

# Cooling Temperatures of Binary Mixed Refrigerants: Vapor-Liquid-Liquid Equilibrium versus Vapor-Liquid Equilibrium

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## ABSTRACT

Joule-Thomson cryocoolers which operate with pure gases provide stable cooling temperatures at their respective boiling points. Mixed-refrigerants have enhanced specific cooling power and they, therefore, enable operating at much lower pressures, relative to pure refrigerants. An attractive method for allowing a stable cooling temperature with binary mixed refrigerants is to choose mixtures that form vapor-liquid-liquid equilibria. In previous research, the cooling temperatures of binary mixtures were estimated by calculating their vapor-liquid equilibrium states. Recently, the vapor-liquid-liquid equilibrium of those mixtures was calculated and the current paper presents a comparison between the results of the two methods.

## INTRODUCTION

Joule-Thomson (JT) cryocoolers operating with pure gases allow steady cooling temperatures without any active control, absence of fluid composition shifts, and performance independence on ambient temperature. Nevertheless, mixed refrigerants (MR) for JT cryocoolers have been widely investigated for various cooling temperatures due to two main advantages: lower pressure ratios and higher coefficient of performance (COP). Multi-component mixtures are usually in use in order to obtain enhanced performance [1-3]. Since binary mixtures are not optimal, they are rarely considered as JT refrigerants; however, they lend themselves to analytical investigation in a more convenient manner. According to the Gibbs phase rule, binary mixtures with an equilibrium of three phases behave like a pure gas in the sense that at a fixed pressure a constant temperature phase transition is obtained. In a previous study [4], the temperatures of the phase transition for several binary mixtures were estimated by Vapor-Liquid Equilibria (VLE) calculations, which were experimentally validated. Recently, we established a method for calculating the Vapor-Liquid-Liquid Equilibria (VLLE) of binary mixtures to improve the prediction of the cooling temperature and to allow extensive search for new mixed refrigerants [5]. In the present paper we calculate the VLLE of some binary MRs, using the method we developed, and compare the results with the VLE results.

## METHOD

### Calculating VLE

The liquid line in the phase diagram is calculated by the activity coefficient method:

$$\sum_i x_i \gamma_i(T, p, \underline{x}) p_i^{vap}(T) = p \quad (1)$$

where  $x_i$  is the liquid phase mole fraction,  $\gamma_i$  is the activity coefficient,  $p_i^{vap}$  is the vaporization pressure of component  $i$ , and  $p$  is the pressure. In the current research the van Laar equation is used to determine the activity coefficients of the components in binary mixtures [6]:

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

where the parameters  $\alpha$  and  $\beta$  are functions of the van der Waals parameters  $a$  and  $b$  of each of the components.

The complete procedure for calculating the VLE of binary mixture is described in details elsewhere [4].

### Calculating VLLE

To obtain the separation of a liquid phase into two different liquid phases in equilibrium the summation of the Gibbs free energies of the two phases has to be lower than the Gibbs free energy of the single phase liquid. Therefore, it is necessary to be able to calculate the Gibbs free energy of real mixtures:

$$\underline{G} = \sum_i^N x_i \underline{G}_i + RT \sum_i^N x_i \ln x_i + \underline{G}^E \quad (3)$$

Here,  $\underline{G}$  is the total molar Gibbs energy of the mixture,  $x_i$  is the molar fraction of component  $i$ ,  $\underline{G}_i$  is the Gibbs energy of the pure component  $i$ ,  $R$  is the universal gas constant, and  $T$  is the temperature. The first term at the right side of Eq. (3) is a linear summation of the pure component properties, whereas the other two terms represent the Gibbs energy of mixing. The former of these two represents the mixing Gibbs energy for an ideal mixture whereas the latter term is the excess Gibbs energy that represents the deviation of a real mixture from an ideal one. Different methods are proposed for evaluating this excess Gibbs energy ( $\underline{G}^E$ ), and they all rely on the activity coefficients of the components. In the current research we use the two-constant Margules expansion [6]:

$$\underline{G}^E = x_1 x_2 [A + B(x_1 - x_2)] \quad (4)$$

$$\begin{bmatrix} x_2^2 & 3x_2^2 - 4x_2^3 \\ x_1^2 & 4x_1^3 - 3x_1^2 \end{bmatrix} \times \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} RT \ln \gamma_1 \\ RT \ln \gamma_2 \end{bmatrix} \quad (5)$$

Here, the activity coefficients are calculated by the regular solution theory (RST), which assumes nearly zero excess mixing entropy. According to the RST, the solubility is defined as a function of the internal energy change of vaporization, and the volume fraction of the components is defined as a function of the mixture volume. To calculate the internal energy of vaporization we use the vaporization pressure of the pure components, and the Soave-Redlich Kwong (SRK) equation of state (EOS) is used to calculate the mixture volume. The interaction parameters are then required for the SRK EOS. As a consequence, the pure component vaporization pressures and the interaction parameters for the SRK EOS are the only input data that is required, and they are readily available. The complete procedure for calculating the VLLE of binary mixtures is described in detail elsewhere [5].

In binary mixtures, a single liquid phase is separated into two liquid phases if

$$\frac{\partial^2 G}{\partial x_1^2} > 0 \tag{6}$$

Incorporating Eq. (3) and (4), applying  $x_2 = 1 - x_1$  and differentiating the result twice yields:

$$\left[ \frac{\partial^2 G}{\partial x_1^2} \right]_{T,p} = \frac{RT}{x_1(1-x_1)} + 6B - 2A - 12Bx_1 \tag{7}$$

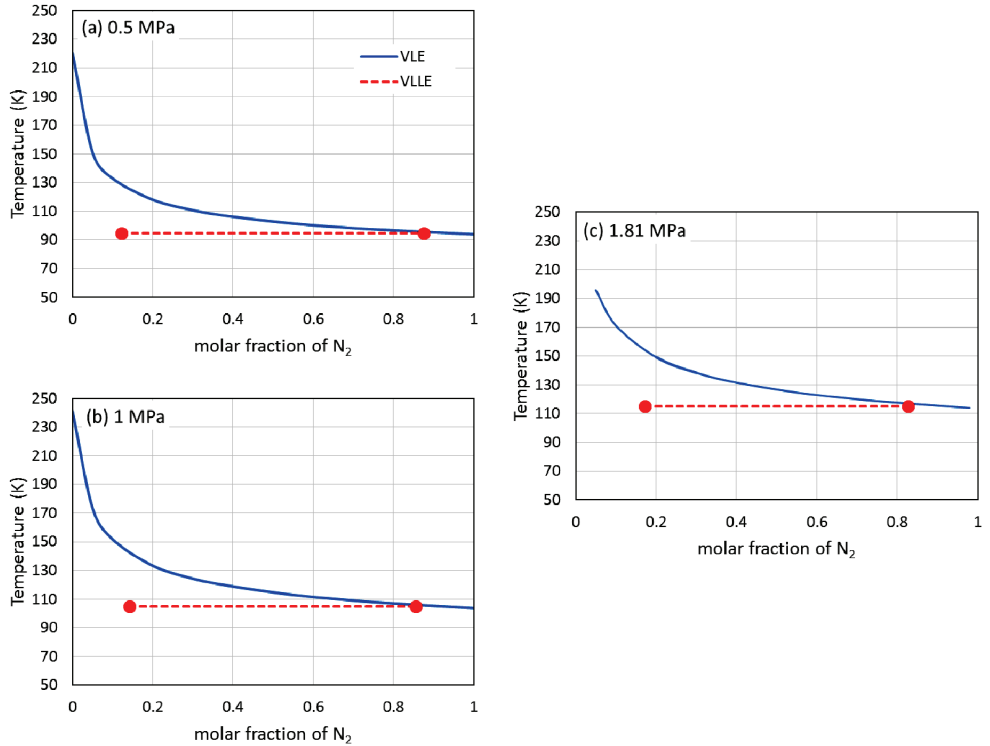
The temperature where VLLE exists is determined by:

$$f_i^{L1}(p, T, \underline{x}_1) = f_i^{L2}(p, T, \underline{x}_2) = f_i^V(p, T, \underline{y}) \tag{8}$$

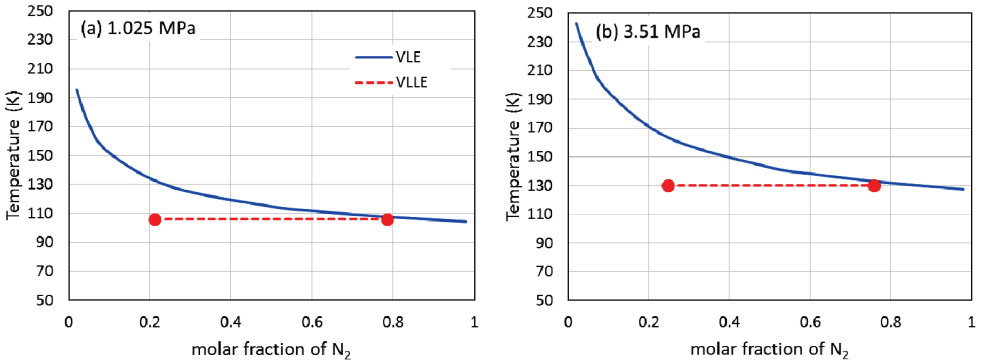
Where the superscript *L1* and *L2* denote the two liquid phases and *V* represents the vapour phase.  $f_i$  is the fugacity of component *i*.  $p$  is the pressure,  $T$  is the temperature,  $\underline{x}$  is the molar composition of a liquid phase, and  $\underline{y}$  is the molar composition of the vapor phase.

**RESULTS AND DISCUSSION**

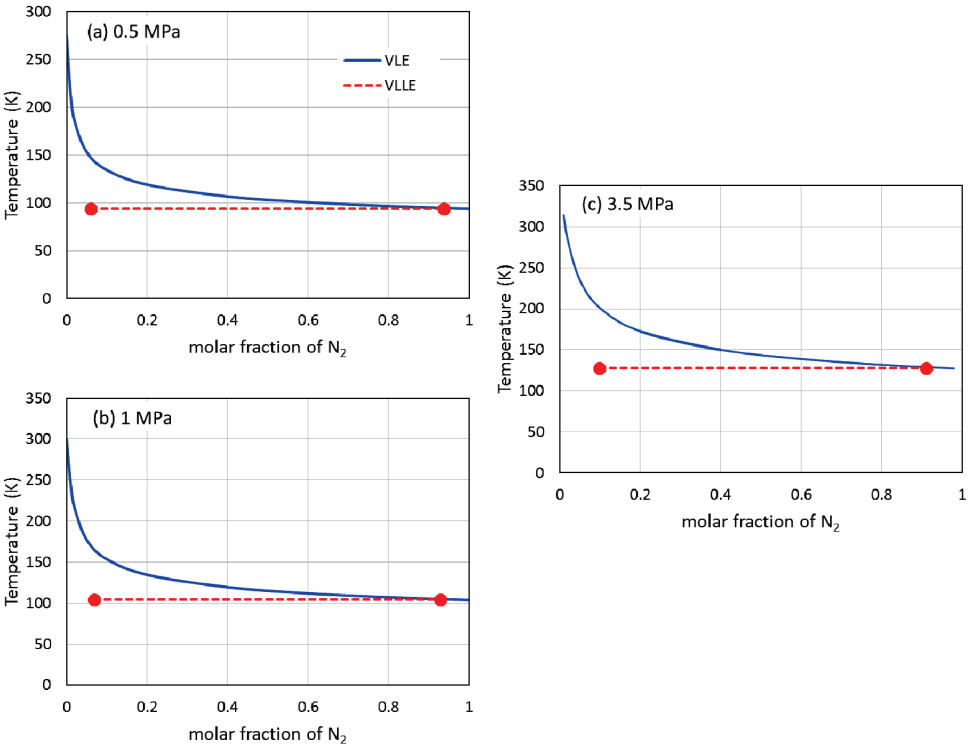
Figures 1 to 3 show comparisons between the VLE results and the VLLE results for nitrogen-ethane, nitrogen-ethylene, and nitrogen-propane mixtures, respectively. The VLE results are presented by solid lines and show the temperature of each mixture composition at a specific pressure. The VLLE results are presented by dashed lines enclosed between two big dots, which indicate the compositions of the two liquid phases. Any mixture with a composition in between (along the dashed lines) separates into these two liquid phases. The results for nitrogen-ethane mixtures, Figure 1, are given at 0.5, 1, and 1.81 MPa, the results for nitrogen-ethylene mixtures, Figure 2, are given at 1.025 and 3.51 MPa, and the results for nitrogen-propane mixtures, Figure 3, are given at 0.5, 1, and 3.5 MPa.



**Figure 1.** The liquid line of VLE calculation (solid line) versus the VLLE existence, for nitrogen-ethane mixtures at (a) 0.5 MPa, (b) 1 MPa, and (c) 1.81 MPa.

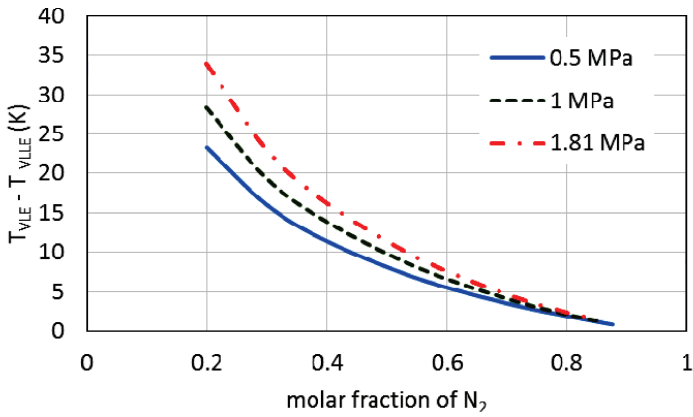


**Figure 2.** The liquid line of VLE calculation (solid line) versus the VLLE existence, for nitrogen-ethylene mixtures at (a) 1.025 MPa and (b) 3.51 MPa.

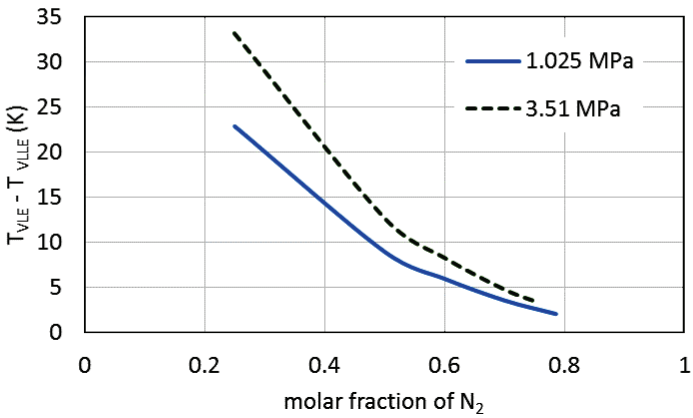


**Figure 3.** The liquid line of VLE calculation (solid line) versus the VLLE existence, for nitrogen-propane mixtures at (a) 0.5 MPa, (b) 1 MPa, and (c) 3.5 MPa.

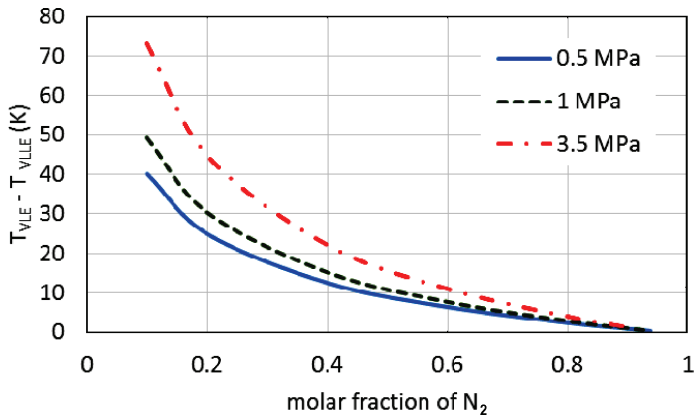
One should notice that at VLLE, all the dots which refer to nitrogen enriched compositions meet the VLE curves. Moreover, all the VLLE results show lower temperatures than the VLE results, as expected, to allow a lower free Gibbs energy, which is temperature dependent. Figures 4 – 6 show these differences for nitrogen-ethane, nitrogen-ethylene, and nitrogen-propane, respectively, at different pressures. As the molar fraction of the nitrogen decreases the difference between the VLE and the VLLE results increases. It is also evident that at higher pressures the differences between the VLE and the VLLE results are larger. The absolute differences between the VLE and the VLLE results are quite similar for the three mixtures. For example, the VLE temperatures of mixtures with



**Figure 4.** Temperature differences between VLE and VLLE calculations for nitrogen-ethane mixtures at 0.5, 1, and 1.81 MPa.



**Figure 5.** Temperature differences between VLE and VLLE calculations for nitrogen-ethylene mixtures at 1.025 and 3.51 MPa.



**Figure 6.** Temperature differences between VLE and VLLE calculations for nitrogen-propane mixtures at 0.5, 1, and 3.5 MPa.

nitrogen molar fraction of 0.3 at about 1 MPa are all about 20 K higher (19.4 K, 20 K, and 22 K for nitrogen-ethane, nitrogen-ethylene, and nitrogen-propane, respectively). Moreover, at about 1 MPa, to have a temperature difference of less than 5 K the nitrogen molar fraction has to be above 0.62, 0.64, and 0.71 for nitrogen-ethane, nitrogen-ethylene, and nitrogen-propane, respectively.

## CONCLUSIONS

JT cryocoolers that operate with MRs are aimed to reach the liquid line of the phase diagram. Using VLE calculation for binary mixtures, which actually form VLLE, provides a limited estimation of the cooling temperature. For the three mixtures presented in this paper, having a large molar fraction of nitrogen in the mixture allows a relatively small deviation between the VLE and the VLLE temperatures. It is recommended to use phase diagrams with VLE prediction to roughly estimate the cooling temperatures of binary MRs; however, it is recommended to use complete phase diagrams, which incorporate the VLLE prediction, for more accurate analyses.

## ACKNOWLEDGMENT

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