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Determination of the Thermodynamic Properties of Refrigerant-Oil Mixtures

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ABSTRACT

The errors associated with thermodynamic performance calculations are discussed with particular reference to systems with a high oil charge. It is shown that calculations made using published refrigerant data can be very misleading as no account is taken of the oil solubility effects.

Pressure-enthalpy charts are presented for refrigerant R12 oil mixtures, for a range of oil concentrations. The effect that the existence of this mixture has on evaporator performance and COP of a refrigeration or heat pump system is discussed and some results are compared with the pure refrigerant cycle normally considered.

INTRODUCTION

The solubility of fluorinated refrigerants in lubricating oil is a phenomenon which has been recognised for a long time, and a considerable amount of work has been done to study the effects of this solubility on refrigeration systems. It is widely recognised that the presence of oil in a vapour compression refrigeration or heat pump system reduces its capacity. Briefly this is because, at the evaporator outlet, liquid refrigerant remains dissolved in the oil, thus being unavailable for evaporation, and hence to carry latent heat. While there has been a certain amount of work concerned with the physics and chemistry of the interaction between the refrigerant and the oil (1,2,3,4), most previous work on the engineering aspects of the subject has looked at the influence of oil on the evaporator heat transfer performance (see e.g. reference 7), and at its effect on system capacity (5). However it has not been generally appreciated that the presence of oil in a refrigeration or heat pump system would have a serious deleterious effect on the coefficient of performance. It should be noted, however, that Spauschus (2) did observe that "... For accurate compressor design, engineering calculations should be based on an enthalpy chart for the refrigerant-oil solution, as opposed to the accepted practice of relying on thermodynamic data for the pure refrigerant."

It appears to us that, in general, this advice has not been acted upon.

In a previous paper (8) it was shown how, theoretically, the COP can be reduced by as much as 30% in systems which require relatively high oil-refrigerant ratios, such as those using rotary sliding-vane or screw compressors. This results from the fact that, while evaporator capacity is reduced, compressor power is largely unaffected by the oil circulation. The analysis set out in this previous paper was based on the oil-refrigerant solubility equation developed by Bambach (1) for R12-paraffinic oil mixtures. Subsequent experimental work by the authors (9) verified the general validity of the theoretical analysis.

It is worth summarising the effects of oil on a typical system using a fluorocarbon refrigerant. Refrigerants are soluble in lubricating oils to a varying degree, depending on the refrigerant and the type of oil. In the case of liquid R12, as with certain other refrigerants, the miscibility is total, the mixture forming a single phase at all temperatures and pressures. Under some conditions (for example when using R22 under typical refrigeration conditions) a single phase is not always formed and separate oil-rich and refrigerant-rich phases may exist. Even here, however, there is still a critical solution temperature above which complete miscibility again appears.

Our interest in these phenomena was aroused when it proved to be impossible to reproduce the manufacturer's published performance data for a particular range of compressors which required a high oil charge (about 10%). Several effects were observed, including a clearly defined optimal evaporator superheat setting and a compressor coefficient of performance some
This was discussed in an earlier paper (8), and the issue was not fully resolved until we finally realised that the manufacturer's calibration rig was a "gas loop" type of test rig, as commonly used in the refrigeration industry, and not the calorimeter we had believed it to be. In this type of test rig, the refrigerant is always in the gas phase with the condenser and evaporator being simulated by throttling and cooling the refrigerant gas to the required suction conditions. The heat extraction rate is then calculated from the measured temperatures, pressures and flow rates using published refrigerant property tables. This is the heart of the problem. The published refrigerant tables present the properties of pure refrigerants, and not those of the oil-refrigerant mixtures that obtain in a practical refrigeration system. Thus the manufacturer's performance charts were deduced from inappropriate refrigerant data. Further, since the refrigerant is assumed always to be in the gas phase, any problems which would arise in the evaporator (or indeed in the condenser) because of the oil-refrigerant interaction cannot be observed.

With increasing interest in rotary and screw compressors, in many cases requiring a high oil charge in the system, it is essential that more accurate methods are available for handling experimental and test data. The normal technique of using the thermodynamic property charts for pure refrigerant to calculate performance from pressure and temperature measurements is strictly invalid when any oil is present in the system, but we have found that it is usable at very low oil concentrations. It appears to be an insufficiently accurate approximation, however, when the oil concentration is greater than about 1%. This paper presents thermodynamic property (pressure-enthalpy) charts for a range of R12-oil mixtures. These charts can be used directly for heat pump cycle analysis using measured state point properties in the normal way.

**ANALYTICAL APPROACH**

The fundamental approach adopted in the present work was to take the solubility equation derived by Bambach (1) for R12 in a paraffinic oil, and to use it, together with published data for R12, to calculate the thermodynamic properties of an oil-refrigerant mixture. The results are then presented in a graphical form similar to the well known refrigerant pressure-enthalpy charts.

The particular paraffinic oil considered by Bambach is not really typical of currently used refrigeration oils, but Pawlinney (11) has shown that the solubility of R12 in Shell Clavus 33, a commonly used naphthenic oil, is remarkably similar. Consequently we felt that the use of Bambach's data was justified, particularly since our primary interest at this stage was in demonstrating typical effects and the validity of our approach. Other refrigerants or lubricants can easily be handled provided that the appropriate solubility data is available.

The calculations centre on a program suite which was developed in our laboratory for determining the thermodynamic and thermophysical properties of a number of pure fluorocarbon refrigerants. Computer programs and data for calculating the state point properties of pure refrigerants have been available for a number of years, and our approach does not differ significantly from that of Kartsounes and Drth (10) except that we put considerable effort into improving the convergence of some routines. We also expanded the treatment to increase flexibility and speed of calculation. This will be discussed elsewhere (12). The refrigerant data is as published by Downing (6). The program allows all of the thermodynamic and thermophysical properties of the refrigerant to be calculated, for any conditions, from the pressure and any one other property. It also allows the data to be presented graphically in various formats, e.g. as the familiar pressure-enthalpy or temperature-entropy charts. This program was modified to take account of the oil-refrigerant solubility data and used to generate the pressure-enthalpy charts shown later.

A heat pump is charged with fluid which consists of two components, refrigerant and oil. At different parts of the cycle, the proportions of oil, liquid refrigerant and vapour refrigerant in the circulating fluid will vary. Thus, at the condenser outlet the vapour refrigerant fraction is zero, while at the evaporator outlet, the liquid refrigerant fraction is limited to that amount which is dissolved in the oil. This can be represented by the following definitions.

\[
\begin{align*}
    w &= \text{refrigerant fraction in the liquid mixture} \\
    &= \frac{\text{mass of refrigerant}}{\text{mass of liquid refrigerant + oil}} \\
    x &= \text{oil fraction in the total mixture} \\
    &= \frac{\text{mass of oil}}{\text{total mass of refrigerant + oil}}
\end{align*}
\]
z = liquid fraction in total mixture
\[ \frac{\text{mass of liquid refrigerant + oil}}{\text{total mass of refrigerant + oil}} \]

(1-z) = vapour fraction in total mixture
\[ \frac{\text{mass of refrigerant vapour}}{\text{total mass of refrigerant + oil}} \]

y = ref. vapour fraction (quality)
\[ \frac{\text{mass of refrigerant vapour}}{\text{total mass of refrigerant}} \]

Hence
\[ x = \frac{1 - z}{1 - w} \]
\[ y = \frac{1 - x}{1 - w} \]

Fambach's equations for the solubility of refrigerant R12 in the paraffinic oil are

for \( t < 0 \) deg C
\[ \log P = a - b w - \frac{c - d w}{10} = A \]

for \( t > 0 \) deg C
\[ \log P = A - (T - 273.16)(e(w - 0.6) - f) \]
\[ \frac{2}{10} \]

where
\[ P \] is the absolute pressure in bar
\[ T \] is the absolute temperature in deg K
\[ a = 4.9972 \]
\[ b = 0.558 \]
\[ c = 1177.67 \]
\[ d = 98.753 \]
\[ e = 0.0002338 \]
\[ f = 0.000075 \]

From these equations the maximum amount of refrigerant, \( w \), dissolved in the oil can be determined if the temperature and pressure are known. This allows the fraction of the total refrigerant which is dissolved in the oil to be determined from the known oil fraction, \( x \). Hence the total liquid fraction, \( z \), can be calculated. Under conditions in which pure refrigerant would be liquid in any case, the liquid fraction of the oil-refrigerant mixture must obviously be unity and the solubility of the refrigerant in the oil has little significance. For our purposes the fluid can be treated as a mixture rather than as a solution. In normal practice this condition only appears at the outlet from a subcooled condenser.

In the more interesting case where refrigerant vapour is also present the solubility effect takes on a much greater significance. Under conditions in which a pure refrigerant would be entirely in the vapour phase, an oil-refrigerant mixture may have a substantial fraction of the refrigerant dissolved in the oil and consequently still in the liquid state. This is the effect which causes the dramatic changes observed in heat pick up at the evaporator. The enthalpy of the mixture is the sum of four components: the enthalpies of the refrigerant liquid, the refrigerant vapour, and the oil, together with the heat of solution of the refrigerant in the oil. We will assume that this last quantity is small enough to be neglected. This has been shown to be a reasonable assumption (5). Thus, three terms must be calculated to evaluate the mixture enthalpy.

The enthalpy of the refrigerant vapour is determined from the refrigerant properties program suite described earlier, and that of the refrigerant liquid is calculated by extrapolation of the subcooled liquid refrigerant properties at the particular pressure to the higher temperature appropriate to the experimental conditions. The enthalpy of the oil can be approximated by integrating its specific heat and taking the reference temperature as -40 deg C for consistency with the refrigerant data. The equation used was

\[ h_{\text{oil}} = 67.12 + 1.754 t + 0.0019 t^2 \]

Hence the total enthalpy of the mixture can be calculated as

\[ h_{\text{mix}} = zh_{\text{liq}} + (1-z)h_{\text{rvap}} \]

where
\[ h_{\text{liq}} = (1 - w)h_{\text{liq}} + wh_{\text{rvap}} \]
\[ h_{\text{oil}} = d_{\text{rliq}} - d_{\text{rvap}} \]

The specific volume of the mixture was determined in an analogous manner from the sum of the partial volumes of each of the components. The density of a typical paraffinic oil is given by

\[ d_{\text{oil}} = 932.47 - 0.6298t \]

The refrigerant densities \( d_{\text{rliq}} \) and \( d_{\text{rvap}} \)
are determined from the refrigerant property equations in the usual way. The mixture specific volume, \( v_{\text{mix}} \), is then given by

\[
v_{\text{mix}} = \frac{z}{d_{\text{liq}}} + \frac{1-z}{d_{\text{vap}}} \]

where \( d_{\text{liq}} \), the liquid mixture density, is given by

\[
d_{\text{liq}} = \frac{1-w}{d_{\text{d}}} + \frac{w}{d_{\text{vap}}} \]

These equations are all that is required to generate the refrigerant - oil mixture property charts. The computer program to solve the equations will be described elsewhere (12).

PRESSURE - ENTHALPY CHARTS

Sample pressure - enthalpy charts are shown in figures 1 to 6, for oil fractions ranging from 0.1% to 15%. The influence of the oil is readily discernible. Probably the most noticeable effect is the disappearance of the saturated vapour line which is characteristic of the pure refrigerant curves. This occurs, of course, because the boiling liquid is no longer pure, so that no unique boiling point exists. What is not obvious from these charts is the relationship between these curves and their pure refrigerant equivalent. This is shown in Figure 7, where the curves for an oil fraction of 8% are superimposed on the pure refrigerant set. The differences are immediately obvious. Boiling begins in the mixture at a lower pressure and a higher enthalpy; there is no distinct boiling point (the slope of the solid curves is more apparent in this diagram); and a significant level of superheat appears at much lower mixture enthalpies. The effect of this on performance is best illustrated by the example drawn on the chart of Figure 7, and showing the implications of using the same measurements for pressure, temperature and mass flow rate to determine system performance using pure R12 refrigerant curves (dotted and cycle 1) and the present oil-refrigerant curves for an 8% oil mixture (solid and cycle 2). The effect is immediately obvious; evaporator capacity is seriously reduced and compressor work is increased. Using the idealised cycle shown, with an evaporating temperature of 0 deg C, 5 deg C evaporator superheat, discharge temperature of 75 deg C, condensing temperature of 50 deg C, and no condenser subcooling, the heat transferred at the evaporator is reduced from 107 kJ/kg to 97 kJ/kg, and the COP from 3.97 to 2.55. When a motor efficiency of about 80% is allowed for, these become 3.18 and 2.07. The latter figure is very close to the value which we observe experimentally under similar conditions.

It is worth noting that this example and the pressure enthalpy charts presented earlier are referred to total mass flow as would be measured by a flow meter in the liquid line. If it is preferred to have the data expressed in terms of refrigerant mass flow alone, then the horizontal axes for the oil-refrigerant data must be rescaled by dividing the numbers by (1-x). This will have no effect on the performance, but gives the evaporator capacity in kJ/kg of refrigerant. In our example above, the evaporator capacity then appears as 85.3 kJ/kg, but the COP is unaffected as the compressor work is increased by the same ratio.

ACKNOWLEDGEMENTS

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REFERENCES


Fig 1  THERMODYNAMIC PROPERTIES OF R12/OIL MIXTURE (0.1% OIL)
Fig 2  THERMODYNAMIC PROPERTIES OF R 12/OIL MIXTURE (1.0 % OIL)

Fig 3  THERMODYNAMIC PROPERTIES OF R 12/OIL MIXTURE (2.0 % OIL)
Fig 4  THERMODYNAMIC PROPERTIES OF R 12/OIL MIXTURE (5.0 % OIL)

Fig 5  THERMODYNAMIC PROPERTIES OF R 12/OIL MIXTURE (10.0 % OIL)
Fig 6  THERMODYNAMIC PROPERTIES OF R 12/OIL MIXTURE (15.0 % OIL)

Fig 7  THERMODYNAMIC PROPERTIES OF R 12/OIL MIXTURE (8.0 % OIL)