

Logarithmic Mean Temperature Difference in heat exchangers employing ammonia-water mixtures

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Abstract

The temperature of zeotropic mixtures does not remain constant throughout a heat exchanger. Furthermore, Zeotropes often exhibit a nonlinear temperature-enthalpy relationship. These factors contradict some of the assumptions made in deriving the log mean temperature difference (LMTD), which is used in computing the size of a heat exchanger (UA). In this paper an ammonia-water mixture in a counter-flow heat exchanger will be examined as an example of a zeotropic mixture. The actual (UA) obtained via numerical analysis will be compared to the (UA) found using (LMTD), and representative error scales shall be developed for this purpose.

Keywords: Zeotropic mixtures, Ammonia-water, Log mean temperature difference, Heat exchanger size, Error scales, Energy equation solver.

Nomenclature

A	Heat transfer area (m^2)
C_p	Specific heat at constant pressure (kJ/kg K)
h	Enthalpy (kJ/Kg)
LER	Log Error Ratio (Dimensionless)
\dot{m}	Mass flow rate (Kg/s)
P	Pressure (bar, kpa)
PP	Pinch Point (C° , K)
Q	Heat transfer rate (kW)
SE	Standard Error (%)
T	Temperature (C° , K)
U	Overall heat transfer coefficient (kW/ m^2 K)

Greek Symbols

Δ	Property difference
δ	Change in a quantity which is not property

Subscripts

c	Cold stream
h	Hot stream
m	Refrigerant mixture stream
w	Water stream

1. Introduction

The use of synthetic mixtures in refrigeration emerged as a consequence of the need for replacing refrigerants. These mixtures may be azeotropic, near-azeotropic, or zeotropic.

In 1985 the World Metrological Organization and the United Nations Environment Program (WMO/UNEP) released a quantitative statement that tied chlorofluorocarbons (CFCs) to the depletion of ozone. The Montreal Protocol (1987) froze CFC consumption in 1989 and pledged to cut it in half by 1998. In 1992, the Copenhagen Amendments halted the production of CFCs in developed countries by 1996.

Hydro-chlorofluorocarbons (HCFCs) and HCFC mixtures were developed that they could serve as drop-in replacements for most of the CFCs in use. However, the Vienna Convention of 1995 not only accelerated the HCFC- reduction timetable, but also required that their production effectively cease by 2020, with a complete cessation by 2030.

2. Zeotropic Mixture Properties

During a phase change of a zeotropic mixture, a temperature glide is created (at which point the concentrations of the vapor and the liquid are continually changing). Zeotropic mixtures are the most common type of refrigerant blends. An example of a zeotropic mixture is ammonia and water. As it is evident from (Figure 1), at no point do the bubble point and dew point curves meet (except, of course, where pure ammonia or pure water exists). Upon cooling the mixture, liquid starts forming at the dew point temperature, but this is not completed until the bubble point temperature.

This difference between the dew point and bubble temperatures is known as the temperature glide. The smaller this glide, the less loss of heat transfer due to concentration differences. In general, zeotropic mixtures should not be placed in existing equipment, but can bring performance improvements with modified systems.

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Because of the varying liquid and vapor compositions, systems employing ammonia-water mixtures must be liquid charged. Otherwise, mixture's composition could change, which could result in decreased performance and increased safety risks over time.

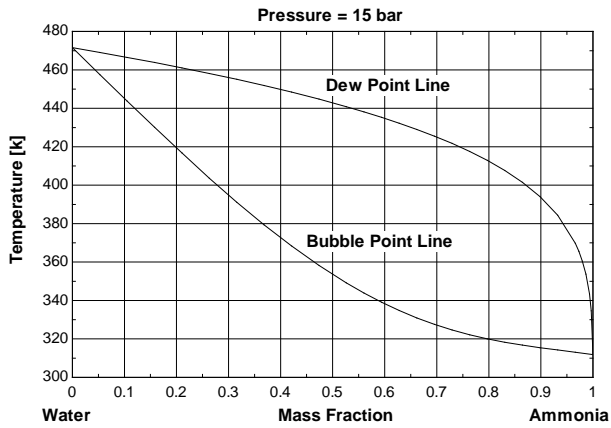


Figure 1: A Zeotropic Mixture of Ammonia and Water

Another feature common to zeotropic mixtures is a nonlinear temperature versus enthalpy profile. A single-component or azeotropic refrigerant will have a linear temperature profile, as in (Figure 2), but a zeotropic mixture's profile can be strikingly nonlinear, as seen in (Figure 3). This sort of temperature-enthalpy behavior results in a varying specific heat and raises the possibility of a temperature pinch within a heat exchanger, both of which complicate traditional heat exchanger calculations.

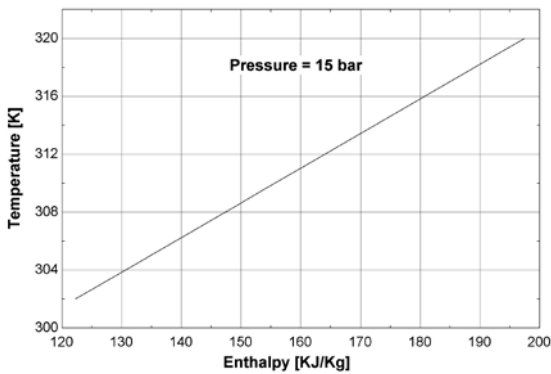


Figure 2: Temperature versus Enthalpy for Water

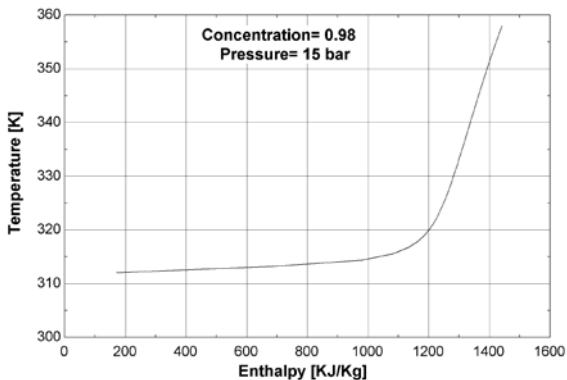


Figure 3: Ammonia-Water, Concentration = 0.98

3. Heat Exchanger Analysis for Mixtures

In the analysis of heat exchangers, the Log Mean Temperature Difference (LMTD) is a standard calculation used to compute the required size (indicated by UA). The LMTD ceases to be valid, however, when a zeotropic mixture that exhibits a nonlinear temperature glide is used as the working fluid. Examining (fig. 1), it is obvious that errors would result from using the LMTD to calculate the heat exchanger size for the mixture. While the inadequacy of the LMTD has been briefly commented on by Lundqvist (1995), he has only examined the differences between subcooling, condensing, and superheating, and ignored the nonlinearities in the two-phase region.

In order to ascertain the magnitude of the error, a numerical analysis must be performed. It is of interest to determine an alternative calculation that is applicable to Zeotropes. The first step is to return to the definition of the mean temperature difference in a heat exchanger. Some assumptions that are made in the formulation of the LMTD are acceptable: for example, that the overall heat transfer coefficient will remain nearly constant over the heat exchanger area. Obviously, though, it cannot be assumed that the temperature will be an easily-determined function of the heat exchanger. As a result, the integral evaluation of the variance in temperature between the two streams over a differential amount of heat transferred must instead be transformed into a summation.

Since the accuracy of this method will increase with the number of steps that are taken, the step size will be made sufficiently small so as to minimize numerical error. The UA that is found using the traditional LMTD can be contrasted with that found using the numerical method.

Heat transferred in a heat exchanger using LMTD is calculated via the familiar equation (Fig. 4):

$$Q = UA \frac{\Delta T_1 - \Delta T_2}{\ln \left[\frac{\Delta T_1}{\Delta T_2} \right]}$$

$$\Delta T_{\text{Log Mean}} = \frac{\Delta T_1 - \Delta T_2}{\ln \left[\frac{\Delta T_1}{\Delta T_2} \right]} \quad (1)$$

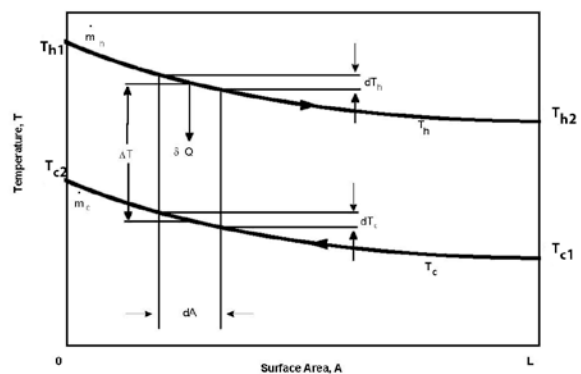


Figure 4: Counter-Flow Temperature Variation over Area

It should be remembered that this equation is only applicable under a number of limiting assumptions. The mass flow rate has to be constant throughout the heat exchanger. The conductive and convective coefficients may vary over the heat exchanger area, but only slightly. The enthalpy-temperature relationship must be linear, and the specific heats are considered to be independent of both temperature and area. In order to better magnify the error resulting from the LMTD, only counter-flow heat exchanger configuration will be studied, since that LMTD represents the maximum temperature potential for heat transfer. For counter-flow, eqn. 1 is

$$Q = UA \frac{(T_{h1}-T_{c2})-(T_{h2}-T_{c1})}{\ln\left[\frac{T_{h1}-T_{c2}}{T_{h2}-T_{c1}}\right]}$$

Rearranging to find the overall conductance multiplied by the area (UA)

$$UA = \frac{Q}{\Delta T_{\text{Log Mean}}} \quad (2)$$

4. A Numerical Method for Calculating the Mean Temperature

For zeotropic refrigerants, some of the assumptions made when deriving the LMTD must be discarded. The mass flow rate through the heat exchanger is still assumed to be constant, but the specific heats for both the cold and the hot streams are not constant now. In the derivation of the classical LMTD, it was assumed that the fluids would not undergo a phase change and that they would have constant specific heats. In this investigation, however, the more general case is studied, allowing a two-phase region of mixtures with nonlinear temperature-enthalpy curves. As said in the introduction, this nonlinearity results in varying specific heats. In fact, the specific heat is a function of both temperature and area. Then, for the heat transferred between two streams in a heat exchanger,

$$\delta Q = U \Delta T_{mw} dA \quad (3)$$

where ΔT_{mw} is the temperature difference between the zeotropic refrigerant mixture and the water at any given point. To find the total heat transferred, equation (3) is integrated over the entire area of the heat exchanger.

$$\int_0^{Q_0} \frac{\delta Q}{\Delta T_{mw}} = \int_0^{A_0} U dA$$

A_0 = the total heat exchanger area

Q_0 = the total amount of heat transferred

It is still reasonable to assume that the overall heat transfer coefficient will be fairly constant over the area (hereafter denoted as U_0). The area is nondimensionalized so that $A' = A/A_0$, and the above equation becomes

$$\int_0^{Q_0} \frac{\delta Q}{\Delta T_{mw}} = U_0 A_0 \int_0^1 dA' = U_0 A_0 \quad (4)$$

It should be noted that, by definition, UA is inversely proportional to the total thermal resistance. This

resistance is obviously not strictly constant over the heat exchanger area; the condensation or evaporation of the fluids and the changes in temperature will affect both the thermal conductivity and the convection coefficients. However, the magnitude of these variations is assumed to be small, so as to only insignificantly affect the overall heat transfer coefficient. If this is not the case, the right hand side of equation (4) could become quite complicated, and would require as parameters the exact specifications of the heat exchanger under consideration.

An examination of equation (4) reveals its similarity to equation (2). However, because the temperature can be radically nonlinear, the above integral cannot be evaluated in closed form (recalling that δQ is a function of enthalpy). Instead, it must be replaced by a numerical integration in which the temperature difference between the streams is found at incremental steps of the amount of heat transferred in the heat exchanger.

$$U_0 A_0 = \sum_{i=0}^{Q_0} \frac{1}{\Delta T_{mw}} \delta Q \quad (5)$$

As the number of steps approaches infinity, equation (5) becomes identical to equation (2).

Calculations such as those above would once have required hours of expensive computer time to solve. Given the current computational power and accurate properties in computer-readable form, however, they can now be performed in minutes on a desktop PC. The number of steps, then, can be made sufficiently large so as to give a reasonably accurate solution without demanding a significant increase in solution time.

Two other numerical approaches for finding a mean temperature have been suggested by Granryd and Conklin (1990). In the first method, the temperature profiles are linearized in small segments, from which an effective specific heat can be calculated. The second method also focuses on the specific heat. A polynomial approximation for C_p is developed from a curve fit, and then integrated where appropriate. A disadvantage to both methods is the complexity of the calculations that must still be performed once C_p is found, in order to determine the heat exchanger size.

5. Application of the Numerical Technique

5.1. Engineering Equation Solver

Engineering Equation Solver (EES) is a software package by Dr. Stanford Klein of the University of Wisconsin. EES incorporates the programming structure of C and FORTRAN with a built-in iterator, thermodynamic and transport property relations, graphical capabilities, numerical integration, and many other useful mathematical functions. By grouping equations that are to be solved simultaneously, EES is able to function at a high rate of computational speed. EES can also be used to perform parametric studies.

EES was chosen for this research due to its ability to seamlessly incorporate fluid property calls. Steam tables, air tables, JANAF data, psychrometric functions, property tables for ammonia, and other fluids are built into EES. Ammonia-water mixture properties are calculated in EES

using the correlation developed by Ibrahim and Klein (1993). To expand the number of available refrigerants, an interface has been developed by Dr. Klein that allows EES to utilize the National Institute of Standards and Technology's *Thermodynamic Properties of Refrigerants and Mixtures Database* (REFPROP).

5.2. Calculation of the UA

In order to find the UA derived in equation (5), the total heat transferred and the temperature difference between the water and mixture streams should be calculated at a number of points in the heat exchanger. The heat transferred can be found by applying the energy equation to the water flowing through the heat exchanger:

$$\dot{Q}_{Tot} = \dot{m}_{water} (h_{water,entrance} - h_{water,exit}) \quad (6)$$

Or for the refrigerant:

$$\dot{Q}_{Tot} = \dot{m}_{mixture} (h_{mix,exit} - h_{mix,entrance}) \quad (7)$$

Where \dot{m} is the mass flow rate and h is the enthalpy. By equating (6) and (7), a mass flow ratio can be stated.

$$\dot{m}_{ratio} = \frac{\dot{m}_{water}}{\dot{m}_{mix}} = \frac{h_{mix,exit} - h_{mix,entrance}}{h_{water,entrance} - h_{water,exit}} \quad (8)$$

The end point states for both the water and the mixture must now be determined. A pinch point (PP) and concentration has to be chosen. For air conditioning applications, a typical condenser entrance temperature for the water side is 29 °C with a 5 °C rise, which are the values used. The pressure in the heat exchanger (P_{hi}) is then found by evaluating the mixture at its exit, where the concentration, the quality (saturated liquid), and the temperature (29 °C + PP) are known. With two independent properties (pressure and temperature) given, the endpoint enthalpies of the water stream can be found. Subcooling is not considered, so the mixture is entirely in the two-phase region, and its endpoint properties can be found using the pressure, concentration, and qualities of zero and one.

In order to better visualize the transfer of heat between the water and the mixture streams, the total heat transferred will be redefined on a per refrigerant mass flow rate basis. The heat exchanger can then be divided into an arbitrary number of sections (n) of equal $\delta\dot{Q}/\dot{m}_{mix}$. The heat transfer per unit mass flow rate of the mixture is directly related to the enthalpy, so an enthalpy step shall be defined as:

$$h_{mix,step} = \frac{h_{mix,exit} - h_{mix,entrance}}{n}$$

The initial temperature difference between the refrigerant and the water and the amount of heat transferred are known from the endpoint specifications and the values at each successive point in the heat exchanger ($n_1 = 1, 2, 3 \dots$) are calculated using the following equations.

From equation (7):

$$\frac{\dot{Q}_{cumulative}}{\dot{m}_{mix}} = q_{cum} = h_{mix,step} \times n_i \quad (9)$$

$$h_{mix} = q_{cum} + h_{mix,entrance} \quad (10)$$

$$h_{water} = \frac{q_{cum}}{\dot{m}_{ratio}} + h_{water,exit} \quad (11)$$

From fluid properties:

$$T_{water} = T(h_{water}, P_{hi})$$

$$T_{mix} = T(h_{mix}, P_{hi}, \text{Concentration})$$

$$\Delta T_{mw} = T_{mix} - T_{water} \quad (12)$$

For each desired pinch point, the values of q_{cum} and ΔT_{mw} calculated in equations (9-12) are numerically integrated by EES to find the actual UA (equation (9) is an implicit equation in EES). When performing the numerical integration, EES decides how many sections the heat exchanger should be divided into. This step size is either chosen using an automatic step size adjustment algorithm, or is directly specified by the user. For this application, one hundred steps deemed to be sufficient, as smaller heat exchanger segments increased the computational time without increasing the accuracy. A variant of the trapezoidal rule is used to examine the preceding values and to calculate the next step. In order to evaluate the integral, EES uses a second order predictor-corrector algorithm. This algorithm was designed to solve problems where the integrand is a complex function of other variables. It estimates what the value of the integral should be at each variable step, iterates until convergence, and then moves to the next step. When each step has been evaluated, the integral is solved and the UA is known.

5.3. Comparison of the UAs: Development of error scales

Once the UA is known, it can be compared with the heat exchanger area that is found using the traditional log mean temperature difference method (UA_{LMTD}). This can be calculated using a slightly altered version of equation 2:

$$\delta T_1 = T_{mix,entrance} - T_{water,exit}$$

$$\delta T_2 = T_{mix,exit} - T_{water,entrance}$$

$$LMTD = \frac{\delta T_2 - \delta T_1}{\ln \frac{\delta T_2}{\delta T_1}}$$

$$UA_{LMTD} = \frac{\dot{Q}_{total} / \dot{m}_{mix}}{LMTD} \quad (13)$$

Two separate error scales were developed to account for both major and minor discrepancies between

the UA and the UA_{LMTD}. For small differences, a standard error (SE) is adequate:

$$SE = \frac{|UA - UA_{LMTD}|}{UA} \times 100\%$$

In this study, however, standard errors ranged from twenty percent to over three thousand percent for some mixtures. In order to provide a meaningful scale for evaluation of errors over such large ranges, a log error ratio (LER) is defined as:

$$LER = -\log\left(\frac{UA_{LMTD}}{UA}\right)$$

By using either the SE or the LER, every possible range of refrigerant UA error can be analyzed.

6. Results and discussion

6.1. Properties

As can be seen from the temperature versus enthalpy profile of Figure (1), ammonia-water (NH₃/H₂O) mixtures generally have extremely nonlinear temperature profiles. This nonlinearity indicates a potential for large error when the LMTD is used to compute the size of a heat exchanger. Therefore, an ammonia-water mixture is an ideal case for the initial application of the methods developed in sections 4 and 5.

Three separate mixture concentrations were studied: 95%, 98%, and 99% ammonia. These are typical concentrations for condensers in ammonia-water absorption refrigeration cycles. Furthermore, each mixture was analyzed at five pinch points (at the refrigerant mixture entrance) ranging from 1-10 K. For each concentration and pinch, the NH₃/H₂O EES program (Appendix) was executed.

Given the above conditions, the temperature of the NH₃/H₂O refrigerant stream was found to range widely, from approximately 30 to 100 °C. While the temperature glides and the operating pressures vary with both pinch and concentration, glide increases significantly with concentration while pressure is a weak function of pinch, as expected. The pressure and temperature glides for all the runs are listed in (Table 1).

Table 1. Operating pressures and temperature glides for NH₃/H₂O

Concentration = 0.95					
Pinch (K)	2	4	6	8	10
P (bar)	11.45	12.14	12.86	13.61	14.4
T _{glide} (K)	65.76	65.41	65.06	64.71	64.34

Concentration = 0.98					
Pinch (K)	2	4	6	8	10
P (bar)	11.78	12.49	13.24	14.01	14.82
T _{glide} (K)	49.59	49.13	48.66	48.18	47.69

Concentration = 0.99					
Pinch (K)	2	4	6	8	10
P (bar)	11.9	12.62	13.37	14.16	14.98
T _{glide} (K)	38.95	38.42	37.89	37.35	36.8

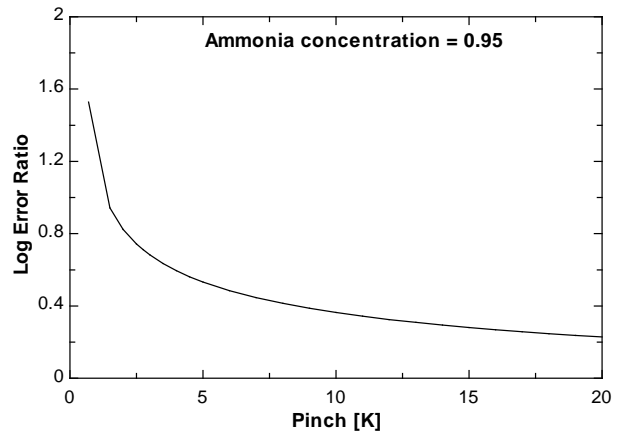
6.2. Log- error ratio for ammonia-water

As predicted, differences between the LMTD-calculated and the actual UA were observed at every concentration and pinch point. Since these differences can be quite large, the log error ratio was utilized. The LER does indeed provide a meaningful scale for evaluation, as the error can easily be graphically displayed (Figure 5). Furthermore, the values of the UA, UA_{LMTD}, and LER are compiled in (Table 2) for every run.

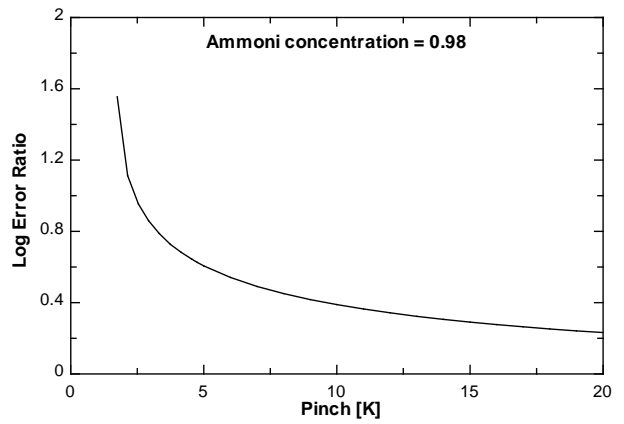
The UAs at the smallest pinch points may appear to be excessive, but this is because the streams at these points only narrowly avoid converging in temperature. For the water and refrigerant streams to actually converge to the same temperature, the heat exchanger area would need to be infinite, a reality reflected in the large actual UAs.

Table 2. UA, UA_{LMTD}, and LER for NH₃/H₂O

Concentration = 0.95					
Pinch (K)	2	4	6	8	10
UA	535.6	255	170.7	129.2	104.3
UA _{LMTD}	80.35	64.8	55.94	49.8	45.16
LER	0.8238	0.595	0.4846	0.4142	0.3637



Concentration = 0.98					
Pinch (K)	2	4	6	8	10
UA	1476	368.3	219.2	156.9	122.4
UA _{LMTD}	93.17	73.91	63.05	55.6	50
LER	1.2	0.697	0.541	0.451	0.389



Concentration = 0.99					
Pinch (K)	2.5	4	6	8	10
UA	2805	479.5	253.7	174.1	132.6
UA _{LMTD}	100.3	84.35	71.11	62.12	55.41
LER	1.447	0.7547	0.5523	0.4475	0.3791

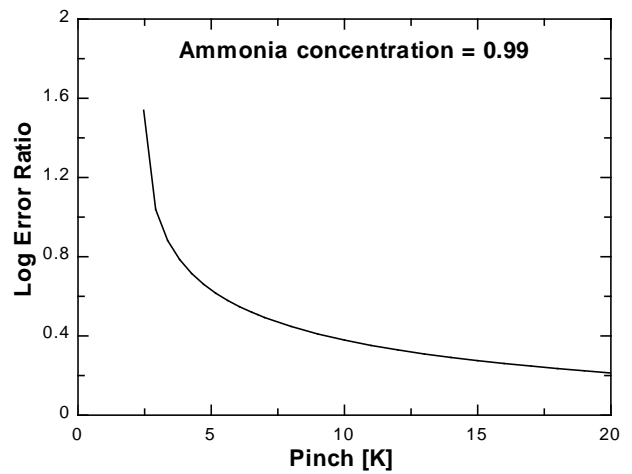


Figure 5. Log error ratio vs. pinch point for NH₃/H₂O

6. Conclusions and recommendations

While the Log Mean Temperature Difference is often used to compute the size (UA) of a heat exchanger, this calculation becomes invalid for mixtures when the working fluid exhibits a nonlinear temperature glide. An analysis of the derivation of the LMTD reveals assumptions that must be discarded. Most notably, it can no longer be assumed that the temperature will be an easily-determined function of the heat exchanged.

In the case of ammonia-water, which was selected for study due to its strong nonlinearity, calculation utilizing the LMTD resulted in dramatic errors. For small pinch points, these errors may lead to heat exchangers that are undersized by as much as a factor of fifty. The LMTD is simply not valid, and a numerically calculated mean

temperature should be used instead. For a given pinch point, the error generally increases with the ammonia concentration. At large pinch points, however, the magnitude of the differences in the error decreases between concentrations.

In general, the UA error decreases as the size of the pinch increases for both NH₃/H₂O and the replacement refrigerants. The change in the error also decreases with increasing pinch, which is both numerically and conceptually logical.

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APPENDIX

Ammonia-water EES program

{Comments are enclosed by quotes or brackets}

FUNCTION tk(T) "converts from C to K"

tk:=T+273.15

END

Conc=0.98 "Concentration of the Ammonia-Water Mixture"

Pinch=5 "Pinch Point"

{Calculates the m dot ratio from the end point data}

m_ratio=(h_end_mix-h_start_mix)/(h_end_h20-h_start_h20)

CALL NH3H2O(138,TK(29)+Pinch,Conc,0:T_hi,P_hi,x_hi,h_hi,s_hi,u_hi,v_hi,Qu_hi)

CALL NH3H2O(238,P_hi,Conc,0:T_1m,P_1m,x_1m,h_start_mix,s_1m,u_1m,v_1m,Qu_1m)

CALL NH3H2O(238,P_hi,Conc,1:T_Nm,P_Nm,x_Nm,h_end_mix,s_Nm,u_Nm,v_Nm,Qu_Nm)

h_start_h20=enthalpy(WATER,T=TK(29),P=P_hi)

h_end_h20=enthalpy(WATER,T=TK(34),P=P_hi)

T1w=temperature(WATER,h=h_start_h20,P=P_hi)

T2w=temperature(WATER,h=h_end_h20,P=P_hi)

{Entered values}

EndPtQ=h_end_mix-h_start_mix "The total heat transferred in the heat exchanger"

h_m=Qtot+h_start_mix

h_w=(Qtot/m_ratio)+h_start_h20

T_w=temperature(WATER,h=h_w,P=P_hi)

CALL NH3H2O(234,P_hi,Conc,h_m:T_m,P_m,x_m,hom,sm,um,vm,Qum)

DELTAT_mw=T_m-T_w

Delta_T_1=T_1m-T1w "Calculation of the LMTD and U0A0 using"

Delta_T_2=T_Nm-T2w "the traditional method"

LMTD=(Delta_T_2-Delta_T_1)/(ln(Delta_T_2/Delta_T_1))

U0A0_LMTD=(h_end_mix-h_start_mix)/LMTD

{Integrates to find the actual UA}

U0A0_act=integral(1/DELTAT_mw,Qtot,0,EndPtQ)

{Calculates the error using two error scales}

LER=-log10(U0A0_LMTD/U0A0_act)

SE=(abs(U0A0_act-U0A0_LMTD)/U0A0_act)*100