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REPORT ON THE DESIGN AND TESTING OF A NEW HIGH PRESSURE EBULLIOMETER FOR STUDYING THE THERMODYNAMICS OF REFRIGERANT MIXTURES

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ABSTRACT

We describe the design and testing of a new all-metal differential ebulliometer which is capable of working in the range 230 to 400 K at pressures to 3 MPa. It can be used to measure pure fluid vapor pressures and P, T, x, y and infinite dilution activity coefficient data for binary mixtures. Tests for superheating and adjustments for condensed vapor holdup are described. Results are shown for pure refrigerant vapor pressures and for the vapor-liquid equilibrium conditions of the system R22 + R143a at 272 K.

INTRODUCTION

An ebulliometer is an instrument used to measure the boiling temperature of a liquid at a selected superimposed pressure. In construction, it is similar to an ordinary open reflux condenser/boiler that operates at ambient pressure. Modifications such as sophisticated design, pressure control, energy flux control, and accurate temperature measurement transform an ordinary laboratory apparatus into a precision measurement device. Because the liquid is actively boiling in the apparatus, this technique is known as a "dynamic" one to distinguish it from "static" techniques in which the liquid is quiescent.

Ebulliometry is a relatively old technique [1], and many different boiler designs have evolved. The goal of any design is the promotion of smooth, even boiling and the minimization of superheating. The two main applications are the study of the boiling points of pure fluids and of binary mixtures. The results of these measurements are the vapor pressures of pure fluids and the determination of the thermodynamic properties of binary mixtures through the measurement of the limiting activity coefficients of the two components at infinite dilution, γ_i^∞ and γ_j^∞ . These two activity coefficients of a binary system can be directly related to the two adjustable parameters in one of the widely-used models for the Gibbs free energy of mixtures, such as the Wilson equation. This model can then be used to calculate the activity coefficients and excess Gibbs free energy of the binary system at all compositions, and it can be extended to multicomponent systems once γ_i^∞ and γ_j^∞ have been determined for all binary pairs.

Most ebulliometers have been made of glass, and they have been used at pressures less than about 0.3 MPa and at temperatures from ambient up to about 373 K. In the following sections we will describe a new all-metal ebulliometer which we have built for the purpose of making measurements on pure and mixed refrigerants over a wide range of temperatures and pressures. We will describe the design and construction, calibration, and testing of its operation, and we will give some results of measurements on the binary system R22 + R143a at 272 K.

EXPERIMENTAL

Design

The technique employed here is known as comparative ebulliometry because it compares the temperatures in two boilers operating at the same pressure. The apparatus is shown schematically in Figure

1. Two boilers, fitted with reflux condensers, are connected through a manifold which contains helium gas. Each boiler employs a Cottrell, or vapor–lift pump. Electrical energy supplied by a capsule heater causes the liquid to boil in the interior of the pump which operates like a percolator–type coffee pot. Rising vapor bubbles lift slugs of liquid and vapor above the average liquid level and spray them onto the thermometer well in the upper, or equilibrium chamber. The intimate mixture of liquid and vapor in the pump facilitates equilibrium of the phases, and any superheating dissipates while the sample is rising. Platinum resistance thermometers measure the temperatures of the spray in each boiler with a precision of ± 5 mK or better. Temperatures were constant within this amount when the heater power input was varied from 5 to 30 W. The body of the boiler is a heavy–wall stainless steel cylinder fitted with a long glass window for viewing the liquid level. Each boiler is surrounded by a metal shield which is thermostated by coils containing methanol supplied by thermostated baths. The apparatus was designed to operate in the temperature range 230 – 400 K at pressures up to 3 MPa or more.

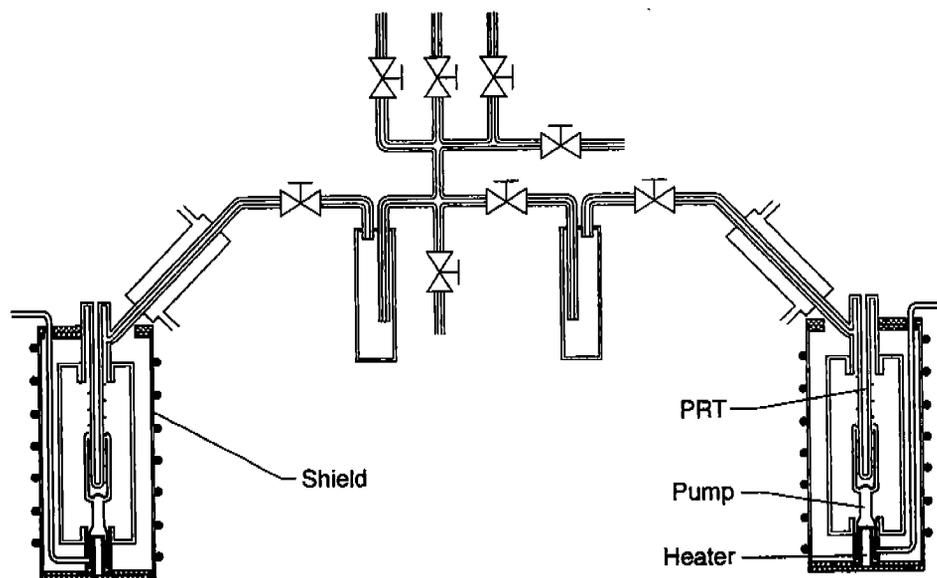


Figure 1. Schematic drawing of the metal ebulliometer.

A pressure controller sets and maintains the pressure of the helium gas with a tolerance of ± 20 Pa. This establishes the system pressure and the boiling temperature. The boiling action of the sample forces the pressurizing helium and any noncondensable impurities out of the boiler and into the manifold. A dynamic fluid interface forms in each reflux condenser. Above the interface the gas is essentially pure helium. Below the interface the gas is the condensing vapor of the fluid in the boiler. This dynamic interface has the great advantage that it eliminates the loss of sensitivity and hysteresis associated with mechanical separators that are used to isolate samples in static measurements. A small hydrostatic pressure correction accounts for the pressure difference between the condenser and the thermometer well. Two liquid nitrogen–cooled traps in the manifold ensure that there is no cross contamination between the boilers.

Operation

The apparatus can be used in either of two modes. For measuring the vapor pressure of pure fluids, a reference fluid is placed in one boiler, and the test fluid is placed in the other one. We have used R123 as a reference fluid because it has a volatility which allows the boiler to operate in a convenient temperature range. We have previously measured the vapor pressure of R123 [2]. The temperature of the boiling R123 allows accurate calculation of the system pressure. We do not rely on a pressure gage.

The apparatus can also be used to determine the bubble pressure curves of binary mixtures. In this

mode of operation, measured amounts (approximately 50 cm³, determined by weight) of the solvent are loaded into each boiler. The helium pressure is set with the controller, the reflux condensers are cooled, and the heaters are activated. After a period of time, when both boilers are operating normally, the temperature of each is measured to ensure that they are both operating at the same temperature. Then a small measured amount of the solute is added to one boiler. The equilibrium temperature, at constant pressure, of that boiler will change by a small amount, ΔT . In classical ebulliometry the solute is introduced through a septum by means of a syringe. For these studies, however, the solutes are gases at pressures in the range 0.4 – 1.6 MPa at room temperature. Therefore we have developed a solute loading system which uses a multi-port, two-position rotary valve of the type that is used in gas chromatography. Gaseous solute from a supply cylinder, at a measured pressure, is loaded into a calibrated sample loop which is connected across two ports of the valve. When the valve is rotated the solute is flushed into the boiler by helium gas supplied from a high-pressure hand pump. The pressure of the ebulliometer system is upset by this process; however, the pressure controller ejects the excess helium, and the system returns to a steady state in about 30 minutes. The exact amount of solute is determined from the measured pressure, the calibrated volume of the sample loop, and an estimated virial equation of state [3]. Several such additions are made until the total solute mole fraction is in the range 0.01 – 0.04. Then ΔT may be plotted against z_2 , the overall mole fraction of the solute (the feed fraction). The dependence of ΔT on z_2 is a nearly straight line which passes through the origin. From this curve we determine $(\partial T/\partial z_2)_P^\infty$, the slope at infinite dilution. However, this slope must be adjusted in order to obtain the desired quantity, $(\partial T/\partial x_2)_P^\infty$.

Holdup Correction

The overall mole fraction, z_2 , must be adjusted to find x_2 , the mole fraction in the liquid phase by accounting for the amount of sample elsewhere in the boiler. This adjustment is expressed in terms of the fraction, $f = n_v/n_l$, the number of moles in the "vapor" phase divided by the number of moles in the liquid phase. The "vapor" phase has two parts, the vapor volume itself (≈ 300 cm³), and the vapor which has condensed in the reflux condenser and which is running down the walls of the boiler in the form of a liquid film. The first correction is made with the aid of the virial coefficients. The second is called the holdup correction, and it must be measured in a calibration experiment.

To measure the holdup correction in this apparatus, we chose the system R124 (solute) + R123 (solvent) at a temperature of 297 K. At this temperature the system pressure was only 90 kPa (the vapor pressure of R123), and, therefore, the correction due to the vapor volume was small. Solute was added to one boiler until $z_2 \approx 0.01$. A small sample of the liquid phase was taken and analysed with a gas chromatograph. Then the entire sample was withdrawn, mixed well, and another sample was analysed. The ratio of the peak areas of these two samples determined x_2/z_2 without the necessity of finding the chromatograph response factors. The relationship between z_2 , x_2 and f has the form [4],

$$x_2/z_2 = (1 + f)/(1 + K_2^\infty f) \quad (1)$$

where $K_2^\infty = y_2/x_2$ was evaluated by the method shown below. It has the value 5.4 for this system at 297 K. Equation (1) was solved for f , and, after the small amount of sample in the vapor phase was subtracted, the liquid film in the holdup correction was found to have a volume of 1.8 cm³ when the power input to the boiler was 18 W. This volume depends on the power input and also on the heat of vaporization of the liquid. The power input is kept constant, and a small correction is made for the heat of vaporization of the system. Then knowledge of the liquid density, estimated via a properties package such

as REFPROP [5], allows the determination of the number of moles of condensed vapor. This quantity added to the amount of free vapor allows the holdup correction to be determined for any system. Because K_2^∞ is usually also unknown, the solution for x_2 involves an iterative solution of Eqs.(1,2,5). Since the working pressures in these measurements are higher than those usually encountered in ebulliometry f also has a larger value, in the range 0.05 – 0.40. The difference between z_2 and x_2 also depends on the relative volatility of the components and it varies from 0 (same volatility) to about 25%. The liquid holdup constitutes an important correction, and it justifies the considerable effort expended in its determination. It makes possible the calculation of $(\partial T/\partial x_2)_P^\infty$, the initial slope of the bubble curve, from the experimental measurements.

Analysis

The relationship between the initial slope of the bubble curve and the activity coefficient was given by Gautreaux and Coates [6] and Eckert and coworkers [7]. It has the form,

$$\gamma_2^\infty = \frac{\varphi_2 P_1^\sigma}{\varphi_2^\sigma P_2^\sigma} \left[\frac{1 - \left[1 - \frac{P_1^\sigma v_1}{RT} + \frac{P_1^\sigma}{\varphi_1^\sigma} \left(\frac{\partial \varphi_1}{\partial P} \right)_T^\sigma \right] \left(\frac{d \ln P_1^\sigma}{dT} \right) \left(\frac{\partial T}{\partial x_2} \right)_P^\infty}{\exp[(P_1^\sigma - P_2^\sigma) v_2 / RT]} \right] \quad (2)$$

where P_1^σ and P_2^σ are the vapor pressures of the pure components, the φ 's are fugacity coefficients obtained from a virial coefficient model, and the v 's are liquid molar volumes. By interchanging the solvent and the solute, γ_1^∞ can also be determined.

The results are used in Wilson's [8] semi-theoretical expression for the excess Gibbs free energy for a binary mixture,

$$g^E = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \quad (3)$$

where the Λ 's are parameters related to the molar volumes and to characteristic energy differences between molecular interactions, as denoted by the subscripts. The corresponding expressions for the activity coefficients at infinite dilution are,

$$\ln \gamma_1^\infty = 1 - \ln \Lambda_{12} - \Lambda_{21} \quad (4a)$$

and

$$\ln \gamma_2^\infty = 1 - \ln \Lambda_{21} - \Lambda_{12} \quad (4b)$$

The distribution coefficient, K_2^∞ , may be found from,

$$K_2^\infty = \gamma_2^\infty \frac{P_2^\sigma}{P_1^\sigma} \frac{\varphi_2^\sigma}{\varphi_2} \exp[v_2(P_1^\sigma - P_2^\sigma)/RT], \quad (5)$$

where γ_2^∞ is a first estimate for the activity coefficient. The final values are found by iteration.

RESULTS

Figure 2 illustrates the precision and accuracy of the apparatus when measuring the vapor pressure of a pure fluid. The figure shows deviations of our data from a fitted vapor pressure curve. The data measured here are flanked on the low temperature side by measurements made in our glass ebulliometer [9], and at higher temperatures by data measured in our Burnett/isochoric PVT apparatus (static data) [10]. The figure shows that there are no systematic deviations between the three data sets. The standard deviation for the data from this metal ebulliometer is 0.02% in P.

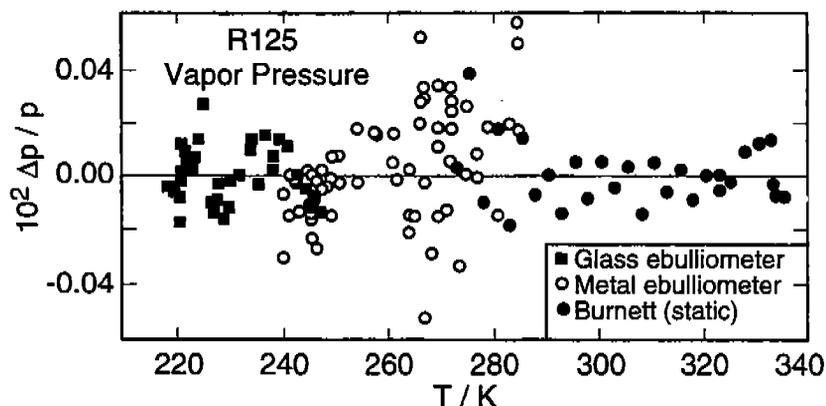


Figure 2. Deviations of the vapor pressure data for R125 from a smooth curve; comparison of three different apparatuses.

Figure 3 shows the experimental results from the metal ebulliometer for the binary system R22 + R143a at a starting temperature of 272 K. From this figure and the corrections given in Eq. (1) we obtain

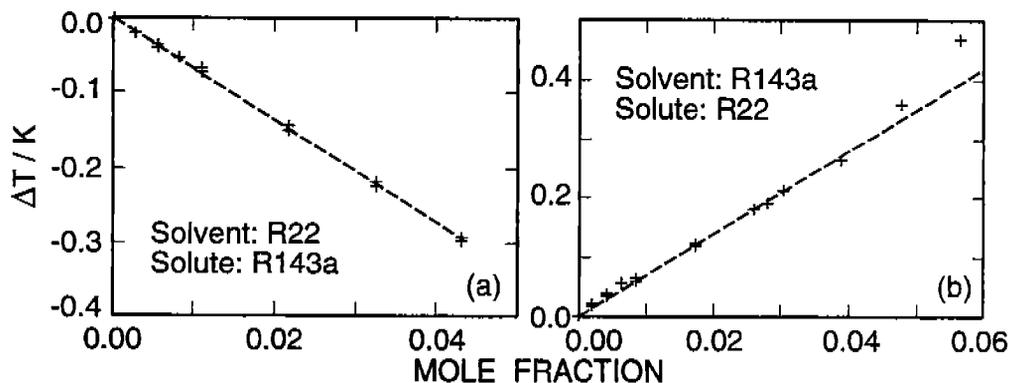


Figure 3. Experimental results for the system R22 + R143a; change in temperature at constant pressure as a function of the overall mole fraction of the solute.

$(\partial T/\partial x_1)_P^\infty$ and $(\partial T/\partial x_2)_P^\infty$. Application of Eqs. (2-5) gives the results shown in Fig.(4a-4c). Figure 4a

shows that the excess Gibbs energy is very small (< 10 J/mol) for this system, and Fig. 4b shows that the activity coefficients are very close to unity. Morrison and McLinden [11] predicted that this system would be very nearly ideal. Figure 4c shows the calculated phase boundaries at 272 K.

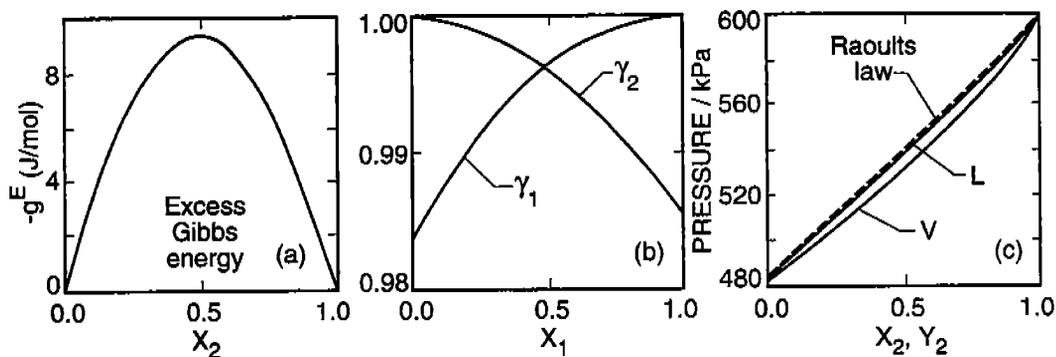


Figure 4. Calculated results for the system R22 + R143a at 272 K; (a) excess Gibbs free energy, (b) activity coefficients, (c) phase boundaries.

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