

PREDICTION OF THERMODYNAMIC PROPERTIES OF REFRIGERANTS IN THE SUPERHEATED REGION

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Abstract This paper demonstrates the capabilities of the PFGC-MES equation of state (EOS) for calculating the thermodynamic properties in the superheated region for pure refrigerants. In addition the ability of this EOS is also tested for predicting the VLE behavior of binary mixtures. For pure compounds several properties in the superheated region are predicted. The calculated results and the experimental data are presented as pressure-enthalpy diagrams and also summarized in tables for five selected refrigerants. For mixtures the predicted results for different properties are also compared with the experimental data.

چکیده با توجه به کارآیی بسیار خوبی که معادله حالت PFGC-MES در پیش بینی خواص تعادلی مواد مبرد (خالص مخلوط) از خود نشان داده است، بررسی قابلیت‌های این معادله حالت در تعیین خواص ترمودینامیکی این مواد در منطقه بس تا فته کاملاً ضروری بنظر میرسد. مقاله حاضر نتایج تحقیقات انجام شده در این موضوع را ارائه می کند. مبردهای خالص را از لحاظ ساختمان مولکولی می توان در پنج گروه مختلف طبقه بندی کرد. در این مقاله جهت ارائه نتایج از هر گروه یک مبرد انتخاب شده و خواص پیش بینی شده برای این مواد در منطقه بس تا فته در نمودارهای فشار-انتالپی ضمیمه شده است. در زمینه مخلوطها نتایج حاصل از بررسی چند سیستم ارائه شده و در هر مورد مقایسه ای بین نتایج پیش بینی شده و مقادیر تجربی نیز ارائه شده است.

INTRODUCTION

The halogenated compounds have been extensively used as refrigerants and heat transfer agents. There are also other fields in which the unusual properties of these compounds have led to significant commercial or social benefit [1]. Therefore, it is obvious that the development of equations of state to accurately describe the thermodynamic properties of these compounds is of considerable importance. Earlier work [2,3] has showed that the PFGC-MES provides an accurate method for predicting the thermodynamic properties of saturated pure refrigerants. This EOS has been also successfully applied to describe the vapor-liquid equilibria behavior of refrigerants and light hydrocarbon mixtures [4].

In this paper, the capabilities of this EOS

for predicting the thermodynamic properties of superheated pure refrigerants and their binary mixtures are tested.

PFGC – MES EOS

The Parameters From Group Contribution (PFGC) EOS was presented by Cunningham and Wilson [5]. In this equation of state, the parameters are functions only of the groups making up the individual molecules present in the system. Wilson and Cunningham presented only four parameters, namely, b_k , S_k , $E_k^{(0)}$, $E_k^{(1)}$ in the original version of the PFGC equation of state. Moshfeghian et al. [6] introduced the fifth parameter, $E_k^{(2)}$, for better accuracy and extension of capabilities of this equation of state. In order to distinguish between the two versions, the latter one will be referred to PFGC-MES*

* Appendix A presents the equations for the PFGC-MES EOS, along with expressions for calculating enthalpy and chemical potential. The mixing rules are also presented.

EOS.

In order to perform any thermodynamic property calculations, the PFGC parameters must be known. Moshfeghian [2] has presented the parameters for several groups and compounds. For those compounds and groups for which parameters were not available, the procedure suggested by Moshfeghian et al. [3] was followed. The binary interaction parameter between groups i and j also had to be determined. In PFGC-MES EOS different binary interaction parameters are defined for each phase presented; i. e. one interaction parameter per binary pair for vapor phase and another one for liquid phase. A detail calculation procedure for finding the binary interaction parameter and the results of these calculations for several binary systems are reported by Moshfeghian et al. [4] Justification for selecting two sets of a_{ij} for different phases was also discussed by Mehranbod [3]. In order to improve the accuracy of the predicted results and due to the complexity of refrigerant molecules, each molecule was treated as a group.

RESULTS

Pure Compounds

As mentioned previously, the PFGC-MES EOS has been successfully applied to describe the thermodynamic properties of saturated pure refrigerants [2, 3]. In this work, in order to show the capabilities of this EOS, the thermodynamic properties are predicted in the superheated region and are compared with the experimental data for different refrigerants. All of the refrigerant molecules could be divided into five distinct chemical categories. These categories are:

- 1) Methane derivatives
- 2) Ethane derivatives
- 3) Cyclic molecules
- 4) Azeotrope mixtures
- 5) Unsaturated molecules

Typical calculated results for each of the above categories are presented. The selected compounds from each category are R-12, R-114, R-C318, R-502, R-1150. For each of these

compounds the calculated values are compared with the experimental data at different conditions. These conditions are as follows:

- 1) Constant temperature
- 2) Constant entropy
- 3) Constant volume

For each condition three arbitrary curves are selected in the superheated region (e. g. three different isotherms are selected). Some arbitrary data points are selected along each of these curves. For each of these data points the experimental temperature and pressure are specified. For each case at the specified temperature and pressure, the enthalpy is predicted and then compared with the experimental value. In this way the relative error in enthalpy is determined for each data point. A summary of the comparison results for the five selected compounds are presented in Table 1. For obtaining a complete phase diagram it is also necessary to calculate the saturated vapor and liquid enthalpies. The predicted results for saturated data were obtained from references [2] and [3]. The calculated values and experimental data for each of these five pure compounds are plotted in pressure-enthalpy (P-H) diagrams. These diagrams are presented in Figures 1 to 5. As can be seen in Table 1, the predicted results in the superheated region are in good agreement with the experimental data. In no case of the five selected pure compounds is the average absolute percent deviation between the predicted values and the experimental data more than 4%.

Mixtures

In earlier works [2,4], the interaction coefficient in the liquid and vapor phases was optimized for several binary mixtures. Based on these parameters the VLE of the binary mixtures under study is accurately predicted. In this work, as an extension of the previous work, it is intended to show the capabilities of the PFGC-MES EOS in predicting other thermodynamic properties of mixtures. For mixtures, these properties are bubble point pressure, saturated vapor and liquid volume, and saturated vapor and liquid enthalpies. The

mixtures under study are:

- 1) $\text{CBrF}_3 + \text{CH}_3\text{CHF}_2$
- 2) $\text{CHClF}_2 + \text{CF}_3\text{CClF}_2$
- 3) $\text{CO}_2 + \text{CH}_2\text{Cl}_2$

For the first mixture, saturated liquid and vapor volumes are predicted at two isotherms. For each point, comparison between the experimental data and predicted values is made and the results are plotted in Figures 6 and 7. The second mixture is an azeotrope at a specific composition (the mole fractions are 48.8 and 51.2 for R-22 and R-115, respectively). This mixture could be treated by two different approaches for predicting the thermodynamic properties. The first approach is to treat it as a pure compound, and the second is to treat it as a mixture of specified composition. For this mixture the following properties are predicted by using the above two methods:

- 1) Vapor pressure (when treated as pure) or bubble point pressure (when treated as a mixture)
- 2) Saturated vapor and liquid enthalpies
- 3) Saturated vapor volume
- 4) Saturated liquid density.

The predicted results from the two different approaches and the experimental data are reported together in Table 2. For a better comparison between the two approaches these results are also plotted in Figures 8 to 12. For all of the properties under study the results by the first method are better than the other approach. The difference between these two methods is more pronounced in the case of saturated vapor volume. For the third mixture the bubble point pressure is predicted at different conditions. The predicted results and experimental data are plotted in Figure 13. The range of CO_2 composition in the liquid phase is from 0.0 to 0.3 mole percent. The predicted results show good agreement at 327.6 (K) and 310.93 (K) isotherms. At 294.26 (K) the predicted results show considerable negative deviation in the upper range of composition. For all data points under study, the average absolute percent

deviation is about 5.5%.

CONCLUSION

The capabilities of the PFGC-MES EOS were investigated for two different categories:

- 1) Predicting the thermodynamic properties in the superheated region for pure refrigerants
- 2) Predicting the thermodynamic properties for binary mixtures.

For the first category several refrigerants were studied, and the predicted results for five selected compounds are presented in pressure-enthalpy diagrams. In the case of mixtures, different thermodynamic properties are predicted for several binary mixtures. The calculated results and experimental data are presented both in tabulated and graphical format.

Based on the results presented in this study, it could be concluded that the PFGC-MES EOS is a practical and reliable tool for describing the thermodynamic properties of superheated pure refrigerants and light hydrocarbon mixtures.

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Table 1. The Ability of PFGC MES in Predicting Enthalpies of Refrigerants in the Superheated Region

Refrigerant No	The Average Absolute Percent Deviation		
	isotherm curves	isoentropy curves	isovolume curve
12	1.306	1.546	1.626
114	1.300	1.649	1.583
502	0.180	0.641	0.578
C-318	3.249	2.890	3.534
1150	0.182	0.281	0.247

Table 2. The Comparison Results between the Two Methods for Predicting the Thermodynamic Properties of R-502

Method No.	The Average Absolute Percent Deviation				
	Vapor Pressure	Saturated Vapor Enthalpy	Saturated Liquid Enthalpy	Saturated Vapor Volume	Saturated Liquid Density
1	0.2840	0.5430	2.6950	0.6760	5.2160
2	4.9800	3.7270	5.1270	11.443	5.5280

1 = first method (treated as pure)
 2 = second method (treated as a mixture)

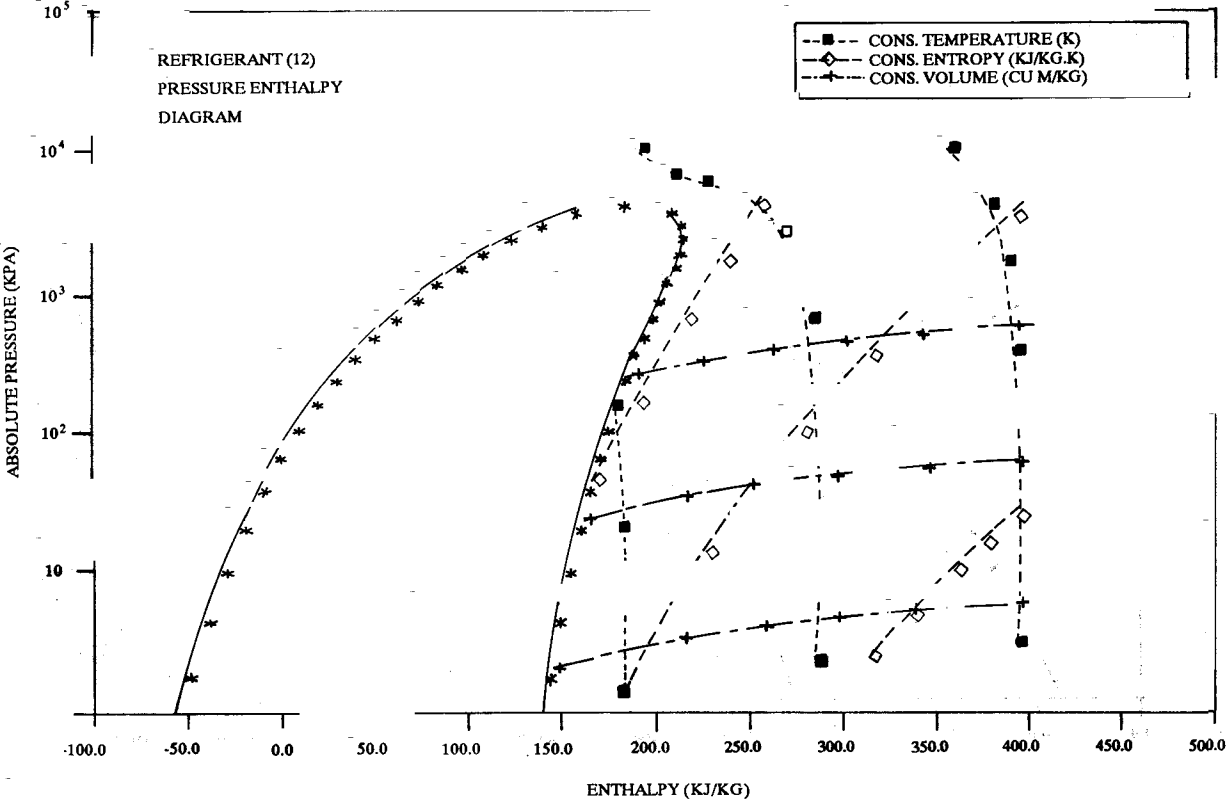


Figure 1. Pressure-enthalpy diagram for refrigerant 12

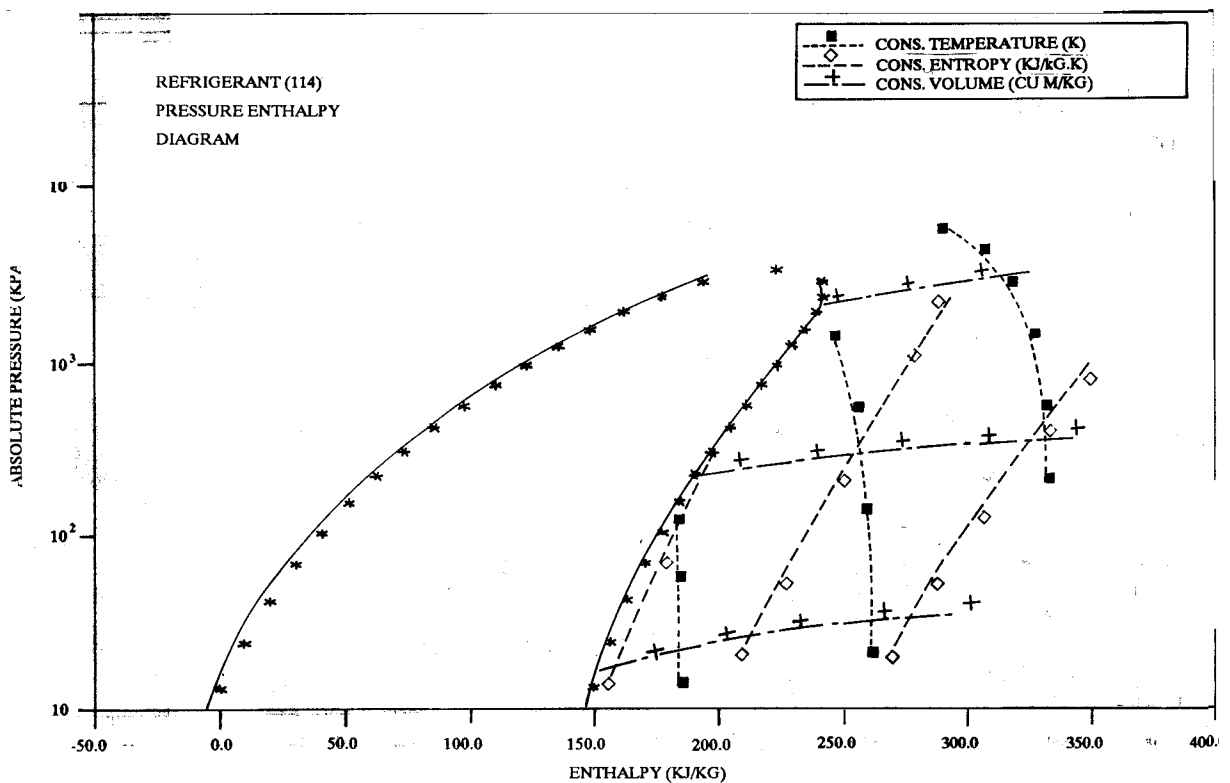


Figure 2. Pressure-enthalpy diagram for refrigerant 114

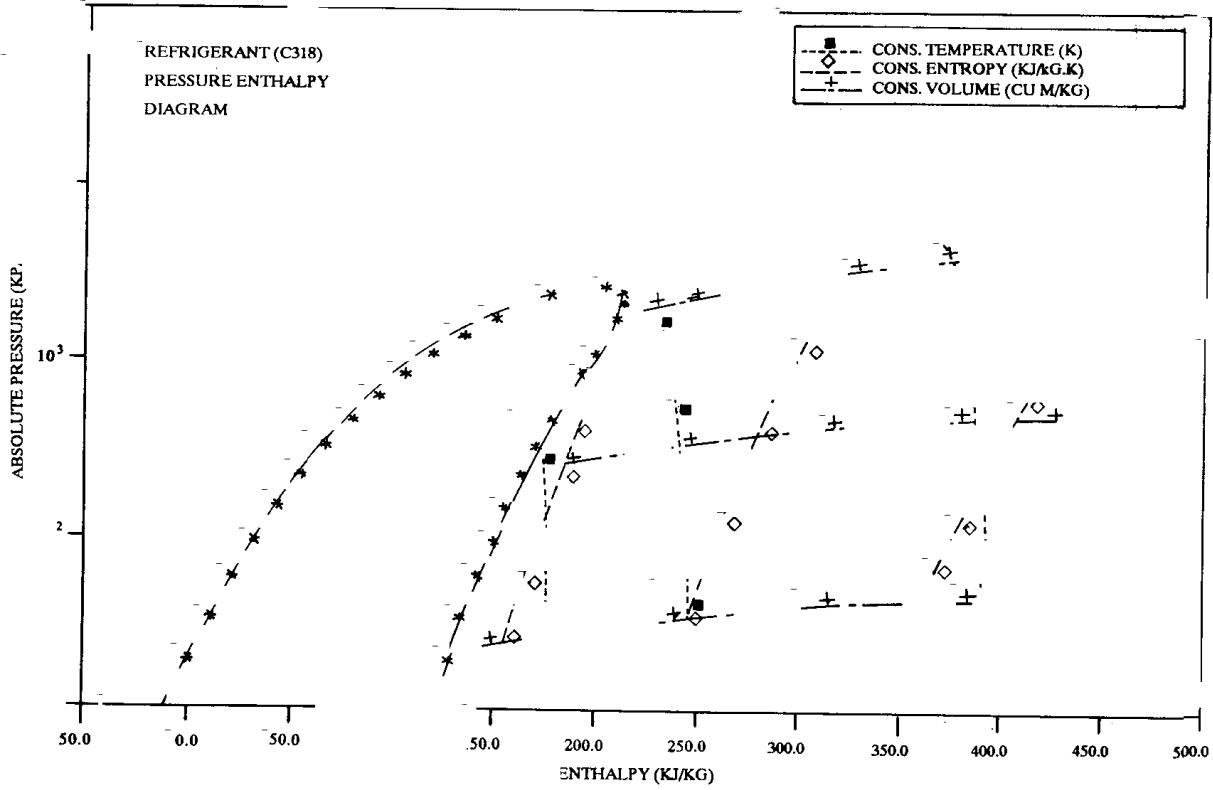


Figure 3. Pressure-enthalpy diagram for refrigerant C 318

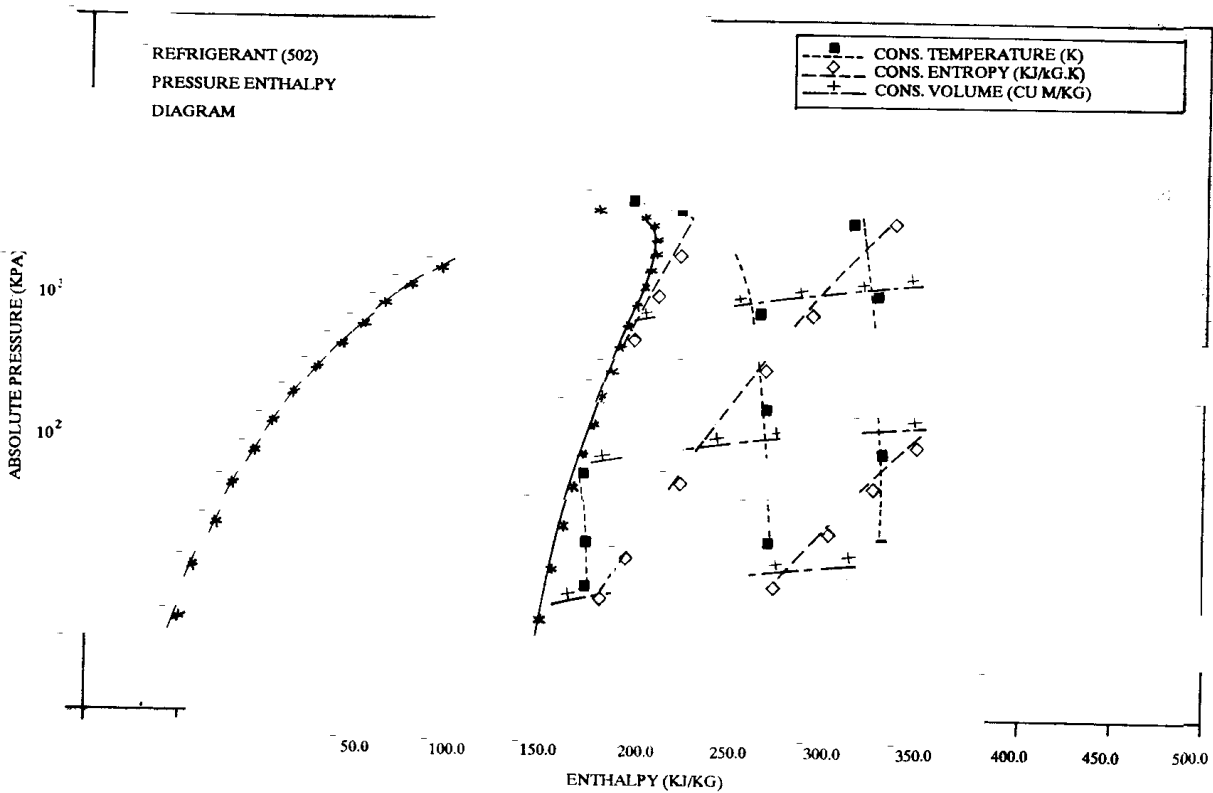


Figure 4. Pressure-enthalpy diagram for refrigerant 502

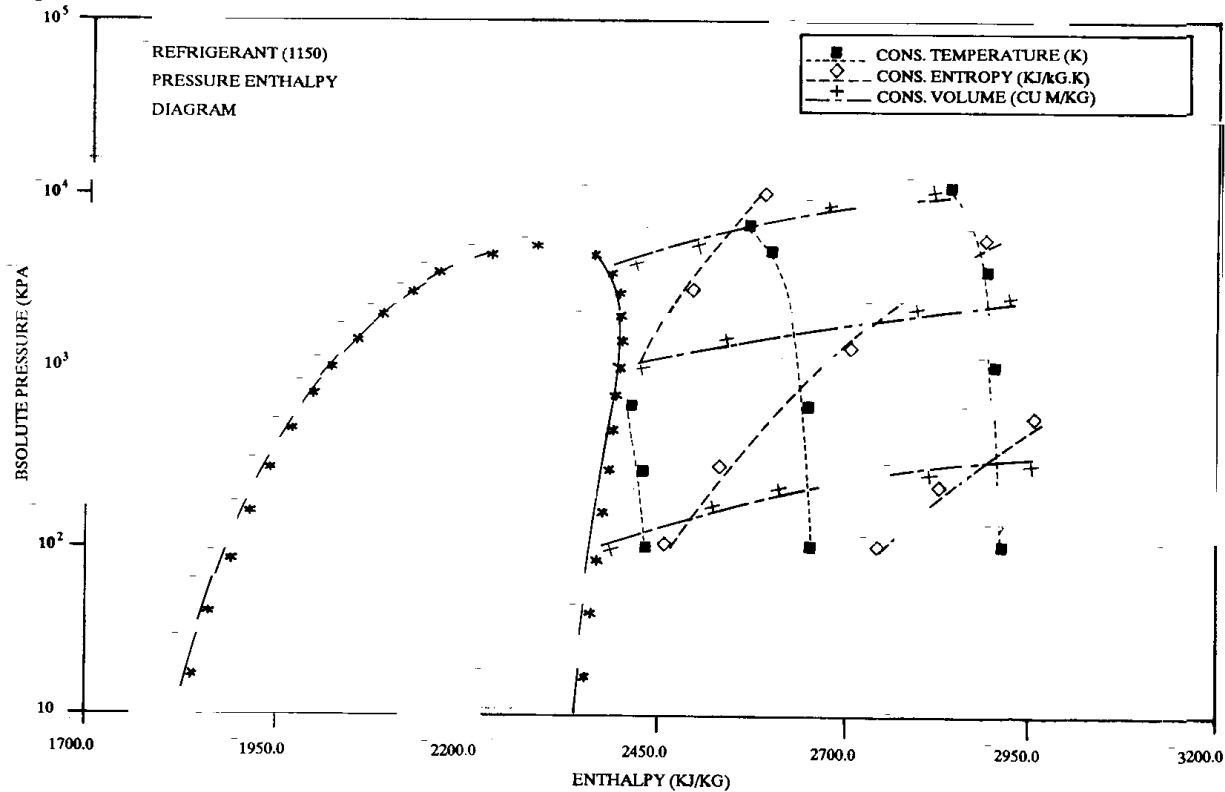


Figure 5. Pressure-enthalpy diagram for refrigerant 1150

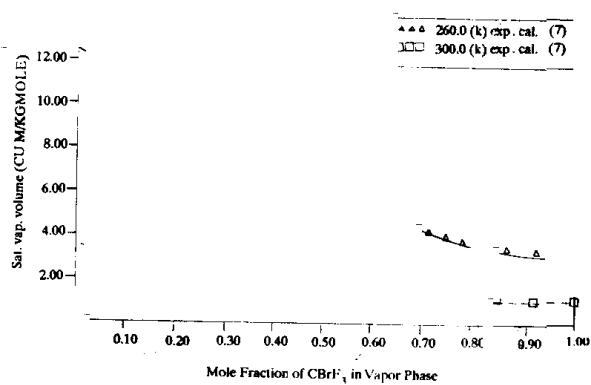
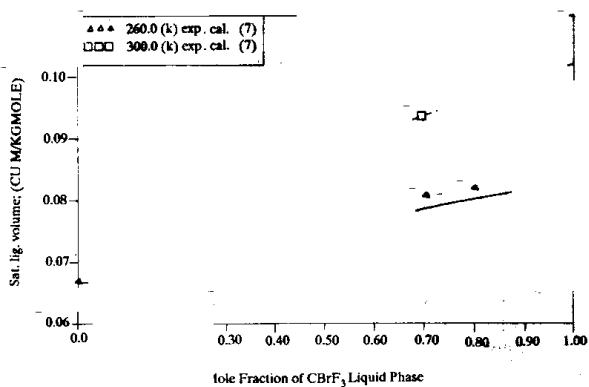


Figure 6. Saturated liquid volume for $CBrF_3-CH_3CHF_2$ system

Figure 7. Saturated vapor volume for $CBrF_3-CH_3CHF_2$ system

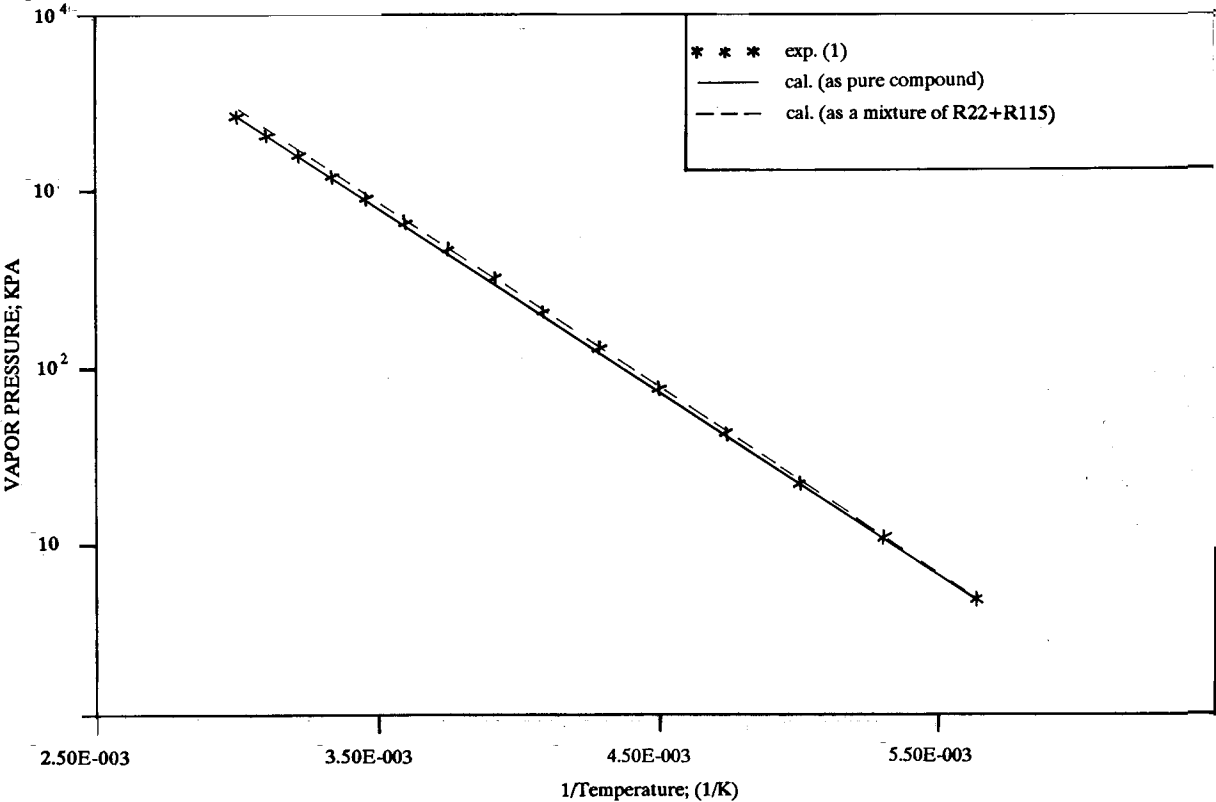


Figure 8. Comparison between calculated and experimental vapor pressure of refrigerant 502

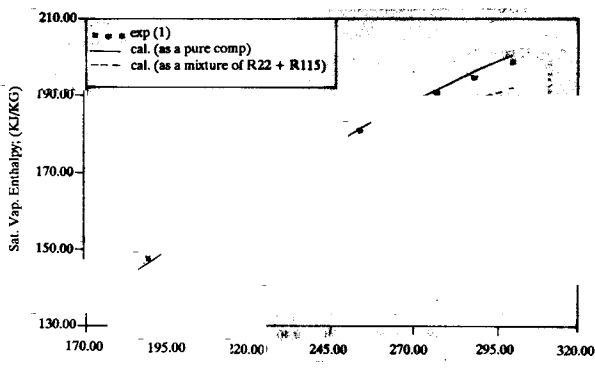


Figure 9. Comparison between calculated and experimental sat. vap. enthalpy for refrigerant 502

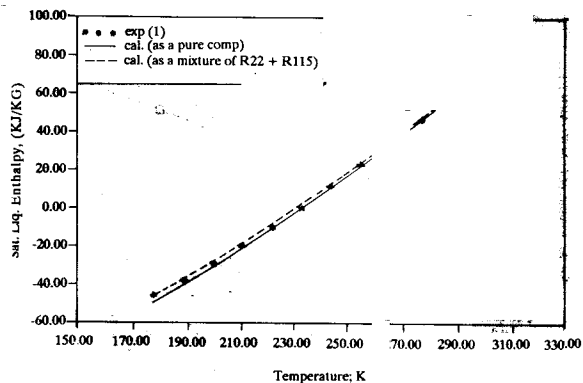


Figure 10. Comparison between calculated and experimental sat. liq. enthalpy for refrigerant 502

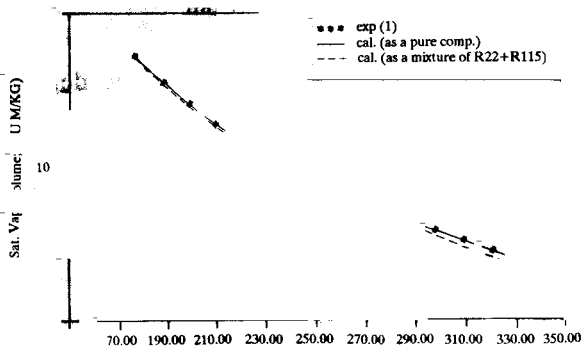


Figure 11. Comparison between calculated and experimental sat. vap. volume for refrigerant 502

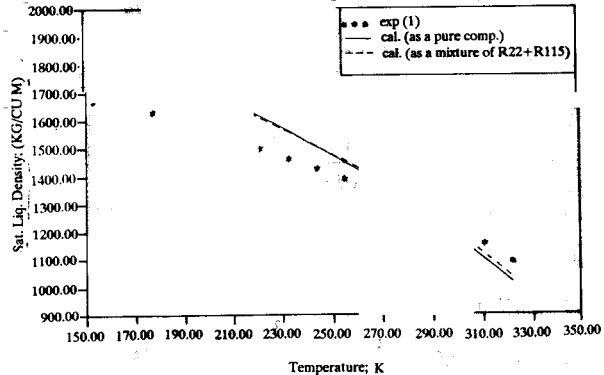


Figure 12. Comparison between calculated and experimental sat. liq. density for refrigerant 502

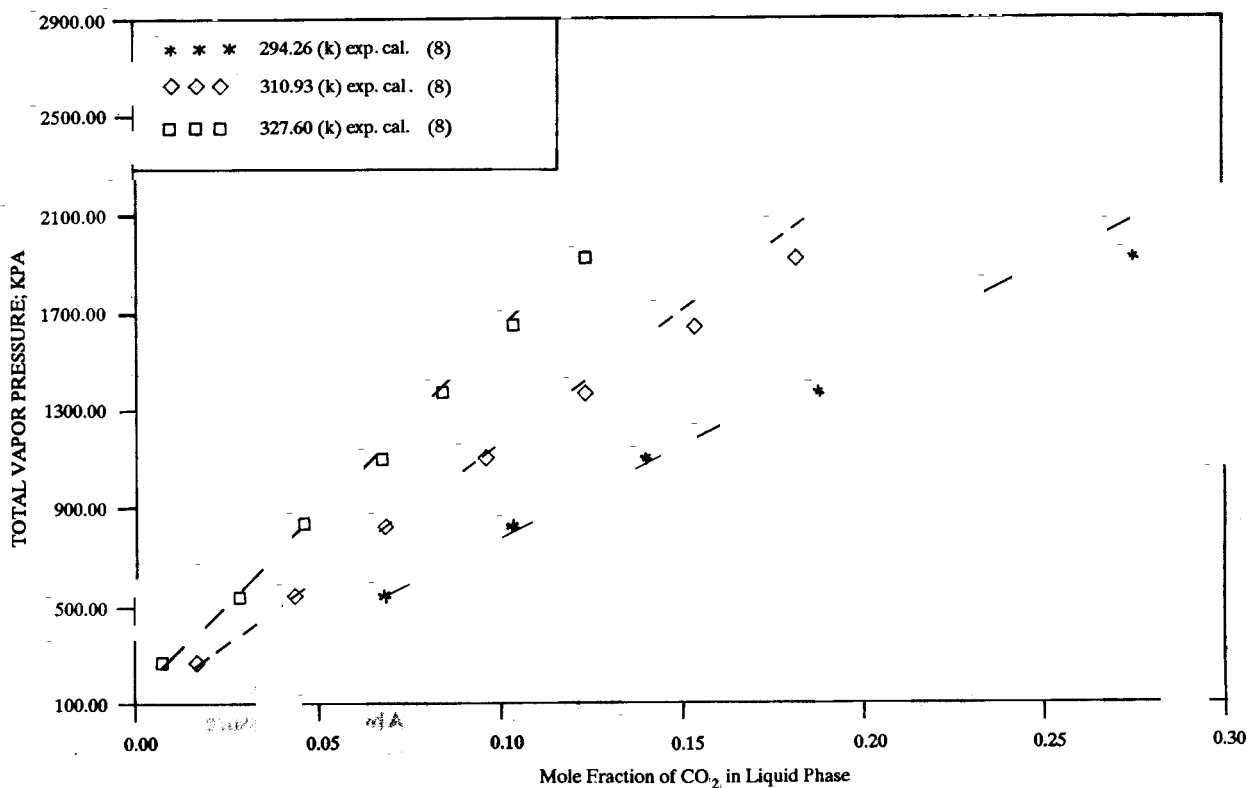


Figure 13. Total vapor pressure of solution of CO₂ in methylene chloride

Compressibility factor:

$$\frac{PV}{RT} = Z = \frac{sV}{b} \ln \left[1 - \frac{b}{V} \right] - s + b \left(\frac{C}{bH} \right) \sum_i^g \left[\frac{b - b \sum_j^g \epsilon_j \tau_{ij}}{V - b + b \sum_j^g \epsilon_j \tau_{ij}} \right]$$

Chemical Potential:

$$\frac{\mu_i}{RT} = S_i \left[\left[\frac{V}{b} - 1 \right] \ln \left[1 - \frac{b}{V} \right] \right] + \ln \left[\frac{RT}{V} \right] - s \frac{b_i}{b} \left[\dots \right] + \frac{C}{bH} \left[\dots \right] + b \sum_j^g \epsilon_j \ln \left[\frac{-b_i + \sum_j^g m_{ij} b_j \tau_{ij}}{V - nb + nb \sum_j^g \epsilon_j \tau_{ij}} \right]$$

Enthalpy departure:

$$\frac{\Delta H}{RT} = (Z - 1) + \left(\frac{C}{bH} \right) (Tb^2) \sum_i^g \left[\epsilon_i \frac{\sum_j^g \epsilon_j \left[\frac{\delta \tau_{ij}}{\delta T} \right]}{V - b + b \sum_j^g \epsilon_j \tau_{ij}} \right]$$

Mixing Rules:

$b_i = \sum_j^g m_j b_j$, component covolume

$b = \sum_i^c x_i b_i$, mixture covolume

$s_i = \sum_j^g m_j s_j$, proportional to component degrees of freedom

$s = \sum_i^c x_i s_i$, proportional to mixture degrees of freedom

$\tau_{ij} = \text{Exp}(-E_{ij}/KT)$, interaction energy parameter between groups i and j

where:

$E_{ij} = a_{ij}(E_i + E_j)/2.0$, interaction energy between groups i and j

$$E_i = E_i^{(0)} + E_i^{(1)} \left[\frac{509.7}{T} \right] + E_i^{(2)} \left[\left[\frac{509.7}{T} \right] \right]$$

interaction energy between groups i and j

$$\sum_i^c x_i m_i b_j \tau_{ij} / b$$

where:

- i i^{th} component of c total components
- i i^{th} group of g total groups
- j j^{th} group of g total groups
- C/bH Universal constant = 12.
- m_{ij} Number of groups j in component i
- a_{ij} Interaction coefficient between groups i and j
- V Molar volume
- P Absolute pressure
- R Universal gas constant
- Absolute temperature