Table 2 Standard errors of flooding limit predictions

Prediction	Standard error W	Standard error %
Faghri et al.[6]	42.5	9.3
Tien and Chung[2]	99.8	16.7
Imura et al.[7]	68.1	18.2
Nejat et al.[7]	146.3	22.8
Katto and Watanabe[8]	157.7	46.8

data. The maximum error is approximately 30%, which is consistent with the original claims of accuracy of this empirical correlation.

The method presented by Katto and Watanabe[8] overpredicts most of the data by a large amount. The error tends to increase as the vapor/liquid density ratio increases. For the data with the lowest vapor/liquid density ratios (ethanol at low saturation temperatures), this model yields the best accuracy. This trend in the error can be attributed to the assumption that the liquid/vapor density ratio is sufficiently high that the liquid film thickness will not affect the vapor velocity. As a fluid approaches its critical point, the liquid film must grow thicker, resulting in higher vapor velocities and interfacial shear stresses and lower heat transport limits than those predicted by Katto and Watanabe.[8] Also, the assumption of laminar liquid flow does not agree with the visual observations of the current experiments. The higher liquid shear stress associated with turbulent flow would result in a decrease in the heat transport limits predicted by this method, and an improvement in the overall accuracy of the predictions.

Conclusions

The current study has measured the flooding limit for three fluids over a range of saturation conditions in a thermosyphon with a high fill ratio. Visual observations indicate that the transition from annular flow to churn flow occurs at a heat transport rate well below the flooding limit. Accumulation of liquid in the condenser caused abrupt increases in the thermal resistance of the thermosyphon at the flooding limit. Of the five predictive methods considered, the correlation by Faghri et al.[6] yielded the most accurate predictions of the flooding limit. The predictive method proposed by Katto and Watanabe[8] could be improved by making minor changes to the physical model.

Acknowledgment

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Measurement of Small Concentrations of Gas in a Low-Pressure Water Vapor Mixture

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Introduction

ABSORPTION of water vapor in liquid films is an important process in a chemical heat pump system such as a LiBr/water chiller, where the LiBr solution is in contact with a gas containing water vapor, a refrigerant, and other gases that do not participate directly in the absorption process (nonabsorbable gas). The nonabsorbable gas may include hydrogen gas evolving as a byproduct of the corrosion process of the construction material and/or air caused by leaks resulting from the subatmospheric pressure operation. It is well understood that the nonabsorbable gas retards the overall heat and mass transfer.[1–4] The nonabsorbable gas accumulates at the liquid–vapor interface as a result of the combined effects of convective bulk transport, along with water vapor toward the interface and the diffusion transport away from the interface. The higher concentration of nonabsorbable gas at the interface relative to that in the bulk, reduces the partial pressure of water vapor at the interface, which leads to a reduction in the absorption rate. This situation is quite similar to the condensation problem with the presence of noncondensibles.[5,6]

In 1929, Othmer[7] developed a unique method for the determination of air concentration in water vapor at moderate pressures (on the order of 1 bar). One end of a manometer is connected to liquid water, the other is connected to the air–water vapor mixture. The pressure differential indicates air partial pressure leading to a concentration measurement. The advantage of Othmer's method[7] is that it uses an apparatus that indicates the partial pressure of the air directly on the manometer to eliminate the undesirable multiplicity of corrections and tedious calibrations. The accuracy of the Othmer method[7] was claimed to be within ±0.1% on an ordinary scale, when the water vapor is slightly above 1 bar. Knowing that the typical

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absorber pressure of an LiBr chiller is approximately 0.01 bar, 1% nonabsorbable gas concentration corresponds to a manometer reading of 0.0001 bar. Therefore, the direct adaptation of Othmer's method[7] to determine the nonabsorbable concentration under a typical LiBr absorber condition can result in significant error. The major objective of this study is to devise a convenient and accurate apparatus for in-situ determination of the nonabsorbable gas concentration under an absorber condition similar to an LiBr chiller. These conditions include a nonabsorbable gas concentration of less than 10% by volume, and an absorber pressure on the order of 0.01 bar.

Experimental Method and Discussion

In this study, two different methods were employed to determine the volumetric concentration C_A of the nonabsorbable gas (air) in the absorber. One method utilized a mass spectrometer gas analyzer to determine the individual gas species contained in the gas, whereas the second, more direct and convenient method, utilized a gas sample container in which the temperature and pressure were measured before and after the enclosed water vapor was condensed. The former method provides qualitative real-time data that facilitates control of the experiment, whereas the latter method provides the desired quantitative data with good accuracy.

Mass Spectrometer Method

As shown in Fig. 1, the gas analyzer includes a leak valve, an ion pump, a small high-vacuum chamber, a quadrapole mass spectrometer total and partial pressure gauge, and a control unit. The leak valve is adjusted to continuously admit a small gas sample into the vacuum chamber, which is maintained at a pressure on the order of 10^{-10} bar by the ion pump. The quadrapole mass spectrometer partial pressure gauge is used to indicate the partial pressures of all the components in the gas sample. A typical mass spectrum, with the ordinate denoting intensity, for an air– water vapor mixture, is shown in Fig. 2. The intensities for the mass spectrum can be converted to partial pressure values by using calibration factors provided by the manufacturer. The vendor-supplied software used to control the data acquisition and reduction was modified so that the volumetric concentration of nonabsorbable gas in the sample can be determined continuously from the mass spectrum data. With this information, the relative amount of air in the absorber could be modified to achieve the desired volumetric concentration by either admitting small amounts of air through a leak valve, by decreasing the absorber pressure through additional pumping, or by changing the evaporator temperature.

The mass spectrometer method has the advantages of ease of operation, computer control, real-time data acquisition and data reduction, and several means of data output. There are several disadvantages, however, that eventually produce a less than desired accuracy and repeatability for C_A. The ion pump used to maintain the required low-vacuum pressure for the mass spectrometer gave rise to an inconsistency when trying to determine the air partial pressure as well as the total pressure. In typical ion pumps, a gas that reaches the cathode as positive ions has a high probability of being desorbed by succeeding ion bombardment. This is especially true for inert gases, such as argon, which may only be ion-pumped and then held at the cathode by the physical adsorption. Including the argon partial pressure in the calculations results in significant error in C_A.

A second procedure introduces additional uncertainty. The true intensity of a particular gas, from which the partial pressures of each species is computed, must include the intensities of its fragment ions. The process of accounting for the fragment ions is based on the expected ion fragmentation pattern, and it is highly qualitative. Two numerical integrations of the mass spectrum are required to compute the air concentration,

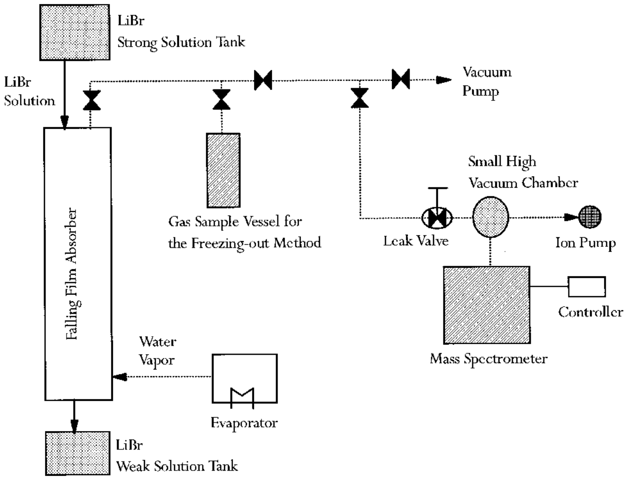

Fig. 1 Schematic of the gas analyzer setup and the freezing-out method.

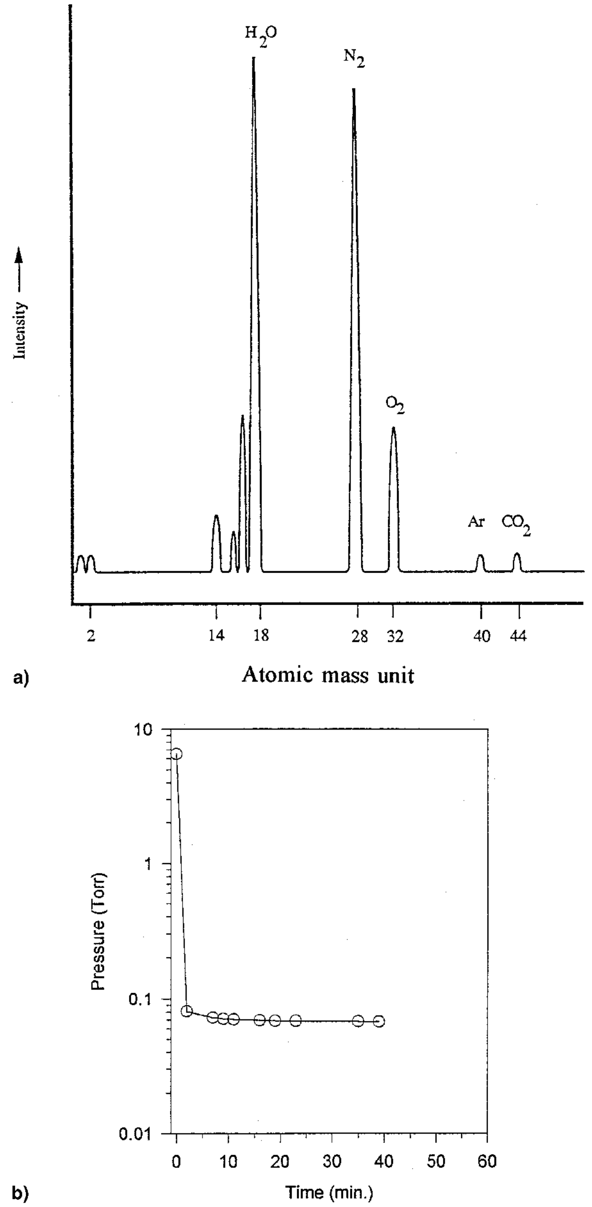

Fig. 2 a) Typical mass spectrum for an air– water vapor mixture and b) a typical pressure profile for the vessel submerged in the cold slurry.

introducing additional error. The complete spectrum must be integrated to determine total pressure, whereas mass spectrum data for the principle species in air are integrated separately. One further change had to be made in the calculation of the total pressure when integrating the entire partial pressure spectrum. The indicated partial pressure for H_2 is typically larger than could be expected, because the signal at mass number = 2 arises from many sources. Literally, any hydrocarbon that is ionized in the mass spectrometer has a fragment at mass number = 2, and these fragments are additive. The result is that the hydrogen concentration is an unknown; therefore, the integration undertaken to determine the total pressure started at mass number = 3, skipping the erroneous hydrogen data. A further complication arises from the frequent calibration required to achieve accurate measurements of the partial pressures of gases with nonoverlapping spectra. For these reasons, it was concluded that the calculated values of C_A from the mass spectroscopy analysis were not acceptable for the final data analysis; however, the qualitative results do provide information useful in experiment control.[8]

Freezing-Out Method

As the mass spectrometer was deemed inappropriate for an accurate measurement of the nonabsorbable gas concentration, an alternative method was devised for C_A measurement. The freezing-out method involved cooling an air– water vapor sample to condense all of the water vapor. The sample was contained in a stainless-steel vessel having a 10.2 cm o.d., and a height of 15.9 cm with connections for a pirani gauge, a K-type thermocouple, and a vacuum valve (for connection to the absorber and for flow control). The pirani gauge and the vacuum valve were connected to the vessel by relatively long lengths of tubing, such that both were located outside of the cold slurry container. This location prevented leakage that would result from damage to the clamping ring rubber seal by the cold slurry. Likewise, the pirani gauge must be maintained in a warm environment to remain calibrated.

Initially, the vessel was evacuated by a roughing pump, down to a pressure on the order of 10^{-2} torr. When the desired conditions were achieved in the absorber, a gas sample was admitted into the gas sample vessel. The pressure within the vessel at this point was the same as that in the absorber (approximately 7.6 torr). The vacuum valve was closed and the vessel was detached from the experimental system. The vessel was then submerged in a dry ice slurry contained in a wide-mouth dewar flask. The cold slurry (approximately -70°C) caused the water vapor within the vessel to condense and solidify, leaving a gas consisting primarily of air. The temperature T and pressure P within the vessel were recorded after the initial evacuation, following the sample addition, and at steady state following the freeze out. Figure 2 shows a representative data set for the pressure response in the vessel submerged in the cold slurry. The sharp decrease in the pressure, right after submersion, is mainly caused by water vapor condensation on the vessel inside surface.

The air– water vapor mixture was assumed to behave ideally, which is justified, based on the low pressures at the initial and final states. Neglecting the volume of the condensate, such that the condensing of the water vapor can be assumed to be a constant volume process, allows the following equation to be developed from the ideal gas equation of state:

$$C_A = V_A/V = P_2T_1/P_1T_2 \tag{1}$$

where states 1 and 2 represent the gas before and after the freezing process, respectively. The error introduced by not accounting for the volume of the condensate can be shown to be much less than 1%, and is therefore neglected. The gas contained in the vessel after the initial evacuation is nearly 100% water vapor, and can be accounted for in the determination of C_A. Assuming the water vapor to be an ideal gas allows Eq. (1) to be rewritten in the following form:

$$C_A = \frac{V_A}{V} = \frac{P_2(T_1T_i)}{T_2(P_1T_i - P_iT_1)} \tag{2}$$

where state i represents the initial evacuated condition before the gas sample is introduced into the vessel.

A second correction must be made to account for the partial pressure of the remaining water vapor at state 2. The saturation pressure of water vapor over ice must be subtracted from the value of P_2 to determine the actual partial pressure of air at state 2. This correction was implemented using an equation for the saturation pressure of water vapor over ice as a function of T only.[9]

One further correction must be made to Eq. (2) to account for the fact that the Pirani gauges are calibrated by the manufacturer for air. At state 1 and state i, the gas consists primarily of water vapor. Since the thermal conductivity of water is different than that for air, a correction to the pressure reading is required. The manufacturer has provided calibration data for various gases relating the measured pressure to the true pressure. These data were curve-fit over two pressure ranges, and then employed to adjust the measured pressure for the state 1 and state i conditions.

The potential error in the freezing-out method arises from four different sources: 1) the volume of the condensate, 2) the residual gas, 3) thermocouple uncertainty, and 4) the pirani gauge calibration. The water vapor residing in the valve and pirani gauge stems does not condense as readily as that in the vessel; however, the error introduced by this additional volume has been calculated to be less than 1%. As noted previously, the potential error induced by neglecting the residual gas was corrected by subtracting the partial pressure of the residual gas from the total pressure. To reduce uncertainty in the temperature measurement, the thermocouple was calibrated with a constant temperature bath to an accuracy of ±0.2°C. Finally, the manufacturer's suggested calibration corrections for the pirani gauge were implemented to eliminate errors introduced by a gas other than air.

An uncertainty analysis was performed using a typical set of data and the computational method described by Moffat.[10] The thermocouple and pirani gauge measurement uncertainties were 0.2 K and 1%, respectively. The sensitivity coefficient for P_2 is 3 orders of magnitude greater than those of the other variables, indicating that C_A is most sensitive to P_2. The relative uncertainty in C_A is 2.0%, a typical value obtained for most data sets.

Conclusions

Two methods have been introduced for determining the air concentration in an air– water vapor mixture at low pressure when the air concentration is less than 10% by volume. The mass spectrometer method is fairly difficult to employ, requires frequent calibration, and depends upon predicted ion fragmentation data. Thus, the method provides only qualitative data; however, the data may be used for comparative purposes and for experimental control. The freezing-out method is simple, inexpensive, and requires a minimal amount of measured data. However, the method does not provide a direct measurement of air concentration. The air concentration, determined by the freezing-out method, has a low uncertainty that depends only on the temperature and pressure measurement uncertainty.

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