

Chapter 15

Thermodynamics of Refrigerant Mixtures and Refrigerant-Oil Mixtures

SUMMARY: The principles of phase equilibrium of zeotropic mixtures are presented in an abbreviated form, including the phase diagram and preparation of enthalpy profiles for describing their evaporation (or condensation) over a temperature glide. Next the thermodynamic description of refrigerant-oil mixtures is presented, including methods to predict the local oil mass fraction, the local bubble point temperature rise caused by the oil, enthalpy changes for their evaporation (or condensation) and the effect of oil on log mean temperature differences. This chapter focuses on the thermodynamics of mixtures during their evaporation but these methods are equally applicable to condensation.

15.1 Introduction

A basic working knowledge of phase equilibria is required to understand the evaporation (and condensation) of zeotropic mixtures and also is an important prerequisite for the design of evaporators that properly take into account the effect of oil on thermal performance. The objective of this chapter is to provide this necessary background. Topics covered include the phase equilibrium diagram, the dew point temperature, the bubble point temperature, the boiling range or temperature glide, the phase equilibria of refrigerant-oil mixtures, enthalpy curves for mixtures and a few other concepts important to the subject. For a more detailed introduction to phase equilibria, the reader is referred to Chapter 12 in Collier and Thome (1994, 1996). Instead, for a comprehensive treatment of prediction of phase equilibria, numerous chemical engineering textbooks are available, such as that by Prausnitz (1969), or can be found in the chapter by Smith, Block and Hickman (1963) appearing in the Chemical Engineer's Handbook (available in more recent editions).

A zeotropic mixture refers to a mixture whose components have different mass fractions in the liquid phase than in the vapor phase at equilibrium conditions. An example of such a mixture is R-407C, which has three components. In contrast, an azeotropic mixture refers to a mixture whose components have the same compositions in both phases. A well-known example is refrigerant R-502, which is a binary refrigerant mixture at the azeotropic composition of its two components. An azeotropic fluid functions just like a pure fluid and hence pure fluid design methods can be applied. Instead, a zeotropic mixture evaporates (or condenses) over a temperature range and hence this must be taken into account in thermal design methods.

A refrigerant-oil mixture functions as an azeotropic mixture in which the refrigerant (either a pure refrigerant such as R-134a or a zeotropic mixture such as R-407C) is combined with a miscible, lubricating oil. The oil for our purposes here can be considered to be one component in such a mixture, even though normally lubricating oil is a multi-component mixture including various additives, long-chain molecules, etc. In this chapter, only refrigerant-oil mixtures that are completely miscible will be considered. These mixtures act as zeotropic mixtures and the refrigerant and oil are miscible in the liquid phase. Some refrigerant-oil mixtures are not miscible, which means they do not mix together in equilibrium conditions, such as is also true for water and oil. Immiscible refrigerant-oil mixtures are not addressed here. One must be careful, however, as some refrigerant-oil mixtures are miscible only within a certain range of temperature or up to a certain oil mass fraction, so that part of the refrigerant cycle or test facility fluid loop may pass outside the miscible range.

15.2 Simple Principles of Phase Equilibrium

This section presents a very brief description of the thermodynamics of zeotropic mixtures. For a more extensive treatment, refer to a chemical engineering handbook or textbook. The following discussion is for a binary mixture, i.e. a mixture with two different fluids for its components. These ideas can be extended to ternary mixtures and multi-component mixtures in general.

15.2.1 Phase Equilibrium Diagram

Phase equilibria of binary mixtures are represented on phase diagrams. Figure 15.1 depicts a phase diagram for a binary mixture system at constant pressure. Temperature is plotted along the vertical axis while vapor and liquid compositions are plotted along the horizontal axis, in this case shown in mole fractions. The dew point line represents the dew point temperatures of all the possible mixture compositions, where T_{dew} is defined as the temperature at which a superheated vapor mixture will first begin to condense upon cooling. The bubble point line represents the bubble point temperatures of all the possible mixture compositions, where T_{bub} is defined as the temperature at which a subcooled mixture will first begin to evaporate upon heating. The composition of one of the components, in this case the component with the lowest boiling point, is depicted on the lower axis, where the equilibrium vapor composition Y is that which corresponds to the liquid composition X at the same temperature.

In Figure 15.1 the saturation temperature of one pure component is on the left vertical axis while that of the other component is on the right vertical axis. The boiling point temperatures for evaporation of the mixtures correspond to the bubble point line. The condensing temperatures for condensation of the mixtures correspond to the dew point line. The temperature difference between the dew point temperature and the bubble point temperature for a specific liquid composition is defined as the *boiling range* ($BR = T_{\text{dew}} - T_{\text{bub}}$). For evaporation of a mixture, the parameter BR is used in modeling the effect of mass transfer. The boiling range is also referred to as the *temperature glide* in literature referring to zeotropic refrigerant mixtures.

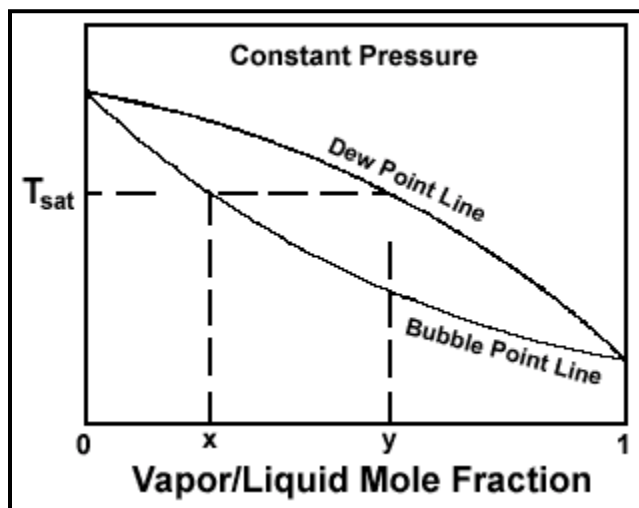


Figure 15.1. Phase equilibrium diagram at constant pressure for a binary mixture.

15.2.2 Definition of Mixture Compositions and Components

On a phase diagram, the compositions can be depicted in units of mass fraction, mole fraction or volume fraction. Refrigerant-oil mixtures are usually referred to in ASHRAE publications in terms of *weight fraction* or weight percent, where the first of these is a colloquial term for *mass fraction*. The mass fraction of a component is defined as its mass in kg (or lb.) divided by the total mass of the mixture in kg (or lb.), respectively, in a particular phase (liquid or vapor). For instance, if a liquid refrigerant-oil mixture weighs 10.0 kg (11.0 lb.) and the oil in this mixture is measured to weigh 0.5 kg (1.1 lb.), then the mass fraction of the oil in the mixture is 0.05 and its mass percent is 5.0%. The mass fraction of the refrigerant is thus 0.95 (i.e. $1.0 - 0.05$) and its mass percent is 95.0%.

Referring again to the phase diagram in Figure 15.1, the more volatile component (also referred to as the lighter component) is defined as the fluid that has the lower boiling point temperature at the pressure of the diagram. This is the fluid with its saturation temperature on the right vertical axis in Figure 15.1. This fluid is more volatile in the sense that this component is always above its normal boiling point. For a refrigerant-oil mixture, the refrigerant will always be the more volatile component since the boiling point temperatures of lubricating oils are in the range from 300 °C to 510 °C (570-950°F), and are thus much larger than those of refrigerants. Hence, the oil will be the less volatile component (also referred to as the heavier component).

For the present situation, a refrigerant-oil mixture can be considered as a zeotropic binary mixture, which is a mixture with two components that does not form an azeotrope. One component is the pure refrigerant, be it R-134a, R-22, or any other single-component refrigerant (R-123, R-125, ammonia, etc.) and the second component is the oil. Even though lubricating oils are multi-component blends of oil plus additives, for the present purposes it is more than adequate to consider them here as a single component fluid.

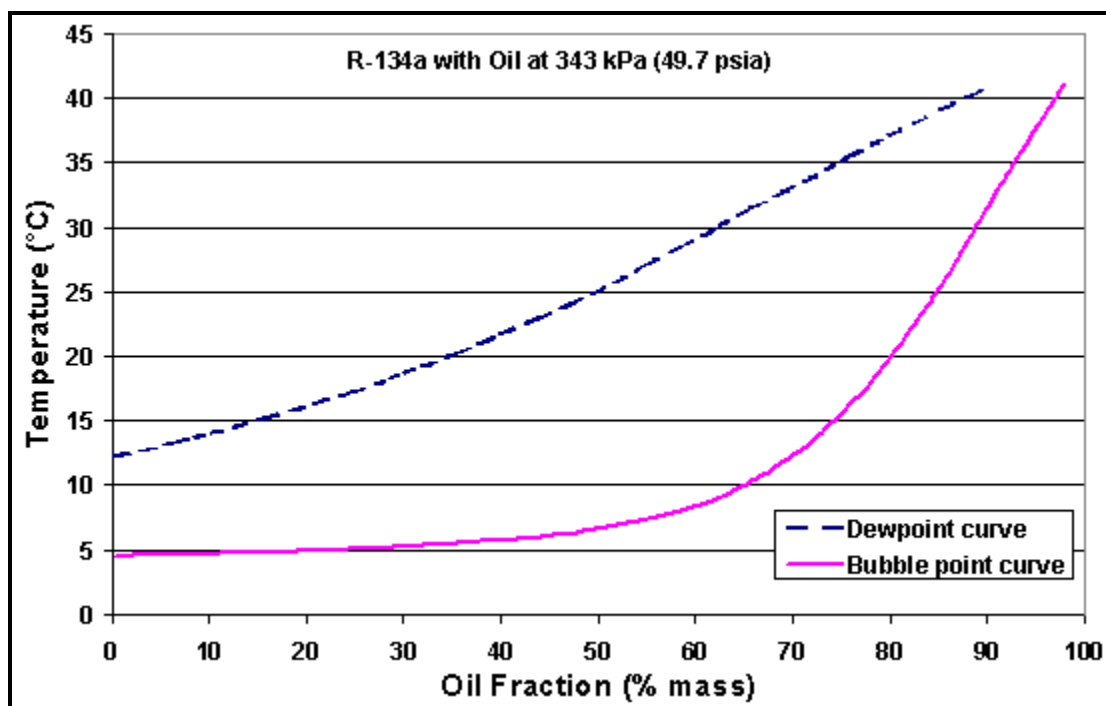


Figure 15.2. Phase equilibrium diagram for a binary mixture of R-134a and oil at a pressure of 3.43 bar (49.7 psia).

Figure 15.2 depicts an approximate phase diagram for R-134a mixed with Mobil Arctic EAL 68 lubricating oil at 3.43 bar (49.7 psia). In this case, the horizontal axis shows the oil composition in mass %. At the left axis of the diagram, the saturation temperature of pure R-134a is 4.44°C (40°F). Near the right axis, the dew and bubble point temperatures rise rapidly towards the saturation temperature of the pure oil (not shown), which is in the neighborhood of 350°C (662°F). The bubble point curve is nearly horizontal with a slightly upward slope from left to right at low oil compositions. It then begins to rise more rapidly at intermediate compositions and then rises rapidly when above 70 mass % oil. The actual location of the dew point curve is not known for refrigerant-oil mixtures; it was drawn assuming negligible amounts of oil enter the vapor phase at liquid oil compositions below 70 mass %, i.e. the part of the dew point line on the left y-axis at 0.0 mass % oil. Above this value its composition is represented

here by a simple extrapolation towards the pure oil value. The method for predicting the bubble point curve shown here is given later in this Chapter.

15.2.3 Piston-and-Cylinder Analogy for a Binary Mixture

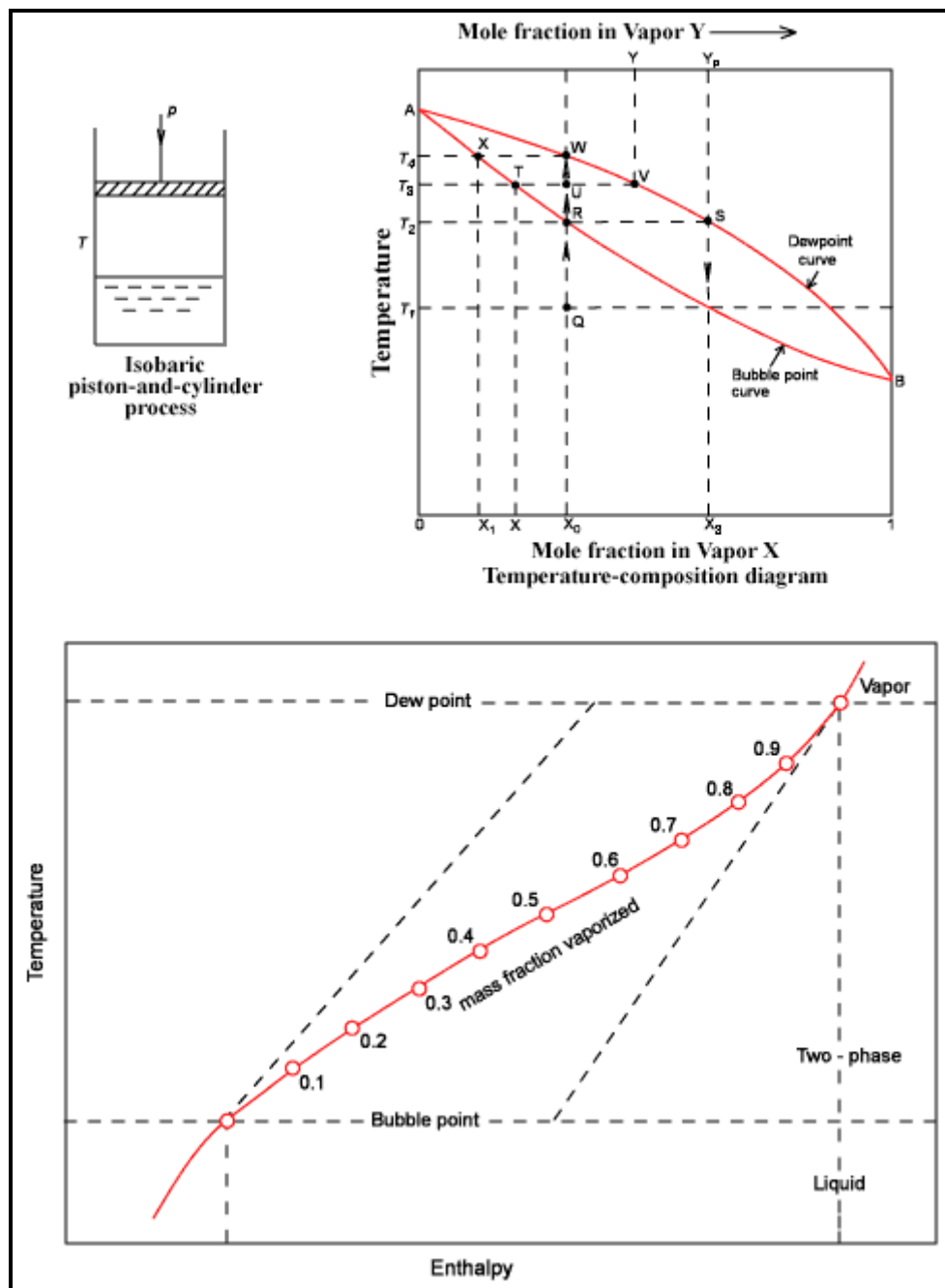


Figure 15.3. Isobaric process path and enthalpy curve of a binary mixture.

To better illustrate these concepts, consider now a situation excerpted from Collier and Thome (1994, 1996). Figure 15.3 shows a piston-and-cylinder setup that contains a binary liquid mixture whose mole fraction of the more volatile component is x_0 and which is held at a fixed pressure of p and temperature of T_1 . What happens to the liquid mixture as it evaporates is conveniently depicted on the temperature-

composition phase diagram at the right, where the mole fraction of the more volatile component is plotted along the horizontal axis and the temperature of the mixture on the vertical axis. Denoting the initial conditions in the vessel by point Q, the piston-and-cylinder is now heated under constant pressure maintaining an isothermal temperature throughout the vessel. When the temperature T_2 is reached, liquid will begin to evaporate at point R. The vapor formed at temperature T_2 has a composition Y_o as shown by point S. This vapor is richer in the more volatile component than the liquid. If this procedure is repeated for the complete range of initial liquid compositions, then a series of points R, T and X will be found. The locus of the curve formed by points AXTRB is known as the bubble point curve and the curve formed by points AWVSB is the dew point curve.

If the vessel is heated above point R, the composition of the liquid will change because of the loss of some of its more volatile component to the vapor. The boiling point temperature will rise to some new temperature T_3 and the compositions in both the liquid and vapor phases will change, both becoming richer in the less volatile component represented by points T and V, respectively. Since no material is lost, the relative volumes occupied by the two phases also change during this process; the volume occupied by the liquid decreases while that of the vapor increases. On still further heating to temperature T_4 , all the liquid is evaporated and the vapor in the vessel at point W has the same composition as the original liquid X_o . The last drop of liquid in the vessel disappears at the temperature T_4 with a composition of X_1 , indicated by point X on the phase diagram, and is very rich in the less volatile component.

During this experiment the amount of heat added to the system could be noted. In addition, there is a clear analogy between this isobaric evaporation process in the piston-and cylinder chamber and evaporation of a refrigerant-oil mixture inside an evaporator tube. Similar to evaporation of the liquid mixture in the vessel, a refrigerant-oil mixture will evaporate along its bubble point curve. However, since essentially none of the oil enters the vapor phase because of the extremely low vapor pressure of the oil relative to the refrigerant (on the order of one millionth that of the refrigerant), the situation is simplified. Thus, as one moves along an evaporator tube from the inlet towards the outlet, the local oil mass percent in the remaining liquid increases, the vapor phase composition remains pure refrigerant, and the local boiling point temperature T_{bub} increases. The amount of heat necessary to evaporate the refrigerant-oil mixture is therefore equal to the sensible heating of the liquid and vapor phases caused by the increase in the bubble point temperature along the tube plus the latent heat for vaporizing the refrigerant from the liquid to the vapor phase. These points will be discussed in more detail in the following sections.

15.2.4 Oil "Contamination" Approach

Until recently, a small fraction of lubricating oil in a refrigerant charge has been treated by refrigeration and air-conditioning system manufacturers as a contaminant in an otherwise pure refrigerant. Thus, pure refrigerant saturation temperatures and properties have been utilized for determining heat transfer coefficients while the oil composition has been considered an independent "contamination" parameter. In practice, this means that during flow boiling experiments with oil to determine local heat transfer coefficients, the local wall temperature difference ($T_w - T_{sat}$) has been determined using T_{sat} from the vapor pressure curve of the pure refrigerant and the measured pressure, where T_w is the inner tube wall temperature.

This oil "contamination" approach has hindered a better understanding of the problem and created a roadblock to development of accurate generalized design methods. The reason for this is that the "contamination" approach is not thermodynamically correct. That is, it ignores the influence of the oil on the boiling point temperature, specific heat, latent heat, viscosity, density, etc. This in turn alters energy balances, local boiling temperature superheats, local vapor qualities and so on in the data reduction process to calculate heat transfer coefficients and two-phase pressure drops. To put this approach in

perspective, it is analogous to assuming that a zeotropic refrigerant mixture, such as R-407C, may be modeled using the vapor pressure curve of only one of its three components, say R-134a. Clearly that is not correct thermodynamically. Thus, the "contamination" approach will not lead to a resolution of the long-standing problem of how to model the influence of oil on flow boiling of refrigerants.

15.2.5 Thermodynamic Approach to Modeling Refrigerant-Oil Mixtures

The thermodynamically correct approach is to treat the refrigerant-oil mixture as the real mixture that it in fact is. This will be referred to as the Thermodynamic Approach. It requires methods to determine the boiling point temperature and enthalpy changes during evaporation (or condensation). Methods for doing this are now available from Thome (1995) and are presented in the next section. The additional complexity is not that great since the oil remains very predominately in the liquid phase (the vapor pressures of lubricating oils are on the order of one-millionth that of refrigerants) and hence its composition in the vapor phase is negligible and happily does *not* have to be predicted. Consequently, dealing with a refrigerant-oil mixture is in this context easier than modeling zeotropic refrigerant mixtures, whose vapor-phase compositions change as the zeotrope evaporates along an evaporator tube.

15.3 Thermodynamics of Refrigerant-Oil Mixtures

15.3.1. Definition of Boiling Heat Transfer Coefficient

To include oil effects correctly in measuring and modeling flow boiling coefficients, the local bubble point temperature and the temperature-enthalpy-vapor quality (T - h - x) relationship have to be calculated. They are then used in determining the local temperature differences and energy balances, and hence the local vapor quality, analogous to how these concepts are applied to zeotropic refrigerant mixtures. Adding miscible oil to a refrigerant increases the bubble point temperature at which the fluid evaporates.

The boiling heat transfer coefficient α is defined as

$$\alpha = \frac{q}{T_w - T_{bub}} \quad [15.3.1]$$

where q is the heat flux through the wall to the evaporating fluid, T_w is the wall temperature and T_{bub} is the bubble point temperature of the fluid. Since the value of T_{bub} for a refrigerant-oil mixture is higher than T_{sat} for the pure refrigerant, reducing raw test data in this correct manner (rather than reducing it using T_{sat} as has been incorrectly but widely done in the past) results in an increase in the heat transfer coefficient. On the other hand, use of T_{bub} rather than T_{sat} for the pure refrigerant in an incremental log mean temperature difference (LMTD) calculation for an evaporator will decrease the value of the LMTD, which partially compensates for the larger boiling coefficient when using T_{bub} in the definition of α . In any case, it should be remembered that the difference between using T_{bub} or T_{sat} typically only becomes significant when reducing test data at vapor qualities greater than about 80%. Thome (1995) presented a detailed discussion of the thermodynamic effects on boiling points and enthalpy caused by oil and these are discussed below.

15.3.2. Bubble Point Temperatures

Takaishi and Oguchi (1987) proposed the following empirical method to predict bubble point temperatures for a specific lubricating oil mixed with R-22 based on their measurements:

$$\ln(p_{\text{sat}}) = [A/T_{\text{bub}}] + B \quad [15.3.2]$$

where p_{sat} is the saturation pressure in MPa and T_{bub} is the bubble point temperature in K. Rearranging [15.3.2] in order to calculate the bubble point temperature for a given saturation pressure and oil mass fraction, it becomes:

$$T_{\text{bub}} = A / [\ln(p_{\text{sat}}) + B] \quad [15.3.3]$$

The amount of oil in the liquid-phase is given by w , i.e. in mass *fraction*, not mass *percent*. A and B are given by the following empirical expressions:

$$A = a_0 + a_1w + a_2w^3 + a_3w^5 + a_4w^7 \quad [15.3.4]$$

$$B = b_0 + b_1w + b_2w^3 + b_3w^5 + b_4w^7 \quad [15.3.5]$$

where the values of the empirical constants are:

$$\begin{array}{ll} a_0 = -2394.5 & b_0 = 8.0736 \\ a_1 = 182.52 & b_1 = -0.72212 \\ a_2 = -724.21 & b_2 = 2.3914 \\ a_3 = 3868.0 & b_3 = -13.779 \\ a_4 = -5268.9 & b_4 = 17.066 \end{array}$$

Evaluating [15.3.3] at a saturation pressure of 0.55 MPa (79.8 psia), Table 15.1 depicts the effect of oil mass fraction on the bubble point temperature for R-22 mixed with various mass fractions of oil. The right column shows the difference between the bubble point temperatures of the mixtures and the saturation temperature of pure R-22 ($T_{\text{R-22}}$) at this pressure.

Table 15.1. Bubble point temperatures of R22/oil mixtures at 0.55 MPa (79.8 psia).

w (mass fraction)	T_{bub} (°C)	$T_{\text{bub}} - T_{\text{R-22}}$ (°C)	w (mass fraction)	T_{bub} (°C)	$T_{\text{bub}} - T_{\text{R-22}}$ (°C)
0.00	2.99	0.00	0.09	3.17	0.18
0.01	3.01	0.02	0.10	3.19	0.20
0.02	3.03	0.04	0.20	3.44	0.45
0.03	3.04	0.05	0.30	3.79	0.80
0.04	3.06	0.07	0.40	4.31	1.32
0.05	3.09	0.10	0.50	5.25	2.26
0.06	3.11	0.12	0.60	7.22	4.23
0.07	3.13	0.14	0.70	11.53	8.54
0.08	3.15	0.16	0.80	[19.95]	[16.96]

[] - Extrapolated value.

Thome (1995) generalized the above method for application to refrigerants other than R-22 and also temperatures outside the original experimental range. This was accomplished by replacing the original values of a_0 and b_0 that are specifically for R-22 with new ones for the desired refrigerant, such as R-134a. Since the vapor pressure of oil is very small compared to that of the refrigerant, it was demonstrated that the effect of the specific type of oil on the empirical constants a_1 to a_4 and b_1 to b_4 is negligible for oil

fractions below 0.50 of oil (50% mass). Rather than using fixed values of a_o and b_o for a particular pure refrigerant, an accurate equation of state for the pure refrigerant vapor pressure curve is used to determine the values of a_o and b_o at the specified saturation pressure instead of the simple Antoine expression, i.e. [15.3.2]. Using these new values of a_o and b_o , [15.3.2] and [15.3.3] are now accurate for predicting saturation temperatures and bubble point temperatures over narrow temperature ranges for essentially any miscible mixture of commonly used refrigerants and oil. Thome (1997b) [also see Zürcher, Thome and Favrat (1998b)] has also applied this method to zeotropic refrigerant blends mixed with miscible oils (in particular R-407C/oil mixtures) and showed that it accurately matched experimental measurements over a wide range of oil mass fractions.

The procedure to use the expression [15.3.3] for any refrigerant is thus:

- Determine the pure refrigerant saturation temperature and pressure just above and just below the design pressure with an accurate equation-of-state of the user's choice;
- Use these two sets of values for T_{bub} and p_{sat} to solve for a_o and b_o in [15.3.3] with w set to zero. The solution is straightforward with two equations and two unknowns.
- These new values of a_o and b_o replace those of $a_o = -2394.5$ and $b_o = 8.0736$ for R-22, respectively. All the other values of a_1 to a_4 and b_1 to b_4 remain the same since they only refer to the effect of the oil on T_{bub} .
- Equations [15.3.3], [15.3.4] and [15.3.5] are then evaluated for the desired oil mass fraction, w , to obtain T_{bub} for the desired value of p_{sat} and w ; instead, p_{sat} can be obtained for specified values of T_{bub} and w using [15.3.2], [15.3.4] and [15.3.5].

15.3.3 Local Oil Mass Fractions

Preparation of a T-h-x (temperature-enthalpy-vapor quality) curve and determination of local thermodynamic and transport properties of refrigerant-oil mixtures require knowledge of the local oil mass fraction in the liquid at locations along the evaporator tube. From a thermodynamic viewpoint, the ideal evaporation process is infinitesimally slow such that thermodynamic equilibrium exists and consequently the liquid phase has a uniform oil mass fraction and temperature at any cross-sectional location along the tube. Enthalpy curves are prepared assuming that thermodynamic equilibrium exists throughout the process, exactly the same as assumed for evaporating a pure fluid.

The liquid-phase mass fraction of the oil circulating in a refrigeration system is a function of its location in the system. Thus, to unequivocally define this mass fraction, a point is chosen where all the circulating fluid is in the liquid-phase, which occurs in the refrigerant line between the exit of the condenser and the entrance into the expansion valve or expansion device. The oil mass fraction at this location is defined as w_{inlet} . When the local vapor quality x is 0.0, the local oil mass fraction w is equal to w_{inlet} . If all the refrigerant could be evaporated out of the liquid-phase, then the local vapor quality x would be equal to $(1-w_{inlet})$ at that point since all of the refrigerant would be in the vapor-phase and all the oil in the liquid-phase; w would be equal to 1.0 at this point since only oil remains in the liquid-phase. Hence, the maximum exit vapor quality is equal to $(1-w_{inlet})$. This is an important limiting point to remember in designing a system with say 3 (% mass) oil, since the exit vapor quality from the evaporator has to be less than 0.97. Also, for refrigerant-oil flow boiling experiments the maximum outlet vapor quality must be less than $(1-w_{inlet})$.

From a design viewpoint, the local oil mass fraction as a function of vapor quality is required. The expression that relates the local oil mass fraction, w , to the local vapor quality, x , and the inlet oil mass fraction w_{inlet} is obtained from a conservation of mass and is a simple expression:

$$w = w_{\text{inlet}} / (1 - x) \quad [15.3.6]$$

As an illustration, assume that 100 g of refrigerant-oil mixture enters the expansion valve with an inlet oil mass fraction, w_{inlet} , equal to 0.05 (thus, there are 5 g of oil and 95 g of refrigerant):

1. Before the expansion valve the local vapor quality is 0.0 and $w = w_{\text{inlet}} = 0.05$ as indicated by [15.3.6];
2. For a local vapor quality equal to 0.20 immediately after the expansion valve, w is 0.0625 [i.e. $0.05/(1-0.20)$];
3. For a local vapor quality of 0.90, w is 0.50 or 50 mass % oil, i.e. $[0.05/(1-0.90)]$;
4. If the entire refrigerant was evaporated from the liquid mixture, the local vapor quality would be $(1 - w_{\text{inlet}})$ or 0.95 and [15.3.6] appropriately predicts that w for this situation is 1.0 [i.e. $0.05/(1-0.95)$].

15.3.4 Enthalpy Curves

The change in enthalpy dh of a mixture during evaporation is referred to as the enthalpy curve. The change in dh with respect to h_L for completely saturated liquid, i.e. with respect to h at $x = 0$, as the bubble point temperature rises is comprised of three contributions:

- The latent heat to the fraction of liquid vaporized, x ;
- The sensible heat to the fraction of fluid in the liquid phase $(1-x)$;
- The sensible heat to the fraction of fluid in the vapor phase x .

In mathematical terms for a refrigerant-oil mixture this is:

$$dh = h_{LG}x + (1-x)dT_{\text{bub}}c_{pL} + xdT_{\text{bub}}c_{pG} \quad [15.3.7]$$

where x is the local vapor quality, h_{LG} is the latent heat of vaporization of the pure refrigerant since no oil enters the vapor-phase, c_{pL} is the specific heat of the liquid-phase refrigerant-oil mixture and c_{pG} is the specific heat of the pure refrigerant vapor. The values of h_{LG} and c_{pG} are obtained from equations for the pure refrigerant at the local saturation temperature while c_{pL} is a function of the local oil composition and bubble point temperature. Equation [15.3.7] reduces to only the latent heat for a pure refrigerant without oil.

A heat release curve is not actually implemented as a curve. Instead, it is prepared as a table of values at set intervals of temperature or vapor quality that gives the amount of heat absorbed by the fluid per unit mass (i.e. dh is in J/kg or Btu/lb) relative to its inlet state together with the bubble point temperature and vapor qualities that correspond to these points.

At a standard evaporation temperature of 4.44°C (40°F) in a refrigeration system, for pure R-134a this corresponds to a saturation pressure of 3.43 bar (49.7 psia) absolute. For a mixture with 3 (% mass) oil in R-134a at this saturation pressure, Table 15.2 lists the enthalpy curve in tabular form at this pressure covering the vapor quality range from 0.15 to 0.95 utilizing the method of Thome (1995). The oil is Mobil Arctic EAL 68 whose density is 971 kg/m³ (60.7 lb/ft³) at 15.56°C (60°F) {Note: the oil's density is utilized to predict its liquid specific heat, cf. Thome (1995) and thus that of the refrigerant-oil mixture}. The first column in Table 15.2 shows the local vapor quality intervals along the evaporator tube. The next two columns list T_{bub} and w . The total heat absorbed relative to the inlet condition is shown in the 4th column (in kJ/kg). The contributions of the heat absorbed as latent heat dh_{latent} and as sensible heating of the liquid and vapor dh_{sensible} are given in the last two columns (in kJ/kg), respectively. As can be seen, the rise in the bubble point temperature and oil mass fraction in the liquid is most rapid at high vapor

qualities. The contribution of sensible heat is important at high vapor qualities since its effect is directly dependent on the rise in T_{bub} .

Table 15.2. An enthalpy curve for R-134a/3 (% mass) oil mixture at 3.43 bar.

x	T_{bub} (°C)	w	dh _{total} (kJ/kg)	dh _{latent} (kJ/kg)	dh _{sensible} (kJ/kg)
0.150	4.509	3.53	0.00	0.00	0.00
0.230	4.516	3.90	15.64	15.63	0.01
0.310	4.525	4.35	31.28	31.26	0.02
0.390	4.536	4.92	46.92	46.29	0.03
0.470	4.550	5.66	62.56	62.51	0.05
0.550	4.570	6.67	78.20	78.13	0.07
0.630	4.598	8.11	93.85	93.75	0.10
0.710	4.643	10.34	109.52	109.37	0.15
0.790	4.729	14.29	125.23	124.99	0.24
0.870	4.954	23.08	141.05	140.59	0.46
0.950	8.289	60.00	159.76	156.07	3.69

Table 15.2 also illustrates the influence of oil on T_{bub} with respect to the pure refrigerant (R-134a) saturation temperature T_{sat} of 4.44°C (40°F). For $x < 0.50$, the increase in boiling point tends to be 0.1°C (0.2°F) or less, for $0.50 < x < 0.80$, the rise increases up to about 0.3°C (0.54°F), and for $x > 0.80$ the elevation of the boiling point can become very significant (3.845°C or 6.921°F at $x = 0.95$ in Table 15.2!). The temperature difference between T_{bub} and T_{sat} depends on the local vapor quality and the inlet oil mass fraction.

For refrigerant-oil mixtures, it is preferable to use set intervals of vapor quality for determining the points on a heat release curve rather than set intervals of temperature. If an evaporator is to be designed with an inlet vapor quality after the expansion valve of 0.20 and an outlet vapor quality of 0.90, then the heat absorbed and bubble point temperatures might be determined at vapor qualities of 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90. The heat absorbed at $x = 0.20$ would be zero and would serve as the datum for the other values. In practice, the number of intervals to use is up to the designer and should be sufficient to accurately represent the heat release curve and also the variation in the two-phase heat transfer coefficient as a function of vapor quality. Normally eight to ten intervals are recommended, but more can be used as desired.

For refrigerant-oil mixtures, the following procedure is used for preparation of a heat release curve at a fixed, isobaric pressure:

1. Select the desired pressure p_{sat} and inlet oil mass fraction before the expansion valve, w_{inlet} .
2. Determine two sets of pure refrigerant saturation temperature and pressure just above and just below p_{sat} with an accurate equation-of-state;
3. Use these two sets of values for T_{bub} and p_{sat} to solve for a_0 and b_0 with w set to zero from the two equations and two unknowns.
4. The new values of a_0 and b_0 are used in place of $a_0 = -2394.5$ and $b_0 = 8.0736$, respectively. All the other values of a_1 to a_4 and b_1 to b_4 remain the same.

5. Choose the inlet vapor quality, the exit vapor quality (always less than the value of $1-w_{\text{inlet}}$), and the number of design intervals desired (for example, if the evaporator is divided into ten heat transfer zones, then 11 points are needed in the heat release curve).
6. Calculate the local oil fractions corresponding to the local vapor qualities using [15.3.6] (for example, determine w for each of the eleven vapor quality points above).
7. Calculate the local bubble point temperatures corresponding to the local vapor qualities and local oil mass fractions at each point.
8. Calculate the values of h_{LG} and c_{pG} at these bubble point temperatures using methods for pure refrigerants. Determine the liquid specific heat of the refrigerant-oil mixture c_{pL} for each point based on the local values of w and T_{bub} using [15.4.1] and [15.4.2].
9. Determine the heat absorbed by the refrigerant-oil fluid in each interval, dh , and then add these up to obtain the total heat absorbed per unit mass of fluid from inlet to outlet.

The heat release curve preparation is now complete and the following values required for thermal design of the evaporator are known at each local vapor quality x : w , T_{bub} and dh .

15.4 Liquid Specific Heats of Oils and Refrigerant-Oil Mixtures

15.4.1 Liquid Specific Heat of Lubricating Oils

Liquid specific heats of lubricating oils are often not available from their manufacturers; hence a general correlating equation is required for their estimation. Based on a literature search, Thome (1995) recommended the following equation cited by Liley and Gambill (1973) for predicting liquid specific heats of petroleum oils, specified to be accurate to within 5%:

$$(c_{\text{pL}})_{\text{oil}} = 4.186 \{ [0.388 + 0.00045(1.8T + 32)] / s^{1/2} \} \quad [15.4.1]$$

where the liquid specific heat $(c_{\text{pL}})_{\text{oil}}$ is in units of $\text{kJ/kg}^\circ\text{C}$, the temperature of the oil, T , must be in $^\circ\text{C}$ (valid for $-18 < T < 204^\circ\text{C}$) and s is the liquid specific gravity at 15.56°C (60°F) and is valid for $0.75 < s < 0.96$. Literature furnished by manufacturers of lubricating oils usually provides the density or specific gravity of the oil at a temperature of 60°F (15.56°C). Thus, application of [15.4.1] for general use for lubricating oils presents no problem. In preparation of a heat release curve, the temperature, T , in [15.4.1] is the bubble point temperature T_{bub} for the local vapor quality in question.

The above correlation compares well with tabular values for engine lubricating oil in Incropera and DeWitt (1981), giving maximum deviations of -2% and +7%. This equation has also been double-checked against numerous heavy hydrocarbons and viscous commercial heat transfer fluids with good results over the temperature range of interest for lubricating oils. Thus it should be sufficiently accurate since liquid sensible heat normally only contributes a small fraction of the total heat absorbed by an evaporating refrigerant-oil mixture.

Some lubricating oils have a specific gravity as high as 1.05, i.e. not very far outside the range cited by Liley and Gambill, and use of [15.4.1] is still recommended in the absence of values from the

manufacturer. As an example calculation, consider an oil at 4.44°C (40°F) with a specific gravity of 0.890 at 15.56°C (60°F). Equation [15.4.1] predicts the liquid specific heat to be 1.80 kJ/kg°C (0.43 Btu/lb°F). In comparison, the values for R-134a and R-22 at 4.44°C (40°F) are 1.354 and 1.187 kJ/kg°C, respectively (0.323 and 0.283 Btu/lb°F).

15.4.2 Liquid Specific Heat of Refrigerant-Oil Mixtures

For preparation of a heat release curve, the liquid specific heat of the refrigerant-oil mixture is required at each local vapor quality as a function of oil fraction, w , and bubble point temperature, T_{bub} . In the absence of experimental data, the only practical approach for predicting specific heats of liquid mixtures is to weigh the single-component values by their mass fractions, according to Liley and Gambill (1973). Thus, heats of mixing are ignored, unless specific information is available, and ideal mixing is assumed. Sophisticated methods in the literature involving corresponding states cannot be applied because the molecular weight of the oil and its critical properties are not known.

Working in the units of kJ/kgK (Btu/lb°F), a linear mixing law based on mass fractions of liquid phase is used. For liquid specific heats the mixture expression is

$$c_{pL} = w(c_{pL})_{\text{oil}} + (1 - w)(c_{pL})_{\text{ref}} \quad [15.4.2]$$

The above equation is evaluated with the refrigerant and oil properties at the local bubble point temperature of the mixture. For example for 30 mass % oil ($w = 0.30$), if the specific heat at 4.44°C for the oil is 1.80 kJ/kgK while that of R-22 is 1.187 kJ/kgK, then the liquid specific heat of the mixture is 1.371 kJ/kgK [= 0.3 (1.80) + (1.0-0.3)(1.187)].

15.5 Example of Application of Thermodynamic Approach

Using the new Thermodynamic Approach, Table 15.3 shows a temperature-enthalpy curve in tabular form calculated for R-134a mixed with 5 mass % oil. The oil is Mobil Arctic EAL 68 whose properties are: specific gravity of 0.971 at 15°C, viscosities of 62.5 and 8.1 mm²/s at 40°C and 100°C, respectively, and assumed molecular weight of 590) at the isobar of 2.93 bar (where $T_{\text{sat}} = 0.0^\circ\text{C}$ for pure R-134a at this pressure). Column one gives the local vapor qualities used in the calculation while columns 2 and 3 list the calculated bubble point temperatures and local oil mass fractions, w . The total heat absorbed by the fluid dh_{total} (in kJ/kg of flowing fluid) is given in column 4 while the next two columns show the individual contributions of latent heat dh_{latent} and sensible heat dh_{sensible} .

As can be observed, the bubble point temperature at first increases slowly relative to T_{sat} of pure R-134a and then rises rapidly at vapor qualities above 0.80. For $x < 0.90$, the contribution of sensible heat is less than 1% of the total but its influence rises rapidly afterwards; thus for test data for $x > 0.90$, the reported vapor qualities become ever too high. For example, if 181.41 kJ/kg of heat is added to the refrigerant-oil mixture, its local vapor quality should be 0.902 according to Table 15.3; using only the latent heat and neglecting sensible heat the vapor quality would be calculated to be 0.9114, i.e. 0.0112 too high. Thus, the error in reported vapor qualities is not very significant except at vapor qualities approaching 1.0. It should be pointed out however that many data reported in the literature incorrectly use a vapor quality based on the local mass of refrigerant vapor divided by the total mass of refrigerant, i.e. ignoring the presence of the oil, while instead the thermodynamic vapor quality x is the local mass of vapor divided the total mass of refrigerant and oil. For the highest vapor quality shown in the table, $x = 0.93$, the bubble point temperature is predicted to be 8.015°C (14.4°F) above the pure refrigerant value.

Table 15.3. R134a-oil temperature-enthalpy curve at 2.93 bar (42.5 psia) for 5 mass % oil at inlet.

x	T _{bub} (°C)	w (%)	dh _{total} (kJ/kg)	dh _{latent} (kJ/kg)	dh _{sensible} (kJ/kg)	5°C %Error	2°C %Error
0.000	0.076	5.00	0.00	0.00	0.00	-1.5	-3.8
0.093	0.084	5.51	18.53	18.52	0.01	-1.7	-4.2
0.186	0.094	6.14	37.06	37.04	0.02	-1.9	-4.7
0.279	0.106	6.93	55.60	55.56	0.04	-2.1	-5.3
0.372	0.123	7.96	74.14	74.08	0.06	-2.5	-6.2
0.465	0.146	9.35	92.68	92.59	0.06	-2.9	-7.3
0.558	0.180	11.31	111.23	111.10	0.13	-3.6	-9.0
0.651	0.236	14.33	129.80	129.63	0.16	-4.7	-11.8
0.744	0.346	19.53	148.42	148.11	0.31	-6.9	-17.3
0.837	0.663	30.67	167.22	166.59	0.63	-13.3	-33.2
0.846	0.729	32.47	169.14	168.44	0.70	-14.6	-36.5
0.856	0.819	34.72	171.08	170.29	0.79	-16.4	-41.0
0.865	0.922	37.04	173.03	172.14	0.89	-19.4	-46.1
0.874	1.056	39.68	175.00	173.98	1.02	-21.1	-52.8
0.883	1.240	42.74	177.02	175.82	1.20	-24.8	-62.0
0.893	1.541	46.73	179.15	177.66	1.49	-30.8	-
0.902	1.974	51.02	181.41	179.50	1.91	-39.5	-
0.911	2.726	56.18	183.93	181.33	2.63	-54.5	-
0.921	4.435	63.29	187.43	183.15	4.28	-	-
0.930	8.015	71.43	192.70	184.95	7.75	-	-

(% errors determined assuming a heat flux of 10,000 W/m²).

In the last two columns in Table 15.3, the effect of erroneously using T_{sat} in place of T_{bub} in converting "raw" data to experimental heat transfer coefficients is shown for wall superheats of 5°C (9°F) and 2°C (3.6°F). It is evident that existing published data using T_{sat} are always too low compared to their more correct values. For instance, at a vapor quality of 0.837 and a wall superheat of 5°C (9°F), published values would be 13.3% lower than the thermodynamically correct values.

For a plain tube the effect of the oil on flow boiling heat transfer becomes significant (> 5%) at a local oil mass fraction greater than 15% while for a micro fin tube it becomes significant at w > 6.5%. At high vapor qualities and oil mass fractions, the effect becomes very significant, substantially changing the trends reported in the literature. Published test data reduced with the "oil contamination" method that fall in these ranges should be used with caution or better yet, the heat transfer coefficients should be recalculated.

15.6 Illustration of Physical Properties of Refrigerant-Oil Mixtures

Thome (1993) put together a comprehensive set of prediction methods that may be the best currently available (but would really benefit from further research). Table 15.4 shows the calculated physical properties that correspond to the enthalpy curve in Table 15.3 at several vapor qualities using his methods. Note that since the vapor pressures of oils are about one-ten millionth those of refrigerants, no oil enters the vapor-phase and hence vapor properties are determined for the pure refrigerant at a saturation temperature corresponding to the local bubble point temperature. For the present conditions, the physical properties that demonstrate a significant change from inlet to outlet (> 5%) are: liquid density

(-17.2%), liquid viscosity (+9003%), liquid specific heat (+23.6%), liquid thermal conductivity (+11.7%), critical pressure (-58.1%), critical temperature (+103%) and liquid Prandtl number (+10,021%). Also shown is the ratio of the liquid Reynolds number relative to than for the inlet at $x = 0.0$, which decreases drastically as the liquid viscosity rises. Thus, the variation in local physical properties can potentially have a significant effect on the local heat transfer coefficients, both for nucleate pool boiling and for flow boiling.

Table 15.4. R134a-oil properties at 2.93 bar for 5 mass % oil at inlet over a range of vapor qualities.

Local Vapor Quality	0.000	0.279	0.558	0.744	0.930
Oil Mass Fraction %	5.00	6.93	11.31	19.53	71.43
Liquid Molecular Weight	126.4	135.9	157.2	197.3	450.6
Bubble Point Temp. (°C)	0.076	0.106	0.180	0.346	8.015
Heat Absorbed (kJ/kg)	0.00	55.6	37.1	148.4	192.6
Liquid Density (kg/m ³)	1276	1270	1256	1230	1057
Vapor Density (kg/m ³)	14.5	14.5	14.5	14.6	16.8
Liquid Viscosity (cp)	0.398	0.458	0.628	1.137	35.83
Vapor Viscosity (cp)	0.011	0.011	0.011	0.011	0.011
Liquid Sp. Heat (kJ/kg K)	136.3	1.372	1.391	1.428	1.684
Vapor Sp. Heat (kJ/kg K)	0.889	0.889	0.889	0.889	0.906
Liquid Th. Cond. (W/m K)	0.094	0.095	0.095	0.096	0.105
Vapor Th. Cond. (W/m K)	0.012	0.012	0.012	0.012	0.013
Surface Tension (dyne/cm)	11.7	11.7	11.7	11.8	17.2
Latent Heat (kJ/kg)	199.1	191.1	1.991	198.9	195.5
Critical Pressure (bar)	38.9	38.2	36.7	33.9	16.3
Critical Temperature (K)	405.7	417.9	445.5	497.4	824.7
Liquid Prandtl Number	5.75	6.64	9.20	16.9	576.2
Relative Liquid Re Number	1.000	0.869	0.634	0.350	0.011

15.7 Online Measurement of Refrigerant-Oil Mass Fractions

The Thermodynamic Approach allows the local bubble point temperature, local oil mass fraction, local heat transfer coefficient, change in enthalpy and (potentially) local physical properties to be calculated for an evaporator from knowledge of w_{inlet} for any refrigerant and lubricating oil mixture, as long as they are miscible and the local oil mass fraction is below 70% oil. To implement the Thermodynamic Approach, an accurate method is required for measurement of the oil composition. For this purpose, a new online measurement system was developed and described in Bayini, Thome and Favrat (1995).

15.7.1 Previous Test Methods

Over the years, oil mass fractions circulating in test facilities and equipment qualification facilities have been inferred from: (i) measuring the masses of refrigerant and oil charged into the system, (ii) measuring the separate oil and refrigerant flow rates leaving an oil separator, or (iii) by withdrawing liquid samples during tests. The 1st approach is often not able to be implemented. The 2nd method is not necessarily accurate since an oil separator actually acts as a liquid-vapor separator and thus some refrigerant remains in the oil leaving the separator as liquid but gets counted as if it were oil. The 3rd method uses ASHRAE Standard 41.4-1994 to determine oil compositions for liquid samples withdrawn from the flow circuit. Each sample is weighed together with its bottle and then the refrigerant is allowed to slowly evaporate off through a valve. To be accurate, the sample must also be evacuated with a vacuum pump and heated up to

150°C (302°F) to drive off the refrigerant, then weighed again with a top loading balance accurate to 0.01 g or better. The oil composition can then be calculated from the initial and final weights. While this method is appropriate as a standard, it is not very convenient for practice. Shortcuts to the standard method, i.e. dispensing with the heating and/or evacuation procedures, result in overstating the oil concentration by as much as 1.5 mass % oil or more. Consequently, it is felt that an online method is imperative in order to measure the oil compositions conveniently and accurately over the range of test conditions to be encountered.

Various methods for determining oil compositions online have been proposed and several have been tested. Baustian, Pate and Bergles (1988a, 1988b, 1988c) have used a Coriolis density meter, an acoustic velocity sensor and a viscosity meter, respectively, to measure oil concentrations with accuracies in the range of 1-2 mass % oil. The Coriolis meter used in their tests had a density measurement accuracy of 10 kg/m³ (0.6 lb/ft³) and the effect of compressibility on the subcooled liquid passing through the meter was not accounted for; however, newer more accurate Coriolis meters are now available and may suit industrial use. Meyer and Saiz Jabardo (1994) built an ultrasonic acoustic velocity device and accurately calibrated it for measuring concentrations for R-12 and R-134a with various oils (95% confidence level accuracy of 0.23-0.26 mass % oil). Suzuki, Fujisawa, Nakarazawa and Matsuoka (1993) instead have used a light absorption method for measuring oil concentrations online.

15.7.2 Online Density Flowmeter

A very high accuracy, commercially available density flowmeter was used Bayini, Thome and Favrat (1995) as the measuring device, a model available from Schlumberger (Liquid Density Transducer type 7847 in stainless steel). This method will be described in some detail here. The meter is a vibrating tube type, where the tube is a 25.4 mm diameter, stainless steel corrugated tube about 1.0 meter long. The meter has a calibrated accuracy of 0.1 kg/m³ (0.006 lb/ft³) over a wide range of density and temperature, including compensating equations to account for nonlinear temperature effects on the instrument's operation. A digital display gives the density and temperature and a digital signal for the density, which was read into our data acquisition system. It operates with subcooled refrigerant-oil flowing through the meter, such that measurements are continuous and no bypass circuit is required.

The density flowmeter is used to measure the density of subcooled liquid, either pure refrigerant or refrigerant-oil mixture, after it leaves the flow loop's condenser. To avoid cavitation in the vibrating corrugated tube (apparently caused by its high vibration frequency), a minimum of 8°C (14.4°F) of subcooling was required at its outlet. A further consideration is the sensitivity of the density flowmeter. The density difference between pure R-134a and the oil is approximately 300 kg/m³ at the test conditions. Thus, in order to determine oil concentrations accurate to 0.1 mass % oil, one must measure density to an accuracy of ±0.30 kg/m³ (±0.019 lb/ft³) including temperature and liquid compressibility effects.

15.7.3 Oil Concentration Calibration Correlation

Measured liquid densities are not only a function of temperature and oil concentration but also liquid compressibility. For example, the density of compressed R-134a increases by about 0.3-0.4 kg/m³ (0.019-0.025 lb/ft³) for each increase of 1 bar (14.5 psi) with respect to the saturation pressure at the measured temperature. The calibration should thus take the liquid compressibility into account, which for mixtures in the range from 0-6 mass % oil can reasonably be assumed to match that of the pure refrigerant. Compressed liquid densities for R-134a were reported for instance by Hou et al. (1992) over a wide range of temperature and pressure. They fit the Tait equation to their data with separate empirical parameters for each isotherm they tested. Refer to Bayini, Thome and Favrat (1995) for further details on this and the calibration procedure.

Their calibration correlation had an average error of 0.09 mass % oil for all 246 data points measured for the oil concentrations of 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 mass %, a maximum error of 0.69 mass % oil and a 95% confidence limit of 0.21 mass % oil.

15.7.4 Industrial Application of a Density Flowmeter

As a shortcut "industrial" method, the saturation density of the refrigerant-oil mixture can be determined using a linear mixing law of the specific volume. The refrigerant-oil saturation density ρ is defined by this ideal mixing law as:

$$\rho = \rho_{\text{oil}} / [1 + (1 - w)(\rho_{\text{oil}} / \rho_{\text{ref}} - 1)] \quad [15.6.1]$$

Solving this expression to obtain the oil mass fraction w (in mass fraction, not mass %) gives

$$w = [(\rho_{\text{oil}} / \rho)(\rho_{\text{ref}} - \rho)] / (\rho_{\text{ref}} - \rho_{\text{oil}}) \quad [15.6.2]$$

The refrigerant saturation density ρ_{ref} in this equation is calculated from an accurate equation for the refrigerant (such as ASHRAE methods). The lubricating oil density ρ_{oil} can either be measured as a function of temperature or obtained from data supplied by the manufacturer. Otherwise, using a method adapted from Thome (1992), it can be estimated from the following equation for lubricating oils:

$$\rho_{\text{oil}} = \rho_{\text{man}} [(T_{\text{crit}} - T) / (T_{\text{crit}} - (T_{\text{man}} + 273.15))]^{0.29} \quad [15.6.3]$$

where ρ_{man} is the oil density (kg/m^3) at the temperature provided by the manufacturer T_{man} (normally 15°C), T_{crit} is the critical temperature of the oil (assume equal to 760 K for all oils as an approximation), and T is the measured temperature (K). Subtracting the density difference due to compressibility from the measured density ρ and using the pure refrigerant and oil densities determined as discussed, the oil composition is determined with [15.6.2]. This simplified method has been successfully compared to R-134a/oil density test data of Bayini, Thome and Favrat (1995) with a mean error of ± 0.22 mass % oil. Because of nonlinear variations in density with composition, the accuracy varies from about ± 0.1 mass % mean error for the 0.5 mass % mixture up to about ± 0.5 mass % mean error for the 6.0 mass % mixture, which is more than satisfactory for most applications.

To get the best results, the meter should be calibrated against the pure refrigerant first, i.e. measure the pure refrigerant's density with the meter, correct this value for liquid compressibility and then compare it against the calculated saturated refrigerant density.

Example Calculation: Assume a density meter is used to measure oil mass fraction of a slightly subcooled mixture of R-134a and oil at the conditions of 0°C and 2.93 bar. R-134a has a density of 1276 kg/m^3 at this temperature while the oil has a density of 900 kg/m^3 at the 15°C according to the manufacturer. If the density measured is 1270 kg/m^3 , what is the oil mass fraction?

Solution: The density of the oil at 0°C (273.15 K) is obtained with [15.6.3]:

$$\begin{aligned} \rho_{\text{oil}} &= \rho_{\text{man}} [(T_{\text{crit}} - T) / (T_{\text{crit}} - (T_{\text{man}} + 273.15))]^{0.29} \\ \rho_{\text{oil}} &= 900 [(760 - 273.15) / (760 - (15 + 273.15))]^{0.29} = 908.2 \text{ kg/m}^3 \end{aligned}$$

The oil mass fraction w (in mass fraction) is obtained with [15.6.2]:

$$w = [(\rho_{\text{oil}}/\rho)(\rho_{\text{ref}} - \rho)]/(\rho_{\text{ref}} - \rho_{\text{oil}})$$

$$w = [(908.2/1270)(1276 - 1270)]/(1276 - 908.2) = 0.0117$$

Thus, the oil mass fraction is 0.0117 or 1.17 % oil.