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CRITERIA FOR ESTABLISHING ACCURATE VAPOR PRESSURE CURVES

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Abstract

We use standard thermodynamic relationships to demonstrate the accuracy of new vapor pressure measurements by using them in the calculation of liquid-phase heat capacities and comparing the results with recently published experimental values. Results for the new alternative refrigerants R134a and R123 are used as examples.

Introduction

The importance of good vapor pressure measurements is generally well recognized in the refrigeration industry. In fact, this property, and in particular the normal boiling point, is often the first characteristic examined when one seeks candidates for alternatives to the currently used chlorofluorocarbons (CFC's). For this reason a rather large body of information on the vapor pressures of the hydrochlorofluorocarbons (HCFC's) and hydrofluorocarbons (HFC's) has appeared in the literature in recent years. Within the limits of the instrumentation used, these measurements generally are mutually consistent at higher temperatures and pressures. In the low temperature, low pressure region, however, the consistency is often less satisfactory. This situation is particularly true at subambient pressures.

Recently we have made new vapor pressure measurements [1,2,3,4] on several candidate alternative refrigerants using a reflux boiler, dynamic technique which has not been previously applied to this class of fluids. This technique is particularly applicable to low pressure measurements. However, it has often yielded vapor pressures that are much lower than other published low-pressure data of high precision that were obtained using static techniques.

In the next section we briefly describe the measurements. Then we compare our results with others and describe simple thermodynamic tests which resolve these discrepancies and imply that the dynamic measurements are more accurate than the static measurements.

Experimental

The apparatus has been previously described [1,2] and only a brief explanation of the technique will be given here. An ebulliometer is a refluxing boiler which is used to measure the boiling temperature or more accurately, the condensing temperature, of a liquid at a user-selected superimposed pressure. As the pressure is varied externally, the condensing temperature is measured, resulting in the vapor pressure curve of the liquid. The boiler has been designed to be a precision measurement device through the use of improved control of the pressure and the energy flux and accurate thermometry. In comparative ebulliometry a second boiler, containing a "standard fluid," is connected to the first through a manifold. The pressure is not measured but is calculated from the condensing temperature of this standard fluid. The liquids in both vessels are actively boiling, hence the method is "dynamic".

A diagram of our apparatus is shown in figure 1. One boiler contained the sample of refrigerant and the other contained water, which was used for the standard fluid. The two condensers and two liquid nitrogen cold traps prevented cross contamination of the fluids. A large insulated ballast tank helped to maintain a constant pressure and damped out fluctuations. The design and arrangement of the boilers is such as to minimize or eliminate the effects of superheating or bumping, Ambrose [5]. The

water boiler was surrounded by a heated shield and by insulation. For low temperature work the refrigerant boiler was placed inside an insulated shield that was cooled with methanol which was supplied by an external refrigerated circulation bath. The shield could be cooled to temperatures as low as 203 K. The apparatus was built of glass, and therefore experimental pressures were always less than about 210 kPa. Two calibrated platinum resistance thermometers and a digital multimeter allowed temperature measurements with an accuracy of about 0.003-0.004 K. Pressure was calculated from the condensing temperature of the water, utilizing either the NBS/NRC Steam Tables [22] or a vapor pressure equation fit to the very accurate data for water. Comparison of our water boiler with a NIST standard barometer showed that they agreed to within 10 Pa at atmospheric pressure.

This measurement technique has several advantages over the more common static measurements. The symmetry of the apparatus causes many small errors to cancel. The presence of very volatile impurities (such as air) and of very involatile impurities has little effect on the condensation temperature. Degassing of the samples occurs naturally during the course of measurement. Accurate, reliable thermometers are substituted in place of a pressure gage. Pressure gages in this range tend to be fragile and to require frequent recalibration using facilities which are often not available in the average laboratory.

Results

We have used this apparatus to measure the vapor pressures of several halogenated hydrocarbons of interest in the field of refrigeration, namely R22, R134a, R123, and R141b. The numerical results are reported elsewhere [1,2,3,4]. They include the pressures from 10 to 210 kPa, which correspond to temperatures between 210 K and 320 K, depending on the volatility of the fluid. The precision of the results is consistent with the accuracy estimates given above, and the standard relative deviations are 0.03% or better.

In several cases, however, we noticed that our vapor pressures are systematically lower than published values. The relative deviations become larger at lower temperatures in a manner which seems to correspond to an approximately constant pressure offset. A typical example is shown in figure 2 for R134a. In the figure the baseline is the curve based on the vapor pressure data for R134a, published by Basu and Wilson [6]. Our ebulliometric measurements are systematically lower than the curve. Data at still lower temperatures deviated by as much as 2.5%, at 215 K. From the figure we see that the deviations can be explained by a constant pressure difference from the baseline of about 0.4 kPa. Two other published vapor pressure curves are also shown in figure 2, and they generally agree with the temperature dependence of the baseline data. Similar deviations between our results and published values were seen from other data sets for this and other refrigerants.

The most likely explanation for this offset in pressure is the presence of a small amount of a volatile impurity (probably air) in the samples used in the static measurements. The dynamic measurements would not be affected by such an impurity. The "freezing, pumping, thawing" cycle purification technique, usually employed in this work, can in principle remove these volatile impurities. However, we have found that in practice many such cycles are needed, requiring very tedious repetition, in order to remove the very small amounts of impurity of concern here. At low reduced temperatures the effect of a volatile impurity on static measurements can be calculated approximately from,

$$\delta P \approx RT\bar{\rho} \chi / (1 - \bar{\rho}/\rho_c) \quad (1)$$

where δP is the increase in pressure, $\bar{\rho}$ is the average density of the refrigerant in the sample cell, ρ_c is the critical density of the refrigerant, R is the gas constant, T the absolute temperature, and χ is the mole fraction of impurity. Here we assume that the impurity is an ideal gas which has only negligible solubility in the liquid phase of the refrigerant. These assumptions are very good in the region of interest. In the situation, often encountered experimentally, where $\bar{\rho} = \rho_c$, equation (1) reduces to,

$$\delta P = (3/2) RT\rho_c \chi \quad (2)$$

Applying equation (2) to the data in figure 2, we find that the deviation of our data from the baseline could be explained by an air impurity (in the static measurements) with a concentration of only about 26 parts per million (ppm). Such a sample would be considered quite pure by most standards. Comparisons with other static data sets, including some of our own static data for the fluids studied, revealed other instances of the same type discrepancy, all of which could be explained by air impurities with concentrations less than 100 ppm.

Such large relative deviations in the vapor pressures will have noticeable effects on some of the calculated thermodynamic properties of the fluids. Therefore we should be able to use comparisons between calculated and experimental thermodynamic properties to confirm our assertions about the presence of volatile impurities and also to choose amongst the various available vapor pressure curves.

The heat of vaporization, ΔH_v , may be calculated from the Clapeyron equation,

$$\Delta H_v = T (dP/dT)_o (V'' - V') \quad (3)$$

where V'' is the molar volume of the vapor phase, V' is the molar volume of the liquid phase, and $(dP/dT)_o$ is the slope of the vapor pressure curve. At low reduced temperatures we may neglect V' relative to V'' . If we define $\epsilon = \delta P/P$, the relative error in P , then the corresponding error in V'' is, $\epsilon = -\delta V''/V''$. The error in the heat of vaporization is,

$$\Delta H_v = \Delta H_v^0 [(1 - \epsilon) - (RT/\Delta H_v)(1 - \epsilon) \epsilon] \quad (4)$$

where ΔH_v^0 is the correct heat of vaporization. The first term in the square bracket is due to the error in V'' and, in our examples, it accounts for about 90% of the total. The second term arises from the error in the derivative. It is small as we would expect since the error in P is relatively constant and varies only slowly with T , compared to the slope of the vapor pressure curve. Thus a 2% error in P results in about a 2% error in ΔH_v^0 . At present, we are not aware of any experimental measurements of ΔH_v^0 for these fluids, which would allow comparisons with the values calculated using different vapor pressure curves.

However, other calculated properties can also be affected. We may approximate, for the heat capacity of the liquid,

$$C_p' = T \Delta S' / \Delta T \quad (5)$$

where $\Delta S'$ is the change in the entropy of the saturated liquid for a small temperature change, ΔT . At low pressures and temperatures the correction term omitted in equation (5) is negligible. Since the entropy of the saturated liquid is a state function we could calculate $\Delta S'$ by any of a number of different paths. As an example, one such path results in the relationship,

$$C_p' = C_v'' + (RT/V'')(dV''/dT) - T(dV''/dT)(dP/dT)_o - V''T(d^2P/dT^2)_o \quad (6)$$

where C_v'' is the constant volume heat capacity of the vapor. It is easily calculated for our conditions from a simple gas-phase equation of state, provided that the ideal gas heat capacity is known. For the low gas-phase densities encountered here it is very nearly equal to the ideal gas heat capacity. The only approximation in equation (6) is the assumption, in the second term on the right side, that the vapor is an ideal gas. The error introduced by this approximation is negligible in the limit of low reduced

temperature. Evaluation of the four terms on the right hand side of equation (6) for a typical case at low reduced temperatures reveals that the relative magnitudes are approximately in the ratio: 0.57 : 0.68 : 8.9 : 7.8. Thus we see that the behavior of C'_p is dominated by the third and fourth terms and is the small difference between two large terms, both of which involve derivatives of the vapor pressure curve.

The constant pressure heat capacity of R134a in the liquid phase has been measured by Saitoh et al. [7] at temperatures greater than 276 K. The vapor pressure at this temperature is a little over 300 kPa; thus these measurements lie outside the pressure range of our ebulliometer. We have, however, combined our ebulliometric measurements with our static measurements at higher temperatures, ref. [2], and we can make a comparison with calculated values of C'_p based on that curve. In addition, Magee [8] has measured C'_v for R134a in the compressed liquid phase. Magee's measurements extend down to a temperature of 180 K where the vapor pressure is about 1 kPa. We can extrapolate his measurements to the vapor pressure curve to obtain C'_v for the saturated liquid. In order to compare our calculations with C'_v measurements we needed an equation of state for the liquid phase. Here we have used an equation from Huber [9] to calculate the ratio C'_p/C'_v and thus obtain C'_p . Magee also measured values of the heat capacity of the saturated liquid, $C_o(T)$. For most of our range of interest C_o is a very good approximation of C'_p (C_o is in fact the quantity actually calculated in equation (5)), and thus Magee's measurements are valuable input for deciding between the various vapor pressure equations.

Comparisons

Figure 3 shows a comparison between the measured and calculated heat capacities for liquid R134a. The experimental data are from Saitoh and the two types of measurements of Magee, described above. The calculated curves are from a thermodynamics package which uses the ideal gas heat capacity from Goodwin and Moldover [11], a virial equation of state surface [12] for the gas, and several different vapor pressure curves. The baseline represents the results using our vapor pressure equation in ref. [2]. The agreement with the experimental values is quite good, especially with the directly measured C_o data. At low temperatures the C'_p values derived from the C'_v data deviate somewhat. We suspect that these deviations result from imperfections in the equation of state that was used to convert the C'_v data to C'_p values. This conversion requires two derivatives of the PVT surface which must be evaluated at an edge of the surface. In addition, there was probably a paucity of PVT data in this region when the equation of state was constructed. Overall, the agreement is good. Figure 3 also shows the results using three other published vapor pressure curves, [6,13,14]. These curves, which were shown in figure 2, deviate from our curve in a positive direction by amounts which can be explained by the presence of volatile impurities with concentrations from 26 to 35 ppm. We see that these curves produce heat capacities which deviate in a negative direction by amounts which reach 12 % at the lowest temperature shown. The deviations become small at the highest temperatures where the vapor pressure curves all agree relatively well. Each of these vapor pressure curves is based on an independent set of experimental data. Thus it would appear that these impurities are a rather common problem.

Recently Magee and Howley [15] have published new vapor pressure data for R134a in the range 180 - 350 K. They performed a very careful purity analysis on their sample, and they claim that it contained virtually no volatile impurity. Their pressures agree with ours within 0-0.1 % in the temperature range 200 to 240 K, and this agreement supports our hypothesis that volatile impurities affected earlier static measurements. This agreement is consistent with an air impurity having an upper bound of about 1 ppm.

In the case of the refrigerant R123 we have the liquid heat capacity data, C'_p , of Nakagawa et al. [10] for comparison, shown in figure 4. The thermodynamic calculation uses the ideal gas heat capacities of Goodwin and Moldover [16] and the virial equation of state from [17]. For the calculated values on the baseline we have used our vapor pressure equation from [3], which represents our ebulliometric data at low pressures and our static measurements at higher pressures. The agreement with the experimental values is not as good as for R134a, and the deviations are systematic. Curve 1 which

uses vapor pressures from [14] is the result of a correlation of a number of vapor pressure data sets. Some of these data appear to show the effects of volatile impurities and some do not. The correlation averages the effects, and shows deviations similar to the curves in figure 3 at low temperatures. Curve 2 is from the recent publication of Piao et al. [18]. It is based only on data above 308 K, and it has not been extrapolated downward in temperature. All of the calculated values agree quite well above 350 K, and the differences from the experimental heat capacity data are difficult to explain. These differences appear to be too large to be attributed to uncertainty in the ideal gas heat capacities. They might arise from an error in the gas-phase contribution in equation (6) although quite large errors in the virial coefficients would be required. The rather constant offset from the baseline in figure 4 could also be explained by a small systematic error in the heat capacity data. A resolution of this discrepancy would be very desirable since R123 is sometimes used at subambient pressures in centrifugal chillers.

Earlier, we said that in equation (5) we could neglect the correction term as being negligible.

This is true at the lowest temperatures, but for a desired accuracy level of 0.5 % in C'_p we should include this term at vapor pressures higher than about 300 kPa. Its calculation requires the derivatives $(\partial P/\partial T)_V$ and $(\partial P/\partial V)_T$ which must be obtained from a suitable equation of state for the liquid phase. This correction has been made for the comparisons in figures 3 and 4. For R134a we used an empirical equation from Defibaugh [19], while for R123 we made use of a NIST database [20]. For R134a the corrections were small (< 1%), but for R123 they reached approximately 8% at 420 K and a pressure of 1988 kPa. They may add as much as 1% to the uncertainty in the value of C'_p in the worst case, at the highest temperature. However, since all vapor pressures are compared on the same basis, the relative positions of the curves in figures 3 and 4 would be unaffected.

Equations (1) and (2), in a corresponding states sense, are accurate asymptotically in the low temperature limit. As the reduced temperature increases, they become more approximate. This happens in several ways. The factor of (3/2) in eqn. (2) tends to a value of 2 as the temperature approaches the critical temperature of the refrigerant. However, we must also consider the Henry's constant for air dissolved in the refrigerant, which was assumed to be infinite in the equations. Its value decreases as the vapor pressure increases until it reaches a small finite value at the solvent's critical point, and the distribution coefficient, χ''/χ' , approaches unity. Thus the solubility of the air in the liquid phase would modify the calculations somewhat and reduce the effect of the impurity. In the critical region itself other factors become important. For the thermodynamic properties of dilute solutions near the solvent's critical point the reader may refer to a recent publication by Levelt Sengers [21]. For the present work, we terminate our calculations at a temperature where the vapor density is no longer low enough to be adequately calculated by means of a virial equation of state truncated after the third virial coefficient.

One other point deserves comment. In equation (1) we see the factor $\bar{\rho}/(1 - \bar{\rho}/3\rho_c)$. We said that the situation $\bar{\rho} = \rho_c$ is common in reported measurements because this filling density provides the convenience of allowing vapor pressure data to be measured right up to the critical temperature without adding or removing sample. However, we may note that for a given χ , δP in static measurements can be minimized by minimizing the value of $\bar{\rho}$. Therefore for the best results, one should place only a very small amount of liquid in the sample chamber. Two difficulties are encountered when applying this technique. First, after only a short temperature interval more sample must be added in order to stay on the vapor pressure curve. Second, experience has shown that when the volume of the liquid phase becomes a very small fraction of the total one often measures pressures that are too low, due presumably to surface tension effects when the liquid collects in cracks, crevices or corners of the apparatus. The best technique is the removal of the impurity during the filling process.

Conclusions

We have shown that discrepancies between precise vapor pressure data from different laboratories can be explained by the presence of volatile impurities, probably air. At low reduced temperatures, where the vapor pressures are low, very small concentrations of air can have relatively large effects on the assumed vapor pressure curve, which can in turn affect some of the calculated thermodynamic properties used in refrigeration cycle design. Larger quantities of impurity, 200 ppm for example (0.9998 purity), cause appreciable effects at pressures as high as 10 bar. We have also shown that the use of a dynamic measurement technique for vapor pressures can help to avoid these difficulties. We

have applied the calculations to the available data for the refrigerants R134a and R123.

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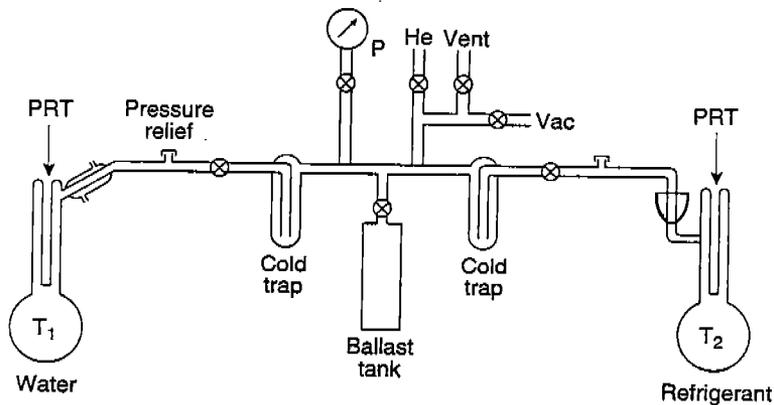


Figure 1. Schematic diagram of the ebullimeter apparatus.

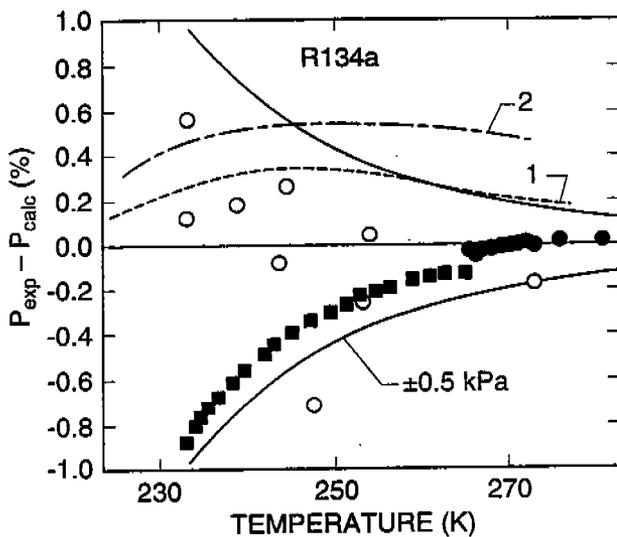


Figure 2. Deviations of our vapor pressure measurements from the curve in ref. [6] for R134a; ● ■ data from [2]; 1 - ref [13], 2 - ref [14].

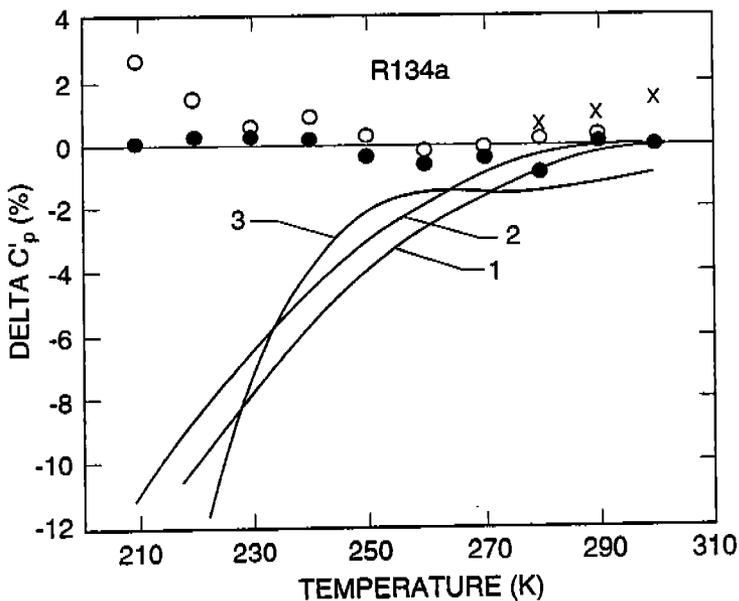


Figure 3. Deviations of liquid-phase heat capacities from the values calculated with our vapor pressure curve, [2] for R134a; 1 - ref [6]; 2 - ref [14]; 3 - ref [13], ● ● ref [8], X ref [7].

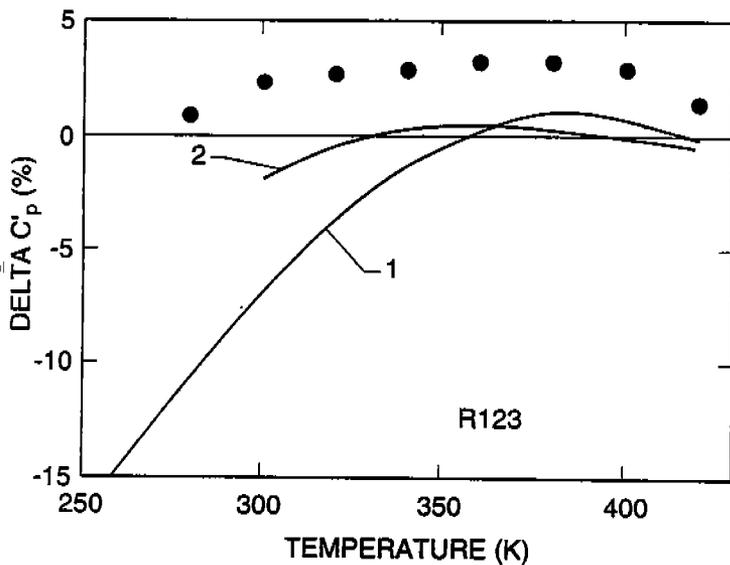


Figure 4. Deviations of liquid-phase heat capacities from values calculated with our vapor pressure curve in ref [3] for R123; 1 - ref [14], 2 - ref [18], ● ref [10].