CONTRIBUTION STUDY OF THE THERMODYNAMICS PROPERTIES OF THE AMMONIA-WATER MIXTURES

by

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The full thermodynamic study of the absorption refrigeration units requires the knowledge of the thermodynamic properties of the used mixture. The present work deals with the mathematical modeling of the thermodynamic properties of ammonia-water mixtures using various models. The presented model covers high vapor-liquid equilibrium pressures up to 110 [bar] and temperatures from 230 to 600 [K]. Furthermore, the calculation of the thermodynamic properties of the ammonia-water mixtures and their pure components was carried out. The obtained results were compared with results given in the literature. This shows a good concordance.

Key words: *ammonia-water; binary solution; thermodynamics properties; Markel; Oldham.*

1. Introduction

The mathematical models of calculation and simulation of the systems with absorption require the knowledge of a great number of operating fluids thermodynamic properties [1]. To achieve this goal, a great number of experimental research was carried out, where the results were presented in a series of tables and diagrams; the known (*H*, *x*) diagram is well realized by Merkel and Bošnjaković [2].

When calculating the performance of an ammonia-water absorption refrigeration cycle, thermodynamic properties of the ammonia-water mixtures need to be known. These properties are usually obtained from equations of states and other general equations [3].

The correlations for thermodynamic properties of ammonia-water mixtures found in literature, can be divided into nine groups: cubic equations of state [4-17], virial equations of state [16, 22, 23, 25], Gibbs excess energy [7, 10, 13, 15-20, 23-32, 44-48], corresponding states method [33-38], perturbation theory [39, 47], group contribution theory [12, 21], Leung-Griffiths model [40], Helmoltz free energy [41] and polynomial functions [42-43].

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Different correlations for the thermodynamic properties of ammonia-water mixtures have been used in studies of ammonia-water absorption refrigeration cycles presented in literature; they were obtained using a library of subroutines developed by Sergio Stecco and Umberto Desideri [30]. Their correlations are based on work presented by Ziegler and Trepp [27] and El-Sayed and Tribus [32]. Different equations are used for the vapor and liquid phases. The vapor is supposed to be an ideal mixture of real gases while the properties of the liquid phase are corrected by a term calculated from the Gibbs excess energy. The functions presented by Ziegler and Trepp [27] have been correlated to experimental data for the mixture up to 240 [°C] and 52 [bar] while El-Sayed and Tribus [32] have taken into account data up to 316 [°C] and 210 [bar]. The maximum pressure for the correlations from Stecco and Desideri [30] has been set to 115 [bar], which is slightly above the critical pressure of ammonia. The critical pressure and temperature of the mixture change with the mass fraction of ammonia. Rainwater and Tillner-Roth [40] presented a model based on the so-called Leung-Griffiths model for the ammonia-water mixture critical region vapor-liquid equilibrium. They conclude that their model is a reasonable representation of the high-pressure phase boundary for the ammonia-water mixture but that more experimental data would be valuable to confirm the model. Furthermore, they mention that there are inconsistencies among the experimental data available today for the ammonia-water mixture in the critical region.

Besides, the correlations presented and used by Xu and Goswami [29] are the same as the correlations of Stecco and Desideri [30]. All but Park and Enick *et al.* [21] use different equations for the liquid and vapor phases. Just as for the correlations of Stecco and Desideri [30] the vapor is supposed to be an ideal mixture of real gases and the properties for the liquid phase are corrected by a term calculated from the Gibbs excess energy for the correlations by El-Sayed and Tribus [32], Kouremenous and Rogdakis [26] and Ibrahim and Klein [28]. Ibrahim and Klein use the equations presented by Ziegler and Trepp [27].

However, the constants in the functions for the Gibbs excess energy have been recalculated with experimental data at higher temperatures and pressures (up to 210 [bar] and 316 [°C]). Ziegler and Trepp [27] have modified the correlations presented by Schulz [25]. By these modifications the correlations are extended from a maximum pressure of 25 [bar] to 50 [bar]. Kouremenos and Rogdakis [26] also use the equations of Ziegler and Trepp [27]. For pressures higher than 50 [bar], they use an expression for the heat capacity given by El-Sayed and Tribus [32] to calculate enthalpy and entropy. Nag and Gupta [31] use the Peng-Robinson equation for the vapor-liquid equilibrium and the Gibbs free energy equations presented by Zielger and Trepp [27] for the vapor and liquid phase properties.

Park [35] uses a generalized equation of state based on the law of corresponding states to calculate the thermodynamic properties of the mixture. Corrections for non-ideal and polar behavior are included. Enick *et al.* [21] use a cubic equation of state, the Peng-Robinson equation of state, with binary interaction parameters estimated from a group contribution model and Gibbs excess energy equations.

Tillner-Roth and Friend [41] presented a new correlation for the ammonia-water mixture thermodynamic properties. It is based on a fundamental equation of state for the Helmholtz free energy and, like the correlation by Park [35]; the entire thermodynamic space of the mixture is described by one single equation. This is formed by the fundamental equations of state of the pure components and a mixing rule for the independent variables, reduced temperature and reduced density. The term for the departure from non-ideal mixture behavior is fitted to the most reliable, available experimental data for the ammonia-water mixture and also to data for the critical region from the modified Leung-Griffiths model presented by Rainwater and Tillner-Roth [40].

Weber [34] has presented a model in order to estimate the second and the third virial coefficient of the ammonia-water mixtures. Rukes and Dooley [44] have calculated the free energy of Helmotz of the components for the derivation after the thermodynamic properties at saturation.

Many researchers have used the calculation of the free enthalpy of Gibbs to formulate the thermodynamic properties of the ammonia-water mixtures [7, 10, 13, 15-20, 23-32, 44-48].

Moreover, M. Barhoumi and co-workers [46], for the liquid phase, have used a three constant Margules model of the excess free enthalpy. The vapor phase is considered as a perfect mixture of real gases, each pure gas being described by a pressure virial equation of state truncated after the third term. Kh. Mejbri and Bellagi [47] have used three different theoretical approaches for the modelling of thermodynamic properties of the ammonia-water mixtures. A comparison of these three methods proves the superiority of PC-SAFT (Perturbed Chain Statistical Associating Fluid Theory) in predicting and extrapolating the thermodynamic properties of ammonia-water system up to very high temperatures and pressures.

Among the mentioned models, we have chosen in this study the one of Michel FEIDT [48], which combines the Gibbs free energy method for the thermal properties and the equations calculating the bubble point and the dew point of the mixture [32]. This method combines the advantages of the both methods. In the same time it avoids the need to make iterations in order to have the equilibrium conditions of phases. The suggested correlations cover equilibrium conditions of phases at high pressures and temperatures: $230<T<600$ [K] and $0.2<P<110$ [bar].

This field is under the critical points of all the components, so that the determination of the equation of state for the mixture, does not take into account features referred to the critical state field. The equation of state does not describe the state in which the solution is in the solid-state aggregation.

The organization of the paper is as follows. The properties of working fluids of the chosen model are given Section 2. The results of calculation of the thermodynamics properties of ammonia-water mixtures and their pure components are presented in section 3. A comparative study of the obtained results with the results provided by the IIR (International Institute of Refrigeration) [50] and Dae.Wen. SUN [49] for the mixtures, and those provided by KUMAN Ražnjevic [51] and L. HAAR *et al.* [52] for the pure components are carried out in the same section. Conclusions are drawn in the last section.

2. Properties of working fluids

2.1. Pure components

2.1.1. Gibbs free energy

The fundamental equation of the Gibbs energy is given in an integral form as (Ziegler and Trepp [27], Ibrahim and Klein [28], Xu and Yogi Goswami [29]):

$$G = H_0 - TS_0 + \int_{T_0}^{T} Cp\, dT + \int_{P_0}^{P} V\, dP - T\int_{T_0}^{T} \frac{Cp}{T}\, dT \qquad (1)$$

The volume *V* and the heat capacity at constant pressure *Cp* for the liquid and vapor phase of both pure water and pure ammonia are assumed to be empirically correlated by the following expression (Ziegler and Trepp [27]):

$$V^L = a_1 + a_2P + a_3T + a_4T^2 \tag{2}$$

$$V^g = \frac{RT}{P} + c_1 + \frac{c_2}{T^3} + \frac{c_3}{T^{11}} + \frac{c_4P^2}{T^{11}} \tag{3}$$

$$Cp^L = b_1 + b_2T + b_3T^2 \tag{4}$$

$$Cp^g = d_1 + d_2T + d_3T^2 - T\int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right) dP \tag{5}$$

The development of eq. (1) with the help of eqs. (2-5) leads to the following equations:

Liquid phase:

$$\begin{aligned} G_r^L = {} & H_{r,0}^L - T_rS_{r,0}^L + B_1(T_r - T_{r,0}) + \frac{B_2}{2}(T_r^2 - T_{r,0}^2) + \frac{B_3}{3}(T_r^3 - T_{r,0}^3) - B_1T_r \ln\left(\frac{T_r}{T_{r,0}}\right) - B_2T_r(T_r - T_{r,0}) \\ & - \frac{B_3}{2}T_r(T_r^2 - T_{r,0}^2) + (A_1 + A_3T_r + A_4T_r^2)(P_r - P_{r,0}) + \frac{A_2}{2}(P_r^2 - P_{r,0}^2) \end{aligned} \tag{6}$$

Vapor phase:

$$\begin{aligned} G_r^g = {} & H_{r,0}^g - T_rS_{r,0}^g + D_1(T_r - T_{r,0}) + \frac{D_2}{2}(T_r^2 - T_{r,0}^2) + \frac{D_3}{3}(T_r^3 - T_{r,0}^3) - D_1T_r \ln\left(\frac{T_r}{T_{r,0}}\right) \\ & - D_2T_r(T_r - T_{r,0}) - \frac{D_3}{2}T_r(T_r^2 - T_{r,0}^2) + T_r \ln\left(\frac{P_r}{P_{r,0}}\right) + C_1(P_r - P_{r,0}) \\ & + C_2\left(\frac{P_r}{T_r^3} - 4\frac{P_{r,0}}{T_{r,0}^3} + 3\frac{P_{r,0}T_r}{T_{r,0}^4}\right) + C_3\left(\frac{P_r}{T_r^{11}} - 12\frac{P_{r,0}}{T_{r,0}^{11}} + 11\frac{P_{r,0}T_r}{T_{r,0}^{12}}\right) \\ & + \frac{C_4}{3}\left(\frac{P_r^3}{T_r^{11}} - 12\frac{P_{r,0}^3}{T_{r,0}^{11}} + 11\frac{P_{r,0}^3T_r}{T_{r,0}^{12}}\right) \end{aligned} \tag{7}$$

The reduced thermodynamic properties (subscript r) are $T_r=T/T_B$, $P_r = P/P_B$, $G_r=G/RT_B$, $h_r=h/RT_B$, $S_r=S/R$ and $V_r=VP_B/RT_B$. The values of the constants R, T_B and P_B are $R=8.314$ [kJkmol^{-1}K^{-1}], $T_B=100$ [K] and $P_B=10$ [bar]. Coefficients for eqs. (6-7) are given in tab. 1.

2.1.2. Thermodynamic properties

The molar specific enthalpy, entropy and volume are related to Gibbs free energy by:

$$H = -RT_BT_r^2\left[\frac{\partial(G_r/T_r)}{\partial T_r}\right]_{P_r} \tag{8}$$

$$S = -R\left[\frac{\partial G_r}{\partial T_r}\right]_{P_r} \tag{9}$$

$$V = \frac{RT_B}{P_B}\left[\frac{\partial G_r}{\partial P_r}\right]_{T_r} \tag{10}$$

	Ammonia	water
A_1	$3.971423.10^{-2}$	$2.748796.10^{-2}$
A_2	$-1.790557.10^{-5}$	$-1.016665.10^{-5}$
A_3	$-1.308905.10^{-2}$	$-4.452025.10^{-3}$
A_4	$3.752836.10^{-3}$	$8.389246.10^{-4}$
B_1	1.634519.101	$1.214557.10^{1}$
B_2	-6.508119	-1.898065
B_3	1.448937	$2.911966.10^{-1}$
C_1	$-1.049377.10^{-2}$	$2.136131.10^{-2}$
C_2	-8.288224	$-3.169291.10^{1}$
C_3	$-6.647257.10^{2}$	$-4.634611.10^{4}$
C_4	$-3.045352.10^{3}$	0
D_1	3.673647	4.019170
D_2	$9.989629.10^{-2}$	$-5.175550.10^{-2}$
D_3	$3.617622.10^{-2}$	$1.951939.10^{-2}$
$H_{r,0}^{L}$	4.878573	21.821141
$H_{r,0}^{g}$	26.468879	60.965058
$S_{r,0}^{L}$	1.644773	5.733498
$S_{r,0}^{g}$	8.339026	13.453430
$T_{r,0}$	3.2252	5.0705
$P_{r,0}$	2	3

Table 1. Coefficients for eqs. (6-7)

2.2. Mixture of ammonia and water

2.2.1. Ammonia-Water liquid mixture

According to the analysis given by Ziegler and Trepp [27], the liquid mixture Gibbs function of ammonia-water is given by the ideal solution mixture relation plus the Gibbs excess energy. This excess energy is limited to three terms and takes into account the deviation from ideal solution behavior.

$$G_r^E = x(1-x)\left[F_1 + F_2(2x-1) + F_3(2x-1)^2\right] \tag{11}$$

where:

$$F_1 = E_1 + E_2P_r + (E_3 + E_4P_r)T_r + \frac{E_5}{T_r} + \frac{E_6}{T_r^2} \tag{12}$$

$$F_2 = E_7 + E_8P_r + (E_9 + E_{10}P_r)T_r + \frac{E_{11}}{T_r} + \frac{E_{12}}{T_r^2} \tag{13}$$

$$F_3 = E_{13} + E_{14}P_r + \frac{E_{15}}{T_r} + \frac{E_{16}}{T_r^2} \tag{14}$$

Coefficients for eqs. (12-14) are given in tab. 2. The excess specific enthalpy, entropy and volume of the liquid mixture can be derived as eqs. (8-10).

E_1	-41.733398	E_9	0.387983
E_2	0.02414	E_{10}	0.004772
E_3	6.702285	E_{11}	-4.648107
E_4	-0.011475	E_{12}	0.836376
E_5	63.608967	E_{13}	-3.553627
E_6	-62.490768	E_{14}	0.000904
E_7	1.761064	E_{15}	24.361723
E_8	0.008626	E_{16}	-20.736547

Table 2. Coefficients for eqs. (12-14)

$$H^E = -RT_B T_r^2 \left[\frac{\partial\left(G_r^E / T_r\right)}{\partial T_r}\right]_{P_r,x} \tag{15}$$

$$S^E = -R\left[\frac{\partial G_r^E}{\partial T_r}\right]_{P_r,x} \tag{16}$$

$$V^E = \frac{RT_B}{P_B}\left[\frac{\partial G_r^E}{\partial P_r}\right]_{T_r,x} \tag{17}$$

Therefore, the specific enthalpy, entropy and volume of the liquid mixture become:

$$H_m^L = xH_{NH_3}^L + (1-x)H_{H_2O}^L + H^E \tag{18}$$

$$S_m^L = xS_{NH_3}^L + (1-x)S_{H_2O}^L + S^E + S^{ml} \tag{19}$$

$$V_m^L = xV_{NH_3}^L + (1-x)V_{H_2O}^L + V^E \tag{20}$$

where:

$$S^{ml} = -R\left[x\ln(x) + (1-x)\ln(1-x)\right] \tag{21}$$

2.2.2. Ammonia-Water vapor mixture

The vapor phase is considered as an ideal solution, so the excess Gibbs function is equal to zero. The specific enthalpy, entropy and volume of the vapor mixture are calculated from:

$$H_m^g = yH_{NH_3}^g + (1-y)H_{H_2O}^g \tag{22}$$

$$S_m^g = yS_{NH_3}^g + (1-y)S_{H_2O}^g + S^{mg} \tag{23}$$

$$V_m^g = yV_{NH_3}^g + (1-y)V_{H_2O}^g \tag{24}$$

where:

$$S^{mg} = -R\left[y\ln(y) + (1-y)\ln(1-y)\right] \tag{25}$$

3. Results and discussions

3.1. Comparison of the results

The comparison is carried out for the calculated thermodynamic properties for the mixtures and pure components.

3.1.1. Ammonia-water mixtures

Comparison between results given by the chosen model and the experimental results provided by IIR [50] and Dae.Wen. SUN [49] data's of ammonia-water mixtures are presented in tab 3. The comparison is made for the saturated pressure and saturated volume for the two states liquid and vapor, in case of two references values of temperatures: low one equal to 283.15 [K] and high temperature equal to 525.15 [K].

	Average error [%]			
	T= 283.15 [K]		T= 525.15 [K]	
	Model 1 : IIR	Model 2 : Dae Wen SUN	Model 1 : IIR	Model 2 : Dae Wen SUN
Saturated pressure	3.6		3.1	
Saturated volume liquid	2.8		9.4	
Saturated volume vapor	4.5		4.1	

Table 3. Average error for comparative study in case of mixtures

From the tab. 3 it is clear that the average error between the calculated saturated pressure and those given by the model 1 and 2 is up to 3.6 % for low temperatures and up to 3.1 % for high temperatures. On the other hand, the average error in case of specific liquid volume is up to 2.8 % for low temperatures and up to 9.4 % for high temperatures. This can be explained by the fact that most of the elaborated models are appropriate for the vapor phase rather than for the liquid phase. Finally, the average error for specific vapor volume is up to 4.5 % for low temperatures and up to 4.1 % for high temperature.

3.1.2. Pure components

The chosen model allows calculating the enthalpy, latent heat, entropy and volume of ammonia and water in case of vapor and liquid states for pure components. The results are compared with the KUMAN Ražnjevic [51] and L. HAAR *et al.* [52] data's and represented in the figs (1-8).

Figure 1. Latent heat of vaporization of ammonia

Figure 2. Latent heat of vaporization of water

The obtained variation of latent heat of vaporization for ammonia and water is compared with KUMAN Ražnjevic and L. HAAR *et al.* data's and shown in the figs (1-2) . As can be seen, the latent heat of vaporization decreases when the temperature is increasing. However, beyond the temperature value of 540 K a little difference is observed. The correlation coefficient between the results of simulation and those of KUMAN Ražnjevic and L. HAAR *et al.* is equal to 0.9999, 0.9977 for ammonia and water respectively. This coefficient is nearly the same for the other results shown in figs (3-8).

Figure 3. Entropy variation of ammonia

Figure 4. Entropy variation of water

Figure 5. Saturated liquid volume of ammonia

Figure 6. Saturated liquid volume of water

Figure 7. Saturated vapor volume of ammonia

Figure 8. Saturated vapor volume of water

Finally, the comparative study shows a good agreement of the results of simulation with those of the authors [51-52].

3.2. Exploring simulation results of the thermodynamic properties of ammonia-water mixtures for the elaboration of the Merkel's and Oldham's diagrams

3.2.1. Merkel's diagram

Merkel's diagram allows doing a full study of the absorption machine, as it provides the heat balances of the various parts of the circuit by direct reading of enthalpy differences. As shown in fig.9, the x-axis is dedicated to the concentration of the liquid phase and the y-axis to the enthalpy.

It includes at its lower part, networks of isobars and isotherms, as well as curves of vapor-liquid equilibrium at equal concentration. At the upper part, the reference curves allow to establish the characteristics of the vapor phase, starting from a determined point of equilibrium in the lower part.

Figure 9. Merkel's diagram

3.2.2. Oldham's diagram

This diagram is the most used and most convenient for the absorption machine study. As shown in fig.10, the x-axis is scaled in (*1/T*) and the y-axis in (Log *P*). In this system of coordinates, the curves reflecting the balance of the binary system in the vapor as well as in the liquid phase are approximately straight lines. The straight line with 100% of concentration corresponds to the vapor-liquid equilibrium of pure ammonia, and the one with 0% of concentration correspond to vapor-liquid equilibrium of pure water.

Figure 10. Oldham's diagram

4. Conclusion

The ammonia-water mixture was the principal binary couple used in the absorption refrigerating machines for several years. As in many studies, this one is conducted on vapor-liquid balance and the thermo-physical properties of mixture. For that the following conclusions were drawn:

- ✓ A method that combines the Gibbs free energy method for mixture properties and bubble and dew point temperature equations for phase equilibrium is used. This method combines the advantages of the two and avoids the need for iterations for phase equilibrium;
- ✓ The proposed correlations cover high vapor-liquid equilibrium pressures and temperatures;
- ✓ It is necessary to note the good agreement of the calculated of the thermodynamic properties for the mixture from the chosen model with the IIR and Dae. Wen. SUN data's;
- ✓ The comparative analysis for the calculated enthalpy, latent heat, entropy and volume of ammonia and water in case of vapor and liquid states for pure components with KUMAN Ražnjevic and L. HAAR *et al.* data's shows a good agreement. This is confirmed by the values of the correlation coefficient equal to *0.999* for ammonia and water.

Nomenclature

H	– molar enthalpy, [kJkmol^{-1}]
V	– molar volume, [m^{3}kmol^{-1}]
S	– molar Entropy, [kJkmol^{-1}K^{-1}]
T	– temperature, [°C, K]
P	– pressure, [bar]
G	– Gibbs free energy, [kJkmol^{-1}]
x	– liquid ammonia mole fraction, [kmol of NH_3 kmol^{-1} of liquid mixture]
y	– vapor ammonia mole fraction, [kmol of NH_3 kmol^{-1} of vapor mixture]
R	– molar gas constant, [kJkmol^{-1} K^{-1}]
Cp	– heat capacity at constant pressure, [kJkg^{-1}K^{-1}]
a, b, c, d	– coefficients, [–]
A, B, C, D, E, F	– dimensionless coefficients, [–]
r	– correlation coefficient, [–]

Subscripts

c	– critical
NH_3	– ammonia
H_2O	– water
r	– reduced
0	– reference state

Superscripts

E	– excess
ml	– liquid mixture
mg	– vapor mixture
L	– liquid
g	– vapor
m	– mixture

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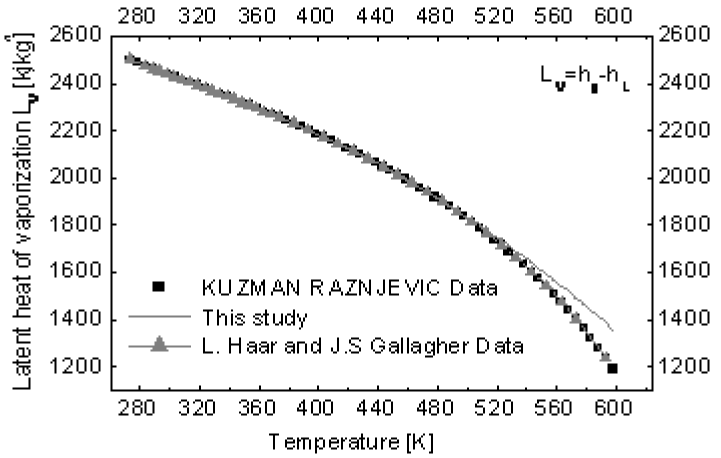


Figure 1. Latent heat of vaporization of ammonia

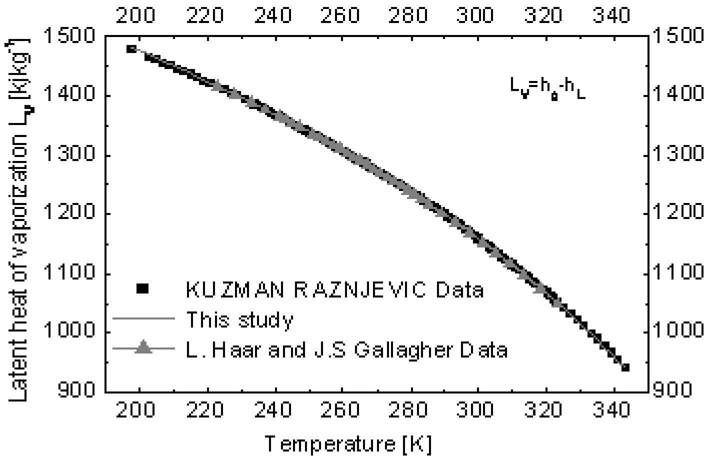


Figure 2. Latent heat of vaporization of water

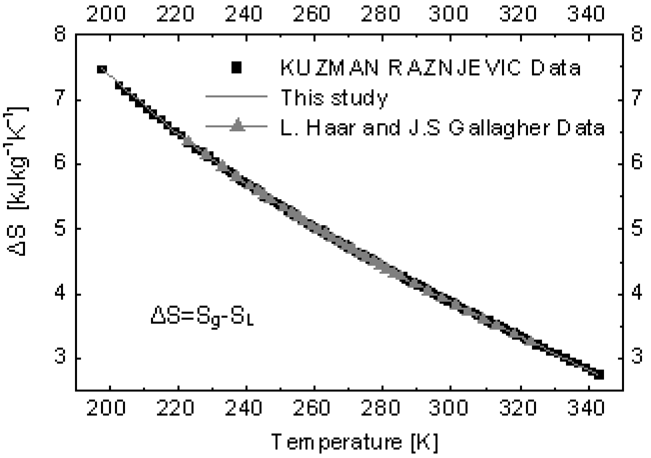
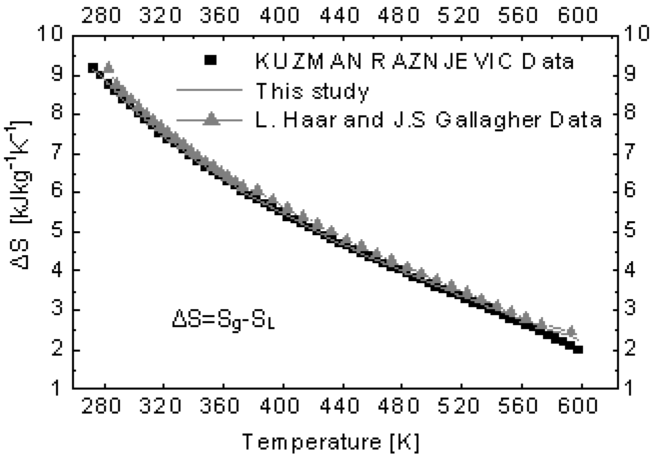


Figure 3. Entropy variation of ammonia



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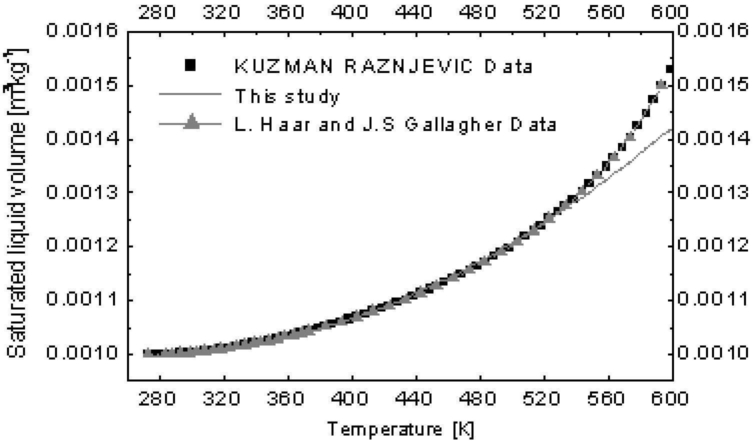
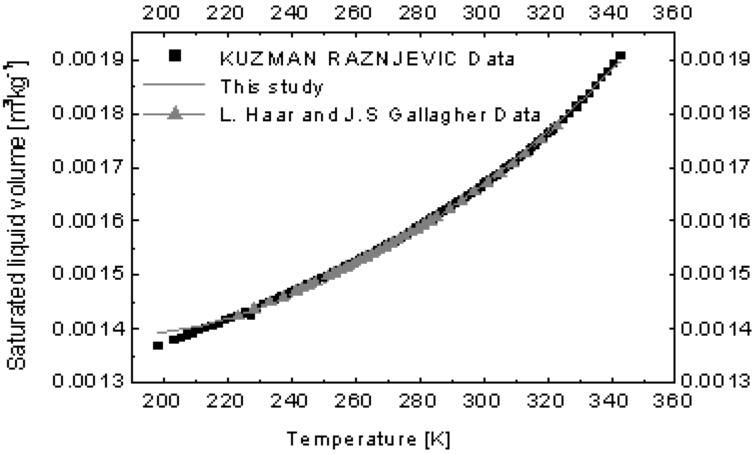


Figure 5. Saturated liquid volume of ammonia



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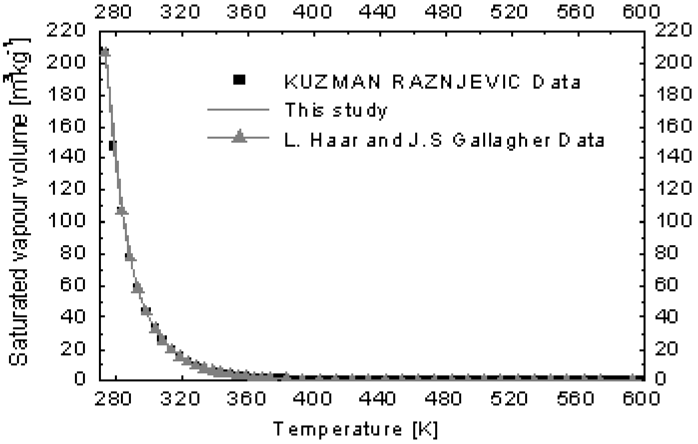

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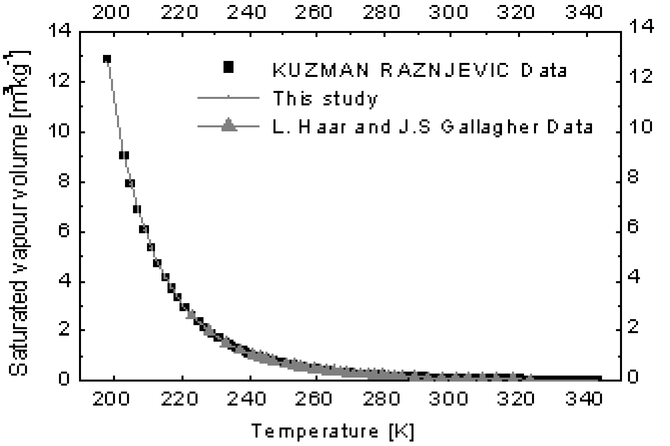

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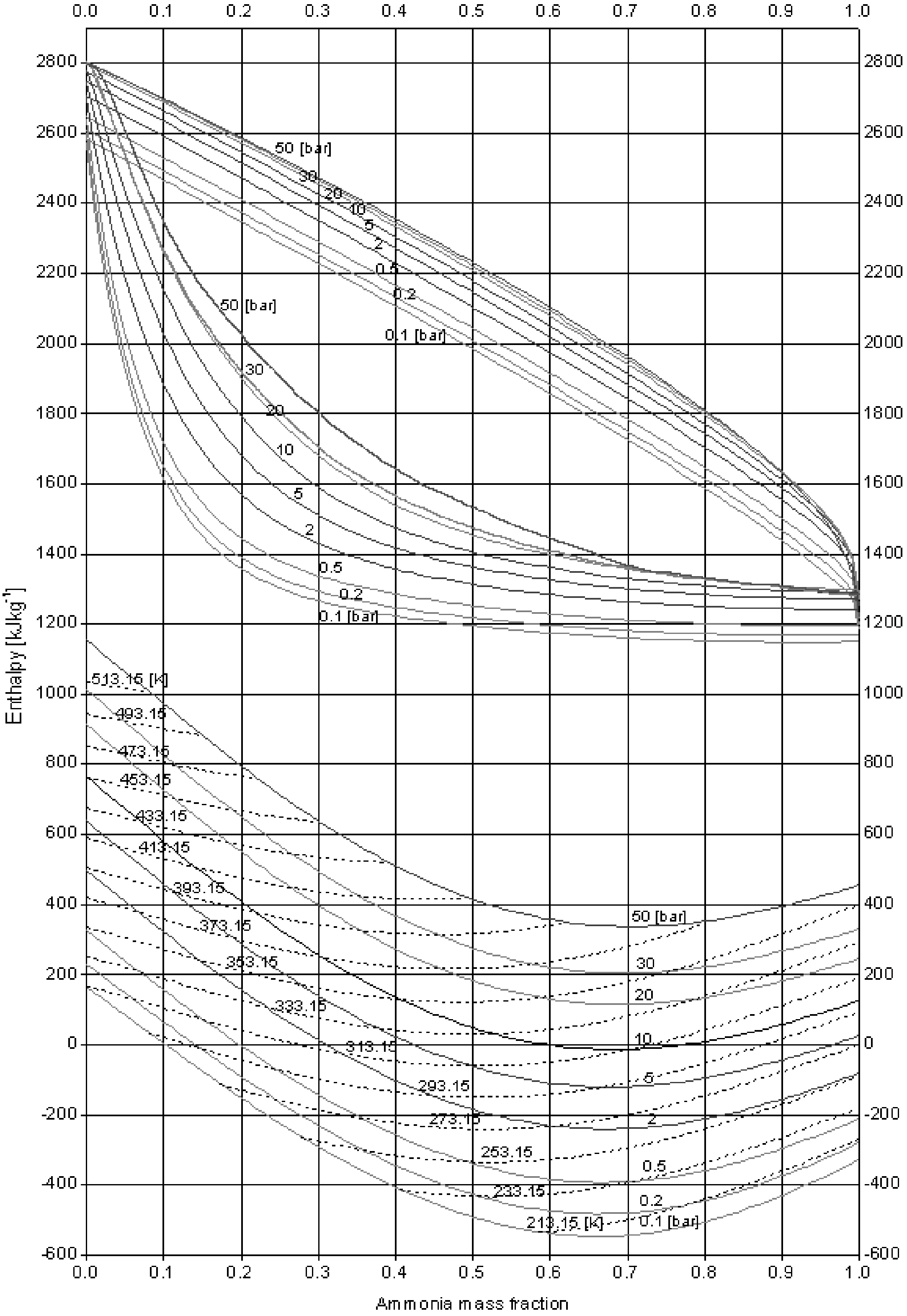

Figure 9. Merkel’s diagram

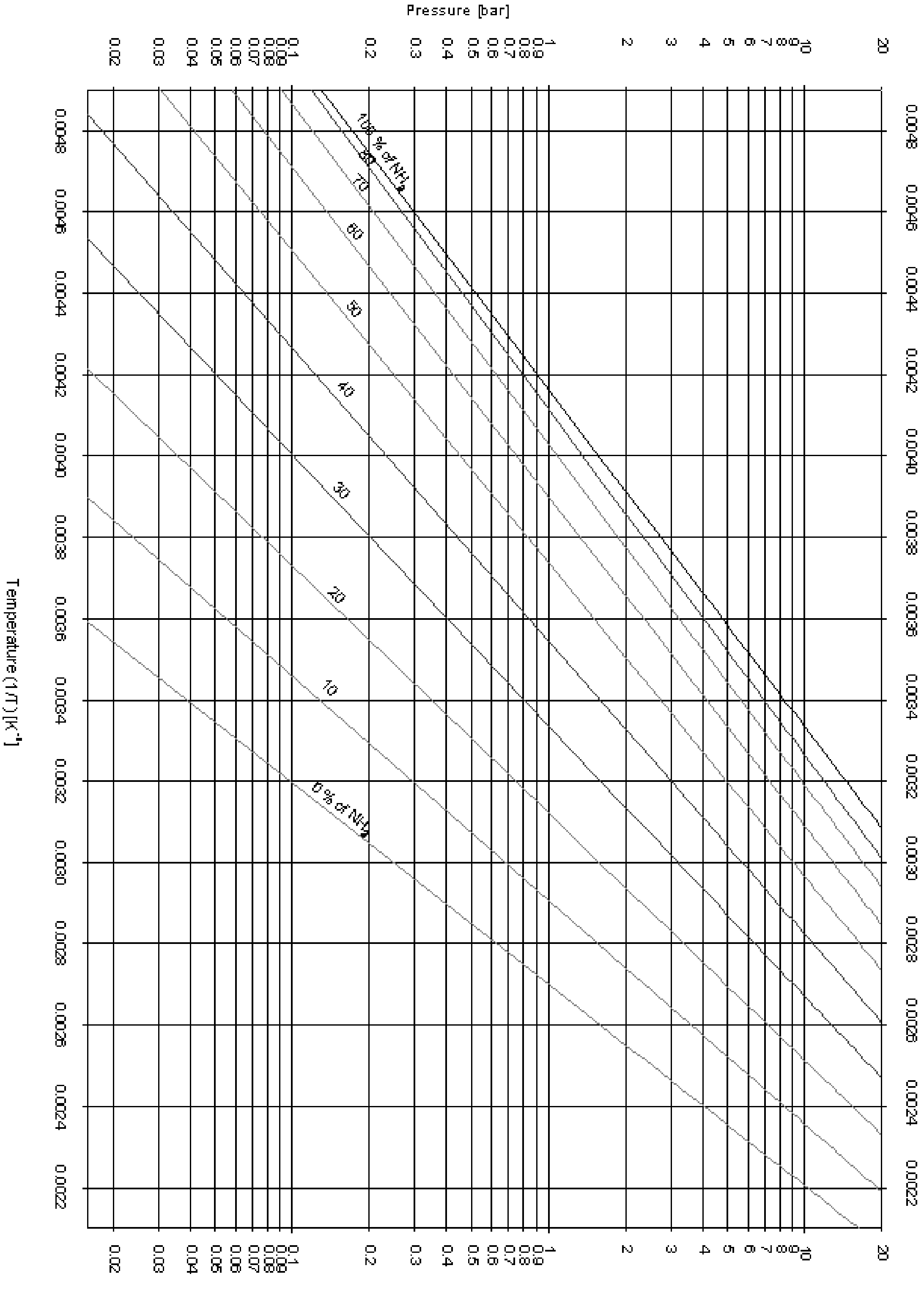

Figure 10. Oldham’s diagram