of the molar concentration

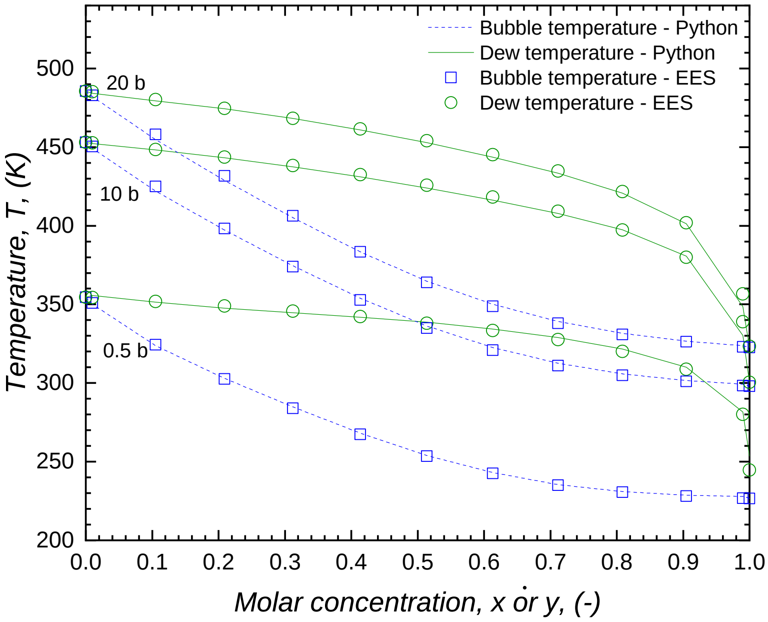

Figure 4. Comparison between the bubble and dew temperature of Ibrahim and Klein (1993) from EES and the current Python routine based on the polynomial correlations developed by Johnson *et al.* (2013).

6. CONCLUSIONS

The present work implemented and developed a Python routine to define the ammonia-water thermodynamic properties for absorption refrigeration applications. The model combined the Gibbs excess energy by using Ziegler and Trepp (1984) equation-of-sate with the polynomial expressions developed by Johnson *et al.* (2013). The Python thermodynamic routine defined the library for the specific volume, specific enthalpy, specific entropy, the bubble curve temperature, and the dew curve temperature. Results showed agreements of the equation-of-state between the Python routine and the *Engineering Equation Solver*-EES procedure. Future attempts will be focused on developing an ammonia-water thermodynamic library that allows the six different input modes based on fixing three independent variables.

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9. RESPONSIBILITY NOTICE