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Thermophysical Properties of Ammonia–Water Mixtures for Prediction of Heat Transfer Areas in Power Cycles[1]

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In power cycles using ammonia–water mixtures as the working fluid, several heat exchangers are used. The influence of different correlations for predicting thermophysical properties on the calculations of the size of the heat exchangers is presented. Different correlations for predicting both the thermodynamic and the transport properties are included. The use of different correlations for the thermodynamic properties gives a difference in the total heat exchanger area of 7%, but for individual heat exchangers, the difference is up to 24%. Different correlations for the mixture transport properties give differences in the predicted heat exchanger areas that are, at most, about 10% for the individual heat exchangers. The influence on the total heat exchanger area is not larger than 3%. A difference in the total heat exchanger area of 7% would probably correspond to less than 2% of the total cost for the process equipment. Experimental data and correlations developed for the ammonia–water mixture transport properties are very scarce. The evaporation and condensation processes involving ammonia–water mixtures are also not fully understood.

KEY WORDS: ammonia–water mixture; heat exchanger; Kalina cycle; power cycle; thermodynamic properties; transport properties.

1. INTRODUCTION

The most well known power cycle using an ammonia–water mixture as a working fluid is the Kalina cycle. This cycle has been shown to be more

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efficient than conventional power cycles for several applications. Binary fluids boil and condense at increasing and decreasing temperatures, respectively. Therefore, better temperature matching in the heat exchange processes is possible compared to when one-component working fluids, which boil and condense at a constant temperature, are used.

Various correlations for predicting the thermodynamic properties of ammonia–water mixtures have been used in studies of ammonia–water mixture cycles described in the literature. The present author has previously compared some of those correlations in power cycle performance calculations [1, 2]. The results of these studies were that even though the correlations showed differences in predicting the properties, the final results of the thermal efficiency cycle simulations were similar.

Besides calculating the thermodynamic performance of the power cycle, its different components have to be designed. In power cycles using ammonia–water mixtures as a working fluid, several heat exchangers are used. In this study the influence of different correlations for predicting thermophysical properties on the calculations of the size of the heat exchangers is examined.

2. TRANSPORT PROPERTIES

The viscosity and thermal conductivity of the fluids are always needed when the heat exchange between two flowing fluids is described. Mass transfer processes can be of importance for the design of heat exchangers when the condensation and evaporation of mixtures are involved, since the vapor and liquid phases during these processes have different compositions. For the mass transfer process, the diffusion coefficient is needed. In the present study, the influence of mass transfer on the heat exchange process has not been considered.

Very little information has been found in the literature regarding transport properties for ammonia–water mixtures. Measurements of the transport properties are very scarce. Two studies [3, 4] presenting experimental data for the viscosity have been found. Data for the liquid thermal conductivity of the mixture are presented in Refs. 5 and 6. The conditions for those measurements are presented in Table I.

Even though several studies can be found in the literature where heat transfer processes involving ammonia–water mixtures are described, the method for calculating the transport properties is seldom mentioned. In some studies, methods described in Reid et al. [7] is used. Reid et al. describe several correlations for predicting mixture transport properties, of which none has been specifically developed for the ammonia–water mixture.

Table I. Experimental Data for Transport Properties of Ammonia–Water Mixtures

Ref.	Year	Type of Data	Temperature range (K)	Mass fraction of ammonia
Pinevic [3]	1948	Saturated liquid viscosity	283.15–423.15	0.10-0.90
Frank et al. [4]	1996	Liquid viscosity	293.00–313.00	0.02-0.20
Riedel [5] [from data of Lees (1898)]	1951	Liquid thermal conductivity	293	0.15–0.30
Riedel [5] [calculated from data of Braune (1937)]	1951	Liquid thermal conductivity	293	0.05–0.10
Baranov et al. [6]	1997	liquid thermal conductivity	303–460	0.00–1.00

In Fig. 1, equations found in the literature for predicting properties of ammonia–water mixtures are shown. Some of the equations have been developed for the ammonia–water mixture, while others are general equations, which have been used for the ammonia–water mixture. The methods described by Stecco and Desideri [8, 9] and El-Sayed [10, 11] have previously been used in calculations of heat exchange areas in power cycles with ammonia–water mixtures as the working fluid.

3. CORRELATIONS USED IN THIS STUDY

Two correlations for predicting the thermodynamic properties are used in the present study: one has been described by Tillner-Roth and Friend [14], and the other is described by Stecco and Desideri [15], which is referred to as the basic case. The correlation by Tillner-Roth and Friend is based on a fundamental equation of state for the Helmholtz free energy. In this correlation, the entire thermodynamic space of the mixture is described by one single equation. The correlation by Stecco and Desideri is based on work presented by Ziegler and Trepp [16] and El-Sayed and Tribus [17]. Here, the basis is expressions for the Gibbs free energy, and different equations are used for the vapor and liquid phases.

The method to calculate the transport properties for the mixture described and used by Stecco and Desideri [8, 9] has been used as the basic case in this study. The predictions of the heat exchanger areas in the basic case are compared to the results using the equations described and used by El-Sayed [10, 11]. The equations for calculations of the transport properties are, however, misprinted in Ref. 10. The correct formulation of the equations [7, 11] is shown in the Appendix here.

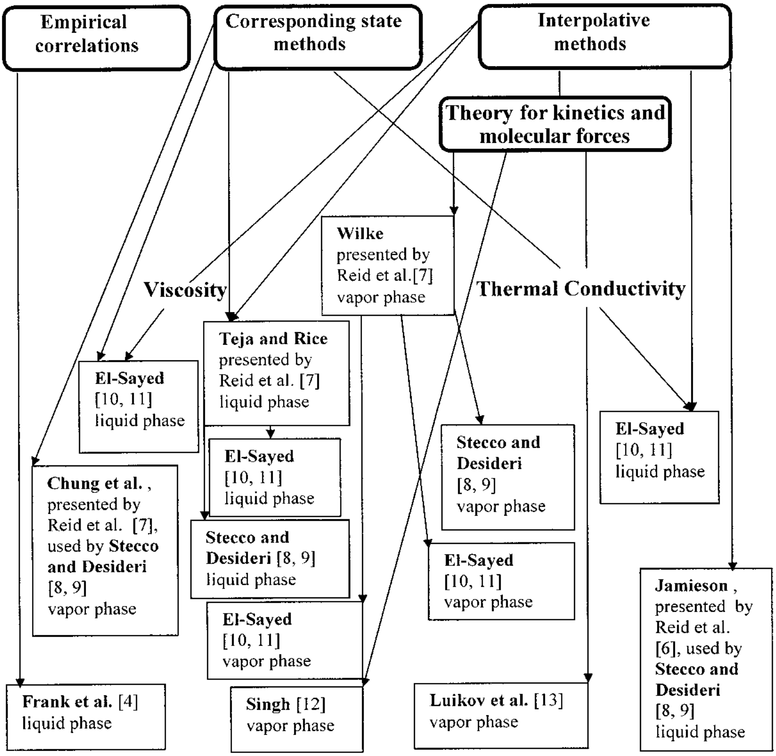

Fig. 1. Correlations found in the literature presented or used for the ammonia–water mixture transport properties.

Stecco and Desideri calculate the mixture viscosities with corresponding-states correlations. The vapor viscosity is calculated with Chung's method as described by Reid et al. [7]. This is a noninterpolative method, which means that the viscosity for the pure substances do not have to be known. However, for the liquid mixture viscosity, equations based on a method by Teja and Rice, as presented by Reid et al., where the pure components are used as reference fluids, are suggested by Stecco and Desideri. In the original Teja–Rice method, the properties for the reference fluids are calculated at a temperature equal to the following relation:

$$T_{\text{reference fluid}} = T_{\text{mixture}} \frac{T_{\text{critical, reference fluid}}}{T_{\text{critical, mixture}}}$$

Stecco and Desideri have modified the Teja–Rice equation by using the mixture temperature, which is the same as when the properties of the pure substances are calculated. The Teja–Rice equation has an interaction parameter, called psi, which must be found from experimental data. Stecco and Desideri use the value 8 for psi. This is something that is also suggested by El-Sayed [10].

El-Sayed used the Wilke method as presented by Reid et al. [7] for the vapor viscosity. For the liquid viscosity, an interpolative correlation based on corresponding-states theory is used.

For the mixture thermal conductivity, Stecco and Desideri use interpolative methods. The thermal conductivity for the vapor is calculated with the Wilke correlation for viscosity calculations, and for the liquid mixtures, a correlation by Jamieson et al. is used. Both methods are described by Reid et al. [7].

El-Sayed used the Wilke correlation for calculation of the vapor thermal conductivity as well. For the liquid thermal conductivity, an interpolative method based on corresponding-states theory is used.

Transport properties for the pure substances have been calculated using the equations suggested by Stecco and Desideri [8, 9] and described by Reid et al. [7]. The thermal conductivities are calculated with polynomial equations originally presented by Miller et al. The vapor viscosities are calculated with the Lucas method, which is a corresponding-states method. The liquid viscosities are calculated with correlations based on experimental data.

A total of seven combinations of correlations for the thermophysical properties, shown in Table II, has been used in the heat exchanger predictions. For the vapor thermal conductivity, Stecco and Desideri and El-Sayed have used the same equation.

4. HEAT TRANSFER AREA PREDICTION

In this study, an estimation of the heat transfer areas in a power cycle using ammonia–water mixtures as the working fluid has been performed. Since it is not clear how the mass transfer resistance in the evaporation and condensation processes should be taken into account, equations valid for pure substances, but with the properties of the mixture, are used. Hultén and Berntsson [18] use correlations for pure substances with the properties of the mixture for the evaporation and condensation processes in their study of the compression/absorption heat pump with ammonia–water mixtures as the working fluid. This will probably lead to an underestimation of the heat transfer areas for these processes, since the possible degradation of the heat transfer coefficients due to mass transfer resistance is not considered.

Table II. Combinations of the Different Methods to Calculate the Thermophysical Properties Used in the Heat Exchanger Predictions

	Thermodynamic properties	Liquid viscosity	Vapor viscosity	Liquid thermal conductivity	Vapor thermal conductivity
Basic case (Case I)	Stecco and Desideri [15]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]; El-Sayed [10, 11]
Case II	Tillner-Roth and Friend [14]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]; El-Sayed [10,11]
Case III	Stecco and Desideri [15]	El-Sayed [10, 11]	El-Sayed [10, 11]	El-Sayed [10, 11]	Stecco and Desideri [8, 9]; El-Sayed [10, 11]
Case IV	Stecco and Desideri [15]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]	El-Sayed [10, 11]	Stecco and Desideri [8, 9]; El-Sayed [10, 11]
Case V	Stecco and Desideri [15]	Stecco and Desideri [8, 9]	El-Sayed [10, 11]	Stecco and Desideri [10, 11]	Stecco and Desideri [8, 9]; El-Sayed [10, 11]
Case VI	Stecco and Desideri [15]	El-Sayed [10, 11]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]	Stecco and Desideri [8, 9]; El-Sayed [10, 11]

The power cycle used as an example for the calculations is shown in Fig. 2. It is the same configuration that has been presented by El-Sayed and Tribus [19], and it also has been simulated in previous studies by the present author [1, 2]. All heat exchangers are assumed to be shell-and-tube heat exchangers.

The boiler has a horizontal shell and vertical finned tubes with a single-pass gas flow outside the tubes and the mixture flow inside the tube bundles. It is a once-through design. The calculations have been performed with a method described by Kays and London [20]. For the evaporator part of the boiler, a constant heat transfer coefficient of $10\ \mathrm{kW \cdot m^{-2} \cdot K^{-1}}$, as used by Stecco and Desideri [8], has been chosen for the boiling side. Since the gas-side heat transfer resistance dominates the overall heat transfer resistance, this approximation should not introduce any large error to the area calculation.

The condensation of the vapor from the turbine and from the separator is done on the shell side in vertical, single-pass, and counter-current

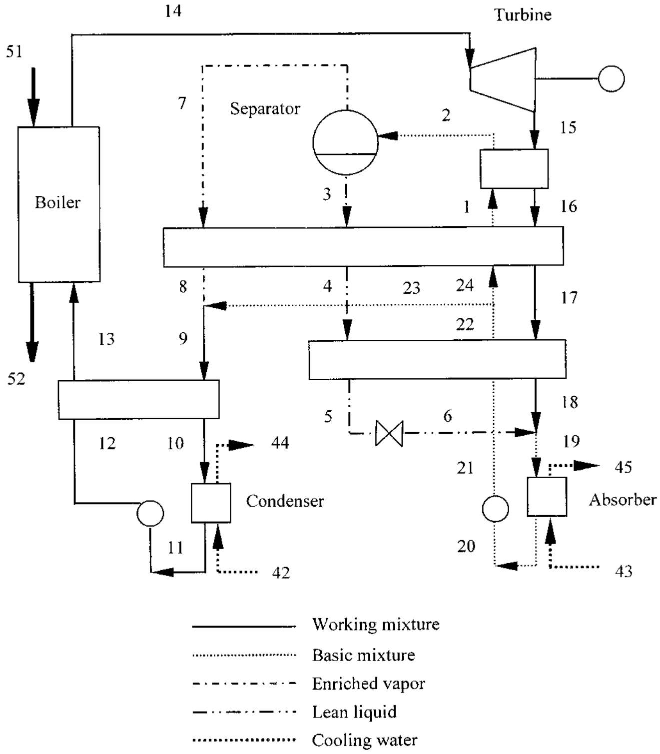

Fig. 2. The configuration of the ammonia–water cycle used in the study.

shell-and-tube heat exchangers. The vapor and liquid that flow into the condenser and absorber are assumed to be ideally mixed. This assumption was made by Hultén and Berntsson [18]. They point out that this, in reality, would require separate mixers. The equations used for the heat transfer processes in the internal heat exchangers, in the condenser, and in the absorber are taken from Refs. 21 and 22.

No complete optimization of the heat transfer areas is performed. Areas giving pressure drops no higher than 5% are chosen, and the tube side liquid velocities are maintained at about 1 to 2 $\text{m} \cdot \text{s}^{-1}$, which, according to Ref. 21, are normal tube-side velocities. Recommendations given in Refs. 20–22 are followed for the design of the tubes and shells. The same dimensions have been used for all the calculated cases. Furthermore, as the present investigation aims at studying the influence on the predicted heat exchanger areas when various correlations for the thermophysical properties are used, no major efforts have been made to find the most reasonable design from a practical point of view.

With regard to the power cycle layout, the results of the simulations presented in Ref. 2 form the basis for this study. The input data that gave the highest cycle efficiency for the case with a maximum pressure of 10.82 MPa in the cycle are used. The gas turbine exhaust gas flow is 12.5 $\text{kg} \cdot \text{s}^{-1}$ giving a power generation from the bottoming cycle of about 2.0 MW. In contrast to the study presented in Ref. 2, the pressure drops over the heat exchangers have been included in the simulations of the process in this study.

5. RESULTS

The results of the heat exchanger area predictions are presented in Tables III and IV. When the process is simulated with the correlations for the thermodynamic properties suggested by Tillner-Roth and Friend [14] (Case II), the total heat exchanger area is larger than when the correlations

Table III. Results of the Heat Exchanger Area Predictions with Different Correlations for the Thermodynamic Properties

		Basic case (Case I)		Case II	
Hot-side stream[a]	Colde-side stream[a]	Heat (MW)	Area (m^2)	Heat (MW)	Area (m^2)
Hot gas	13–13b	1.287	994.1	1.411	1113.9
Hot gas	13b–13d	2.741	482.9	2.616	464.7
Hot gas	13d–14	2.138	529.4	2.133	553.7
Sum		6.166	2006.4	6.160	2132.3
15–15d	2d–2	0.270	110.6	0.191	115.2
15d–16	1–2d	0.510	69.3	0.380	69.4
16–17	24–1	1.104	322.3	1.285	393.0
17–18	21–22	0.351	23.6	0.404	25.6
3–4	24–1	0.460	192.0	0.487	239.7
4–5	21–22	0.790	630.7	0.750	667.0
7–8	24–1	0.204	66.6	0.260	78.9
9–10	12–13	0.324	19.4	0.360	21.1
Sum		4.013	1434.4	4.117	1609.9
19–20	Cooling water	2.621	294.9	2.648	288.0
10–11	Cooling water	1.548	176.6	1.519	168.4
Sum		4.169	471.5	4.167	456.4
Total sum		14.348	3912.3	14.444	4198.6

[a] b refers to the boiling point for the cold side stream, d refers to the dew point for the hot- or cold-side stream

Table IV. Results of the Heat Exchanger Area Predictions with Different Correlations for the Transport Properties

			Area (m^2)				
Hot-side stream[a]	Cold-side stream[a]	Heat (MW)	Basic case (Case I)	Case III	Case IV	Case V	Case VI
Hot gas	13–13b	1.287	994.1	990.3	986.5	994.1	999.3
Hot gas	13b–13d	2.741	482.9	482.9	482.9	482.9	482.1
Hot gas	13d–14	2.138	529.4	528.9	529.4	528.9	529.4
Sum			2006.4	2002.1	1998.8	2006.0	2011.6
15–15d	2d–2	0.270	110.6	107.9	110.3	108.4	110.4
15d–16	1–2d	0.510	69.3	63.7	66.6	69.3	66.3
16–17	24–1	1.104	322.3	311.0	302.1	322.3	332.1
17–18	21–22	0.351	23.6	23.5	21.8	23.6	25.5
3–4	24–1	0.460	192.0	183.0	180.4	192.0	194.8
4–5	21–22	0.790	630.7	646.1	580.7	630.7	702.6
7–8	24–1	0.204	66.6	65.5	61.9	66.6	70.5
9–10	12–13	0.324	19.4	18.5	17.5	19.4	20.5
Sum			1434.4	1419.1	1341.2	1432.2	1522.6
19–20	Cooling water	2.621	294.9	295.6	284.3	294.9	307.3
10–11	Cooling water	1.548	176.6	174.2	168.8	176.6	182.6
Sum			471.5	469.8	453.1	471.5	489.9
Total sum			3912.3	3891.1	3793.0	3909.7	4024.1

[a] b refers to the boiling point for the cold side stream, d refers to the dew point for the hot- or cold-side stream.

by Stecco and Desideri [15] (Case I) are used. The difference is 7%. For some individual heat exchangers, however, Case II shows a smaller area. For the individual heat exchangers, the difference in predicted heat exchanger area can be as large as 24%. The differences in the mixture transport properties between Case I and Case II are small. For both the viscosity and the thermal conductivity, the differences for most streams are about 1–2% of the properties of the streams in the Stecco and Desideri case and no higher than 7%. The variations in transferred heat, temperature differences, and mass flow cause the differences in heat exchanger areas. This is due to the fact that the simulation of the process with the different correlations for the thermodynamic properties give differences in the enthalpies, mass fractions of ammonia, and mass flows for the different streams in the cycle.

Using the method by El-Sayed for calculating all the transport properties (Case III) gives a total predicted heat exchanger area that is only 0.5%

lower compared to when the correlations suggested by Stecco and Desideri (Case I) are used. For the individual heat exchangers, the difference is up to 8%.

The use of the equations for the liquid thermal conductivities presented by El-Sayed give 3 to 20% higher thermal conductivities for the streams in the power cycle than for the equations used by Stecco and Desideri. Thus, the El-Sayed equations for the liquid thermal conductivity (Case IV) result in a total heat exchanger area that is 3% smaller than the area calculated using the equations suggested by Stecco and Desideri. For the individual heat exchangers, the difference is at most 10%.

The use of the different equations for the liquid viscosities (Case I and Case VI) shows the opposite result for most heat exchangers. Here, a 3% larger total heat exchanger area is achieved when the equation presented by El-Sayed is used compared to the equation suggested by Stecco and Desideri. For the individual heat exchangers, the difference is up to 11%. The variation in the liquid viscosities between different correlations is 1 to 18% for the streams in the power cycle. For most streams, the equation presented by El-Sayed gives higher viscosity values than the equation suggested by Stecco and Desideri, but the opposite is sometimes the case.

The correlation by El-Sayed for the vapor viscosity gives viscosities that are about 8% lower than the values from the correlation used by Stecco and Desideri. The resulting differences in the heat exchanger areas are not larger than 2%.

6. DISCUSSION AND CONCLUSIONS

The present study indicates that the use of different correlations for the thermodynamic properties in the simulation of the power cycle causes a noticeable difference in the predicted heat exchanger areas. The difference in the total heat exchanger area for the power cycle studied here is about 7% of the area predicted in the basic case. The influence on the heat exchanger area predictions of using different correlations for the thermodynamic properties is larger than the influence on the cycle performance calculations. The difference in power generation is only 0.2% for the process studied here.

Dvoiris and Mirolli [23] present results from experimental measurements of the condensation of ammonia–water mixtures. They conclude that when the ammonia mass fraction of the vapor phase is 95% or higher and the fraction of liquid is higher than 10%, the mass transfer resistance is low and the process can be treated as the condensation of a pure substance with properties corresponding to the average properties of the mixture. These conditions are present for all condensing heat exchangers, except for streams 15d–16 and 16–17, referring to Fig. 2. Further, convective evaporation, where the degradation of the heat transfer coefficient is small (Rohlin [24]), is present in the internal heat exchangers.

The uncertainties for the equations used to calculate the heat transfer coefficients is said to be about 20% for pure substances. The use of different correlations for thermophysical properties in this study gives a difference in the heat transfer coefficients that in most cases is lower than 10% but in some cases is as large as 30%. Therefore, besides better methods to predict the thermophysical properties, a more thorough study of the heat transfer processes and heat exchanger design for the heat exchangers would be valuable for more accurate heat exchanger area predictions.

In the present study, the same correlations are used for the transport properties of the pure components in all compared cases. If different correlations for the transport properties were used for the pure substances as well, an even larger difference in the predicted heat exchanger areas might be obtained.

An interesting question is, of course, if a more accurate heat exchanger area prediction is necessary from an economic point of view. Three economic evaluations of ammonia–water bottoming cycles to gas turbines can be found in the literature [25–27]. The results of these studies show that the cost for the heat exchangers is from 30 to 70% of the total equipment cost, where the first figure represents a process similar in size and complexity to the process studied here. Assuming the total heat exchanger cost to be 30% of the total equipment cost and that the cost of the heat exchangers is proportional to the heat exchanger area, an increase in the total area of 7% would then correspond to an increase in the total equipment cost of about 2%. A lower increase in the cost could be expected since the extra cost of the heat exchangers will probably not be proportional to the extra heat exchanger area.

In the present study, the same standard tube and shell dimensions, chosen from recommendations in Ref. 21, have been used for all the calculated cases. The results of the calculations show slightly different pressure drops over the heat exchangers in the different cases. The differences in pressure drops are much smaller than what a different choice of standard dimensions would give. Keeping the pressure drop constant instead of keeping the shell dimensions constant gives larger differences in the predicted heat exchanger areas when the different correlations are used for the thermophysical properties. For some heat exchangers in some of the compared cases, the increase in the differences is up to 100%.

Since the experimental data for the transport properties of ammonia–water mixtures are very scarce, it is very difficult to estimate the uncertainties of the calculations of the properties. If the difference between the true and the predicted transport properties is larger than the difference between the properties predicted with different correlations, the uncertainty in the heat exchanger area predictions may be larger than the comparison using different correlations for the properties shown.

APPENDIX

The equations for the transport properties presented by El-Sayed [10] are presented here. In Ref. 10 the equations are misprinted. The correct formulation is as follows [7, 11].

Gas phase (low pressure)

$$\mu_m = \frac{\mu_1 x_1}{(x_1 + F_{12} x_2)} + \frac{\mu_2 x_2}{(x_2 + F_{21} x_1)}$$

$$k_m = \frac{k_1 x_1}{(x_1 + F_{12} x_2)} + \frac{k_2 x_2}{(x_2 + F_{21} x_1)}$$

$$F_{12} = \frac{[1 + (\mu_1/\mu_2)^{0.5}\,(M_2/M_1)^{0.25}]^2}{[8(1 + (M_1/M_2))]^{0.5}}$$

$$F_{21} = F_{12}(\mu_2/\mu_1)(M_1/M_2)$$

Liquid phase

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + F_{12}$$

$$k_m = x_1 k_1 + x_2 k_2$$

$$T_r = \frac{T_m}{T_{cm}} = \frac{T_1}{T_{c1}} = \frac{T_2}{T_{c2}}$$

$$T_{cm} = T_{c2} - 242.4625 w_1 - 440.9283 w_1^2 + 874.8125 w_1^3 - 624.2917 w_1^4$$

$$(T_{cm} \text{ and } T_{c2} \text{ in } {}^\circ\mathrm{F})$$

$$F_{12} = F_t F_x$$

$$F_t = 4.219 - 3.7996 \frac{T_m}{492} + 0.842 \left[\frac{T_m}{492}\right]^2$$

$$(T_m \text{ in } {}^\circ\mathrm{R})$$

$$F_x = [x_1 x_2 - 0.125 x_1^2 x_2][\ln(\mu_1 \mu_2)]^{0.5}$$

$$(\mu \text{ in } \mu\mathrm{Pa} \cdot \mathrm{s})$$

NOMENCLATURE

k = thermal conductivity
M = molar mass
T = temperature
w = mass fraction
x = mole fraction
μ = viscosity

SUBSCRIPTS

c	critical
m	mixture
r	reduced
1	ammonia
2	water

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