

**HEAT EXCHANGER MEAN TEMPERATURE DIFFERENCES  
FOR REFRIGERANT MIXTURES**

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by

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**HEAT EXCHANGER MEAN TEMPERATURE DIFFERENCES  
FOR REFRIGERANT MIXTURES**

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## NOMENCLATURE

### Symbols

$A$	Area over which heat is transferred ( $m^2$ )
$c_p$	Specific Heat at Constant Pressure ( $\frac{kJ}{kg \cdot K}$ )
$h$	Enthalpy ( $\frac{kJ}{kg}$ )
$LER$	Log Error Ratio (-)
$\dot{m}$	Mass flow rate ( $\frac{kg}{s}$ )
$P$	Pressure ( $bar, kPa$ )
$PP$	Pinch Point ( $^{\circ}C, K$ )
$Q$	Heat Transfer Rate ( $kW$ )
$SE$	Standard Error (%)
$T$	Temperature ( $^{\circ}C, K$ )
$U$	Overall Heat Transfer Coefficient ( $\frac{kW}{m^2 \cdot K}$ )

### Greek Characters

$\theta$	Temperature Difference ( $^{\circ}C, K$ )
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### Subscripts

$c$	Cold Stream
$h$	Hot Stream
$m$	Refrigerant Mixture Stream
$w$	Water Stream

## SUMMARY

Recent protocols have reduced, and will eventually eliminate, the production and use of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). While it has been possible to find single-component replacements for CFCs such as R-12, replacements for HCFCs are generally refrigerant mixtures. These mixtures may be azeotropic, in which case single-component behavior is exhibited, near-azeotropic or zeotropic. Azeotropic refrigerant mixtures are uncommon, so it is of interest to study the characteristics of zeotropes and near-azeotropes.

The temperature of a 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 that are made in deriving the Log Mean Temperature Difference (*LMTD*), a calculation that is used to compute the size of a heat exchanger (*UA*). In order to develop a more precise mean temperature difference, the derivation of the *LMTD* must be reevaluated. Since the temperature is not an easily-determined function of enthalpy, the heat transfer process must be discretized and the properties determined at each point.

An ammonia-water mixture is examined first, since it is known to display a highly nonlinear temperature glide. Synthetic mixtures that are being studied by the refrigeration industry as replacements for HCFC-22 are also analyzed. In each case, the actual *UA* is compared to the *UA* found using the *LMTD*, and representative error scales are developed. It is found that these errors can cause a heat exchanger to be undersized by as much as a factor of fifty.

Finally, the advantages of zeotropes are also discussed, as are cycles that can utilize those advantages. Recommendations are made that the effect of the modified  $UA$  calculations on these cycles should be studied, and that the benefits of natural over synthetic refrigerants should also be investigated.

## CHAPTER I

### INTRODUCTION

#### The Need For Replacement Refrigerants

Since their development in 1931, chlorofluorocarbons (CFCs) were thought to be ideal refrigerants. They had chemical stability and relatively low toxicity, making them safe for both residential and industrial use. CFCs were also quite inexpensive, resulting both in a proliferation of refrigerators and air conditioners that utilized them, and in an unwillingness to repair systems with leaks, since they could often be periodically recharged for much less.

In 1974, CFCs were tentatively identified as destructive to the ozone layer (Domanski, 1997). For the next decade, this relationship was investigated, and a quantitative statement that tied CFCs to the depletion of ozone was released by the World Meteorological Organization and the United Nations Environment Programme (WMO/UNEP) in 1985. The Montreal Protocol (1987), which was agreed to by nearly one hundred and fifty countries, froze CFC consumption in 1989 and pledged to cut it in half by 1998. In 1992, the Copenhagen Amendments went even farther, and halted the production of CFCs in developed countries by 1996. The effects of these protocols, assuming international compliance, can be seen in Figure 1-1 (Ennis, 1994).

With CFCs scheduled to be phased out, hydrochlorofluorocarbons (most notably HCFC-22) gained in popularity. While their production levels were controlled by 1992, they were not scheduled for complete elimination. HCFCs were still damaging to the ozone layer, but much less so than CFCs. Their average stratospheric

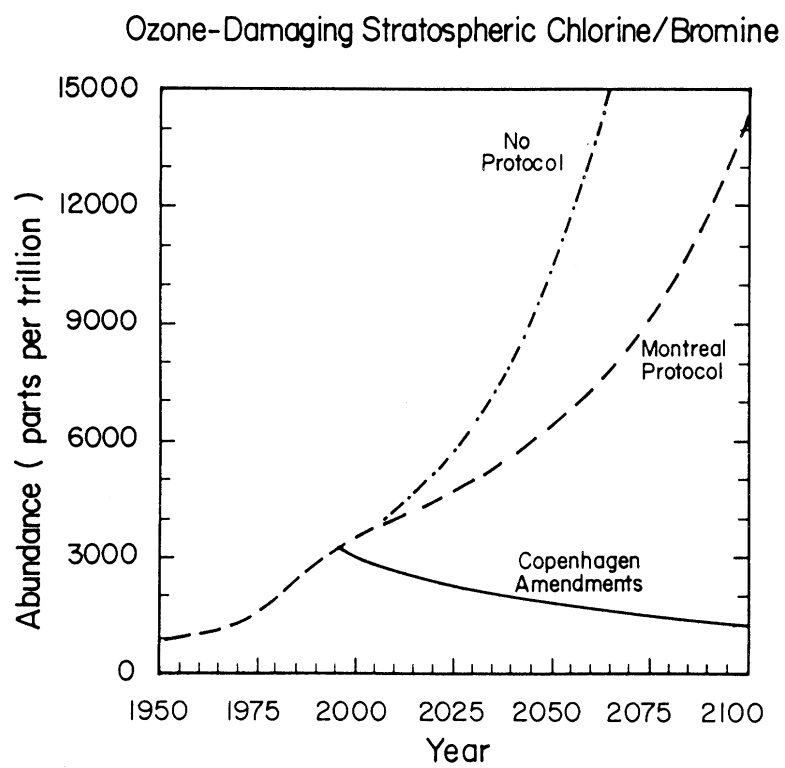


Figure 1-1: Results of International Protocols

lifespan was much shorter, and not as many of them penetrated into the upper atmosphere. For example, CFC-12 has a stratospheric lifetime of 102 years, compared to a lifetime of 13.3 years for HCFC-22. Furthermore, the ozone depletion potential (ODP) of R-22 is only 5.5% of the ODP of R-12 (Sand et al., 1997). HCFCs and HCFC mixtures were developed that could serve as drop-in replacements for most of the CFCs in use. However, the excitement over HCFCs was short-lived, as 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. Japan and some European countries have established cut-off dates that begin much earlier. In Switzerland, for example, HCFCs are banned by 2005.

Once again, replacement refrigerants need to be found, but this time there are no obvious solutions. While some single-component refrigerants present reduced-performance possibilities, the solution appears to lie with synthetic mixtures. These mixtures may be azeotropic, near-azeotropic, or zeotropic.

## Mixture Properties

### **Zeotropes**

For a zeotropic mixture (also known as a non-azeotropic mixture), the concentrations of the liquid and the vapor phase are never equal (Alefeld and Radermacher, 1994). This creates a temperature glide during phase change (at which point the concentrations of the vapor and the liquid are continually changing). Zeotropic mixtures are the most common type of refrigerant blend. An example of a zeotropic mixture is ammonia and water. As can be seen in Figure 1-2, at no point do the bubble and dew point lines meet (except, of course, where there is pure ammonia or pure water). When the mixture is cooled, liquid begins to form at the dew point

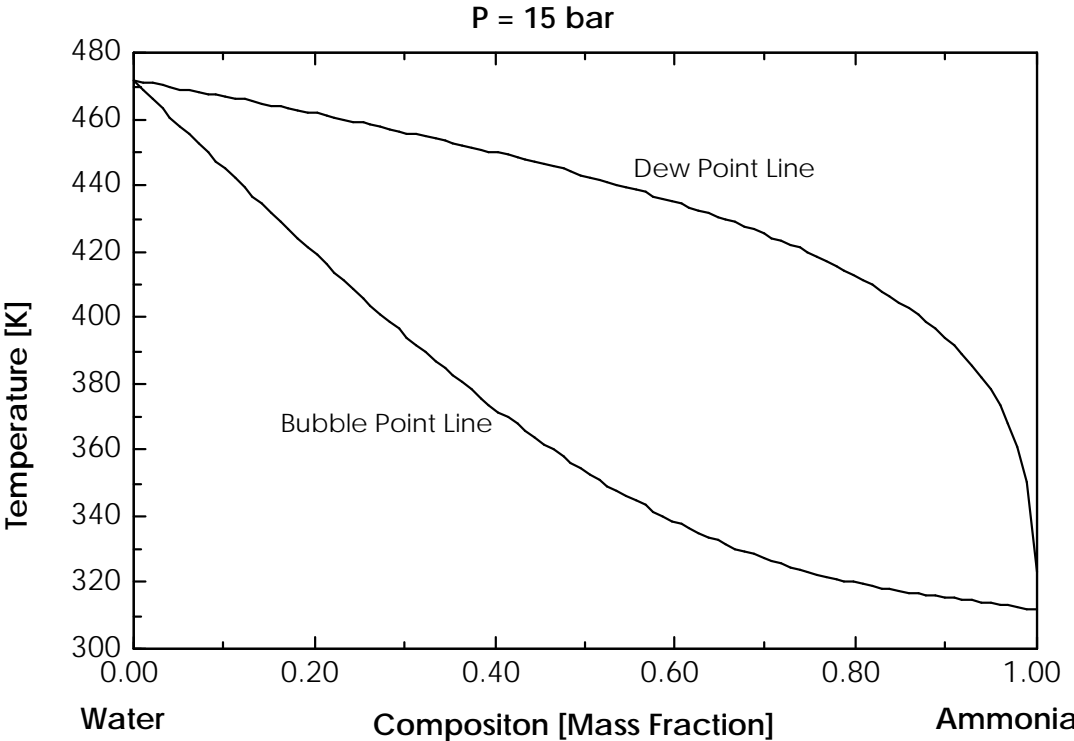


Figure 1-2: A Zeotropic Mixture of Ammonia and Water

temperature, but this is not completed until the bubble point temperature.

This difference between the dew and bubble temperatures is known as a temperature glide. The smaller the temperature glide, the less loss of heat transfer due to concentration differences. Generally, zeotropic mixtures are not ideally suited to be placed in existing equipment, but can bring performance improvements when used with modified systems. Because of the varying liquid and vapor compositions, systems employing zeotropic refrigerant mixtures must be liquid charged. Doing otherwise could change the mixture's composition, which could result in decreased performance and increased safety risks over time.

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 1-3, but a zeotropic mixture's profile can be strikingly nonlinear, as seen in Figure 1-4. 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.

### **Near-azeotropes**

For a near-azeotropic mixture, the vapor and liquid concentrations at a given temperature and pressure differ only slightly. Most azeotropic refrigerant mixtures become near-azeotropic when the pressure or temperature is varied from the azeotrope point. R-410A (which is also known as AZ-20 under the AlliedSignal patent) is a near-azeotropic mixture of R-32 and R-125 (fifty-fifty mass percent). For standard condenser pressures and temperatures, the bubble and dew points for this concentration vary by less than 0.1 °C (see Figure 1-5). Although it appears that this variation could be reduced even further by increasing the concentration of R-125, this is ac-

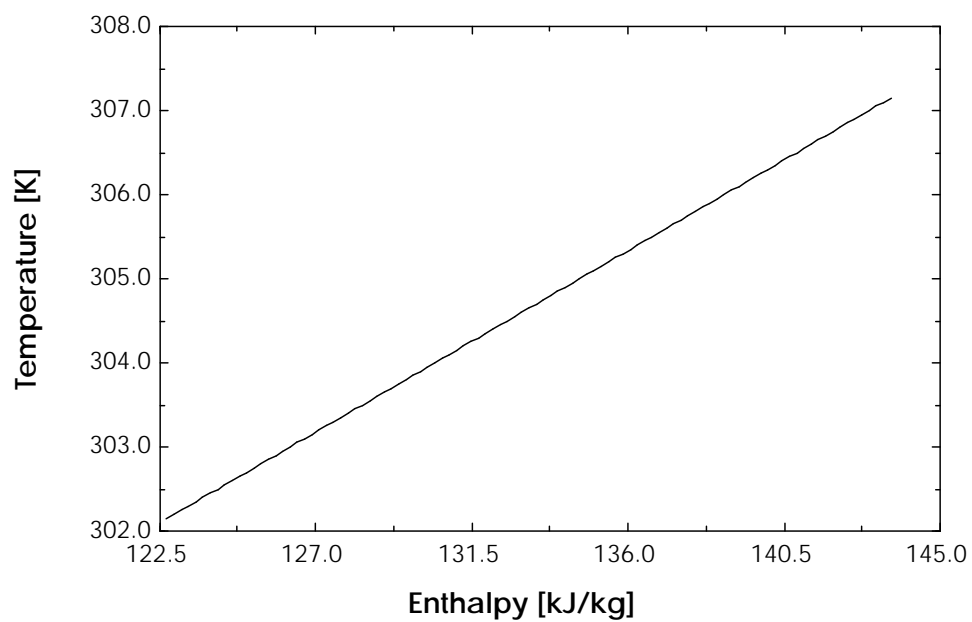


Figure 1-3: Temperature vs. Enthalpy for Water

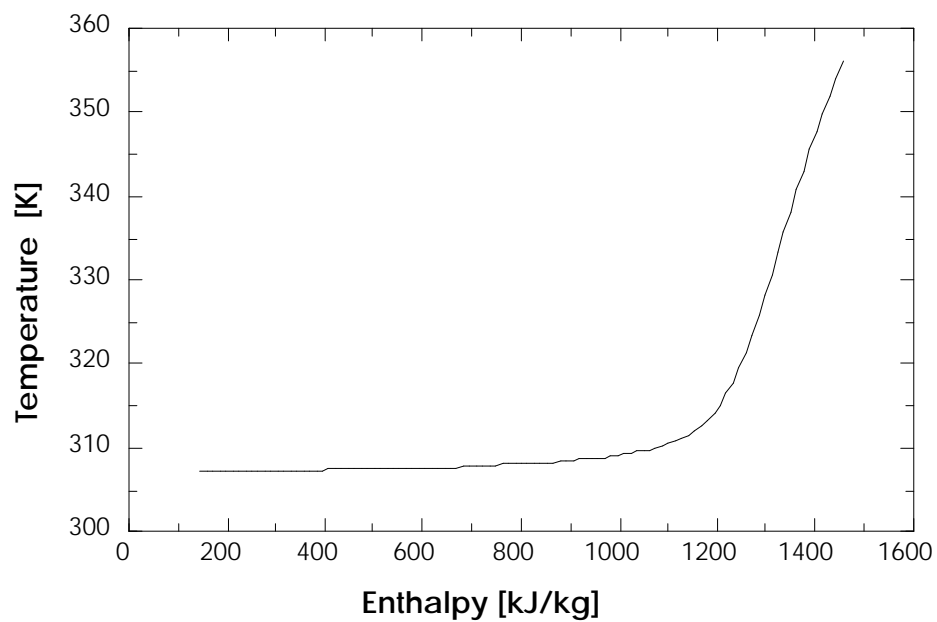


Figure 1-4: Ammonia-Water Mixture, Concentration = 0.98

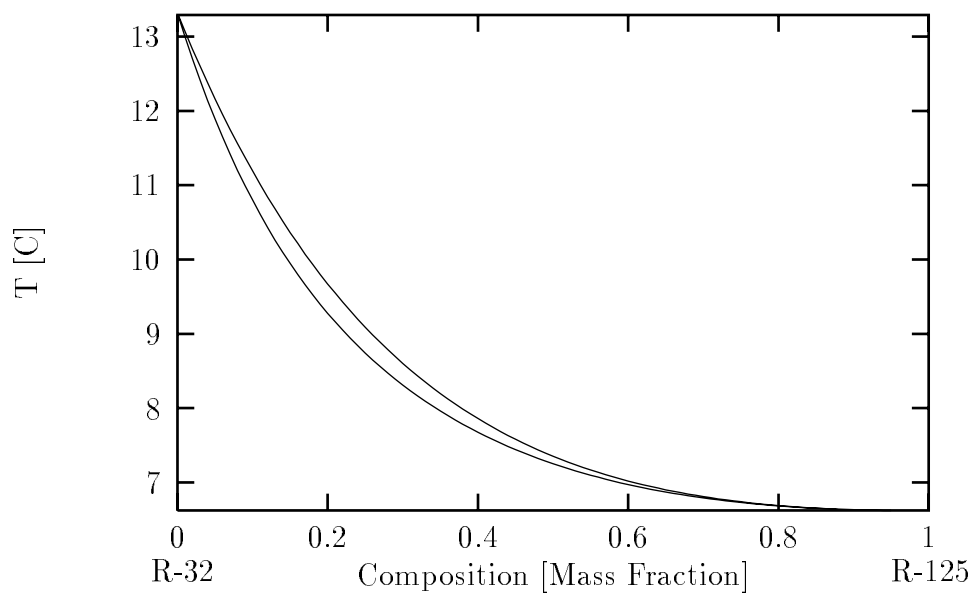


Figure 1-5: A Near-Azeotropic Mixture

tually undesirable. For example, R-410A was developed to serve as a replacement for HCFC-22, and changing its composition reduces its suitability for that role while also increasing its flammability and toxicity. Near-azeotropic mixtures usually work fairly well with existing equipment.

### **Azeotropes**

An azeotrope is defined as a point at which the concentration of the liquid and the vapor phase is the same for a given temperature and pressure. Some mixtures have more than one azeotrope at a fixed pressure or temperature, but this is uncommon. At an azeotrope, a mixture behaves like a single-constituent system. Almost all azeotropic refrigerants have a boiling point lower than either of the constituents (which is known as a minimum temperature or maximum pressure azeotrope). An exception to this is R-507, which is a fifty-fifty weight percent blend of R-125 and R-143a, and is proposed as a replacement for R-502. A plot of temperature versus composition for a mixture of R-125 and R-143a can be found in Figure 1-6. While an azeotropic mixture may appear to be an obvious replacement for a pure refrigerant, there is no azeotropic mixture replacement for R-22, one of the most popular of the HCFCs, which duplicates its cooling capacity and pressures. Azeotropic refrigerant mixtures are uncommon, and it appears unlikely that new azeotropes will be found.

### **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 practice of using the LMTD for heat exchanger calculations dates to the 1950s (Chen, 1988). Other mean temperature methods, such as Underwood's (1933)

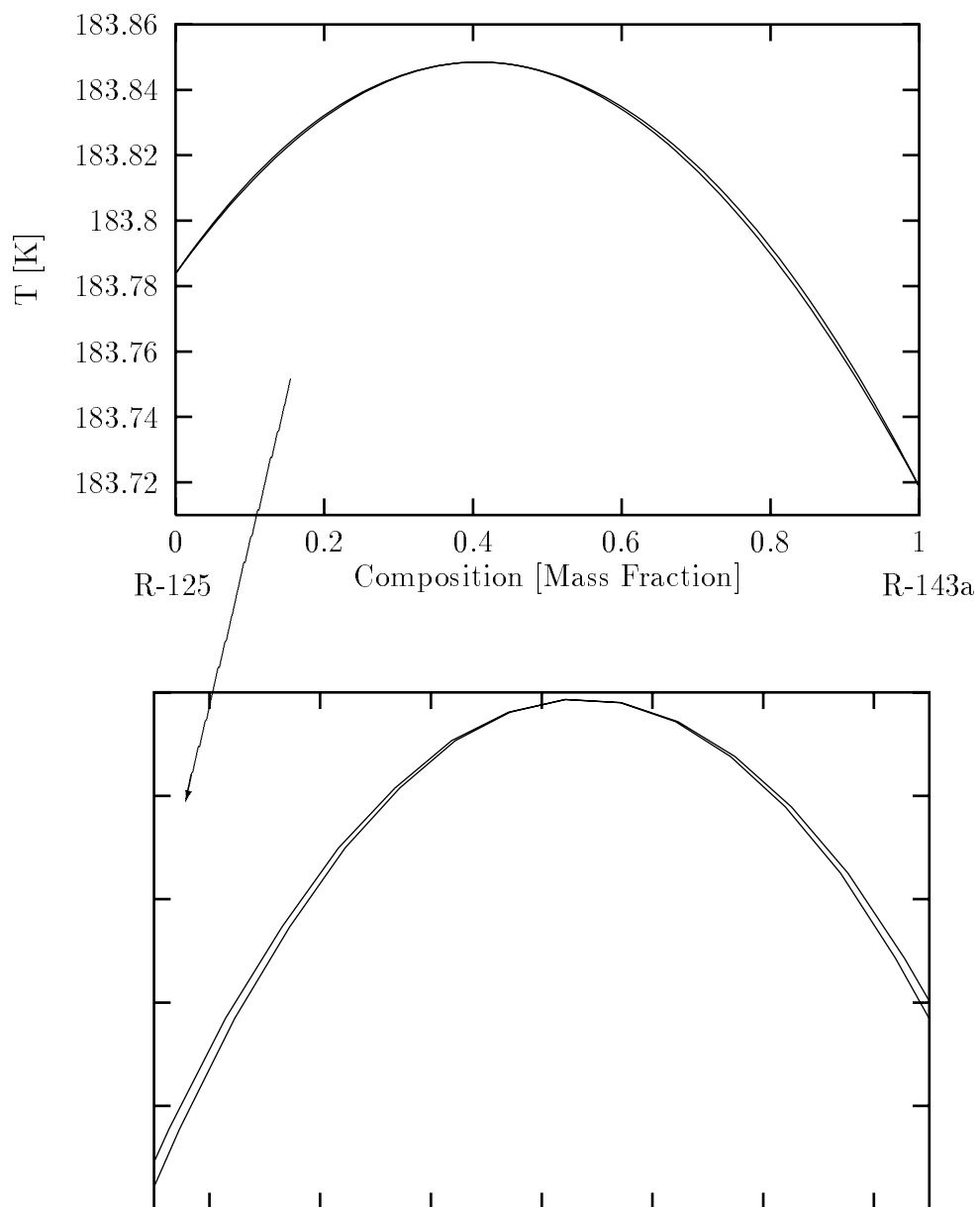


Figure 1-6: A Mixture With an Azeotrope At 41.18% R-125

one-third rule ( $\theta_m^{1/3} = \frac{1}{2}(\theta_1^{1/3} + \theta_2^{1/3})$ ), predate the LMTD, but none of them are as widely used today. The LMTD ceases to be valid, however, when a zeotropic mixture that exhibits a nonlinear temperature glide is used as the working fluid. Examining Figure 1-4, it is obvious that errors would result from using the LMTD to calculate the heat exchanger size for this 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 exchanged. 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, and the deviations compared for various possible refrigerant replacements over a range of pinch points.

## CHAPTER II

### DERIVATION OF THE LOG MEAN TEMPERATURE DIFFERENCE

Using the energy equation to express the heat transferred over a section of a heat exchanger (Figure 2-1)<sup>1</sup>:

$$\delta Q = \dot{m} dh + h d\dot{m} \quad (2.1)$$

If the mass flow rate through the heat exchanger is constant, this reduces to:

$$\delta Q = \dot{m} dh \quad (2.2)$$

For fluids that have constant specific heats and that do not undergo a phase change, a property relation is:

$$dh = c_p dT \quad (2.3)$$

and, therefore:

$$\delta Q = \dot{m} c_p dT \quad (2.4)$$

Using this equation to examine the hot and cold streams separately yields:

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<sup>1</sup>Both Kakaç and Paykoç (1988) and Incropera and DeWitt (1985) provide a more generalized overview of the following derivation.

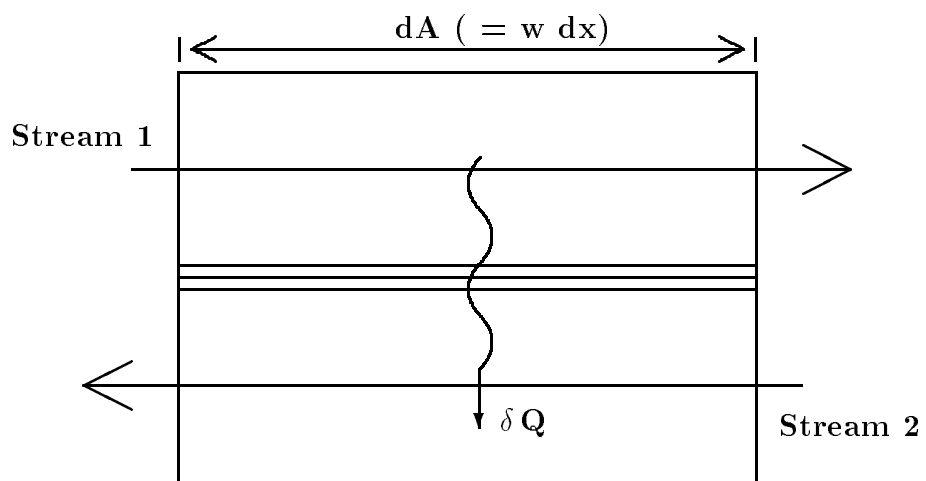


Figure 2-1: A Counterflow Heat Exchanger

$$\delta Q = -C_h dT_h ; C_h = (\dot{m} c_p)_h \quad (2.5)$$

$$\delta Q = \pm C_c dT_c ; C_c = (\dot{m} c_p)_c \quad (2.6)$$

where  $\pm$  or  $\mp$  appears, the top sign designates parallel-flow (Figure 2-2), and the bottom sign designates counterflow (Figure 2-3).

A heat exchanger relationship for expressing the heat transfer between fluids over a differential area is:

$$\delta Q = U (T_h - T_c) dA , \text{ or} \quad (2.7)$$

$$T_h - T_c = \frac{\delta Q}{U dA} \quad (2.8)$$

Rearranging equations 2.5 and 2.6 yields:

$$dT_h = -\frac{\delta Q}{C_h} \text{ and } dT_c = \pm \frac{\delta Q}{C_c} ; \text{ so}$$

$$dT_h - dT_c = d(T_h - T_c) = \delta Q \left( -\frac{1}{C_h} \mp \frac{1}{C_c} \right) \quad (2.9)$$

Dividing the above equation by equation 2.8 results in:

$$\frac{d(T_h - T_c)}{T_h - T_c} = U \left( -\frac{1}{C_h} \mp \frac{1}{C_c} \right) dA \quad (2.10)$$

The conductive and convective coefficients are assumed to vary only slightly over the heat exchanger area, and the temperature-enthalpy relationship is assumed

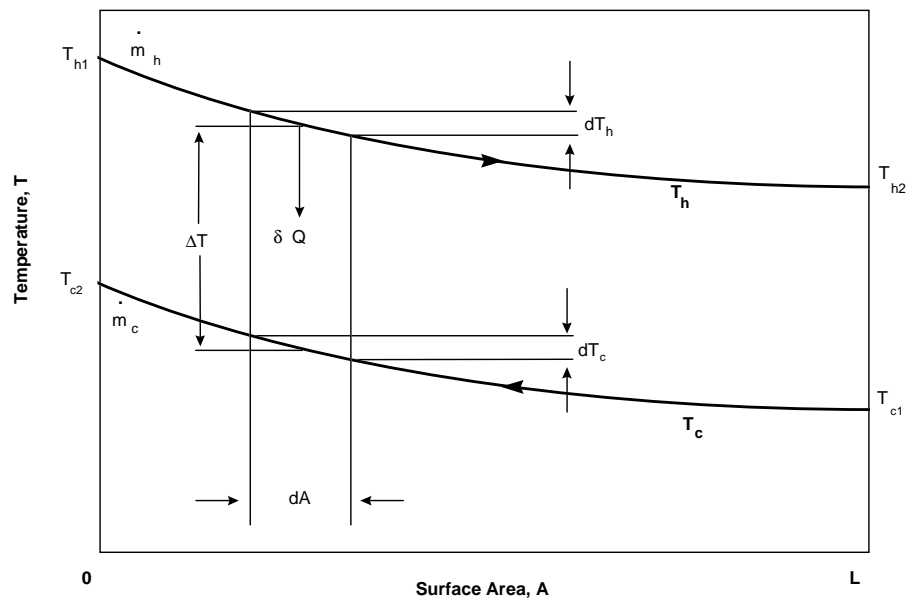
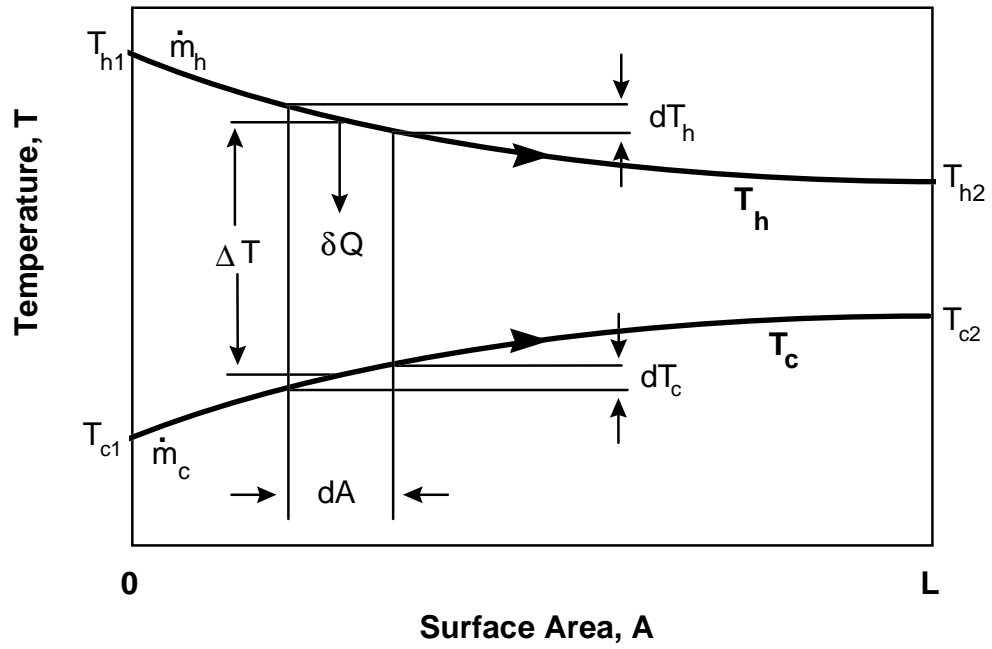


Figure 2-3: Counterflow Temperature Variation Over Area

to be linear, so the overall heat transfer coefficient ( $U$ ) and the specific heats ( $C_c$  and  $C_h$ ) will be considered to be independent of the area. Equation 2.10 can then be integrated over the heat exchanger:

$$\int_{side1}^{side2} \frac{1}{T_h - T_c} d(T_h - T_c) = U \left( -\frac{1}{C_h} \mp \frac{1}{C_c} \right) \int_{s1}^{s2} dA$$

Parallel-flow:

$$\ln \left[ \frac{T_{h2} - T_{c2}}{T_{h1} - T_{c1}} \right] = UA \left( -\frac{1}{C_h} - \frac{1}{C_c} \right)$$

Counterflow:

$$\ln \left[ \frac{T_{h2} - T_{c1}}{T_{h1} - T_{c2}} \right] = UA \left( -\frac{1}{C_h} + \frac{1}{C_c} \right) \quad (2.11)$$

Returning to equations 2.5 and 2.6, expressions incorporating  $C_c$  and  $C_h$  can be found:

$$\int_{side1}^{side2} \delta Q = - \int_{s1}^{s2} C_h dT_h$$

$$\int_{s1}^{s2} \delta Q = \pm \int_{s1}^{s2} C_c dT_c$$

Assuming that the specific heat is also not a function of temperature, this results in:

$$Q = -C_h (T_{h2} - T_{h1}) \quad (2.12)$$

$$Q = C_c (T_{c2} - T_{c1}) \quad (2.13)$$

Replacing the specific heats of equation 2.11 with those found in 2.12 and 2.13 yields

Parallel-flow:

$$\ln\left[\frac{T_{h_2} - T_{c_2}}{T_{h_1} - T_{c_1}}\right] = \frac{UA}{Q}[(T_{h_2} - T_{h_1}) + (T_{c_1} - T_{c_2})]$$

Counterflow:

$$\ln\left[\frac{T_{h_2} - T_{c_1}}{T_{h_1} - T_{c_2}}\right] = \frac{UA}{Q}[(T_{h_2} - T_{h_1}) + (T_{c_2} - T_{c_1})]$$

Rearranging to separate  $Q$  and  $UA$  results in the familiar log mean temperature difference:

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

$$\Delta T_{LogMean} = \frac{\Delta T_1 - \Delta T_2}{\ln\left[\frac{\Delta T_1}{\Delta T_2}\right]} \quad (2.14)$$

It must be remembered that this equation is only applicable under a number of limiting assumptions. The mass flow rate must be constant throughout the heat exchanger. The conductive and the 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.

From equation 2.14 it is evident that:

$$\Delta T_{LogMean,Counterflow} \geq \Delta T_{LogMean,Parallel-flow}$$

for the same inlet and outlet temperatures. In order to better magnify the error resulting from the LMTD, only counterflow heat exchanger configurations will be studied, since that LMTD represents the maximum temperature potential for heat transfer. For counterflow, equation 2.14 is

$$Q = UA \frac{(T_{h_1} - T_{c_2}) - (T_{h_2} - T_{c_1})}{\ln\left[\frac{T_{h_1} - T_{c_2}}{T_{h_2} - T_{c_1}}\right]}$$

This equation is valid only if  $C_c \neq C_h$ ; otherwise,  $T_{h_1} - T_{h_2} = T_{c_2} - T_{c_1}$  and a logarithm of zero results.

Finally, since the objective of this study is to correctly size heat exchangers, equation 2.14 is rearranged to find the overall conductance multiplied by the area ( $UA$ )

$$UA = \frac{Q}{\Delta T_{LogMean}} \quad (2.15)$$

### CHAPTER III

## A NUMERICAL METHOD FOR CALCULATING THE MEAN TEMPERATURE

For zeotropic refrigerants, some of the assumptions from the classical LMTD derivation must be discarded. Beginning with the first equation of Chapter II, 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 now not constant. In the classical LMTD derivation, it was assumed that the fluids would not undergo a phase change and that they would have constant specific heats (so that  $dh = c_p dT$ ). In this investigation, however, the more general case is studied, allowing a two-phase region of mixtures with nonlinear temperature-enthalpy curves. As discussed in the introduction, this nonlinearity results in varying specific heats. In fact, the specific heat is a function of both temperature and area. Returning then instead to the second definition in Chapter II for the heat transferred between two streams in a heat exchanger,

$$\delta Q = U \Delta T_{mw} dA \quad (3.1)$$

where  $\Delta T_{mw}$  is the temperature difference between the zeotropic refrigerant mixture and the water at any given point. To find the total heat transferred, equation 3.1 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

$$\int_0^{Q_0} \frac{\delta Q}{\Delta T_{mw}} = U_0 A_0 \int_0^1 dA' = U_0 A_0 \quad (3.2)$$

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 3.2 could become quite complicated, and would require as parameters the exact specifications of the heat exchanger under consideration.

An examination of equation 3.2 reveals its similarity to equation 2.15. However, because the temperature can be radically nonlinear, the above integral cannot be evaluated in closed form (recalling that  $\delta Q$  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.

$$U_0 A_0 = \sum_{i=0}^{Q_0} \frac{1}{\Delta T_{mw}} \delta Q \quad (3.3)$$

As the number of steps approaches infinity, equation 3.3 becomes identical to equation 2.15.

Calculations like those above would once have required hours of expensive computer time to solve. Given 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. As a graphical representation of this improvement, compare the obvious inaccuracy of Figure 3-1 with the increased precision of Figure 3-2.

Two other numerical approaches to 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 these 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.

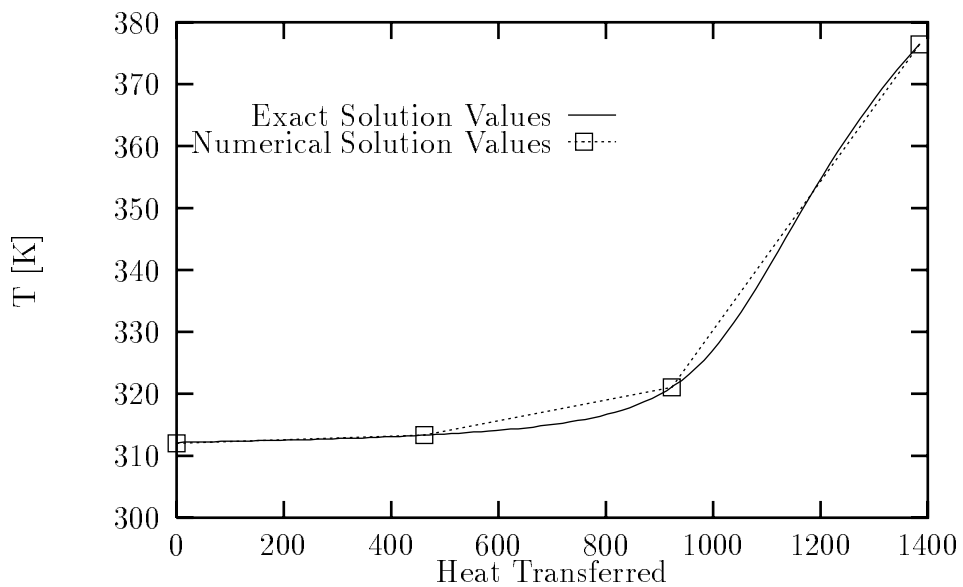


Figure 3-1: A Counterflow Heat Exchanger: Temperature Examined at Four Points

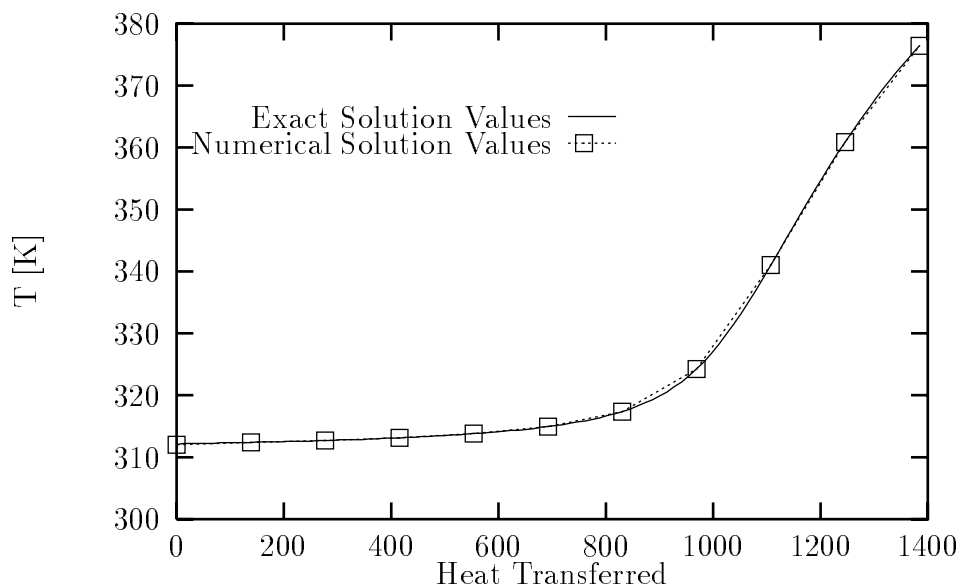


Figure 3-2: A Counterflow Heat Exchanger: Temperature Examined at Eleven Points

## CHAPTER IV

### APPLICATION OF THE NUMERICAL TECHNIQUE

#### Software Tools

##### *Engineering Equation Solver*

*Engineering Equation Solver* (EES) is a software package developed by Dr. Sanford Klein of the University of Wisconsin. EES incorporates the programming structures 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, and property tables for ammonia, methane, carbon dioxide, and other fluids are built into EES. Rather than store each possible data point, the Martin-Hou equation of state (EOS) is used. Water is one exception to this, as several equations of state are used for each phase. 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 Refrigerant Mixtures Database* (REFPROP).

## Refrigerant Database

REFPROP is a *FORTRAN*-based program that allows a user to look up thermodynamic properties for most refrigerants currently in use or under study. In addition to pure refrigerant properties, REFPROP uses either the Carnahan-Starling-DeSantis (CSD) hard sphere equation of state or the modified Benedict-Webb-Rubin (MBWR) equation of state to calculate the properties of refrigerant mixtures (up to five components per mixture are possible). The CSD EOS requires only six adjustable parameters per fluid, making it suitable for fluids where there are limited experimental observations, or where only a narrow range of study is of interest. The MBWR EOS is better for wide ranges of data, but requires a large amount of experimental information in order to fit its thirty-two interaction coefficients. The parameters for a number of mixtures have already been found and entered into REFPROP, but the user is responsible for matching the calculated points to experimental data for new combinations. The EES interface calls a DOS version of REFPROP in order to increase the speed of its calculations, but a Windows version is also available in a beta version still under development. The refrigerants that are available in both the DOS and the Windows versions can be found in Appendix A.

### Calculation of the $UA$

In order to find the  $UA$  derived in equation 3.3, the total heat transferred and the temperature difference between the water and mixture streams must 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:

$$\dot{Q}_{Tot} = \dot{m}_{water}(h_{water,entrance} - h_{water,exit}) \quad (4.1)$$

or for the refrigerant:

$$\dot{Q}_{Tot} = \dot{m}_{mixture}(h_{mix,exit} - h_{mix,entrance}) \quad (4.2)$$

where  $\dot{m}$  is the mass flow rate and  $h$  is the enthalpy. By equating 4.1 and 4.2, a mass flow ratio can be stated.

$$\dot{m}_{ratio} = \frac{\dot{m}_{water}}{\dot{m}_{mix}} = \frac{h_{mix,exit} - h_{mix,entrance}}{h_{water,entrance} - h_{water,exit}} \quad (4.3)$$

The end point states for both the water and the mixture must now be determined. A pinch point (PP) and concentration must also be chosen. For air-conditioning applications, a typical condenser entrance temperature for the water side is 29 °C with a 5 °C rise, so these are the values that will be 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 ( $n_i = 1, 2, 3 \dots$ ) are calculated using the following equations.

From equation 4.2:

$$\frac{\dot{Q}_{cumulative}}{\dot{m}_{mix}} = q_{cum} = h_{mix,step} \times n_i \quad (4.4)$$

$$h_{mix} = q_{cum} + h_{mix,entrance} \quad (4.5)$$

$$h_{water} = \frac{q_{cum}}{\dot{m}_{ratio}} + h_{water,exit} \quad (4.6)$$

From fluid properties:

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

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

$$\Delta T_{mw} = T_{mix} - T_{water} \quad (4.7)$$

For each desired pinch point and refrigerant, the values of  $q_{cum}$  and  $\Delta T_{mw}$  calculated in equations 4.4-4.7 are numerically integrated by EES to find the actual  $UA$  (equation 4.4 is an implicit equation in EES). When performing the numerical integration, EES decides how many sections the heat exchanger should be divided

into. This stepsize is either chosen using an automatic stepsize adjustment algorithm, or is directly specified by the user. For this application, one hundred steps were 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 integrand 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.

### 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 2.15:

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

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

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

$$UA_{LMTD} = \frac{\dot{Q}_{total}/\dot{m}_{mix}}{LMTD} \quad (4.8)$$

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.

## CHAPTER V

### RESULTS AND DISCUSSION

#### Ammonia-Water Mixtures

##### **Properties**

As can be seen from the temperature versus enthalpy profile of Figure 1-4, ammonia-water ( $\text{NH}_3/\text{H}_2\text{O}$ ) 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 Chapters III-IV.

Three separate mixture concentrations were studied: ninety-five percent, ninety-eight percent, and ninety-nine percent 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  $\text{NH}_3/\text{H}_2\text{O}$  EES program (Appendix B) was executed.

Given the above conditions, the temperature of the  $\text{NH}_3/\text{H}_2\text{O}$  refrigerant stream was found to range widely, from approximately 30 to 100  $^{\circ}\text{C}$ . 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 pressures and temperature glides for all the runs are listed in Table 5-1.

Table 5-1: Operating Pressures and Temperature Glides for  $\text{NH}_3/\text{H}_2\text{O}$ **Concentration = 0.95**

	Pinch (K)				
	1	3	5	7	10
$P(\text{bar})$	11.119	11.793	12.497	13.233	14.397
$T_{\text{glide}}(\text{K})$	65.96	65.59	65.24	64.89	64.34

**Concentration = 0.98**

	Pinch (K)				
	1.74	3	5	7	10
$P(\text{bar})$	11.693	12.135	12.862	13.621	14.824
$T_{\text{glide}}(\text{K})$	49.65	49.36	48.89	48.41	47.69

**Concentration = 0.99**

	Pinch (K)				
	2.47	3	5	7	10
$P(\text{bar})$	12.068	12.257	12.992	13.76	14.976
$T_{\text{glide}}(\text{K})$	38.82	38.68	38.15	37.61	36.79

## The Fallacy of an End-Point Pinch

The nonlinearity of  $\text{NH}_3/\text{H}_2\text{O}$  can lead to results that are physically unrealistic. For example, at a concentration of 99% and a pinch point of 1  $K$ , the LMTD is found to be 9.6  $K$ , resulting in a  $UA$  equal to  $132.72 \frac{kJ}{kg \cdot K}$ . In fact, a pinch of 1  $K$  at the mixture inlet is impossible, as demonstrated in Figure 5-1. An identical problem occurs at the same pinch for a concentration of 98%. Furthermore, by comparing the curves for a pinch point of 5  $K$  and concentrations of ninety-five, ninety-eight, and ninety-nine percent ammonia (Figure 5-2) it can be observed that while the nonlinearity increases with ammonia concentration, it remains strong even at ninety-five percent.

To avoid physically impossible calculations, care was taken to select pinch points where the streams' temperatures would not cross. It should be noted, however, that for  $\text{NH}_3/\text{H}_2\text{O}$ , all listed pinch conditions are solely applicable to the mixture entrance, as smaller temperature differences will consistently occur within the heat exchanger. The occurrence of an internal pinch can be predicted by comparing the value of  $\partial h/\partial T$  for the refrigerant mixture at the inlet and the outlet. If

$$\left(\frac{\partial h}{\partial T}\right)_{inlet} > \left(\frac{\partial h}{\partial T}\right)_{outlet}$$

then an interior pinch will occur (Venkatarathnam et al., 1996).

## 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 5-3).

Furthermore, the values of the  $UA$ ,  $UA_{LMTD}$ , and  $LER$  are compiled in Table 5-2 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  $UAs$ .

### Other Refrigerants

#### **Properties**

In addition to ammonia-water mixtures, zeotropic and near-azeotropic refrigerant mixtures that are currently under consideration as replacements for HCFC-22 were also analyzed. A literature search was conducted, and the most promising and/or widely endorsed mixtures were chosen for study, and are listed in Table 5-3 (all refrigerants will henceforth be referred to by their reference number). Refrigerants 1 and 8 are currently being considered by DuPont (Bivens, 1997), and refrigerant 9 (also known as AZ-20) has been developed by Allied Signal, two of the largest refrigerant producers in the United States. Refrigerants 3 through 5 were designated by Radermacher and Jung in their comprehensive survey (1993) as the most promising three-component blends. Refrigerant 2 was endorsed by Mei et al. in a follow-up study to that survey (1995). Refrigerant 2 was also earlier advocated by the Air Conditioning and Refrigeration Institute (ARI), as were refrigerants 6 and 7 (Kondepudi, 1992).

Each refrigerant was analyzed at pinch points of 2 to 7  $K$  at the mixture inlet. Refrigerant 9 is an exception to this; due to its concave rather than convex

Table 5-2:  $UA$ ,  $UA_{LMTD}$ , and  $LER$  for  $\text{NH}_3/\text{H}_2\text{O}$ **Concentration = 0.95**

	Pinch (K)				
	1	3	5	7	10
$UA$	1392.392	342.442	204.114	146.909	104.327
$UA_{LMTD}$	96.175	71.188	59.882	52.63	45.16
$LER$	1.161	0.682	0.533	0.446	0.364

**Concentration = 0.98**

	Pinch (K)				
	1.74	3	5	7	10
$UA$	6206.845	571.118	274.649	182.668	122.328
$UA_{LMTD}$	97.132	81.83	67.895	59.038	50.002
$LER$	1.806	0.844	0.607	0.491	0.389

**Concentration = 0.99**

	Pinch (K)				
	2.47	3	5	7	10
$UA$	7857.926	951.709	330.693	206.368	132.644
$UA_{LMTD}$	100.793	94.104	77.017	66.259	55.415
$LER$	1.892	1.005	0.633	0.493	0.379

Table 5-3: HCFC-22 Alternatives

#	Comp. 1	Comp. 2	Comp. 3	Mass % 1	Mass % 2	Mass % 3	Name
1	32	125	134a	0.23	0.25	0.52	407c
2	32	125	134a	0.3	0.1	0.6	
3	32	152a	124	0.2	0.2	0.6	
4	32	152a	134	0.3	0.4	0.3	
5	32	152a	134a	0.4	0.5	0.1	
6	32	125	134a	0.1	0.7	0.2	407b
7	125	143a	134a	0.4	0.45	0.15	
8	32	134	n/a	0.5	0.5	n/a	
9	32	125	n/a	0.5	0.5	n/a	410A

temperature profile, its pinch was specified at the mixture outlet. Throughout this range, the properties of these refrigerants varied widely, as did their operating pressures and temperature glides. The glides were much smaller than those observed for  $\text{NH}_3/\text{H}_2\text{O}$ , but the pressures were considerably higher. Tables 5-4 - 5-5 contain a complete list of the pressures and glides for comparison purposes. Note that the temperature glides are in the range of 5 to 10 °C, and that the pressures are listed in *kPa* rather than *bar*. The linearity of temperature versus enthalpy has increased, as can be seen at a pinch of 5 *K* for three of refrigerants in Figure 5-4, but there is still the possibility of an interior pinch. For each refrigerant and pinch, the EES program found in Appendix C was executed.

### **Standard Error for R-22 Alternatives**

As would be expected from the smaller temperature glides, the *UA* error for refrigerants 1 through 9 is less than for  $\text{NH}_3/\text{H}_2\text{O}$ . The magnitude of the differences can be seen in Tables 5-6 - 5-7.

Because  $|UA - UA_{LMTD}|$  is relatively small, the standard error calculation will produce values that are easy to evaluate both numerically (Table 5-8) and graphically (Figures 5-5 - 5-7). When a table entry is marked not applicable, an infeasible interior pinch was generated.

### **Drop-In Replacements vs. System Reconfiguration**

In the search for alternatives to R-22, a primary objective of the refrigeration industry has been the discovery of a “drop-in” replacement. A drop-in replacement is one that:

- 1) operates under very similar pressures to,

Table 5-4: Operating Pressures and Temperature Glides for Refrigerants 1-5

**Refrigerant # 1**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	1399.839	1436.386	1473.632	1511.587	1550.259	1589.655
$T_{glide}(K)$	5.189	5.154	5.118	5.081	5.044	5.006

**Refrigerant # 2**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	1381.817	1418.121	1455.124	1492.835	1531.262	1570.413
$T_{glide}(K)$	5.447	5.412	5.377	5.341	5.305	5.268

**Refrigerant # 3**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	1093.765	1121.81	1150.374	1179.461	1209.076	1239.226
$T_{glide}(K)$	10.07	10.03	9.988	9.947	9.904	9.86

**Refrigerant # 4**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	1128.243	1158.306	1188.955	1220.198	1252.042	1284.492
$T_{glide}(K)$	5.971	5.938	5.904	5.87	5.835	5.799

**Refrigerant # 5**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	1240.457	1273.366	1306.912	1341.105	1375.951	1411.458
$T_{glide}(K)$	6.879	6.849	6.819	6.789	6.758	6.726

Table 5-5: Operating Pressures and Temperature Glides for Refrigerants 6-9

**Refrigerant # 6**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	n/a	1593.875	1634.642	1676.177	1718.489	1761.588
$T_{glide}(K)$	n/a	2.813	2.787	2.759	2.732	2.704

**Refrigerant # 7**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	n/a	n/a	1499.032	1537.131	1575.948	1615.493
$T_{glide}(K)$	n/a	n/a	1.245	1.228	1.212	1.196

**Refrigerant # 8**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	1511.117	1550.362	1590.347	1631.08	1672.57	1714.824
$T_{glide}(K)$	8.347	8.302	8.257	8.211	8.164	8.116

**Refrigerant # 9**

	Pinch (K)					
	2	3	4	5	6	7
$P(kPa)$	2197.791	2252.694	2308.622	2365.586	2423.6	2482.678
$T_{glide}(K)$	0.116	0.116	0.116	0.115	0.115	0.114

Table 5-6:  $UA$  and  $UA_{LMTD}$  for Refrigerants 1-5**Refrigerant # 1**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	7254.367	4935.324	3727.552	2986.106	2484.39	2122.149
$UA_{LMTD}$	7157.052	4891.5665	3703.247	2970.873	2474.0563	2114.772

**Refrigerant # 2**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	6840.15	4772.05	3655.525	2955.366	2474.807	2124.406
$UA_{LMTD}$	6840.782	4774.1654	3657.343	2956.769	2475.9275	2125.29

**Refrigerant # 3**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	3466.033	2816.027	2389.221	2080.984	1845.409	1658.438
$UA_{LMTD}$	3692.544	2971.2297	2503.058	2168.255	1914.4263	1714.205

**Refrigerant # 4**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	5032.711	3855.596	3131.735	2636.972	2275.836	1999.993
$UA_{LMTD}$	5437.96	4092.7362	3287.357	2746.599	2356.9411	2062.201

**Refrigerant # 5**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	5676.224	4212.46	3350.749	2779.464	2371.927	2066.072
$UA_{LMTD}$	5933.173	4355.0611	3441.034	2841.484	2416.9026	2100.036

Table 5-7:  $UA$  and  $UA_{LMTD}$  for Refrigerants 6-9**Refrigerant # 6**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	n/a	9792.723	5349.748	3735.791	2870.195	2324.879
$UA_{LMTD}$	n/a	9152.4246	5153.854	3640.876	2814.8496	2289.129

**Refrigerant # 7**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	n/a	n/a	11946.56	5327.101	3671.643	2822.269
$UA_{LMTD}$	n/a	n/a	11423.38	5217.044	3619.7126	2792.065

**Refrigerant # 8**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	5465.339	4024.631	3193.355	2646.892	2258.31	1967.168
$UA_{LMTD}$	4841.3632	3680.786	2975.881	2497.552	2149.9769	1885.358

**Refrigerant # 9**

	Pinch (K)					
	2	3	4	5	6	7
$UA$	3213.858	2483.476	2027.328	1711.092	1477.374	1296.872
$UA_{LMTD}$	3210.3017	2481.3435	2025.898	1710.07	1476.6088	1296.289

Table 5-8: Standard Error for Refrigerants 1-9

Number	Pinch (K)					
	2	3	4	5	6	7
1	1.341	0.887	0.652	0.510	0.416	0.348
2	0.009	0.044	0.050	0.047	0.045	0.042
3	6.535	5.511	4.765	4.194	3.740	3.363
4	8.052	6.151	4.969	4.157	3.564	3.110
5	4.527	3.385	2.694	2.231	1.896	1.644
6	n/a	6.539	3.662	2.541	1.928	1.538
7	n/a	n/a	4.379	2.066	1.414	1.070
8	11.417	8.544	6.810	5.642	4.797	4.159
9	0.111	0.086	0.071	0.060	0.052	0.045

2) has chemical properties compatible with the equipment used with, and  
3) provides a refrigeration capacity at the level of  
the refrigerant that it replaces. While R-134a has proven to be a successful drop-in replacement for CFC-12, no completely satisfactory drop-in replacement has been found for R-22. However, both R-407c and R-410a work fairly well for selected applications, and are likely to become the preferred replacements for existing systems.

Zeotropes and near-azeotropes should not just be thought of as straight replacements, though. For a pure refrigerant, there is usually a trade-off between improving the efficiency and the volumetric capacity. Zeotropic mixtures can mitigate this somewhat (Didion and Bivens, 1990). A zeotropic mixture in the two-phase region constantly changes its composition as temperature changes, making it possible to control composition during operation.

The greatest potential, though, is a result of a zeotrope's gliding temperature. When properly utilized, this can actually result in efficiencies that are higher than those demonstrated by R-22. The diagram for a Lorenz cycle demonstrates that entropy generation can be reduced (below that of a Carnot cycle) if temperature profiles are properly matched (Figure 5-8). The Lorenz cycle consists of two constant-entropy adiabatic expansion or compression processes and two constant-heat capacity heat transfer processes (Cavallini, 1996).

Unfortunately, the nonlinearity of the temperature versus the enthalpy creates difficulties in accurately matching the profiles for a Lorenz cycle. Three ways to correct this are through chemical, mechanical, and thermal controls. The chemical approach uses an additional component to linearize the temperature profile. The mechanical approach cuts off the phase-change process so that the majority of the heat exchanger has a minimum temperature difference. The thermal approach adds additional heat processes so that the heat exchange avoids pinch points. Each of

these approaches also has the advantage of separating the interdependency of the composition and temperature glides (Didion and Bivens, 1990).

The characteristics of zeotropes and near-azeotropes can also be exploited in other ways. For example, the addition of a liquid-line/suction-line heat exchanger (Figure 5-9) results in impressive efficiency improvements. The idea of a desorber-absorber heat exchange cycle (Figure 5-10) is fairly old, but it can take unique advantage of zeotropic properties.

Whatever cycle is chosen, the results of this study can be used to more accurately determine the size of the heat exchangers.

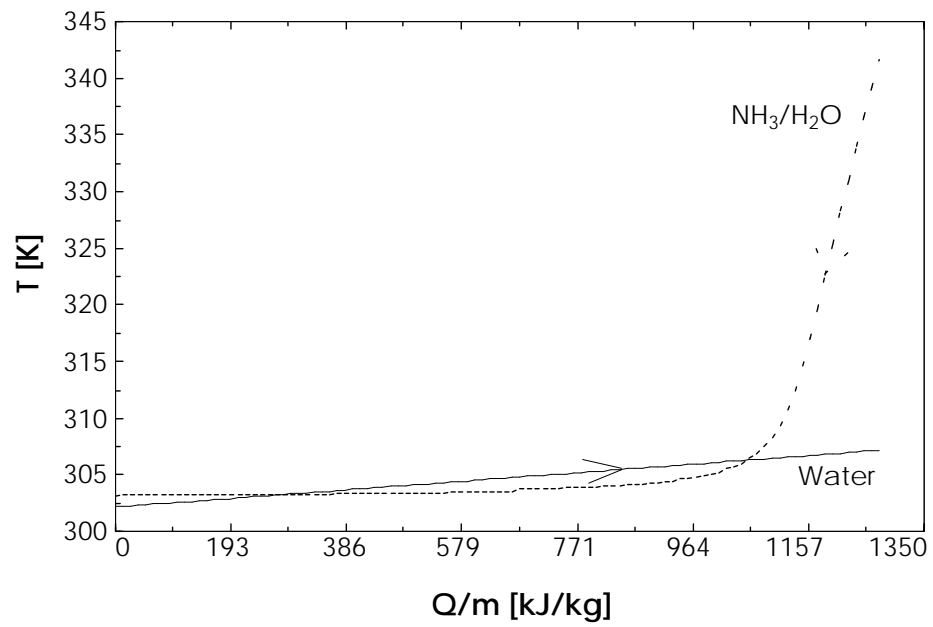


Figure 5-1:  $\text{NH}_3/\text{H}_2\text{O}$ : Concentration = 0.99, Pinch = 1 K

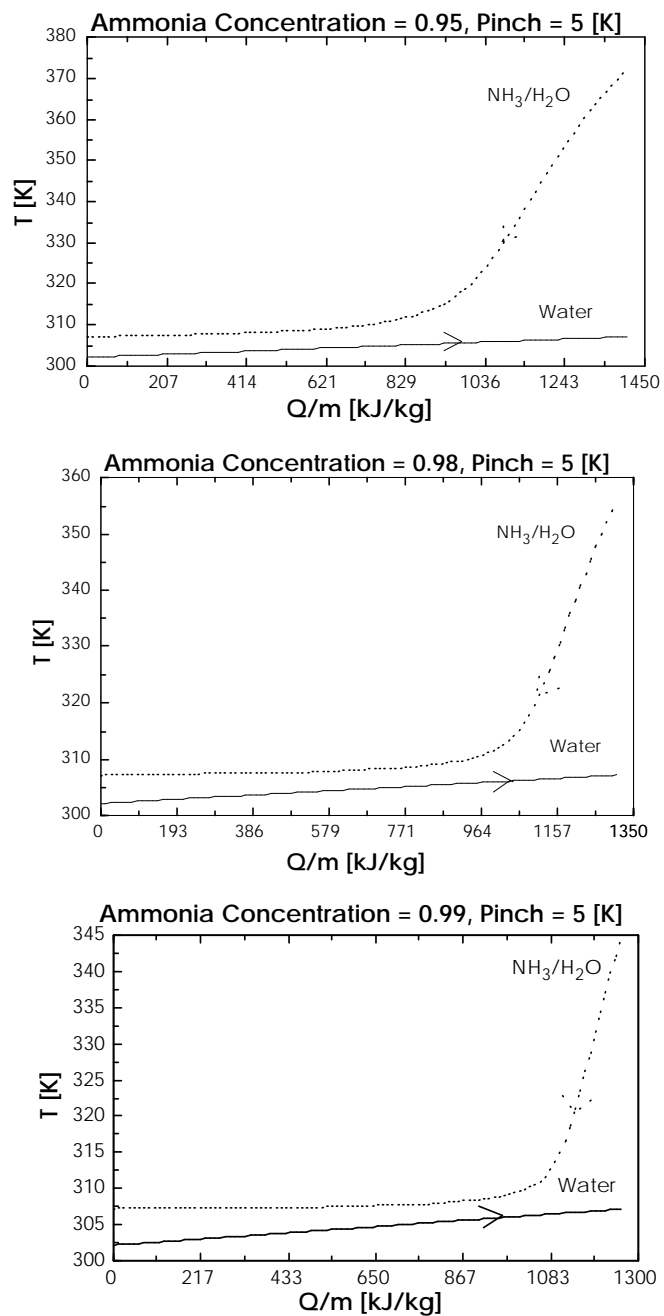


Figure 5-2: Concentration and Nonlinearity for  $\text{NH}_3/\text{H}_2\text{O}$

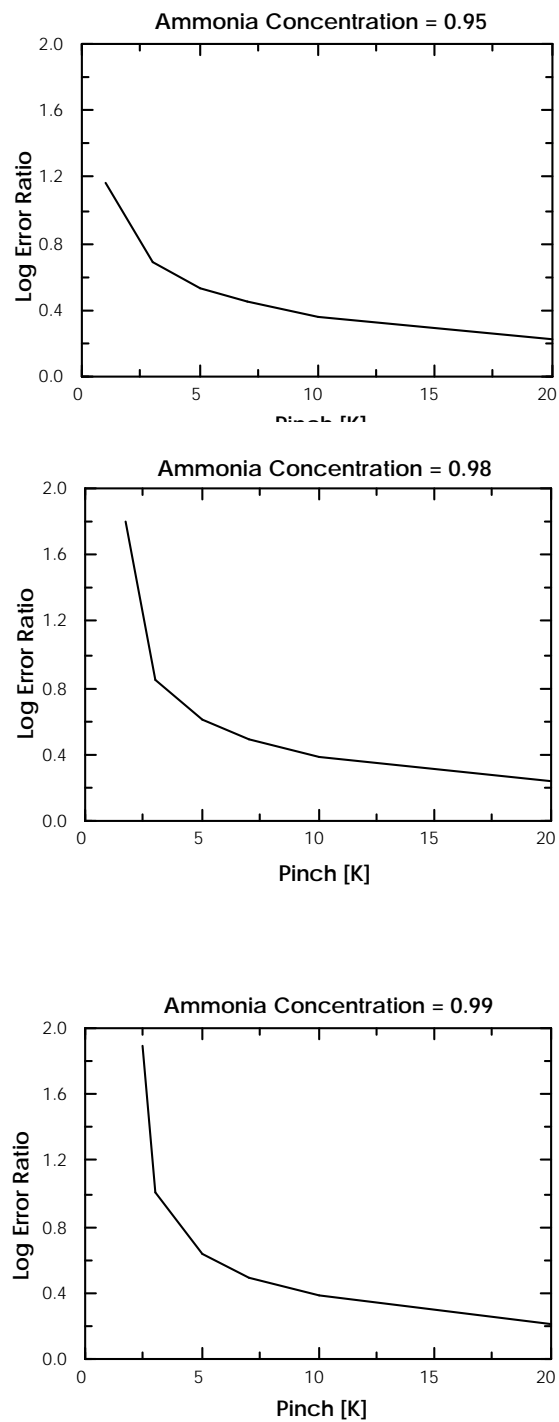


Figure 5-3: Log Error Ratio vs. Pinch Point for  $\text{NH}_3/\text{H}_2\text{O}$

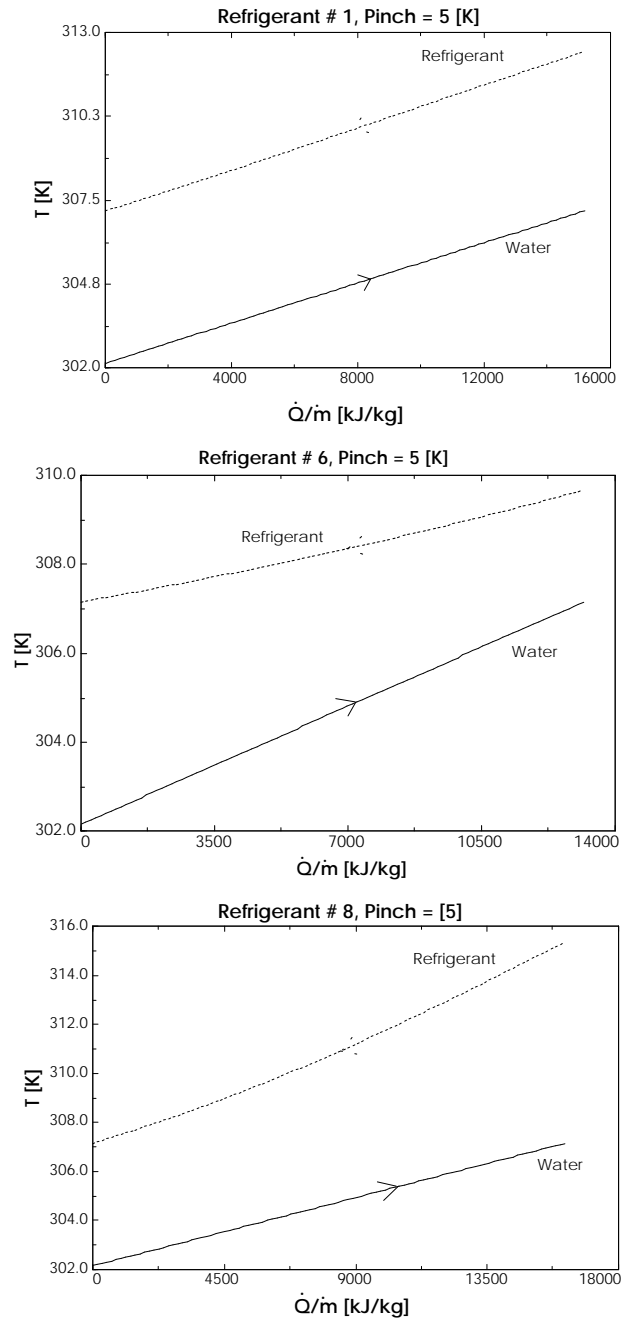


Figure 5-4: Nonlinearity of Refrigerants 1, 6, and 8

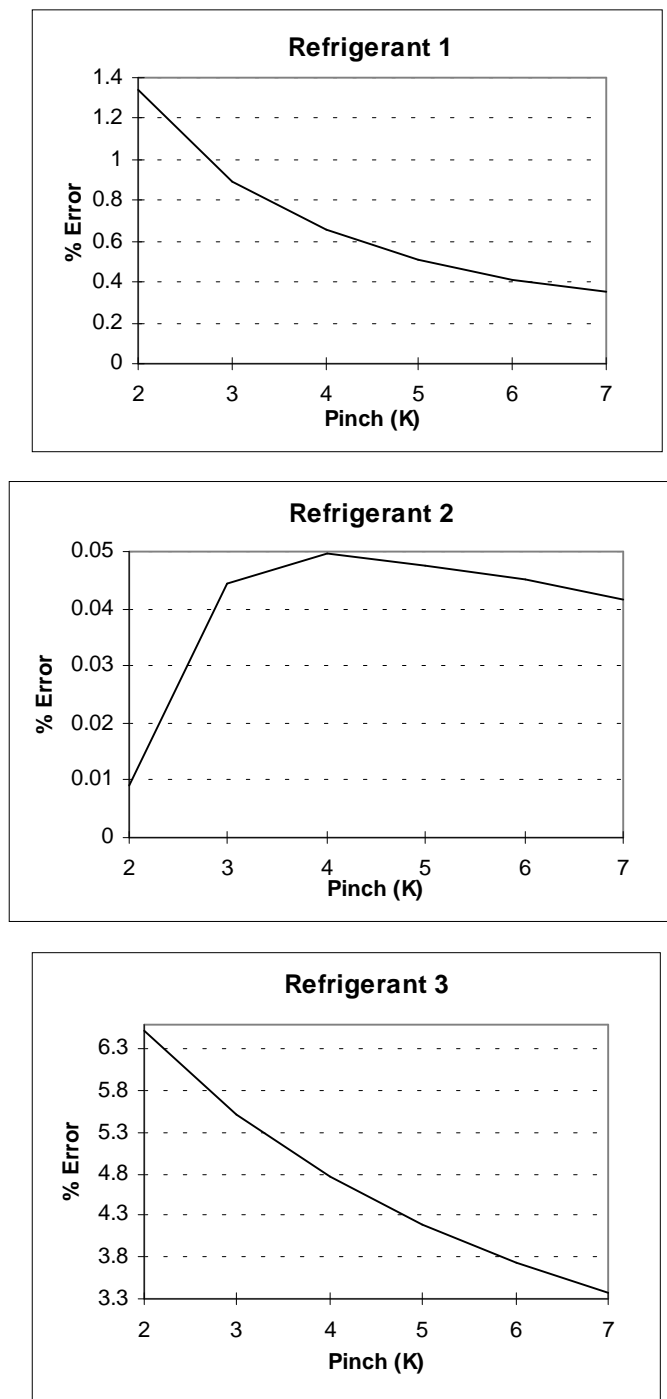


Figure 5-5: Standard Error for Refrigerants 1-3

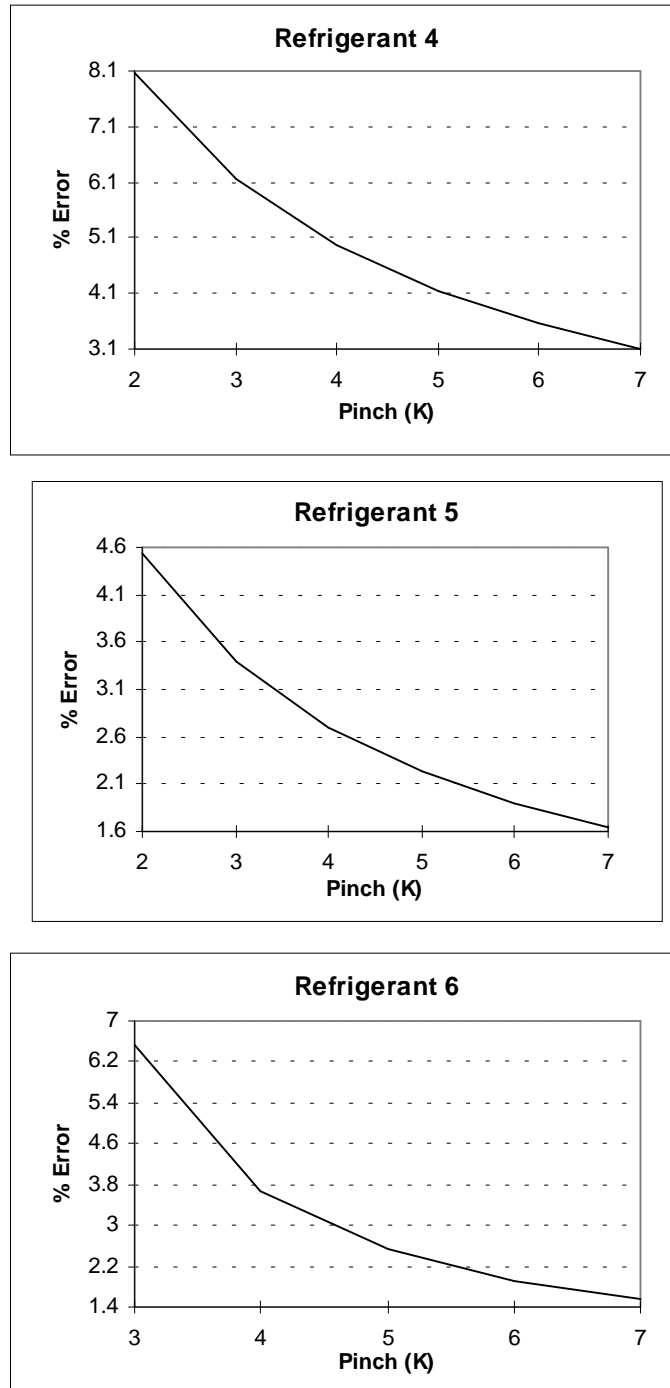


Figure 5-6: Standard Error for Refrigerants 4-6

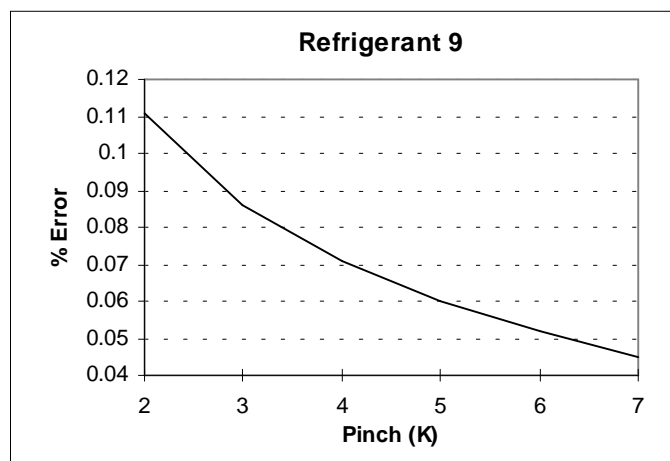
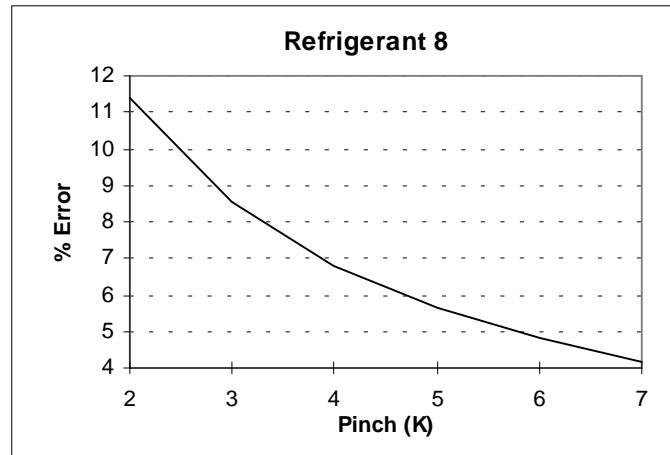
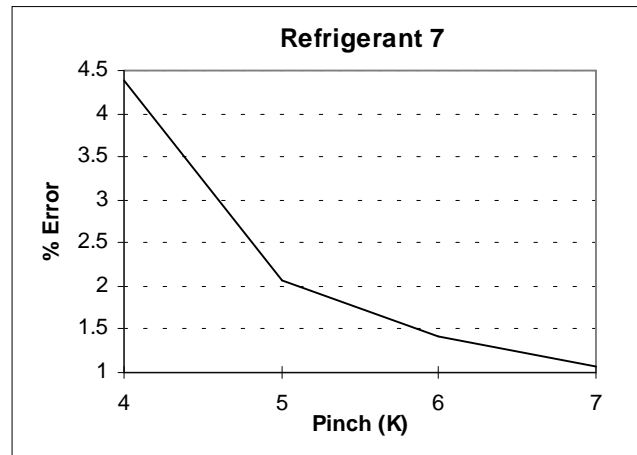


Figure 5-7: Standard Error for Refrigerants 7-9

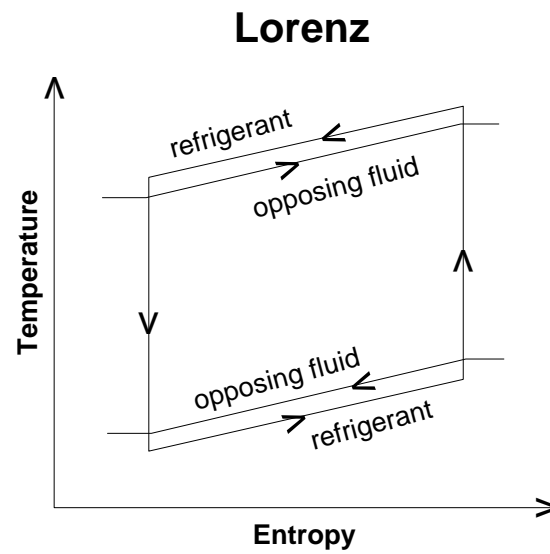
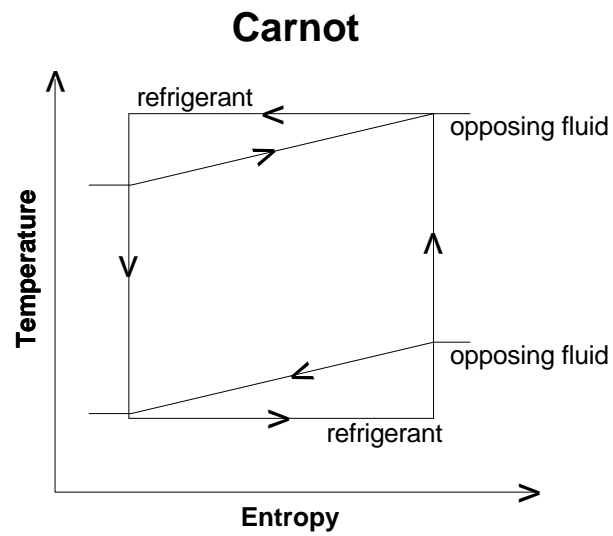


Figure 5-8: Carnot and Lorenz Cycle Diagrams

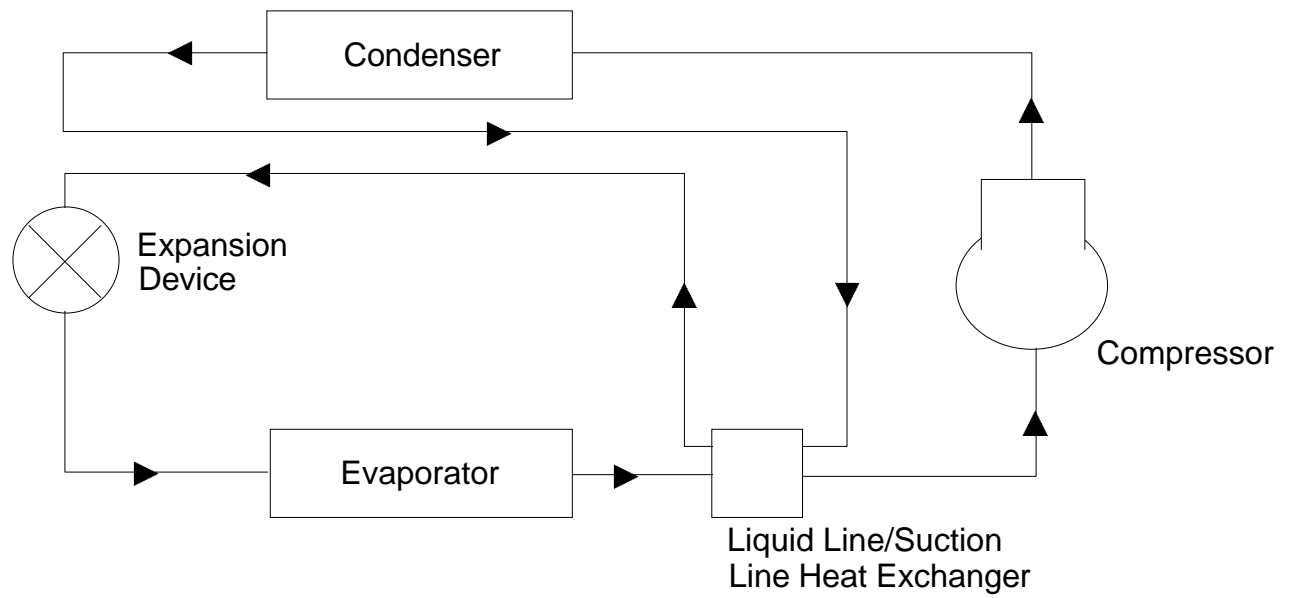


Figure 5-9: The Liquid-Line/Suction-Line Heat Exchanger

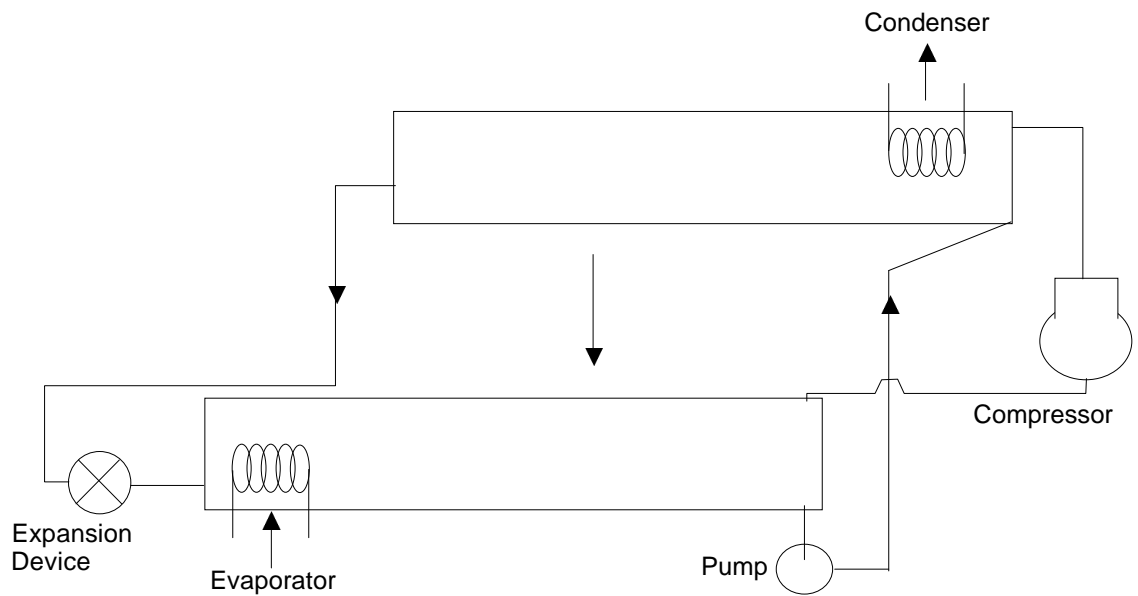


Figure 5-10: The Desorber-Absorber Heat Exchange Cycle

## CHAPTER VI

### 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, calculations 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.

For the refrigerant mixtures proposed as replacements for HCFC-22, the error is less, but clearly still exists. The magnitude of the error does not appear to directly correlate with the size of the temperature glide, as can be observed from comparing refrigerants 1 and 2 at a pinch of 2  $K$ . Both their operating pressures and their glides are nearly the same, but refrigerant 1 has a standard error of 1.34% while refrigerant 2 has a SE of 0.01%.

In general, the  $UA$  error decreases as the size of the pinch increases for both

$\text{NH}_3/\text{H}_2\text{O}$  and the replacement refrigerants. However, this is not the case for refrigerant 2; its error increases until a pinch of 4  $K$ , and at that point begins to decrease. For all other refrigerants, though, the change in the error also decreases with increasing pinch, which is both mathematically and conceptually logical.

Modified cycles to exploit the unique characteristics of mixtures should be analyzed using the correct mean temperature difference. The potential efficiency improvement could then be properly evaluated for these refrigerant mixtures. Since the majority of refrigerants being considered in applications currently satisfied by R-22 are zeotropes, both the desorber-absorber heat exchange (DAHX) cycle and the liquid-line/suction-line heat exchanger (LLSL-HX) should be considered for new systems and for retrofits.

A DAHX cycle incorporates both thermal and mechanical controls to optimize the utility of a temperature glide. Thermal control is achieved through heat exchange between the evaporator and the condenser, while mechanical control is gained through the variable speed liquid pump. This desorber-absorber heat exchange can provide the same temperature lift as a conventional cycle, but over a smaller pressure lift (Didion and Bivens, 1990). So by definition, the working fluid of a DAHX cycle must be a mixture whose constituents have very different boiling points; this means that a large temperature range can be covered at constant pressure through composition shifting (Radermacher, 1987). The DAHX cycle also uses a liquid-line heat exchanger with the evaporating zeotrope. An expansion device is used instead of a turbine in the compression cycle, but adding a liquid-line heat exchanger recovers the lost work.

The LLSL-HX cycle subcools the high-pressure refrigerant by reducing the superheating of the vapor entering the compressor. An LLSL-HX can either improve or worsen a system's performance, depending on what working fluid is used. For R-407c, for example, employing a LLSL-HX with a counterflow evaporator and con-

denser for cooling raises the efficiency to 5-6% above that of R-22, even when the same alterations are made to the R-22 cycle (Bivens et al., 1995). The impact of LLSL-HX on the volumetric capacity can be even greater (Domanski, Didion and Doyle, 1994).

In addition to considering new ways to utilize synthetic refrigerants, the advantages of switching to natural refrigerants should also be considered. While CFCs and HCFCs are currently designated as harmful to the environment, they were considered to be safe, and even ideal, for many years. It is unknown which synthetic refrigerants that are now thought of as benign will prove dangerous in the future. Some studies suggest, in fact, that HFC-134a may be decomposed in the troposphere by sunlight and form acid and poisonous substances (Lorentzen, 1995). On the other hand, natural refrigerants such as ammonia-water, propane, and carbon dioxide have long existed in the biosphere. Furthermore, while refrigerants such as R-410a and R-407c have zero ozone depletion potential (ODP), they do have non-trivial global warming potential (GWP).  $\text{NH}_3/\text{H}_2\text{O}$ , propane, and  $\text{CO}_2$  also have zero ODP, and while it is obvious that  $\text{CO}_2$  has a high GWP, the GWP of both propane and  $\text{NH}_3/\text{H}_2\text{O}$  is negligible.

Throughout the past, the greatest concern with the use of ammonia has been safety. While it is true that ammonia can burn with air and is poisonous, current refrigeration standards and ammonia's other natural properties may offset these difficulties. Ammonia gas is much lighter than air, and can easily be vented away. If it is trapped, its strong smell serves as a warning that there is a leak. In fact, ammonia can be detected at concentrations as low as five parts per million in air, before there is any significant danger. In terms of flammability, the lower ignition limit of ammonia is three to seven times that of natural gas and most hydrocarbons. The pressure of ammonia was also once considered a limiting factor, but compared to

the much higher pressures of the synthetic refrigerants in this study, that should no longer be counted as a concern. Even disregarding these natural safety features, the need to create systems that are tight and stay tight lessens the danger of ammonia as a refrigerant (Lorentzen, 1995).

Ammonia as a refrigerant has been applied to both industrial and residential heating and cooling units. It has been used in water chillers and heat pumps for residential buildings; direct-expansion systems for supermarket refrigeration; large heat pump plants for district heating; and central cooling of gas turbine cogeneration plants (Cavallini, 1996). Ammonia is also becoming more acceptable to the public. While more popular in Europe, especially Scandinavia and Germany, ammonia has the long-term potential to increase its U.S. market share as “green” issues gain in importance. Other natural refrigerants are also becoming more prominent: When a natural refrigerant-powered home refrigerator (marketed under the name “GreenFreeze”) was recently introduced in Germany, the manufacturer sold out within weeks. So, in summary, while systems can be developed that will increase the feasibility of synthetic refrigerants as R-22 replacements, the opportunity to change existing systems should perhaps be redirected toward an effort to reduce the use of all synthetics in favor of natural replacements.

## APPENDIX A

### REFRIGERANTS AVAILABLE IN REFPROP

#### REFPROP, Version 5.0

R-11	R-12	R-13	R-13b1	R-113
R-114	R-115	R-123	R-123a	R-124
R-125	R-134	R-134a	R-141b	R-142b
R-143	R-143a	R-152a	R-218	R-116
RC270	RC318	R-227ea	R-236ea	R-245cb
R-245ca	R-600a	R-236fa	RE134	RE245
propane	butane	isopentane	n-pentane	ammonia
propylene	ether	carbon dioxide		

#### REFPROP, Version 6.0 $\beta$ 21

#### Pure Substances

R-11	R-113	R-115	R-116	R-12
R-123	R-124	R-125	R-13	R-134a
R-142b	R-143a	R-152a	R-22	R-227ea
R-23	R-236fa	R-245ca	R-245fa	R-32
R-41	propane	butane	isobutane	ammonia
propylene	carbon dioxide			

**Mixtures**

R-401a	R-401b	R-401c	R-402a	R-402b
R-404a	R-407a	R-407b	R-407c	R-407d
R-408a	R-409a	R-409b	R-410a	R-410b
R-500	R-501	R-507a	R-32/R-125	
R-22/isobutane/R-142b		ammonia/butane		

## APPENDIX B

### AMMONIA-WATER EES PROGRAM

{Comments are surrounded by quotes or brackets.}

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

tk:=T+273.15

END

Conc=0.95 "Concentration of the Ammonia-Water Mixture"

Pinch=10 "Pinch Point"

{Calculating what the mdot ratio is from the end point data.}

{m\_ratio = m\_w / m\_m}

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,Pm,xm,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

{Integration to find the actual U0A0}

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

{Calculation of the error using two error scales}

LER=-log10(U0A0_LMTD/U0A0_act)
SE=(abs(U0A0_act-U0A0_LMTD)/U0A0_act)*100

```

## APPENDIX C

### REFRIGERANT MIXTURE EES PROGRAM

```

{Comments are surrounded by quotes or brackets.}
FUNCTION tk(T) "converts from C to K"
tk:=T+273.15
END
$INCLUDE /eesw/userlib/REFPROP.TXT

{Calculating what the mdot ratio is from the end point data.}
{m_ratio = m_w / m_m}
m_ratio=(h_end_mix-h_start_mix)/(h_end_h20-h_start_h20)

{The components and compositions listed below vary for each}
{refrigerant mixture.}
CALL REFPROP(3,R32,R125,R134a,TQX,TK(29)+Pinch,0,0.3811,0.1796:
            T_hi,P_hi,v_hi,h_hi,s_hi)
CALL REFPROP(3,R32,R125,R134a,PQX,P_hi,0,0.3811,0.1796:T_1m,
            P_1m,v_1m,h_start_mix,s_1m)
CALL REFPROP(3,R32,R125,R134a,PQX,P_hi,1,0.3811,0.1796:T_Nm,
            P_Nm,v_Nm,h_end_mix,s_Nm)
h_start_h20=enthalpy(WATER,T=TK(29),P=P_hi)
h_end_h20=enthalpy(WATER,T=TK(34),P=P_hi)

```

$T_{1w} = \text{temperature}(\text{WATER}, h = h_{\text{start\_h20}}, P = P_{\text{hi}})$

$T_{2w} = \text{temperature}(\text{WATER}, h = h_{\text{end\_h20}}, P = P_{\text{hi}})$

{Entered Values}

$\text{EndPtQ} = h_{\text{end\_mix}} - h_{\text{start\_mix}}$  "The total heat transferred in the heat exchanger"

$h_m = \text{Qtot} + h_{\text{start\_mix}}$

$h_w = (\text{Qtot} / m_{\text{ratio}}) + h_{\text{start\_h20}}$

$T_w = \text{temperature}(\text{WATER}, h = h_w, P = P_{\text{hi}})$

CALL REFPROP(3, R32, R125, R134a, PHX, P\_hi, h\_m, 0.3811, 0.1796: T\_m,  
P\_m, v\_m, h\_m, s\_m)

$\text{DELTA}_{\text{mw}} = T_m - T_w$

$\text{Delta}_{T_1} = T_{1m} - T_{1w}$  "Calculation of the LMTD and UOA0 using"

$\text{Delta}_{T_2} = T_{Nm} - T_{2w}$  "the traditional method"

$\text{LMTD} = (\text{Delta}_{T_2} - \text{Delta}_{T_1}) / (\ln(\text{Delta}_{T_2} / \text{Delta}_{T_1}))$

$\text{UOA0}_{\text{LMTD}} = (h_{\text{end\_mix}} - h_{\text{start\_mix}}) / \text{LMTD}$

{Integration to find the actual UOA0}

$\text{UOA0}_{\text{act}} = \text{integral}(1 / \text{DELTA}_{\text{mw}}, \text{Qtot}, 0, \text{EndPtQ})$

{Calculation of the error using two error scales}

$\text{LER} = -\log_{10}(\text{UOA0}_{\text{LMTD}} / \text{UOA0}_{\text{act}})$

$\text{SE} = (\text{abs}(\text{UOA0}_{\text{act}} - \text{UOA0}_{\text{LMTD}}) / \text{UOA0}_{\text{act}}) * 100$

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