Proceedings of ICEC 24-ICMC 2012, edited by K. Funaki, A. Nishimura, Y. Kamioka, T. Haruyama and H. Kumakura

Phase Equilibria in Binary Mixtures at Cryogenic Temperatures

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Mixed-Gases are in use as cryogens in Joule-Thomson (JT) cryocoolers due to their enhanced performance relative to pure gases. In the present paper the phase equilibria in binary mixtures is calculated by different methods at cryogenic temperatures. The analysis indicates the preferable methods for calculating the vapor and liquid lines. Experimental verifications with JT cryocooler and nitrogen – ethane mixtures are conducted.

INTRODUCTION

Mixed Refrigerants for Joule-Thomson (JT) cryocoolers are widely investigated for various cooling temperatures. While pure nitrogen and argon are usually in use for cooling to 80 – 100 K, mixed gases are proposed to improve the pure refrigerants performance. Binary mixtures are not the optimum refrigerants for cooling from normal ambient temperatures down to about 80 K; however, they can be analytically investigated in a more convenient manner. Xu et al. have investigated the vapor-liquid and vapor-liquid-liquid equilibrium of flammable [1] and non-flammable mixtures [2]. Hwang et al. have investigated the freezing temperatures of mixtures for JT cryocoolers [3]. In the current work the vapor-liquid equilibrium and solid-liquid equilibrium of nitrogen-methane and nitrogen-ethane are calculated by different methods [4]. Experimental verifications of nitrogen-ethane mixtures were conducted.

VAPOR-LIQUID EQUILIBRIUM (VLE)

The starting point for all vapor-liquid calculations is the equilibrium criterion:

$$\bar{f}_i^L\left(T,p,\underline{x}\right)=\bar{f}_i^V\left(T,p,\underline{y}\right) \tag{1}$$

where $\bar{f}_i$ is the molar fugacity of a species i with the superscripts L and V refer to the liquid and vapor phases, respectively. T is the temperature, p is the pressure, $\underline{x}$ is the set of liquid phase mole fractions, and $\underline{y}$ is the set of vapor phase mole fractions.

Ideal Mixtures

If the liquid forms an ideal mixture the Raoult's law is obtained:

$$x_i p_i^{vap}\left(T\right)=y_i p=p_i \tag{2}$$

$$\sum_i x_i p_i^{vap}\left(T\right)=\sum_i p_i=p \tag{3}$$

where p_i^{vap} is the vaporization pressure of species i. The composition of the liquid phase for a given temperature and a given pressure is calculated by Eq. (3). In cases where the temperature is out of range and pi vap is unavailable, an extrapolation of p_i^{vap} is used. The composition of the vapor phase is found by Eq. (2).

Φ-Φ Method

In this method the fugacity of each species in both phases is calculated by an equation of state. In the current research the fugacity of the species in the liquid phase is assumed to be equal to p_i^{vap}, while the Peng-Robinson Equation of State (PREOS) is used for calculating the fugacity in the vapor phase:

$$\ln\frac{\bar{f}_i^V(T,p,\underline{y})}{y_i p} = \ln\phi_i^V = \frac{B_i}{B_{mix}}\left(Z_{mix}^V - 1\right) - \ln\left(Z_{mix}^V - B_{mix}\right) - \frac{A_{mix}}{2\sqrt{2}B_{mix}}\left[\frac{2\sum_j y_j A_{ij}}{A_{mix}} - \frac{B_i}{B_{mix}}\right]\ln\left[\frac{Z_{mix}^V + \left(1+\sqrt{2}\right)B_{mix}}{Z_{mix}^V \quad \left(1-\sqrt{2}\right)B_{mix}}\right] \tag{4}$$

where

$$A_{mix} = \frac{\sum_i\sum_j y_i y_j \sqrt{a_i a_j}\left(1-k_{ij}\right)}{(RT)^2}p \tag{5}$$

$$B_{mix} = \frac{\sum_i y_i b_i}{RT}p \tag{6}$$

ϕ is the fugacity coefficient, R is the universal gas constant, k_{ij} is the binary interaction coefficient, and a_i and b_i are the Peng-Robinson parameters of species i. The compressibility factor, $Z_{mix,}$ is determined by the cubic form of the PREOS. In binary mixtures $y_2 = 1 - y_1$; therefore, y_1 is chosen and the vapor phase fugacity of both species are calculated at varying temperatures and constant pressure by Eq. (4). The mole fraction of each species at the liquid phase is then calculated:

$$x_i p_i^{sat}(T) = \bar{f}_i^V(T,p,\underline{y}) \tag{7}$$

and the temperature is found by satisfying $\sum_i x_i = 1$

γ-Φ Method

In this method the fugacity of each species in the liquid phase is calculated by the activity coefficient, γ:

$$\sum_i x_i\gamma_i(T,p,\underline{x})p_i^{vap}(T) = p \tag{8}$$

where γ_i is the activity coefficient of species i. There are different methods to determine the activity coefficient. In the current research we used the van Laar equation:

$$\ln\gamma_1 = \frac{\alpha}{\left[1+\frac{\alpha}{\beta}\frac{x_1}{x_2}\right]^2} \quad \text{and} \quad \ln\gamma_2 = \frac{\beta}{\left[1+\frac{\beta}{\alpha}\frac{x_2}{x_1}\right]^2} \tag{9}$$

where the parameters α and β are calculated using the van der Waals parameters a_i and b_i:

$$\alpha = \frac{b_1}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \quad \text{and} \quad \beta = \frac{b_2}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \tag{10}$$

SOLID-LIQUID EQUILIBRIUM (SLE)

The freezing line of each species is calculated as follows:

$$\ln x_i\gamma_i = -\frac{\Delta H_{fus}}{R}\left[\frac{T_m - T_f}{T_m T_f}\right] \tag{11}$$

where T_m is the melting temperature of the pure species, T_f is the freezing temperature of the solute, ΔH_{fus} is the heat of fusion, where all are assumed to be pressure independent. The activity coefficient in this case is calculated according to the regular solution theory.

EXPERIMENTAL VERIFICATION

In order to verify the analytical investigation conclusions, nitrogen – ethane mixtures with three different compositions (in molar fractions) were tested: $0.75N_2 - 0.25C_2H_6$, $0.5N_2 - 0.5C_2H_6$, and $0.3N_2 - 0.7C_2H_6$. The experiments were conducted with an oil-free compressor that includes pressure transducers at the high and low pressure connections. A single JT cryocooler was used for all experiments. The steady state cooling temperatures at evaporator pressures of 0.19 and 0.21 MPa were measured and further compared with the calculated phase diagram. The evaporator pressure is the summation of the measured compressor low pressure and the pressure drop in the JT cryocooler heat exchanger. The pressure drop in the heat exchanger has been evaluated by operating the cryocooler with pure nitrogen while exposed to the ambient pressure and measuring the cooling temperature (which equals the boiling temperature at the evaporator pressure). During the experiments with the mixtures the high pressure has been kept above the minimal required value to enable steady cooling.

RESULTS AND DISCUSSION

Fig. 1 shows the phase diagram of nitrogen – methane mixtures. The phase diagram is calculated at 0.1 MPa and includes the results of the following methods: ideal mixture, ϕ-ϕ method, γ-ϕ method, and REFPROP® results. All vapor lines are similar; however, calculating the vapor line by the γ-ϕ method at low nitrogen concentration is difficult. The different liquid lines have small deviations from each other, especially the line calculated by REFPROP. The example of nitrogen – methane mixtures brought us to the conclusion that the ϕ-ϕ method should be used for calculating the vapor line and the γ-ϕ method should be used for calculating the liquid line. The freezing line is well below the liquid line; therefore, the nitrogen – methane mixture composition is not limited by solidification considerations.

Fig. 2 shows the phase diagram of nitrogen – ethane mixtures. The phase diagram is calculated at 0.1 MPa and includes the results of the following methods: ϕ-ϕ method, γ-ϕ method, and REFPROP® results. Once again, all vapor lines are similar with difficulties for the γ-ϕ method at low nitrogen concentration. However, the liquid line predicted by REFPROP has larger deviations from the other liquid lines in relation to nitrogen – methane mixture. In addition, the REFPROP liquid line is lower than the freezing line at low nitrogen concentrations up to equal-molar mixture which means that these compositions are not suitable for JT cryocooling.

Fig. 3 shows experimental results of JT cooling with nitrogen – ethane mixtures compared to the liquid lines calculated both by γ-ϕ method and REFPROP. The results are at 0.19 and 0.21 MPa, according to the experimental conditions. Three mixtures with different compositions (in molar fractions) have been tested: $0.75N_2 - 0.25C_2H_6$, $0.5N_2 - 0.5C_2H_6$, and $0.3N_2 - 0.7C_2H_6$. The accuracy of the nitrogen mole fraction in the experiments is estimated in ± 0.05 and the accuracy of the measured temperature is ± 2°, mainly due to the uncertainty of the pressure in the JT cryocooler evaporator. Fig. 3 proves that the γ-ϕ method provides satisfactory prediction of the cooling temperature while the REFPROP results have significant deviation in relation to the experimental results.

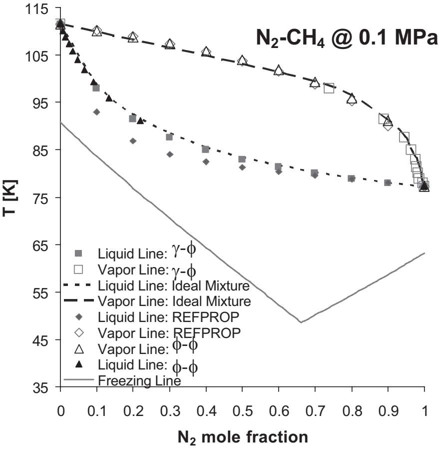

Figure 1 N_2-CH_4 phase diagram at 0.1 MPa.

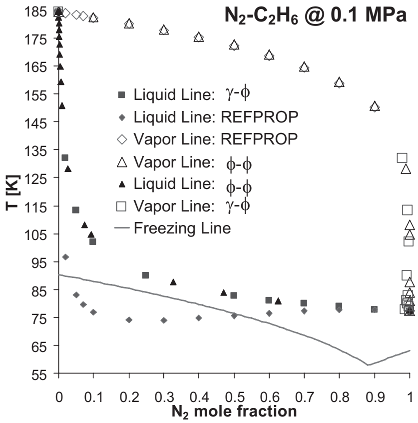

Figure 2 N_2-C_2H_6 phase diagram at 0.1 MPa.

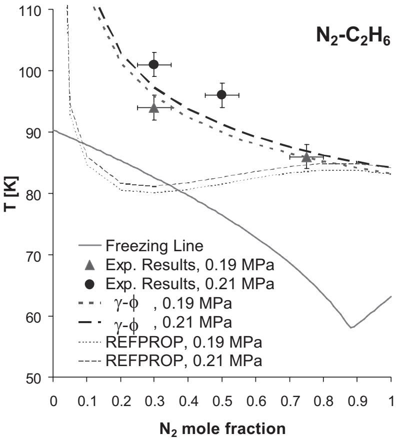

Figure 3 Experimental and calculated results of N_2-C_2H_6 mixtures at varying pressures.

SUMMARY

A few methods for calculating the VLE of binary mixtures are demonstrated. In addition, a method for calculating the freezing line is explained. These phase equilibria calculations provide the basic constrains in choosing mixed refrigerants for JT cryocoolers, according to the required cooling temperature and avoiding solidification. The vapor line is insensitive to the calculation method used; however, it has minor significance for JT cryocooling. In this research the γ-ϕ method has been found the most convenient for calculating the liquid line which has a significant role in determining the cooling temperature. In addition, experimental results of nitrogen- ethane mixtures show good agreement with γ-ϕ method calculated results.

REFERENCES

1. Xu, M., He, Y., and Chen, Z., Analysis of using binary cryogenic mixtures containing nitrogen and alkanes or alkenes in cryocoolers, Cryogenics (1996) 36 69-73
2. Xu, M., He, Y., and Chen, Z., Analysis of using binary cryogenic mixtures containing nitrogen and freon in cryocoolers, Cryogenics (1996) 36 243-247
3. Hwang, G., Lee, J., and Jeong, S., Estimation of freezing point of hydrocarbon and hydrofluorocarbon mixtures for mixed refrigerant JT cryocoolers, Advances in Cryogenic Engineering (2010), 55 95-102
4. Stanley I.S., In: Chemical, biochemical, and engineering thermodynamics 4th edition, John Wiley & Sons Inc., USA (2006)