Int.J. Applied Thermodynamics, **ISSN 1301-9724**
Vol.2 (No.1), pp.19-35, March-1999

The Influence of the Thermophysical Fluid Properties of the New Ozone-Safe Refrigerants on Performance

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Abstract

The selection a working fluid as a refrigerant for the vapor compression cycle is discussed. For thermodynamic performance to be optimized particular attention must be paid to the fluid's critical point and molar heat capacity. To achieve a reasonable balance between volumetric capacity, which implies equipment size, and coefficient of performance, which is efficiency, it is necessary to select a fluid with a critical point such that the application's condenser will operate in a reduced temperature range of approximately 0.7 to 0.9. It is also necessary to select fluids within a rather limited range of molar heat capacity values. The specifics as to how these properties effect the cycle's performance are presented in detail. For a better matching of the working fluid to a given application, both azeotopic and zeotropic mixtures of fluids are used. The characteristics and performance advantages and disadvantages of these mixtures are discussed.

Keywords: ozone-safe refrigerants, thermophysical properties.

1. Background

Perhaps as much as 90% of the world's heat pumping power (i.e., refrigeration, water chilling, air conditioning, various industrial heating and cooling processes, etc.) is based on the vapor compression (reverse Rankine) cycle principle. With the exception of ammonia, which is largely limited to industrial applications, the preeminent working fluids for this cycle are derived from the halogen family. Until the time of the awareness of the stratospheric ozone layer damage, virtually all of these working fluids contained chlorine (Calm and Didion, 1998). The elimination of this important element has caused considerable changes in the design of refrigeration machinery (Didion 1994). It has also caused new interest in the fundamentals of working fluid performance so that the "fluid design" and the "machine system design" are being considered in parallel. It is the fluid design's impact on machinery system design that this paper will address. The review of some of these fundamental connections will be helpful if the pending global warming crisis becomes a political reality. For then, once again, industry will be forced to change refrigerants. This time from the new chlorine-free refrigerants to ones that do not absorb the infrared re-radiation from the earth's surface. Under these circumstances, additional stringent criteria relating to system efficiency will also be necessary so that the new refrigerants do not cause additional CO_2 generation at the power source. These two criteria will pose a significant challenge in that new refrigerants or systems will have to be found that will be environmentally compatible both chemically and as energy performers.

In 1928 the inventor of the halogen family refrigerants (Midgley 1937) determined that only eight elements are suitable to be combined into molecules that could act as refrigerants. All others would form solids, are unstable or toxic, or were so inert (i.e., noble gases) that they could not be reasonably combined at all. In 1987 a search of a database of some 860 industrially important fluids was conducted to seek refrigerant candidates (McLinden and Didion 1987). The criteria for sorting out the candidates was that the liquid / vapor phases would exist at reasonable pressures and temperatures and that the fluid would have an acceptable volumetric heat capacity. In short, the study showed that Midgley's postulate stood the test of time. All but two of the selected 51 fluids contained only Midgley's elements. The two were highly reactive and toxic and thus unsuitable from chemical and health criteria viewpoint. The ozone crisis has eliminated two of Midgley's original eight elements: chlorine and bromine. The surviving six are :carbon, nitrogen, oxygen, sulfur, hydrogen and fluorine. Now the global warming issue threatens those refrigerants that have a carbon-fluorine bond because of its infrared absorption band. In addition to the thermal properties criteria discussed in this paper there are at least ten other chemical, health, safety and miscellaneous criteria that a refrigerant must satisfy to be considered for operation in a modern vapor compression cycle system (Threlkeld 1970). All of this is to say that the pool for future refrigerants is anything but unlimited.

The most fundamental of a working fluid's thermal properties that are needed for the prediction of a refrigerant system's performance are the pressure-volume-temperature (PvT) in an equilibrium state. Other properties, such as enthalpy and entropy as well as the Helmholtz and Gibbs functions, may be derived from a PvT correlation, that is an equation-of-state, utilizing specific heat. There exists a myriad of equations-of-state, which have been classified into families, each of which have a set of advantages and disadvantages. Today, the most widely used refrigerant database is REFPROP (McLinden et.al.,1998). It was developed and is maintained by The National Institute of Standards and Technology and is currently in its sixth edition. It uses several equations-of-state to correlate 33 single component refrigerants and 29 predefined mixtures, along with the ability to construct virtually any desired mixture of up to five components. The data upon which REFPROP is based has been collected through the International Energy Agency Annex 18. This committee of experts gather data submitted from laboratories throughout the world. In order to provide engineers with enthalpy and entropy data of a precision of 0.5 to 1.0%, it is necessary to make PvT measurements to within 0.05 to 0.1%, which is the state-of -the-art of these measurements. The lower precision of enthalpy and entropy is largely due to the derivatives necessary in their derivation from the PvT data and the fact that any correlation (i.e., equation-of-state) will necessarily have some uncertainty band associated with it. The precision of derived properties, for those mixtures that have not been measured directly, is probably an additional 1.0 to 2.0% lower because the uncertainty of each component's data is accumulative and the equations-of-state of the mixtures generally correlate with less precision than for a single component refrigerant. Mixtures that are user defined suffer an additional uncertainty if the mixing coefficients of the specific components are not empirically determined.

As will be discussed in this paper, the working fluid's specific heat capacity is one of the most influential properties for estimating system performance. This property, whether it be molar or mass, constant volume or constant pressure, is by definition dependent, on another derivative (i.e., the change in enthalpy per unit change in tem-perature). Thus, unless heat capacity has been measured directly, independent of the PvT measurements, its predicted numerical value will necessarily be more uncertain than the enthalpy and entropy values.

This estimate of the state-of-the-art of data precision is mentioned to impress upon the reader the value of high quality property data and the need to use only that data for which uncertainty is properly quantified. This important field of property measurement research, although not discussed here, is certainly implicit throughout any quantitative analysis this paper suggests.

2. Cycle Analysis

The ideal vapor compression cycle is shown on the Temperature-Entropy diagram of *Figure 1*. This cycle is comprised of two isobaric heat exchange processes, a constant enthalpy expansion process and an isentropic compression process. The "ideal" vapor compression cycle is, by definition, one in which the refrigerant exit states from the condenser and the evaporator are on the respective saturation lines. Beginning with state point 1, saturated liquid is leaving the condenser and entering the expansion device where some of the refrigerant is flashed at constant enthalpy (1-2) causing the remaining liquid portion to be at the desired temperature and pressure needed for a particular evaporator operating condition. The price paid for this process is that not all of the refrigerant is available for the vaporization process in the evaporator (2-3). The evaporator's heat source is an external fluid, usually air, water, or brine. The heat transferred during this process is called the refrigerating effect, the dimensions of which are Watts per kilogram of refrigerant flow. The saturated vapor leaving the evaporator is compressed isentropically to the desired condenser's saturation pressure by inputting mechanical work (3-4). Finally, the discharged vapor is desuperheated and condensed by expelling heat through the wall of the condenser to another external fluid which is usually air or water. For the purposes of rating either heating or cooling one of the external fluids, the efficiency term is

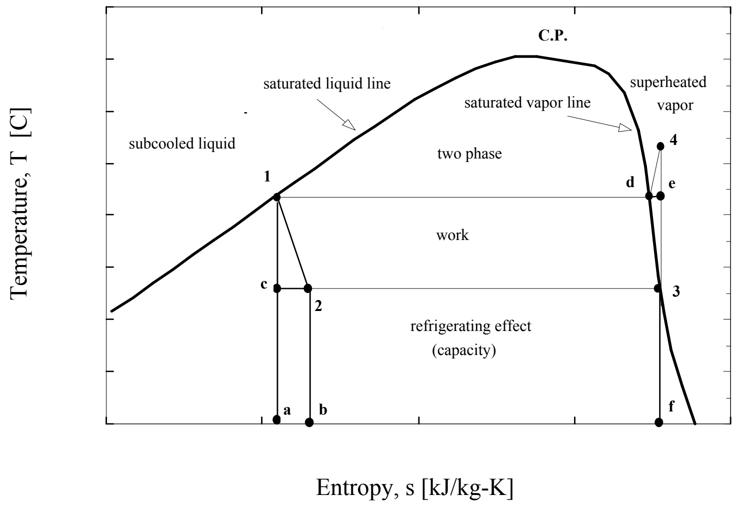

Figure 1. Ideal vapor compression cycle's temperature-entropy diagram.

the coefficient of performance (COP). It is, as all efficiency terms are, the desired product (e.g., the refrigerating effect) divided by the cost which, in this case, is the work input to the compressor. Different refrigerants provide the desired product with more or less effectiveness. The desired product for a cooling application is the heat entering the evaporator ($Area_{2\text{-}b\text{-}f\text{-}3\text{-}2}$). It is important to note that, from the first law, the work is the difference between the heat rejected from the condenser and that entering the evaporator. Since these processes are theoretically isobaric, the general property relationships are:

$$dh = T\,ds + v\,dP$$

where $dP = 0$, thus

$$W = \int_1^4 dh - \int_2^3 dh = \int_1^4 T ds - \int_2^3 T ds$$

and since $h_2 = h_1$, which are the end points of an irreversible process of unknown path, the work is: $W = h_4 - h_3 = Area_{1\text{-}a\text{-}b\text{-}2\text{-}3\text{-}4\text{-}d\text{-}1}$. It is the areas of the T-s diagram that illustrate the academic subtlety of the work not being contained within the boundaries of a cycle that includes an irreversible process. While the quantitative analysis is best obtained using the ln P-h diagram (*Figure 2*) because the enthalpy differences, which designate the quantities desired or paid for, are easily taken from the linear scale of the abscissa. The area designated by a-b-2-c-a represents the lost refrigerating effect (capacity) due to the expansion process. This area is also equivalent to the

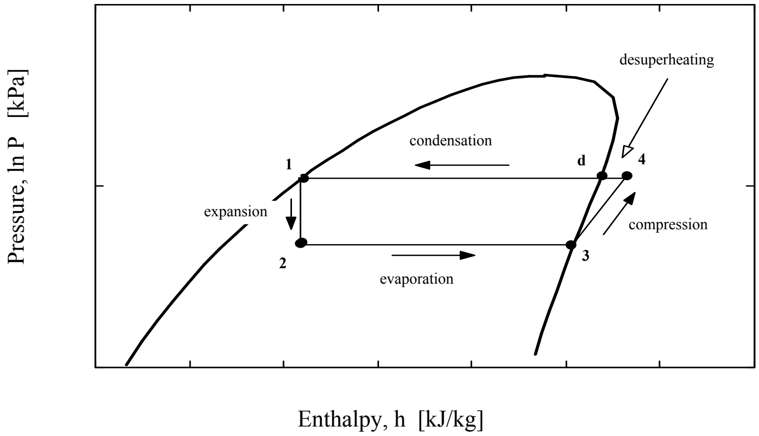

Figure 2. Ideal vapor compression cycle's pressure-enthalpy diagram.

lost isentropic work that the use of an expansion turbine would bring. (For practical reasons the irreversible expansion is almost always preferred.)

The performance of refrigerants is reflected, and perhaps best understood qualitatively, by the relative sizes of these T-s diagram areas and can be easily given a quantitative value based on their respective enthalpy differences from the ln P-h diagram. Actually, the industry rates the performance of each refrigerant by applying to it a COP rating, much the way they do for a compressor or a machinery system. The COP is defined as the numerical value obtained for the ratio of (h_3-h_2) / (h_4-h_3) when the ideal vapor compression cycle is evaluated at the saturated condenser and evaporator temperatures of 30^0 C and -15^0 C, respectively.

3. Single Component Refrigerants

Although each refrigerant has different numerical property values, all fluids have similar vapor domes. A typical shape is shown in *Figure 3*. A saturated liquid line (left side) and a saturated vapor line (right side), with different slopes for each fluid, meet at a critical point (CP) of unique temperature and pressure. Using the CP as one index of refrigerant performance, one can see some consequences different working fluids have on the cycle's performance. Given an ideal vapor compression cycle for a fixed application temperature range, a refrigerant of a higher CP will result in a decreased density at state 3, the point of suction into the compressor. Since most refrigeration compressors run at constant speed and are thus constant volume pumps, this decrease in density translates to a decrease in mass flow rate and thus system capacity, which is equal to the product of mass flow rate times refrigerating effect. For a new system design, the higher CP fluid would require a larger compressor pumping displacement to have an equal capacity rating. Conversely, selecting a fluid that has a lower CP results in more mass flow rate but a higher reduced condenser temperature. (Reduced temperature, T_r, is defined as the ratio of the particular state temperature to the CP temperature.) Since the slope of liquid saturation line decreases as it approaches the CP, the operation at higher reduced temperatures will result in the constant enthalpy expansion process using more flash gas to reduce the remaining liquid to evaporator conditions. Also the latent condensing heat per unit mass flow is less because of the narrowing of the vapor dome near the critical point. These reductions in refrigerating effect result in a decrease in COP since less heat can be transported per unit mass flow and thus per unit work. As a general rule then, when selecting a working fluid, an inherent trade-off exists between the vapor compression cycle's efficiency and capacity. The former is proportional to the CP value and the latter is inversely proportional to it. Therefore no single ideal fluid can exist for all applications (McLinden 1988).

Morrison (1994) showed that the slope of the saturation lines are related to thermodynamic properties of fluids in such a way htatbased on a prospective refrigerant's heat capacity alone, estimates of its expected field performance could be made. Briefly, his analysis started with the expansion of entropy as a function of temperature and volume:

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

and differentiating with respect to temperature along the saturation line, σ, to obtain the inverse slope in a T-s diagram:

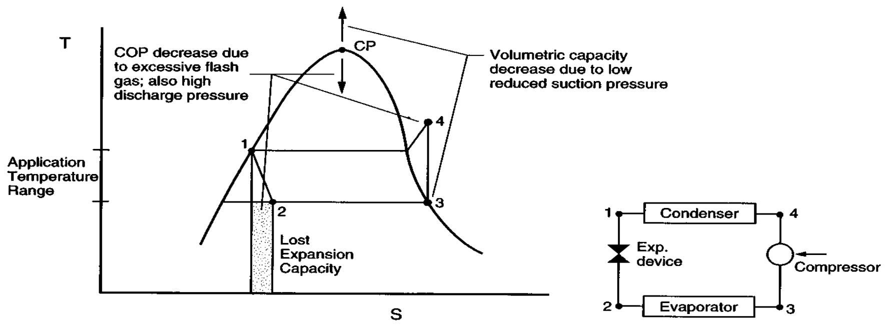

Figure 3. Inherent trade-offs for pure refrigerants.

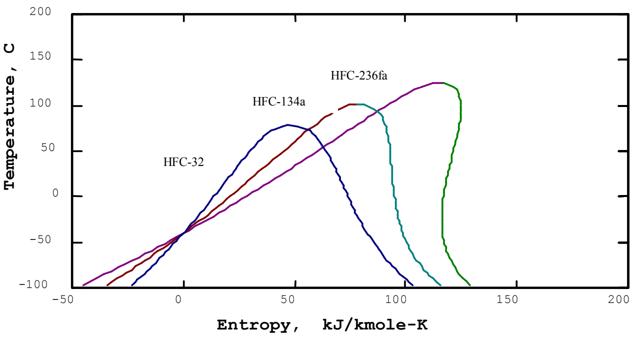

Figure 4. Saturation domes of refrigerants of increasing molecular complexity.

$$\left(\frac{ds}{dT}\right)_\sigma = \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_\sigma .$$

Then by way of a Maxwell relation and the fact that the constant volume heat capacity is:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \text{ and } \left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$$

the slope of the saturation line can be shown to be:

$$\left(\frac{dT}{ds}\right)_\sigma = \left[\frac{c_v}{T} + \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{dv}{dT}\right)_\sigma\right]^{-1} .$$

It should be noted that $\left(\partial P/\partial T\right)_v$ is positive for virtually all saturated liquids and vapors and $\left(\partial P/\partial T\right)_\sigma$ is positive for saturated liquids and negative for saturated vapors. Thus the magnitude of the constant volume molar heat capacity will have a strong influence on the slope of either saturation line. In the case of the vapor side, it can be a matter of whether it will be a positive or negative slope (*Figure 4*). By the second law, the slope of the saturated liquid line cannot be negative. Thus, the heat capacity will influence its slope but it will always remain a positive slope. Molar heat capacity is generally a function of molecular complexity. This is because temperature is a measure of translation energy only and chain molecules have the ability to absorb energy rotational and vibration modes, which is not reflected by an increase the substance's temperature. A rule of thumb might be that the more complex the molecule the higher the molar heat capacity and the more likely the saturated vapor line will bend so that its slope is negative at the lower pressures and positive at the higher pressures. *Figure 4* illustrates the saturation domes of refrigerants of increasing molecular chain length. For refrigerants with three or more in a carbon chain (e.g., HFC-236fa) the isentropic vapor compression process starting from the saturation vapor line at a low pressure, rising vertically can enter the two phase region. This 'wet compression' process over an extended period of time is unacceptable for most compressors; thus, all such fluids are considered doubtful as potential alternative refrigerants. One might be tempted to suggest that the re-entry into the two-phase region could be avoided with a sufficient amount of superheat prior to the compressor suction point. Indeed, superheat is always advisable so as not to 'slug' the compressor with liquid. However, for all fluids, superheat is detrimental to the system COP. This is because the slope of the isentropes on the lnP-h diagram decreases as they get further from the saturation line. This may be reasoned mathematically by comparing the combination of the 1st and 2nd laws to the expansion of enthalpy as a function of entropy and pressure:

$$dh = T\,ds + v\,dP$$

and since h = h(s, P) which can be expanded to:

$$dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP$$

equating coefficients yields:

$$v = \left(\frac{dh}{dP}\right)_s$$

which is the reciprocal of the slope of the isentrope on the ln P-h diagram. For simplicity, consider the ideal gas equation of state to obtain:

$$\left(\frac{\partial P}{\partial h}\right)_s = \frac{1}{v} = \frac{P}{RT}$$

Thus as the superheat temperature increases the isentrope slope decreases and the work (dh) increases for a fixed difference between the saturation pressures of the evaporator and condenser. In other words, it takes more work to compress a hot gas than a cool gas over the same pressure lift. In addition, the suction gas density (and thus the volumetric capacity) decreases. Fundamentally, superheat is so detrimental to performance that it is doubtful that the any potential working fluid is likely to have other properties that off-set this degradation. Therefore, it is safe to say that any halogen or hydrocarbon of carbon chains longer than three or four is unlikely to have acceptable performance, particularly in these energy and environmental conscious days. Bivens and Minor (1997) conducted a rather extensive study of halogenated ethers and failed to show any likely prospects, as well.

Perhaps the more subtle problem of this 'vapor dome tilt' with fluids of high heat capacity is on the saturated liquid side. Here its decreased slope implies an increase in expansion losses. Another explanation is that the increased liquid molar heat capacity requires more latent heat, via more flash gas, to bring it down to the evaporator temperature. In addition to the rather impractical isentropic expansion turbine, several machinery options are available to mitigate this loss. The simplest one is a liquid line / suction line (llsl) heat exchanger, illustrated in *Figure5a*. Its thermodynamic tradeoff , illustrated in *Figure5b*, is an increase in refrigerating effect at the expense of an increased superheat which causes a decrease in flow density and thus the mass flow rate. Domanski, Didion and Doyle (1994) discussed the potential of many different refrigerants' response to this heat exchanger and showed a strong correlation with molar heat capacity. That is, the higher the molar heat capacity the greater the performance increase from the addition of the llsl heat exchanger. So the refrigerants that need it the most will respond the best. However, a rather high heat exchanger effectiveness is necessary for significant improvements, implying a relatively large amount of surface area must be added to the system. A computer simulation study of several of selected recovery systems for expansion side losses has been conducted by Domanski (1998). Only the economizer-cycle, which reduces compressor work, is currently used in practice for the sole purpose of enhancing system efficiency.

While it is true that working fluids suffer performance problems when their heat capacity is too high, it is also true that for different reasons, performance will decrease if heat capacity is too low. In *Figure 1* the triangular area of work, d-4-e, is called the superheat horn. The d-4 line represents the isobaric process of the desuperheat region of the condenser. Obviously the steeper the isobar the more the work because the vapor has to be compressed to a higher temperature to reach the condenser's saturated pressure line.

The dependency of this isobar's slope on heat capacity may be seen by equating the other two coefficients of the previous two enthalpy expressions, to get: $T = \left(\partial h / \partial s\right)_P$. Rearranging by inverting the partial differential and using the definition of heat capacity and T_c as the saturation temperature of the condenser's isobar:

$$\partial h = T ds \text{ for constant pressure}$$

$$\left(\frac{\partial T}{\partial s}\right)_P = \frac{T_c}{T_c}\left(\frac{\partial T}{\partial s}\right)_P = T_c\left(\frac{\partial T}{\partial h}\right)_P = \frac{T_c}{c_P}$$

Thus the slope of the condenser's isobar's in the superheat region is inversely proportional to the molar heat capacity. And so fluids that have a very low molar heat capacity (e.g., ammo-

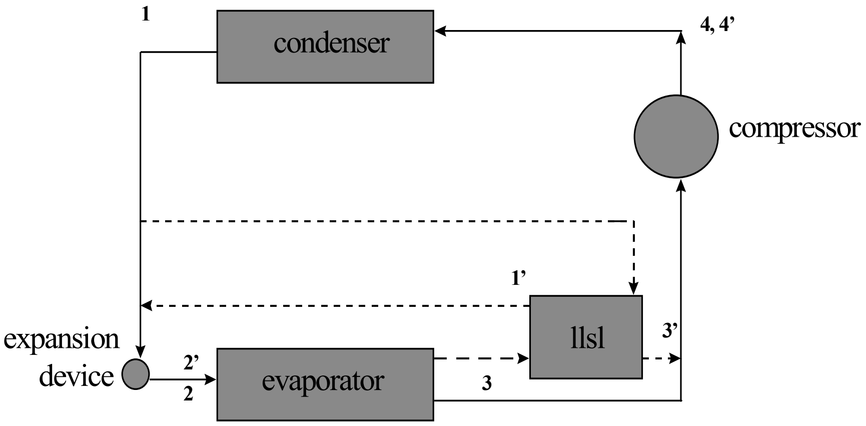

Figure 5a. Schematic of a liquid line- suction line heat exchanger cycle.

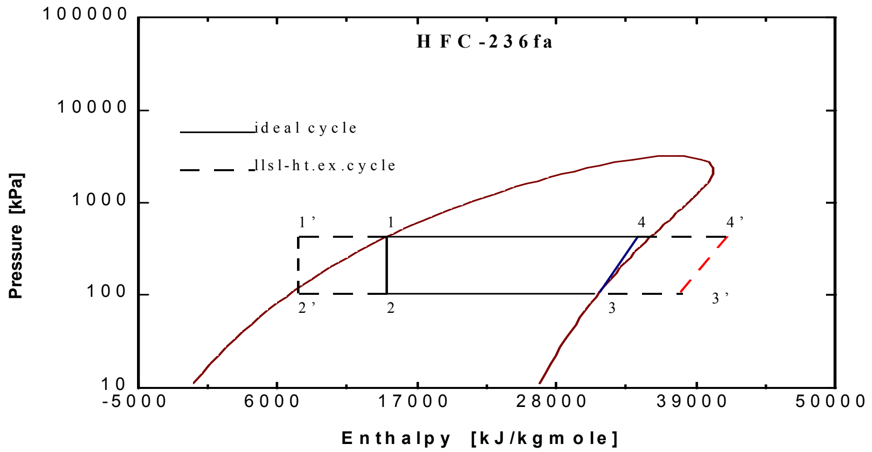

Figure 5b. ln P-h diagram for liquid line-suction line heat exchanger cycle.

nia) will suffer some performance degradation due to an increase in work. However, for the halogenated refrigerants in use today, the magnitude of this effect is generally not as significant as the expansion side effects. A more significant impact is the potential for a high discharge temperature threatens a slow lubricant decomposition.

Additional insight about refrigerants may be gained by the somewhat unconventional, for this Industry, thermodynamic diagram of ln P_{sat} vs -1/T. *Figure 6* is an example of this diagram of saturation pressure versus temperature on nonlinear axes so as to present the data relationship in a near linear fashion. To the thermodynamicist, this graph is based on the following equation:

$$\frac{1}{P}\frac{dP}{dT}=\frac{h_{fg}}{RT^2}$$

which is typically used for estimating the latent heat of vaporization at low reduced temperatures. Over small temperature differences the latent heat, h_{fg}, can be considered constant. Thus an integration of this equation yields:

$$\ln P=-\frac{h_{fg}}{R\,T}+\text{constant}$$

which means that a plot on a (ln P) versus (−1/T) axes will be a straight line with a slope of h_{fg} /R. In light of the approximations, particularly the ideal gas assumption to get the above form of the Clausius-Clapeyron equation, the graph is not quantitatively accurate. It is, however, convenient for defining a fluid's vapor pressure by just two data points (usually c.p. and NBP). These plots are then useful for comparing relative performances of different fluids by noting their magnitudes and slopes.

This data is also what every technician carries, in tabular form, to assist in determining the proper amount of refrigerant charge to put in the system. The graph strikes the heart of what vapor compression working fluids are all about; that is, they enable heat to be transferred from one temperature to another (the X-axis) by which is raising the working fluid from one saturation pressure to another (Y-axis). The four refrigerants shown are two of the most widely used CFCs, CFC-12 and CFC-11 now banned from production, and their respective ozone-safe alternatives, HFC-134a and HCFC-123. It was indeed fortunate that alternatives with such similar vapor pressure curves existed. This means that from a thermodynamic viewpoint at least[1], relatively few machine design changes are necessary and in some instances "drop-in" replacements for existing equipment are possible.

Where the alternative's vapor pressure is lower than the CFC's vapor pressure it can be expected that the refrigerant density is less and thus the capacity of an existing system would be less or the design of a new system would require larger volume components to achieve the same capacity. The alternatives' steeper slopes imply that each is required to overcome a larger pressure difference to achieve to same temperature

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[1] The absence of chlorine in the alternative refrigerants caused the need to change lubricants, in all systems, from mineral oil to either a polyalkylene glycol or ester based lubricant. This change may cause some system design changes.

lift and thus are probably inherently lower in thermodynamic efficiency than their CFC counterparts. As noted earlier the application's reduced temperature operation range has an impact on COP. For most applications, the maximum condenser temperature is somewhat greater than an extreme environmental temperature, thus the fact that each alternative's critical point is lower than its CFC's counterpart is another indication that the theoretical COP will also be lower.

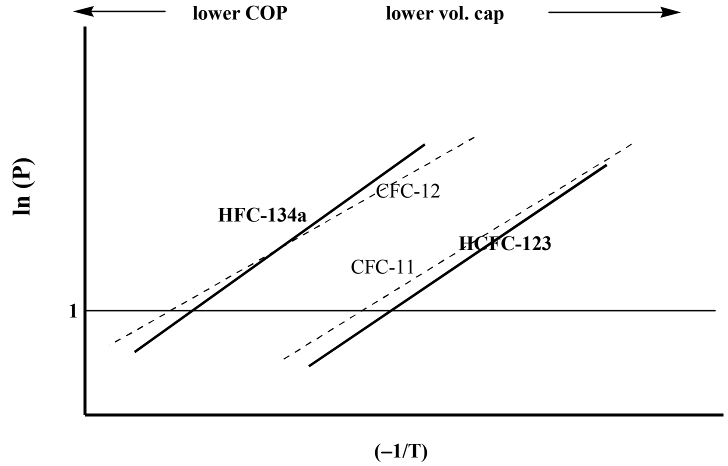

Figure 6. Vapor pressure of CFCs and their alternatives.

Finally, *Figure 6* highlights the atmospheric pressure indicating the normal boiling point (NBP) of each fluid. The value of the NBP gives some insight into the latent heat of the particular working fluid through the empirical chemical rule established by Trouton. It states that the latent heat (h_{fg}) divided by the NBP is equal to a constant. A review of refrigerants listed in ASHRAE's Handbook of Fundamentals (1993) suggests this is true within + or −15%. This means that, in general, the higher the NBP the larger the latent heat and the potential for a larger refrigeration effect which, in turn, means higher COP. *Figure 6* also illustrates that the two most widely used CFCs are so close in vapor pressure to of their alternatives that little or no change in machinery size is required. The increased slope however suggests a decrease in efficiency results with the use of the alternative.

4. Azeotropic[2] Refrigerant Mixtures

The use of more than one working fluid in a refrigerant system usually increases both the complexity and the flexibility of its design and operation. The increase in flexibility comes in the form of more fluids to chose from, which can result in a closer match of the optimum working fluid to the application. The complexity is the introduction of another independent variable, composition, which has both theoretical and practical ramifications. Actually, refrigerant mixtures have been in use by the Industry for several decades. However, the ones that have been in use have been restricted to a rather rare category called azeotropes. The unique property azeotropes have is that, over a locus of specific temperature and pressure values, the mixture's vapor and liquid molar compositions are exactly the same and at these points the temperature and pressure are either a maximum or a minimum of all possible com-positions. A maximum pressure (thus a minimum temperature) azeotrope is illustrated in *Figures 7a and 7b*. It can be seen that azeotropic saturation condition exists only at a single composition. However, there is also a wide band of very minimal composition differences between vapor and liquid. Thus, for all practical purposes, the typical azeotrope acts as a single component refrigerant throughout the various pressure and temperatures of a refrigeration system. As such, azeotropes offer additional opportunity to better match working fluids to a given application without additional equipment. They are the preferred form of mixed working fluids but are relatively rare and difficult to discover. The flexibility azeotropic mixtures can bring to a list of working fluid candidates is illustrated in *Figure 8*, which shows the phase diagram of

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[2] The meaning of azeotrope is best understood by dissecting the word: 'zeo' is the Greek word for 'to boil'; 'trope' is Greek for 'change'; 'A' is the Latin negation prefix. Thus azeotrope means 'there is no change in the boiling behavior' as there is with the zeotrope mixture.

three azeotropes in current commercial use. However all three contain at least one CFC so they are no longer in production. Note all of these are maximum pressure azeotropes, so their saturation curves lie to the left of the components of which they are comprised. CFC-500 is comprised of CFC-12/HFC-152a (73.8/26.2 % by mass) and was developed as a more dense R-12 alternative. A manufacturer of a CFC-12 centrifugal unit rated for 60 Hz operation in the USA could have the same capacity rating using CFC-500 with 50Hz operation in Europe. CFC-502 is comprised of HCFC-22/CFC-115 (48.8/51.2 % by mass) and designed for commercial refrigeration systems.

In general, the lower the evaporator temperature the higher the discharge temperature of the isentropic compression. In deep refrigeration applications, such as food freezing, this discharge temperature in an R-22 system can reach a level so as to endanger system reliability. The purpose of the addition of the higher heat capacity of CFC-115 us to reduce this discharge temperature. The third azeotrope still in use, CFC-503, is a binary of CFC-13/HFC-23 (40.1/59.9 % by mass). Its purpose is simply to provide a higher pressure refrigerant than either of its components. This means that its NBP will be lower which provides for positive pressure operation at lower evaporator temperatures.

Two new azeotropes based on HFCs have been found: HFC-507, which is comprised of HFC-125/143a (50/50% by mass), and HFC-508, which is HFC-23/116 (39/61% by mass). HFC-507 is a substitute for CFC-502. *Figure 9* illustrates the vapor pressure lines for this mixture and its components, as well as the azeotrope it is re-placing. Careful examination reveals that this new azeotrope is a very rare negative pressure one. This was fortunate in that this unusual property lowers the azeotrope's vapor pressure closer to that of CFC-502 than either of the components. Typically azeotropes do not exist over all possible temperature and pressure ranges. In the case of the HFC-507 the azeotrope 'drift' causes it to go out of existence at a lower saturation temperature than most refrigeration applica-

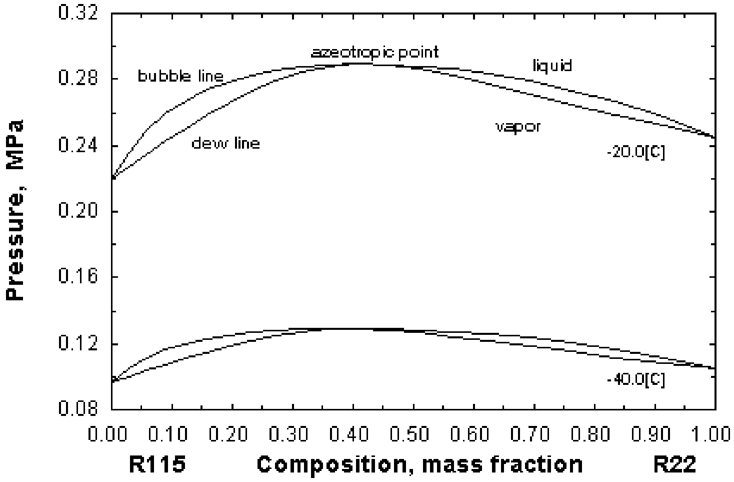

Figure 7a. P-x Phase diagram of CFC-502 azeotrope.

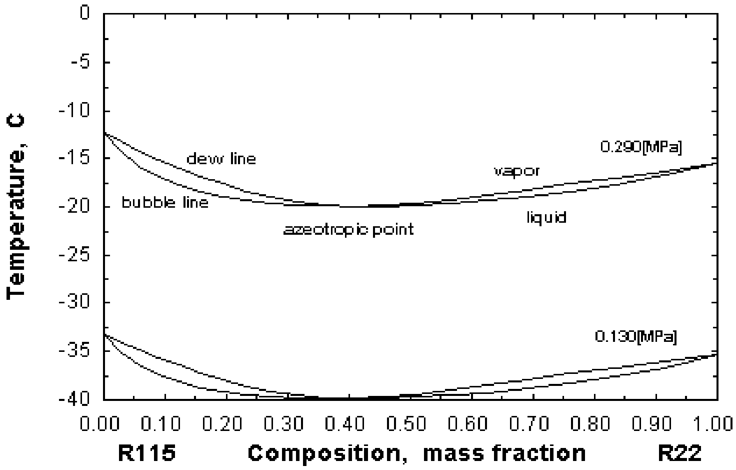

Figure 7b. T-x Phase diagram of CFC-502 azeotrope.

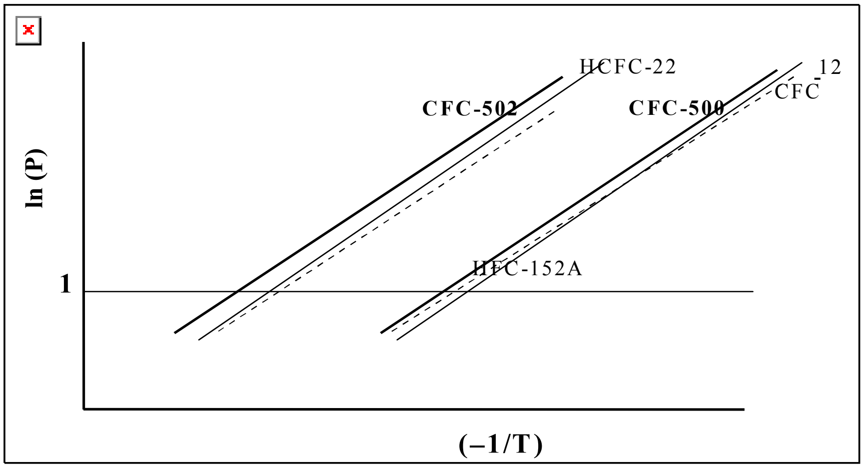

Figure 8. Vapour pressure curves of CFC azeotropes.

tions. However, this is of little practical consequence since the components, HFC-125 and HFC-143a, have NBPs that are only 1^0C apart. Thus any composition change due to liquid pooling within the system or leaks will be so minimal that performance changes would not occur. However, HFC-507 is very close to being flammable because HFC-143a is flammable. For this reason, one refrigerant manufacturer has added 4% HFC-134a to this mixture, trapping the flammable fluid between the two non-flammable ones and ensuring safety under most any conditions.

This very near-azeotropic ternary is known as HFC-404A. Although the third component has a significantly different NBP, its small quantity only creates a difference in dew and bubble point temperatures of 0.8°C. This suggests that only very little composition shift is possible. Unfortunately, HFC-143a has a relatively high global warming potential and so both the azeotropic binary and the near-azeotropic ternary are likely to be in danger of being banned if the global warming crisis come to pass.

The HFC-508 azeotrope is the usual positive pressure type with a vapor pressure similar to the azeotrope CFC-503, which it is intended to replace.

5. Zeotropic Refrigerant Mixtures

No acceptable single component alternative refrigerant has been discovered for HCFC-22. As a result , the industry has searched for and developed several mixtures, two of which appear to be the most likely alternatives. One is a ternary zeotrope, HFC-407C, which is a compound of HFC-32/125/134a (23/25/52 % by mass) and is intended to be used as a ‘drop-in’ because its vapor pressure curve closely approximates that of HCFC-22. The other alternative is a binary near-azeotrope, HFC-410A, which is a composite of HFC-32/125 (50/50 % by mass). Thermodynamically speaking, both are zeotropes, also

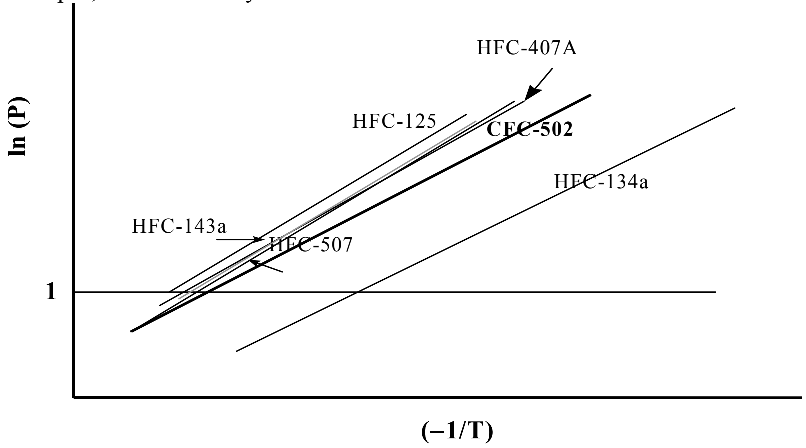

Figure 9. Vapor pressure curves of CFC-502 and alternatives.

known as non-azeotropes, but the binary has a smaller maximum difference between the dew-point temperature and the bubble point temperature. This temperature difference is called the temperature glide and is used to characterize the degree of temperature change a particular mixture has during a liquid / vapor phase change. Zeotropic mixtures tendency to shift composition during the phase change process may be illustrated best on a composition phase diagram. *Figure 10* is a phase diagram of a binary zeotrope of HFC-32/134a (30/70 % by mass) which is being considered by the Japanese industry as an alter-native to HCFC-22. The temperature glide for the evaporator is 7 °C. The maximum amount of the flammable HFC-32 that exists during operation occurs in the evaporator. The liquid charge initially has 30% and as the evaporation process proceeds this quantity decreases to 15%. The HFC-32 vapor composition is initially 57% at the bubble point and decreases to 30% when the evaporation process is completed. At the higher pressure condenser condition all the variations are in the same direction but to a lesser degree. The temperature glide is 5 °C, and the liquid and vapor HFC-32 compositions shift from 30% to 21% and 41% to 30%, respectively. A leak during a two phase condition would permanently change the operating composition and thus the performance of the system. In single phase, the processes are the same as for the single component refrigerants and thus leaks would lower the charge but not change the composition. The composition shift characteristic of zeotropes also causes difficulties in applications where a large portion of the working fluid remains in the liquid state during operation. That is, if only a minor part of the total charge is circulating throughout the vapor compression system at any given time it is difficult to know what the circulating fluid's composition is and thus difficult to size or rate the hardware components. This difficulty is exacerbated when such a system is expected to meet a varying load and the liquid pool becomes a variable during operation. For this reason, only zeotropic mixtures whose components have similar NBPs (i.e., near azeotropes) are being considered for flooded evaporator systems, such as water chillers.

The attempt to construct a 'drop-in' alternative for HFC-22 has been achieved then, at least two ways. Basically it is a matter of straddling the desired vapor pressure curve with at least one alternative above and one below. The first is the binary HFC-32 /134a (30/70% by mass) which is illustrated in *Figures 10* and *11*. However, the 57% proportion of HFC-32 that this mixture's vapor can achieve is considered flammable, at least according to the USA test procedure. As seen in *Figure 11* a ternary was created by adding HFC-125, to create HFC-407C, resulting in some sacrifice in performance because the CP was lowered and in the heat transfer process the mass diffusion dependency among components was increased.

A third HFC-22 alternative has been developed. The NBPs of HFC-32 and HFC-125 are only 3.6 °C apart which means their mixture, HFC-410A, is a near -azeotrope and thus for all

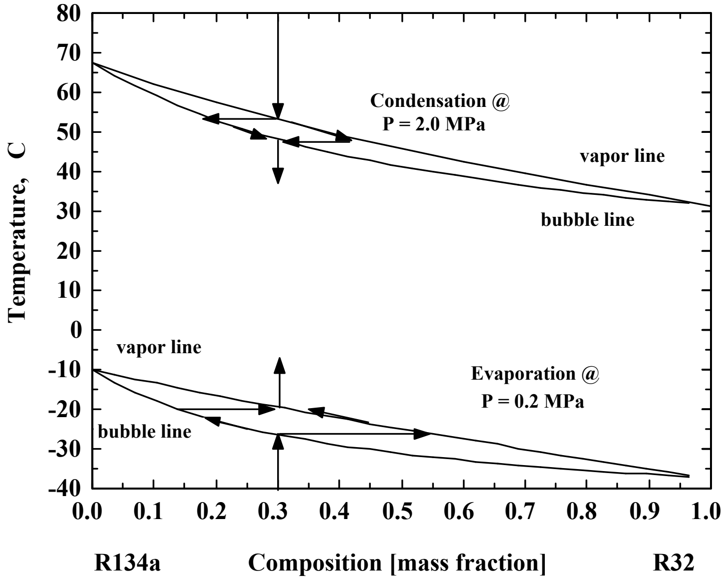

Figure 10. Composition phase diagram of HFC-32 / 134a.

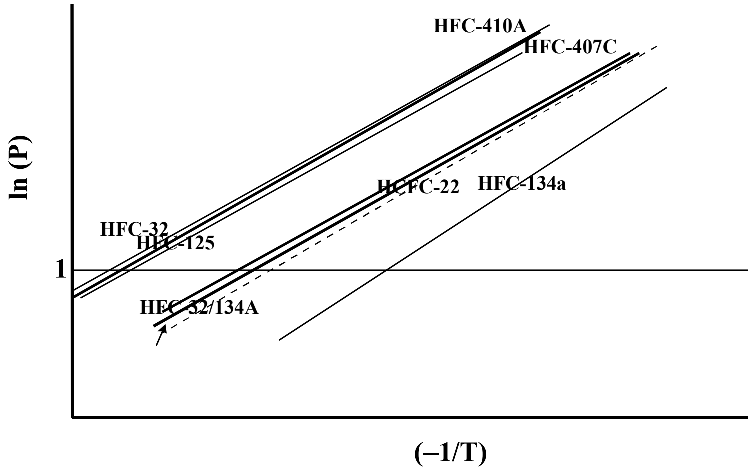

Figure 11. Alternative mixtures for HCFC-22.

practical purposes it acts as a single component refrigerant. But as can be seen from *Figure 11* it is at a significantly higher vapor pressure than HCFC-22. It also lies between the vapor pressures of its components, as all zeotropes do. HFC-410A's high pressure makes it unsuitable for a 'drop-in' for an existing HCFC-22 system; but it is a rather intriguing substitute for HCFC-22 applications utilizing a new system designed specifically for it. Such a system will, in general, be considerably smaller and stronger, but probably with a net decrease in material costs needed for manufacture. Considering that in the refrigeration machinery business more systems contain HCFC-22 than all the other refrigerants put together, one can imagine the R&D effort currently underway. Such fundamental problems as the pressure drops in the new tube sizes, the heat transfer coefficients with the various tube surfaces, solubility with new lubricants have been underway for some years and are necessary before the design of the final product can begin. Property trade-offs are inevitable. For example the relatively high conductivity and low viscosity of HFC-32 make it an attractive fluid from a heat transfer viewpoint but its flammability limits the proportion it can be used in mixtures. By combining it with the non-flammable HFC-125, which has a lower CP, some thermodynamic performance is also sacrificed. However their similar vapor pressure curves guarantee that they will remain in the similar proportions even under leak conditions.

6. Two Phase Heat Transfer in Mixtures

Since mixtures change composition while changing phase there is a non-uniform distribution of the components in each phase particularly near the liquid / vapor interface. In the case of evap-oration, there exists a depletion of the high pressure fluid (HFC-32) in the liquid near the vapor interface. This slows the evaporation process since this more volatile fluid has to diffuse through the low pressure (less volatile) HFC-134a before it can vaporize. *Figure 12* illustrates how a typical zeotropic mixture's evaporative heat transfer coefficient might vary as a function of composition. As with most thermophysical properties of mixtures, one might expect to find the value of a particular composition to be something between the component values. The fact that much of the mixture's composition values are below either component's value is an indication that a phenomena, other than mixing fluids of different properties, is going on. The introduction of these concentration gradients in zeotropic mixtures has been shown to reduce the heat transfer coefficient by more than 40% from the value that a weighted average of the components (Ross, et.al. 1987). This degradation has been seen to increase with increasing composition differences between the vapor and the liquid (Kedzierski, et. al. 1992). This is certainly one of the disadvantages of using wide temperature glide zeotropic mixtures. On the other hand, an azeotropic mixture will inevitably have a heat transfer coefficient that is close to the weighted average of its components, which is at the azeotropic point. At compositions where the azeotrope does not exist, a degradation in heat transfer will occur in proportion to the difference between liquid and vapor composition. This phenomena has been verified in detail through a series of tests performed on the azeotropic mixture CFC-502 (Gorenflo and Bieling 1986).

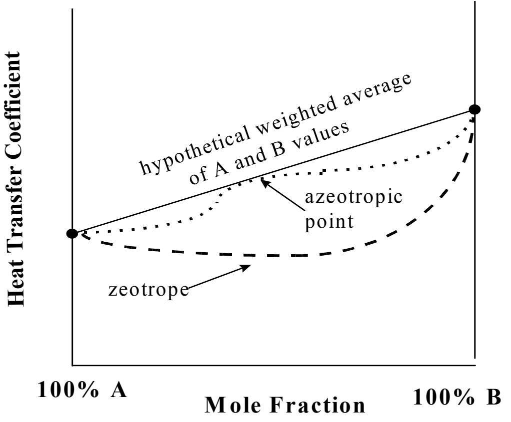

Figure 12. Mixtures evaporative heat transfer coefficients.

The case for the new ozone-safe mixtures may be examined as follows. The evaporative heat transfer coefficients of HFC-407C and HFC-410A and the refrigerants that comprise them, have been measured over the partial range of quality and heat flux, that is found in a typical evaporator. *Figure 13* illustrates a summary of the data for one such heat flux case (Kaul,et al.,1998). The refrigerant HFC-32 is, by far, the most effective heat transfer fluid because it has superior thermophysical properties.

This may be demonstrated by looking at a functional relationship between the convective heat transfer coefficient and the most influential properties derived from the Dittus-Boelter equation[3] (Dittus et.al. 1930):

$$\mathrm{Nu} = 0.023\ \mathrm{Re}^{0.8}\ \mathrm{Pr}^{0.4}$$

where the functional form of the heat transfer coefficient in terms of its properties is:

$$h \sim k_l^{0.6} \left(\frac{c_p}{\mu_l} \right)^{0.4} \rho_l^{0.8}$$

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[3] The Dittus-Boelter equation (Dittus and Boelter, 1930) is based on single phase, fully developed, turbulent tube flow but it is also a starting point for many two-phase evaporative tube flow correlations.

The numerical values for these properties obtained from REFPROP 6.0 are presented in TABLE I. For the single component fluids, the estimated values of TABLE I will be ranked in the same numerical order, within a reasonable margin of error, if one would extrapolate and integrate the average measured values of *Figure 13* over the typical evaporator quality range of 0.2 to 0.9. The measured values of the binary mixture HFC-410A falls between its components, HFC-32 and HFC-125. This is ex-pected for a near-azeotrope where the process is similar to a single component fluid under similar flow conditions because fluid properties are the controlling factor. The TABLE I prediction of properties supports second place position of the near-azeotrope HFC-410A, as well. However, when HFC-134a is added to form the zeotropic ternary mixture HFC-407C, the heat transfer coefficient drops to a value lower than any of its components and its relative position is not estimated very well by the properties relationship of TABLE I. This is because the wide differences in component boiling points creates concentration gradients in the single phase layers near the interface, which fluid properties alone do not take into account A similar phenomena occurs in the zeotropic binary HFC-32/134a, which also has a relatively wide maximum temperature glide between its dew and bubble points and thus concentration gradients at its annular flow's liquid / vapor interface. This binary ranks above HFC-407C in heat transfer coefficient value because it has a larger percentage of HFC-32. This is at least part of the reason it is a better system performer. There also exists a thermodynamic problem with zeotropic mixtures in heat exchangers. The change in composition during the phase change causes the fluid's saturation temperature to change and thus produces the temperature glide (see *Figure 10*). For the evaporation process the temperature glide due to the composition shift is increasing the bulk fluid temperature which tends to offset the saturation temperature drop due to the flow's pressure drop. In the condenser, the composition temperature glide is decreasing which tends to add to the temperature drop due to the decreasing saturation pressure. Depending on the given heat exchanger's circuiting, that is the amount of cross-counter and cross-parallel flow relative to the external fluid's sensible temperature gradient, the additional internal temperature glides can be detrimental or helpful to system performance. In any case, it is a considerable complexity added to the design of azeotropic mixture's heat exchanger.

TABLE I. Thermophysical Properties of Saturated Liquid Refrigerants.

Refrigerant @ -15 C	R-32	R-410A	R-32/134a	R-407C	R-22	R-134a	R-125
Liquid Thermal Conductivity, k_l, (W/m-K)	0.1648	0.1232	0.1178	0.1087	0.1016	0.0988	0.0772
Specific Heat, Cp_l (kJ/kg-K)	1.678	1.443	1.412	1.361	1.133	1.304	1.205
Viscosity, μ_l (μPa-s)	184.8	198.6	253.9	252.3	257.2	329.6	249.3
Density, ρ_l (kg/m^3)	1105	1228	1259	1289	1331	1343	1387
Heat Transfer Coefficient, h (W /m^2 K)	**14.06**	**11.76**	**10.49**	**10.06**	**9.14**	**8.67**	**8.32**

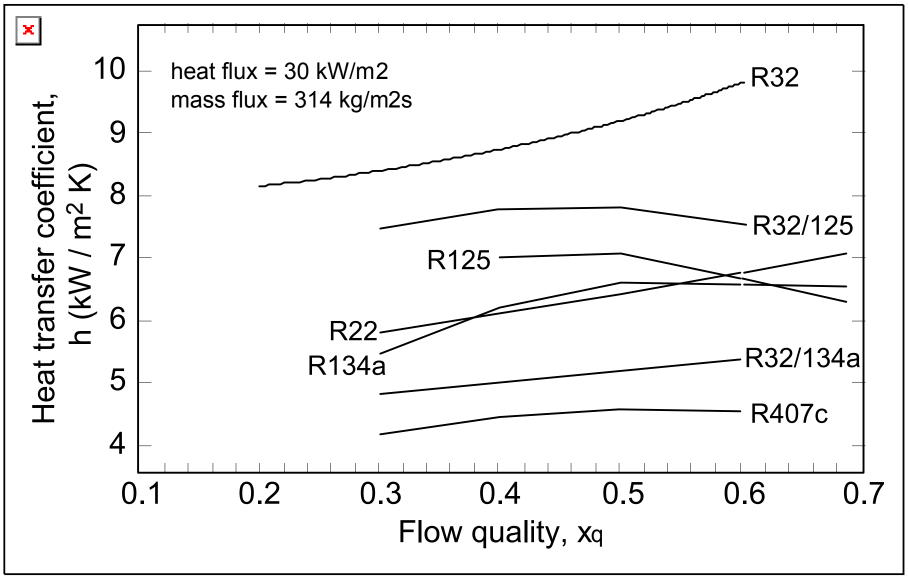

Figure 13. Evaporative flow heat transfer coefficient versus quality.

Performance benefit results when the majority of the heat is transferred under the condition that the internal two phase temperature glide and the external sensible temperature gradient are linear and reasonably parallel to each other in a counter flow arrangement. Difficult design requirements indeed, for real world applications, particularly when one considers that the wider the temperature glide the more nonlinear its gradient becomes and the possibilities of pinch-points abound. Further-more, it has been reported that even under the most ideal conditions significant performance benefits can be realized only when the temperature glides are a significant percentage of the overall temperature lift from the evaporator to the condenser saturation conditions (Marques and Domanski, 1998). Since the fluids designed to be CFC alternatives have temperature glides that are less than 10 ^{o}C, it has not been seen necessary to alter hardware design so as to try to increase performance. On the other hand, minor performance benefits and degradations can result by simply ignoring the zeotropic temperature glide phenomena during the hardware design stage.

7. Summary

Working fluids for refrigeration systems receive COP ratings for their thermodynamic performance just as any refrigeration hardware system. This rating is assessed by superimposing the ideal vapor compression cycle on top of the specific fluid's thermodynamic property map (e.g.,, T-s or ln P-h diagram) at standard rating conditions. This suggests that the position of the fluid's vapor dome, defined by its critical point (CP), relative to the rating points and the shape of the vapor dome, defined by its molar heat capacity, will be an indication of the fluid's inherent performance. The relative position of the fluid's CP temperature to the given application's saturation temperatures quantifies the inherent tradeoff of a fluid's COP with its volumetric capacity. These parameters inverse proportionality suggest the inevitability of a compromise between a system's size and efficiency.

A fluid's molar heat capacity is indicative of the steepness of the vapor dome's slides (i.e., the slope of the liquid saturation line and the vapor saturation line on a temperature - entropy diagram, see *Figure 4*). The higher the molar heat capacity the lower the positive slope of the liquid saturation line, which leads to higher expansion side losses. The effect of both critical point and liquid molar heat capacity on ideal cycle performance may be seen in *Figure 14*. The data of eighteen different fluids from REFPROP 6.0, was correlated for two sets of reduced temperatures of the ideal vapor compression cycle. Since the cycle's work and capacity, for a given application, are a strong function of the mass flow rate, the efficiency of a fluid may be indicated by how much of the fluid pumped is utilized to transport the heat (i.e., the ratio of the refrigerating effect to the latent heat). The analysis shows that the lower critical point or higher molar liquid heat capacity fluids will be poorer performers. The slope of the vapor saturation line is also effected by the molar heat capacity. Being a negative slope for most of the CFCs, it will continue to increase with increasing molar heat capacity until it is virtually vertical, as with

HFC-134a. Additional increase in molar heat capacity results in a positive slope at high reduced saturated vapor pressure / temperature states, while a negative slope remains at the low reduced saturated vapor states (see *Figure 4*). Using a fluid with a saturated vapor line that has a change from positive to negative slope in a vapor compression cycle can result in "wet compression", which for practical reasons, makes it unacceptable as a refrigerant. Since any fluid's molar heat capacity is primarily dependent on its molecular size or complexity, the vast majority of man-made fluids are unacceptable as refrigerants. Certainly any molecule of four or more carbon atoms would be suspect. Theoretically, it is possible to recover much of the expansion losses and even avoid wet compression; however it always requires various additional hardware components and/or cycle modifications. The addition of more components or deviations from the ideal cycle have inherent irreversibilities associated with them and so it is doubtful that the final overall system efficiency of the 'complex' can exceed that of the 'simple'. One might say simple molecules require simple systems and complex molecules require complex systems to achieve the same theoretical efficiency.

The blending of refrigerants to form a fluid mixture with weak chemical bonds offers the opportunity to tailor the thermophysical properties of the working fluid to better match the needs of the application. Mixtures developed in the past have been tailored to reduce compressor discharge temperature, increase volumetric capacity, and lower the normal boiling point temperature. Mixtures developed recently have primarily intended to clone the vapor pressure curve of the CFC or HCFC they were meant to replace. A typical mixture is called a zeotrope and will shift its composition during a change of phase. This composition shifting can lead to several performance and practical problems. To avoid these problems most of the mixtures developed, past and recent, have been limited to the rather rare azeotrope, which doesn't change composition, or the near-azeotrope, which changes composition minimally. However, those zeotropes with a temperature glide greater than 5^0 C have shown a significant decrease in the evaporative heat transfer coefficient compared to their component's values. This is due to concentration gradients at the liquid-vapor interface. These zeotropes also complicate the temperature profile of the flow as it progresses through the phase change by superimposing the composition change on top of the saturation pressure drop, making it difficult to predict the internal flow temperature profile. Theoretically, systems can be designed to take advantage of this phenomena by matching the internal glide with the external fluid's sensible temperature gradient and thus transferring the heat through a minimal temperature difference (minimal irreversibility). However for many applications, such as, building systems, the desired temperature increase in an external fluid's temperature is limited to 10 °C or less. Modeling studies, for such applications, have shown that making significant design changes might yield a potential performance increase, for a zeotrope such as HFC-407C, of the order of 5% (Marques and Domanski, 1998). This probably means that in a real hardware system about half of this improvement would be realized for a significantly

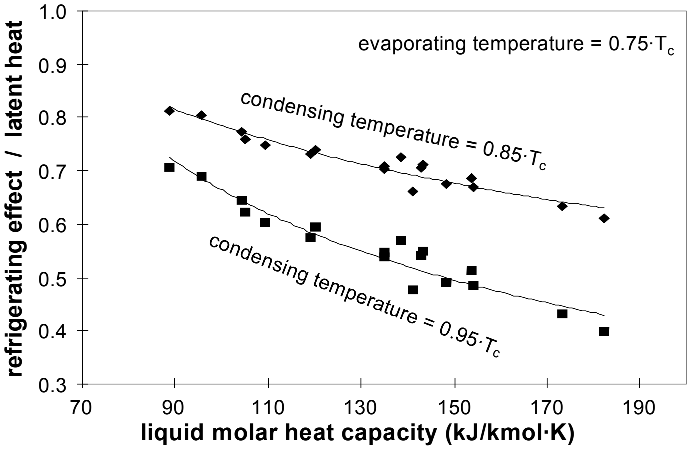

Figure 14. Refrigerant performance as a function of reduced temperature and liquid molar heat capacity.

larger heat exchanger. In turn, not designing for glide matching may result in glide mismatching and thus some additional minor degradations.

The fundamental issue of whether there is a net performance gain through the use of very wide glide zeotropes (i.e., the thermodynamic advantages of glide matching versus the two phase heat transfer degradation) remains unresolved. Perhaps if the global warming threat diminishes the pool of potential refrigerants even more, the use of wide glide zeotropes will be revisited.

Appendix

In order to quantitatively define the thermodynamic state of a mixture it is necessary to introduce an additional dimension, composition, to the pure fluids' three dimensional (P-v-T) system. Constructing a two dimensional plane of one constant thermodynamic property then will not necessarily be sufficient to define all of the saturation states. When a pure fluid is represented on a lnP vs (-1/T) diagram the two phase lines, one for saturated liquid and one for saturated vapor, are projected on top of one. For a zeotropic mixture, the surface of thermodynamic equilibrium states is not flat and normal to the constant specific volume plane and therefore both the saturated liquid line and saturated vapor line are visible. *Figure A1* illustrates the zeotropic mixture HFC-32/134a (30/70%mass) as it truly should be. The two saturation lines are the boundaries of the two phase region, albeit somewhat distorted and not particularly helpful qualitatively. Never-the-less, the temperature glide through the two phase region is seen explicitly; where the lower pressure evaporator glide is always larger than the higher pressure condenser glide (that is the temperature difference between the saturation lines).

Throughout the text of this paper a single saturation line was used to represent a zeotropic mixture for the sake of clarity. Since this single line represents an average value somewhere between the two saturation lines and thus does not accurately represent a quantitative value the numerical scales were left off. The purpose of the single saturation line is to approximate the mixture's relative position to that of its components.

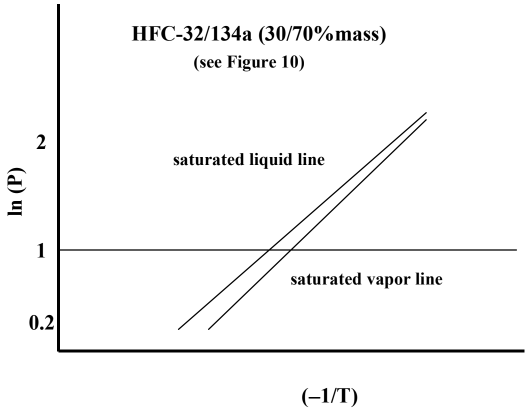

Figure A1. A true representation of a zeotropic mixture.

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