Binary Mixed Refrigerants for Joule-Thomson Cryocooling to 80–100 K

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ABSTRACT

Cooling to 80–100 K with Joule-Thomson (JT) cryocoolers is often implemented with either of two pure gases: nitrogen or argon. Alternatively, mixed gases are suggested as refrigerants. Usually, a mixture with 2 – 3 components is applied in open cycle cryocoolers operating at elevated pressures. The mixed refrigerant objectives are to reduce the cool-down time and to increase the total cooling duration relative to operation with pure refrigerants. Mixtures containing 4 – 7 components are usually used for reducing the operating pressures and thus suit for closed cycle cryocoolers driven by compressors.

In the present research we investigate binary mixtures, which lend themselves to analytical calculations in a convenient manner, as refrigerants for JT cryocoolers. Nitrogen, argon, methane, ethane, ethylene, and propane are considered as components. The phase diagrams at low pressures are calculated and cooling temperature aspects are discussed. The isothermal JT effects (Δh_T) are also calculated to study the cooling power of the different mixtures and the operating pressures of the different mixtures are compared to these of the pure coolants. Finally, experimental results are presented to verify some of the analytical results.

INTRODUCTION

Mixed Refrigerants for Joule-Thomson (JT) cryocoolers have been widely investigated for various cooling temperature. While pure nitrogen and argon are usually in use for cooling to 80 – 100 K, mixed gases are proposed in order to improve on the pure-refrigerant performance. Recently, Nayak and Venkatarathnam [1] have suggested nitrogen, methane, ethane, and propane mixtures and argon, methane, ethane, and propane mixtures for refrigeration temperatures between 90 to 160 K with an auto refrigerant cascade refrigerator. Walimbe et al. [2] have tested flammable and non-flammable mixed refrigerants containing nitrogen, hydrocarbons, hydroflurocarbons, and neon. While their flammable mixture has reached 65 K, their non-flammable mixtures have reached 122 K only. However, Khatri and Boiarski [3] have reported cooling down to about 80 K with non-flammable mixtures due to mixture composition and cooler design. Tzabar and Lapp [4] have demonstrated the performance of a nitrogen-neon-hydrocarbons mixture at varying conditions and a method for stabilizing the cooling temperature. Hwang et al. [5] have investigated the freezing temperature of some flammable and non-flammable mixtures with the same components as in the above-mentioned studies.

Binary mixtures are not the optimum refrigerants for cooling from normal ambient temperature down to about 80 K; however, they are easier than multi-component mixtures to

investigate analytically. Xu et al. have investigated the vapor-liquid and vapor-liquid-liquid equilibrium of flammable [6] and non-flammable mixtures [7]. There are many publications of binary mixture phase diagrams [8-11]; however, the binary mixtures have not been fully investigated as refrigerants in JT cryocoolers. In the current research binary mixtures of nitrogen, argon, methane, ethane, ethylene, and propane are considered. Their vapor-liquid equilibrium, solid-liquid equilibrium, and isothermal JT effect are calculated and discussed. Experimental verifications of nitrogen-ethane mixtures are conducted.

METHOD OF STUDY

Vapor-Liquid Equilibrium (VLE) of Binary Mixtures

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

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

where $\bar{f}_i$ is the molar fugacity of species i with the superscripts L and V referring 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.

The vapor line is found by calculating the fugacity of the vapor phase according to the Peng-Robinson Equation of State (PREOS):

$$\ln\frac{\bar{f}_i^V(T,p,\underline{y})}{y_i p} = \ln\phi_i^V = \frac{B_i}{B_{mix}}\left(Z_{mix}^V - 1\right) - \ln\left(Z_{mix}^V - B_{mix}\right)$$

$$- \frac{A_{mix}}{2\sqrt{2}B_{mix}}\left[\frac{2\sum_j y_j A_{ij}}{A_{mix}} - \frac{B_i}{B_{mix}}\right]\ln\left[\frac{Z_{mix}^V + \left(1+\sqrt{2}\right)B_{mix}}{Z_{mix}^V + \left(1-\sqrt{2}\right)B_{mix}}\right] \tag{2}$$

where

$$A_{mix} = \frac{a_{mix}p}{(RT)^2} \tag{3}$$

$$B_{mix} = \frac{b_{mix}p}{RT} \tag{4}$$

$$a_{mix} = \sum_i \sum_j y_i y_j \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{5}$$

$$b_{mix} = \sum_i y_i b_i \tag{6}$$

$$a = 0.45724\frac{R^2 T_c^2}{p_c}\left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right] \tag{7}$$

$$b = 0.0778\frac{RT_c}{p_c} \tag{8}$$

ϕ is the fugacity coefficient, R is the universal gas constant, ω is the acentric factor, k_{ij} is the binary interaction coefficient, and T_c and p_c are the critical temperature and pressure, respectively. The compressibility factor is determined by the cubic form of the PREOS:

$$Z^3 + (B-1)Z^2 + \left(A - 3B^2 - 2B\right)Z - AB + B^2 + B^3 = 0 \tag{9}$$

In a binary mixture the following relation is used:

$$y_2 = 1 - y_1 \tag{10}$$

therefore, y_1 is chosen and the vapor phase fugacities of both species are calculated at varying temperatures and constant pressure by Eq. (2). The mole fraction of each species at the liquid phase is then calculated:

$$x_i p_i^{sat}(T) = \bar{f}_i^V(T,p,\underline{y}) \tag{11}$$

Finally, the temperature is found by satisfying the relation:

$$\sum_i x_i = 1 \tag{12}$$

The liquid line is determined by the activity coefficient method. At low pressure the following relation is valid:

$$\sum_i x_i \gamma_i (T, p, \underline{x}) p_i^{vap}(T) = p \tag{13}$$

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:

$$\ln \gamma_1 = \frac{\alpha}{\left[1 + \dfrac{\alpha}{\beta} \dfrac{x_1}{x_2}\right]^2} \quad \text{and} \quad \ln \gamma_2 = \frac{\beta}{\left[1 + \dfrac{\beta}{\alpha} \dfrac{x_2}{x_1}\right]^2} \tag{14}$$

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

$$\alpha = \frac{b_1}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \quad \text{and} \quad \beta = \frac{b_2}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \tag{15}$$

The liquid line temperature is found at fixed pressure by Eq. (13).

Solid-Liquid Equilibrium (SLE) of Binary Mixtures

The freezing line of each species is calculated as follows [12]:

$$\ln x_i \gamma_i = -\frac{\Delta H_{fus}}{R}\left[\frac{T_m - T_f}{T_m T_f}\right] \tag{16}$$

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

Isothermal Joule-Thomson Effect, Δh_T

The cooling power of JT cryocoolers is determined as follow:

$$\dot{q} = \dot{m}\Delta h_T \tag{17}$$

where $\dot{m}$ is the flow rate and Δh_T is the difference between the enthalpies of the incoming and leaving flows of the cooler. The Δh_T is examined in two aspects: higher values to provide higher cooling power for constant flow rate, and avoiding a pinch point at the relevant temperature range to enable cooling down to low temperatures. The addition of components with higher boiling temperatures increases Δh_T at a given temperature and thus increases the cooling power of the cryocoolers. In the current research the Δh_T of the discussed mixtures is calculated with the REFPROP® data base for high pressures of 2.5 MPa, 3.0 MPa, and 3.5 MPa, and low pressures of 0.1 MPa, 0.2 MPa, and 0.3 MPa, although most of the discussion focuses on low pressure of 0.1 MPa.

Experimental Verification

In order to verify the analytical investigation conclusions, nitrogen – ethane mixtures with two molar compositions were tested: $0.75N_2 - 0.25C_2H_6$ and $0.30N_2 - 0.70C_2H_6$. The experiments were conducted with an oil-free compressor and a single JT cryocooler. The results are also compared to the cryocooler performances with pure nitrogen.

RESULTS AND DISCUSSION

Phase Diagram Results

Figures 1– 4 show the phase diagrams for binary mixtures of nitrogen with methane, ethane, ethylene, and propane, respectively. Figures 5–8 show the phase diagrams for binary mixtures of argon with methane, ethane, ethylene, and propane, respectively. Figure 9 shows the phase diagrams for binary mixtures of nitrogen – argon, which are usually implemented for different applications than the aforementioned mixtures. The VLE is calculated at four different pressures: 0.05 MPa, 0.1 MPa, 0.2 MPa, and 0.3 MPa, while the SLE is calculated only for 0.1 MPa assuming it is pressure-independent.

The dotted lines in the figures represent the vapor lines and the solid lines represent the liquid lines. A single solid line in each figure shows the freezing line, calculated for 0.1 MPa. All nine figures show that for all compositions an increase in pressure increases the bubble and dew points. However, the freezing lines have minimum points (the eutectic points) that are lower than the pure species melting points.

The existence of vapor-liquid-liquid equilibrium (VLLE) is usually associated with the horizontal section of the liquid lines, for example in $N_2+C_2H_6$, $N_2+C_2H_4$, and $N_2+C_3H_8$ mixtures. Although mixtures that do not form VLLE may be considered as refrigerants for JT cryocoolers, VLLE is desired in order to obtain a constant cooling temperature. In addition, refrigerants for JT cryocoolers must avoid solid phases. One should notice that some mixtures reach a solid state at particular pressures at higher temperatures than the liquid line. For example, $N_2+C_2H_6$ mixtures reach a solid state at low pressures of about 0.05 MPa for nitrogen mole fraction between 0.15 and 0.55, $N_2+C_2H_4$ mixtures reach a solid state at much higher pressures near 0.2 MPa, and all the mixtures that contain argon reach a solid state at low pressures of about 0.05 MPa for argon-enriched compositions. Thus, the phase diagrams indicate preliminary restrictions on the mixed refrigerant composition, according to the operating pressures.

Isothermal Joule-Thomson Effect Results

The isothermal JT effects of all nine mixtures mentioned above were calculated at different compositions for high pressures of 2.5, 3.0, and 3.5 MPa and low pressures of 0.1, 0.2, and 0.3 MPa. It is not possible to present all the results; therefore, they are discussed by citing only a few representative examples.
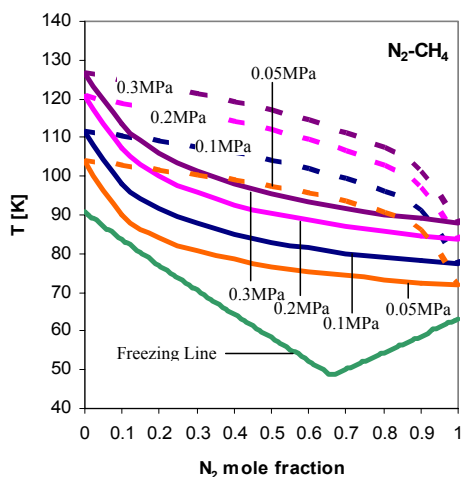

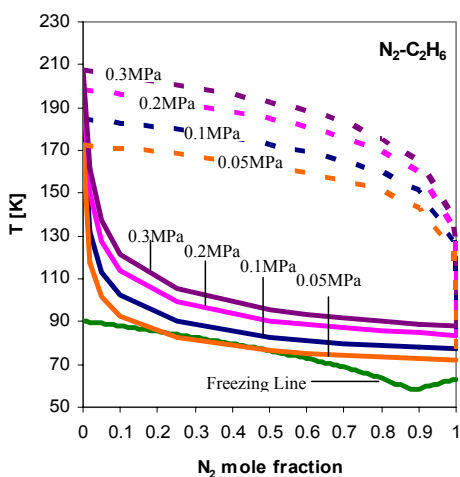**Figure 1.** N_2-CH_4 phase diagram
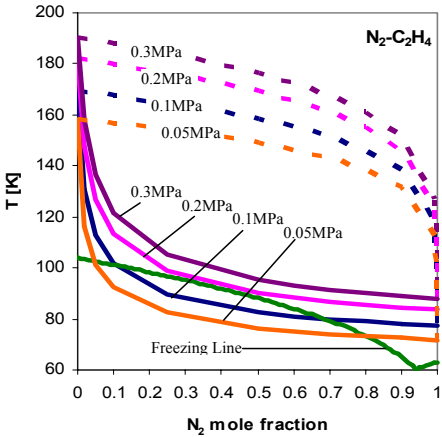

Figure 2. N_2-C_2H_6 phase diagram

Figure 3. N$_2$-C$_2$H$_4$ phase diagram
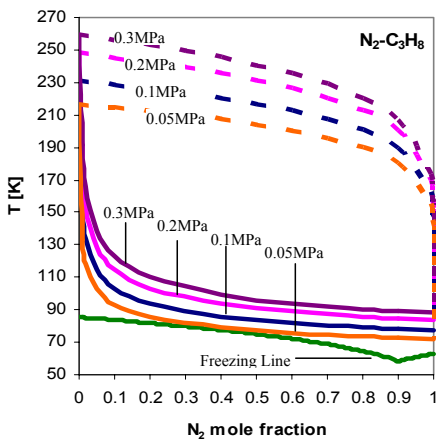
Figure 4. N$_2$-C$_3$H$_8$ phase diagram
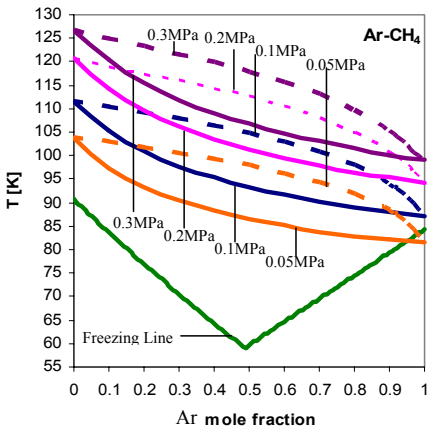
Figure 5. Ar-CH$_4$ phase diagram
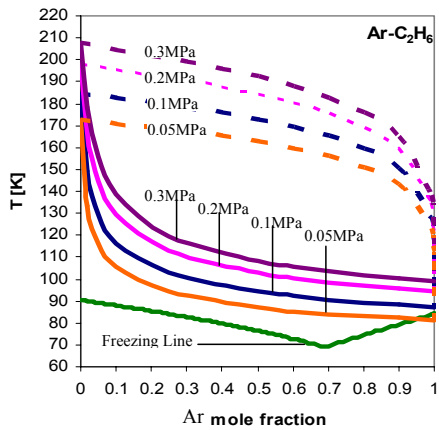
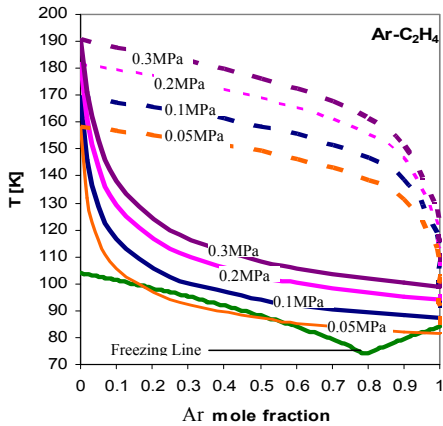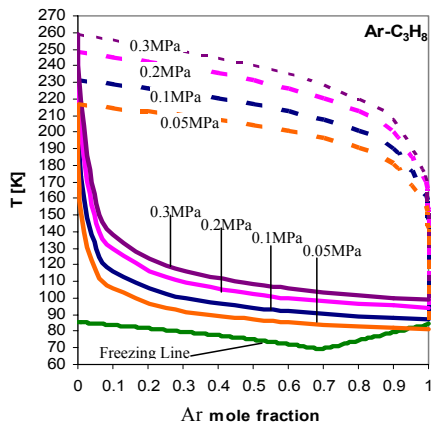**Figure 6**. Ar-C$_2$H$_6$ phase diagram

Figure 7. Ar-C$_2$H$_4$ phase diagram

Figure 8. Ar-C$_3$H$_8$ phase diagram

Species with similar boiling temperatures have similar isothermal JT effects and their mixtures have similar characteristics for the Δh_T versus T plot, as demonstrated in Fig. 10 for N_2 – CH_4 mixtures with high and low pressure of 2.5 and 0.1 MPa, respectively. Figure 10 (a) shows that, as with the pure species, the pinch points of the mixtures are at the warm end, and increase of the higher boiling temperature species concentration increases Δh_T. However, this increase of the high boiling temperature species concentration increases the cooling temperature, as shown in Fig. 10 (b). The shape of this plot is typical for mixtures that do not form VLLE. The drop in Δh_T occurs between the dew point and bubble point of the mixture with the specific composition. The shape of the curves in Fig. 10 (b) indicate that for higher concentration of the low boiling temperature species the cooling temperature is closer to the bubble point and for higher concentration of the high boiling temperature species the cooling temperature is closer to the dew point. This behavior is also obtained for N_2-Ar mixtures. The improvement of Δh_T at the warm end, which increases the cooling power of the refrigerant, is not shown here although it does exist. This aspect is discussed with reference to the next figure.

In case of a large difference between the species boiling temperatures a pinch point in the middle of the temperature range may occur, especially for mixtures that are enriched with the high boiling point species. Such a case is demonstrated in Fig. 11 for Ar-C_2H_6 mixtures in which an about equal molar composition is required to avoid the pinch point in the middle of the desired temperature range. However, two major advantages are apparent in Fig. 11: the vertical drop of Δh_T in the cold temperature is associated with the existence of VLLE that provides a stable cooling temperature, and the increase of Δh_T at the warm end, shown in Fig. 11 (b), that increases the cooling power of the cooler and enables operating in higher ambient temperatures. A similar behavior is obtained with N_2-C_2H_6, N_2-C_2H_4, and Ar-C_2H_4 mixtures. The use of ethylene instead of ethane reduces the value of Δh_T for a given composition; however, it allows higher concentrations of the high boiling point species in the mixture.

Species with a large difference between their boiling temperatures can be used as binary mixtures in JT cryocoolers only with low boiling point species enriched compositions. In the current research propane with either nitrogen or argon represent this type of mixtures. With nitrogen, propane concentration can not exceed about 70% and with argon it cannot exceed about 50%.

The influence of the operating pressures is demonstrated with 0.1Ar-0.9CH_4 mixture in Fig 12. The low temperatures region is shown in Fig. 12 (a). In this region, there is no influence of the high pressure on Δh_T while the low pressure defines the cooling temperature. Figure 12 (b) shows the high temperature region in which the low pressure has a weak influence on Δh_T while the high pressure dominates it.
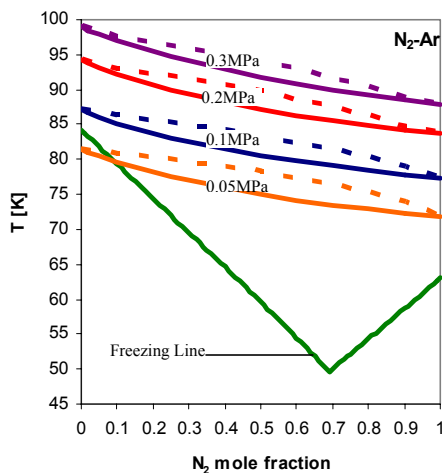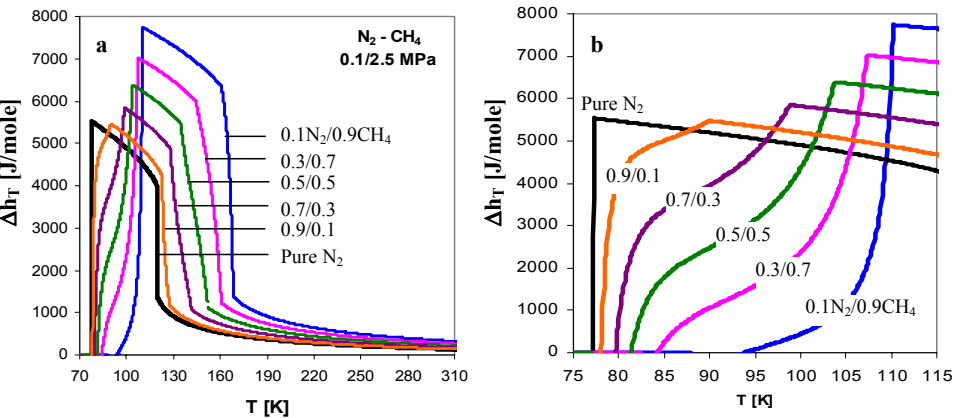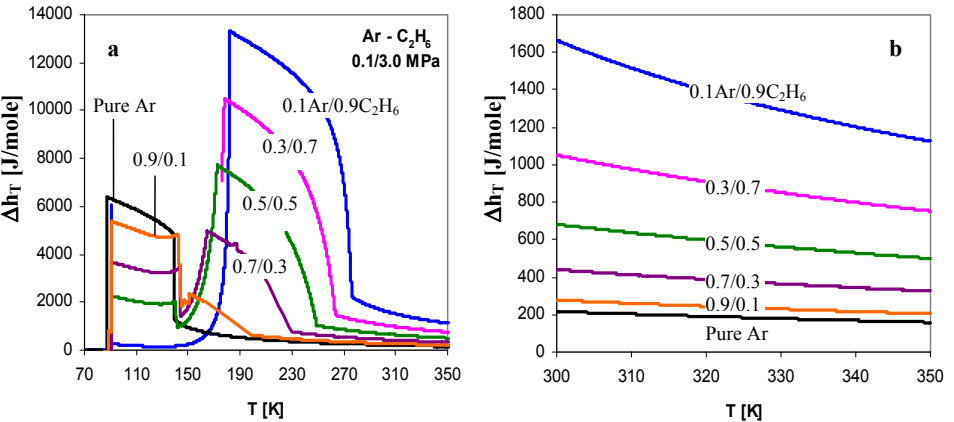

Figure 9. N_2-Ar phase diagram

Figure 10. Isothermal JT effect of pure nitrogen and N_2-CH_4 mixtures for high and low pressures of 2.5 and 0.1 MPa, respectively. (a) complete temperature range, (b) focus on cold temperatures range.

Figure 11. Isothermal JT effect of pure nitrogen and Ar-C_2H_6 mixtures for high and low pressures of 3.0 and 0.1 MPa, respectively. (a) complete temperature range, (b) warm temperatures range.
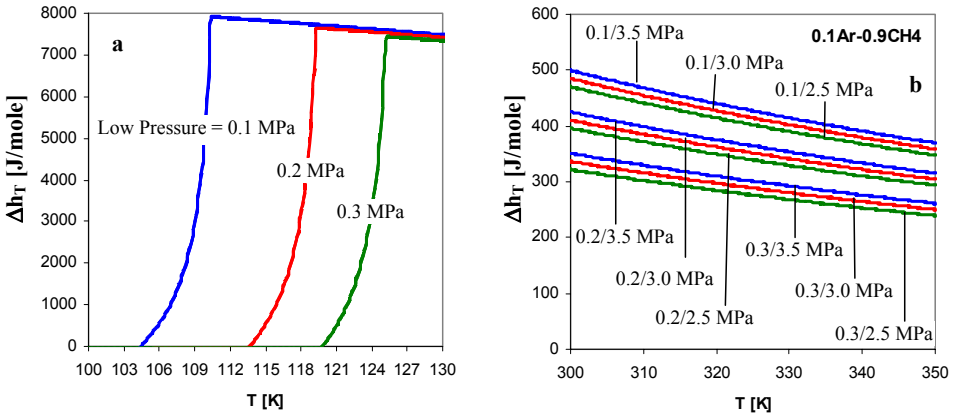
Figure 12. High and low pressures influence on the isothermal JT effect of 0.1Ar-0.9CH_4 mixture. (a) low temperature range, (b) high temperatures range.

Table 1. Operating pressures for 80 K cooling refrigerants with specific cooling power of 300 J/mol

	Pure N_2	0.18 N_2 0.82 CH_4	0.7 N_2 0.3 CH_4	0.7 N_2 0.3 C_2H_6	0.7 N_2 0.3 C_2H_4	0.36 N_2 0.64 C_3H_8	0.72 N_2 0.28 C_3H_8
p_L [MPa]	0.14	0.05	0.1	0.1	0.1	0.05	0.1
p_H [MPa]	5.3	2.3	3.8	2.0	2.4	0.6	1.5
Pressure ratio	38	46	38	20	24	12	15

Table 2. Operating pressures for 90 K cooling refrigerants with specific cooling power of 300 J/mol

	Pure N_2	0.1 N_2 0.9 CH_4	0.23 N_2 0.77 CH_4	0.52 N_2 0.48 CH_4	0.25 N_2 0.75 C_2H_6	0.51 N_2 0.49 C_2H_6	0.5 N_2 0.5 C_2H_4	0.54 N_2 0.46 C_3H_8
p_L [MPa]	0.36	0.05	0.1	0.2	0.1	0.2	0.2	0.2
p_H [MPa]	5.6	2.15	2.4	3.25	0.85	1.4	1.75	1
Press. ratio	15.6	43	24	16.2	8.5	7	8.8	5
	Pure Ar	0.32 Ar 0.68 CH_4	0.73 Ar 0.27 CH_4	0.38 Ar 0.62 C_2H_6	0.74 Ar 0.26 C_2H_6	0.74 Ar 0.26 C_2H_4	0.74 Ar 0.26 C_3H_8	
p_L [MPa]	0.13	0.05	0.1	0.05	0.1	0.1	0.1	
p_H [MPa]	4.15	2.45	3.35	1.1	2.25	2.3	1.8	
Press. ratio	32	49	33.5	22	22.5	23	18	

Table 3. Operating pressures for 100 K cooling refrigerants with specific cooling power of 300 J/mol

	Pure N_2	0.03 N_2 0.97 CH_4	0.08 N_2 0.92 CH_4	0.2 N_2 0.8 CH_4	0.24 N_2 0.76 C_2H_6	0.23 N_2 0.77 C_2H_4
p_L [MPa]	0.78	0.05	0.1	0.2	0.2	0.2
p_H [MPa]	6.0	2	2.15	2.45	0.9	1.15
Pressure ratio	7.7	40	21.5	12.25	4.5	5.8
	Pure Ar	0.06 Ar 0.94 CH_4	0.23 Ar 0.77 CH_4	0.57 Ar 0.43 CH_4	0.32 Ar 0.68 C_2H_6	0.62 Ar 0.38 C_2H_6
p_L [MPa]	0.32	0.05	0.1	0.2	0.1	0.2
p_H [MPa]	4.35	2.05	2.35	3. 05	1.0	1.85
Pressure ratio	13.6	41	23.5	15.3	10	9.25
	Pure Ar	0.16 Ar 0.84 C_2H_4	0.31 Ar 0.69 C_2H_4	0.62 Ar 0.38 C_2H_4	0.62 Ar 0.38 C_3H_8	
p_L [MPa]	0.32	0.05	0.1	0.2	0.2	
p_H [MPa]	4.35	0.9	1.15	1.95	1.4	
Pressure ratio	13.6	18	11.5	9.8	7	

Mixture compositions with their required high pressure, p_H, for specific cooling power of 300 J/mol and cooling temperatures of 80, 90, and 100 K are listed in Tables 1, 2, and 3, respectively. The low pressure, p_L, equals 0.05, 0.1, and 0.2 MPa. The operating pressures of pure nitrogen and argon are provided as well. One should notice that for all cooling temperatures N_2-CH_4 mixtures are not advantageous over pure gases, while the other mixtures allow operation with lower pressure ratios than pure gases. In addition, for all mixtures, operating with higher values of low pressures usually allows lower pressure ratios. Mixtures that are not suggested either form solid state or have a pinch point in the middle of the heat exchanger.

Experimental Results

The results for operating with pure nitrogen are shown in Fig. 13. The cryocooler operated in an open cycle with exhaust to the ambient air; therefore, the low pressure is 0.1 MPa. A minimal high pressure of 4.8 MPa is required and an attempt to reduce it to 4 MPa caused an increase in the cooling temperature. Cooling to 82 K is obtained which is associated with a back pressure in the cryocooler of about 0.17 MPa.
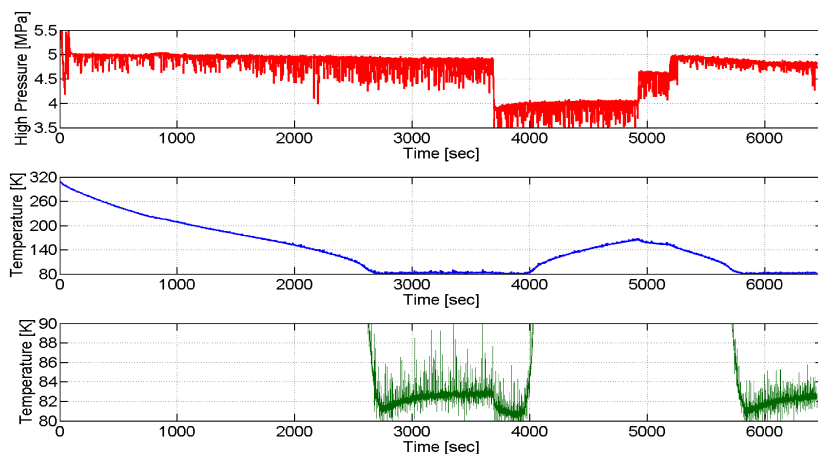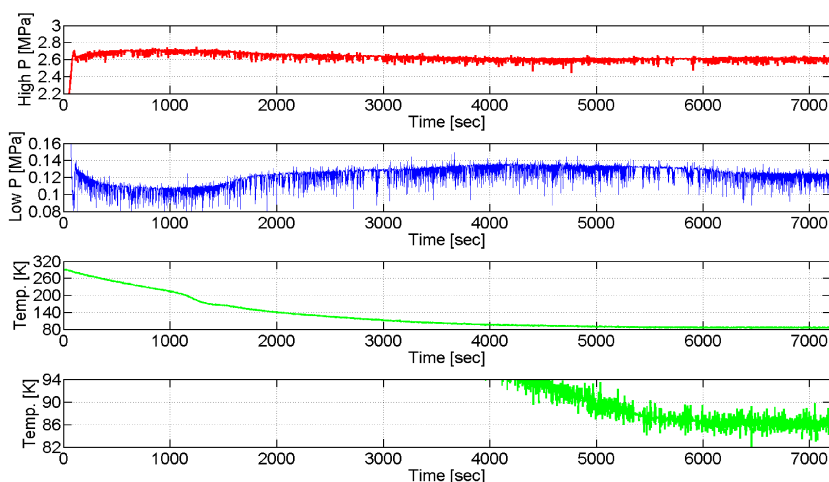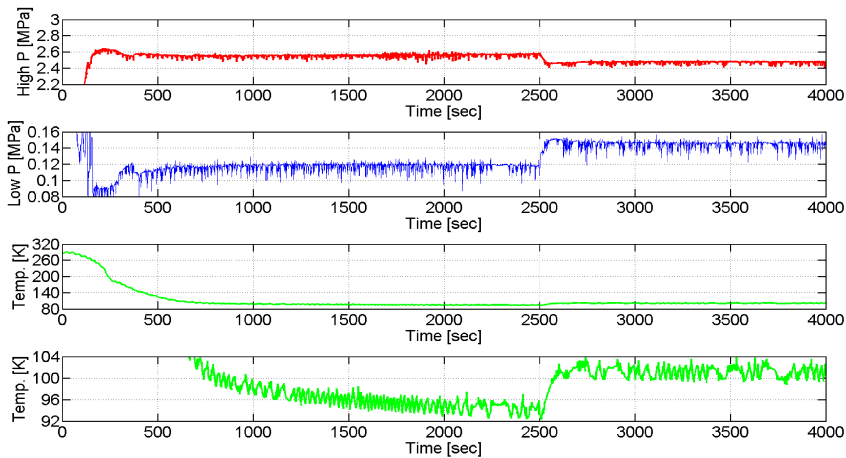
Figure 13. Experimental results for pure nitrogen.

Figure 14. Experimental results for 75%N2-25%C2H6 mixture.

Figure 14 shows the results for $0.75N_2$-$0.25C_2H_6$ mixture. Cooling to 86 K is obtained with a high pressure of 2.6 MPa only and low pressure of 0.12 MPa. Taking into account the back pressure, this cooling temperature is suitable for evaporator pressure of 0.19 MPa, in good agreement with the phase diagram in Fig. 2. Figure 15 shows the results for $0.3N_2$-$0.7C_2H_6$ mixture; 94 K is obtained for low pressure of 0.12 MPa that is associated with 0.19 MPa in the evaporator, and 101 K is obtained for a low pressure of 0.14 MPa that is associated with 0.21 MPa in the evaporator. These results are also in good agreement with the calculated phase diagram that predicts 97 K at 0.2 MPa. Both mixtures operate with a high pressure of about half that required for pure nitrogen, as predicted by the calculated isothermal JT effect.

SUMMARY

A method for calculating the VLE and SLE for plotting the phase diagram of binary mixtures is explained and demonstrated. These phase diagrams provide the basic constrains in choosing the mixture compositions according to the required cooling temperature and avoiding solidification. Furthermore, the isothermal JT effect is calculated to provide additional restrictions on the mixture compositions to avoid a pinch point in the middle of the heat exchanger temperature range. The

Figure 15. Experimental results for 30%N2-70%C2H6 mixture.

isothermal JT effect provides the cooling capacity of refrigerants, and its dependence on the operating pressures and mixture components selection is discussed. Tables 1-3 summarize the mixture compositions for cooling to 80 K, 90 K, and 100 K and their operating pressures. Finally, experimental results for two compositions of nitrogen-ethane mixtures are presented, that show a good agreement with the calculated results. These results prove the advantage of using mixed refrigerants rather than pure nitrogen.

REFERENCES

1. Nayak H.G. and Venkatarathnam G., "Performance of an auto refrigerant cascade refrigerator operating on gas refrigerant supply (GRS) mode with nitrogen-hydrocarbon and argon-hydrocarbon refrigerants," *Cryogenics*, vol. 49 (2009), pp. 350-359.

2. Walimbe N.S., Narayankhedkar K.G., and Atrey M.D., "Experimental investigation on mixed refrigerant Joule-Thomson cryocooler with flammable and non-flammable refrigerant mixtures," *Cryogenics*, vol. 50 (2010), pp. 653-659.

3. Khatri A. and Boiarski M., "Development of JT coolers operating at cryogenic temperatures with nonflammable mixed refrigerants," *Adv. in Cryogenic Engineering - CEC*, vol. 53 (2008), pp. 3-10.

4. Tzabar N. and Lapp Z., "Experimental investigation on mixed refrigerant for closed-cycle Joule-Thomson cryocoolers," *Adv. in Cryogenic Engineering - CEC*, vol. 55 (2010), pp. 1121-1128.

5. Hwang G., Lee J., and Jeong S., "Estimation of freezing point of hydrocarbon and hydrofluorocarbon mixtures for mixed refrigerant JT cryocooler," *Adv. in Cryogenic Engineering - CEC*, vol. 55 (2010), pp. 95-102.

6. Xu M., He Y., and Chen Z., "Analysis of using binary cryogenic mixtures containing nitrogen and alkanes or alkenes in cryocoolers," *Cryogenics*, vol. 36(1996), pp. 69-73.

7. Xu M., He Y., and Chen Z., "Analysis of using binary cryogenic mixtures containing nitrogen and freon in cryocoolers," *Cryogenics*, vol. 36(1996), pp. 243-247.

8. Grauso L., Fredenslund A., and Mollerup J., "Vapour-liquid equilibrium data for the system $C_2H_6+N_2$, $C_2H_4+N_2$, $C_3H_8+N_2$, and $C_3H_6+N_2$," *Fluid phase equilibria*, vol. 1 (1977), pp. 13-26.

9. Gasem K.A.M., Hiza M.J., and Kidnay A.J., "Phase behavior in the nitrogen + ethylene system from 120 to 200 K," *Fluid phase equilibria*, vol. 6 (1981), pp. 181-189.

10. Platzer B. and Maurer G., "Application of a generalized Bender equation of state to the description of vapour-liquid equilibria in binary systems," *Fluid phase equilibria*, vol. 84 (1993), pp. 79-110.

11. Carrero-Mantilla J. and Llano-Restrepo M., "Vapor-liquid equilibria of the binary mixtures nitrogen+ methane, nitrogen+ethane and nitrogen+carbon dioxide, and the ternary mixture nitrogen+methane+ ethane from Gibbs-ensemble molecular simulation," *Fluid phase equilibria*, vol. 208 (2003), pp. 155-169.

12. Stanley IS., *Chemical, Biochemical, and Engineering Thermodynamics,* 4th ed, John Wiley & Sons Inc., USA (2006).