

Prediction of Thermodynamic Properties of Helium and Neon as Working Fluids in Cryogenic Processes using Fundamental Equations of States

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Abstract: Design and optimization of various thermodynamic processes that are used in chemical industries such as low- temperature refrigeration and cryogenic cycles, requires computer software to simulate the thermodynamic cycle and examine the effect of various parameters on the performance of the cycle. So the existence of an equation of state to predict thermodynamic properties of working fluids in a wide range of temperatures and pressures is essential. Despite the greater complexity than the other equations, the fundamental equations of state have higher accuracy in the calculation of the thermodynamic properties and the main advantage of them is that other thermodynamic properties can be obtained with high accuracy by differentiating them. In this study, the thermodynamic properties of Helium and Neon as working fluids in cryogenic processes including density, internal energy, enthalpy, entropy, isobaric specific heat capacity, and isochoric heat capacity, have been calculated based on fundamental equations of state using a developed computer code in MATLAB software. By comparing the results with the valid reference data, a range of temperature and pressure in which the fundamental equations of state can be used with high accuracy, have been presented. In this high accuracy region, the maximum error is related to the isobaric heat capacity that is 3.37 % and 1.1 % respectively for Helium and Neon.

keywords: Fundamental equations of state, Thermodynamic properties, Cryogenic process simulation, Neon, Helium.

1. Introduction

Using a suitable equation is an essential solution for predicting the thermodynamic properties of fluids in the design and simulation of thermodynamic processes. Although there are many thermodynamic tables and charts that provide detailed information on the thermodynamic properties of fluids, an accurate equation is necessary to correctly predict the thermodynamic properties of fluids in a wide range of temperature and pressure using to design and simulate the thermodynamic cycles.

So far, many of equations of state were suggested such as primary simple equations with a few of parameters and modern equations that are complex but accurate. In the primary equation of state, the pressure is a function of other properties such as temperature and volume so these equations are named the pressure-explicit equation of state while new equations are explicated on Helmholtz energy. These

equations that are known as the fundamental equations of state are more complex than pressure-explicit equations but have higher accuracy in the calculation of the thermodynamic properties in a wide range of temperature and pressure. The main advantage of these equations is that there is no need for integration for driving other thermodynamic properties. All required thermodynamic properties can be obtained with differentiating of Helmholtz energy with high accuracy. Due to the applicability of these equations in accurately predicting thermal-physical properties, extensive research is done on the development of these equations. Most of the works were done on this subject are about presenting a model based on Helmholtz energy or using previous models and calculating the thermodynamic properties of fluids and then comparing them with experimental data. Jacobsen et al. presented a thermodynamic property formulation for nitrogen from the freezing line to 2000 K at pressures to 1000 MPa. The given

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relation can be used for thermodynamic property calculation with uncertainty 0.1% for the pressure and density, 0.2% for thermal capacities and 2% for the values of speed of sound. The formulation is not recommended near the critical point (Jacobsen, Stewart, & Jahangiri, 1986). Dillon and Penoncello presented a formulation for the thermodynamic properties of ethanol (C_2H_5OH) in the liquid, vapor, and saturation. The formulation presented may be used to compute densities with uncertainty 0.2%, heat capacities with uncertainty 3%, and speed of sound with uncertainty 1%. Saturation values of the vapor pressure and saturation densities are represented with uncertainty $\pm 0.5\%$, except near the critical point (Dillon & Penoncello, 2004). Leachman et al. developed a form of the fundamental equation of state for para-hydrogen, normal hydrogen, and ortho-hydrogen and then calculated the thermodynamic properties of them. The uncertainties of vapor pressures and saturated liquid densities vary from 0.1% to 0.2%. Heat capacities are generally estimated to be accurate to within 1%, while speed-of-sound values are accurate to within 0.5% below 100MPa (Leachman, Jacobsen, Penoncello, & Lemmon, 2009). Bückner and Wagner calculated the thermodynamic properties of ethane in the temperature range of the melting line up to 675 K and the pressure up to 900 MPa. The uncertainty in the calculation of density was less than 0.02%–0.03% from the melting line up to temperatures of 520 K and pressures of 30 MPa. In the gaseous and supercritical region, the high precision speed of sound data is represented generally within less than 0.015%. The primary data, to which the equation was fitted, cover the fluid region from the melting line to temperatures of 675 K and pressures of 900 MPa. Beyond this range, the equation shows reasonable extrapolation behavior up to very high temperatures and pressures (Bückner & Wagner, 2006). Estela-Urbe developed a model based on Helmholtz energy for calculating the thermodynamic properties of a group of refrigerants. He predicted thermodynamic properties of 19 refrigerant and reported following percentage overall absolute average deviations: 0.187 for p-T data, 0.229 for saturation pressures, 0.206 for saturated-liquid densities, 1.053 for saturated-vapor densities, 1.734 for isochoric heat capacities, 1.238 for isobaric heat capacities and 0.662 for speeds of sound (Estela-Urbe, 2014). Estela-Urbe also predicted the thermodynamic properties of non-polar fluids and their mixtures such as natural gases using an improved Helmholtz energy model (Estela-Urbe, 2013a, 2013b, 2013c). Thol et al. predicted the thermodynamic properties of Hexa-methyldisiloxane (Thol, Dubberke, Rutkai, Windmann, Köster, Span, & Vrabec, 2015) and ethylene oxide (Thol, Rutkai, Köster, Kortmann, Span, & Vrabec, 2015) using fundamental equation of state correlation based on experimental and molecular simulation data. Gernert and Span presented an equation of state and the EOS–CG mixture model for thermodynamic properties of humid gases,

combustion gases and CO₂-rich mixtures typical for Carbon Capture and Storage processes (Gernert & Span, 2016). They use the mathematical structure of Kunz and Wagner in their work (Kunz & Wagner, 2012). Grigoriev et al. proposed a new mixture model, explicit in the reduced Helmholtz energy, for modeling the thermodynamic properties and phase equilibria of technological oil fractions. The model covers a broad temperature and pressure range in gaseous, liquid, and supercritical regions (Grigoriev, Alexandrov & Gerasimov, 2018).

This study aims to predict the thermodynamic properties of cryogenic refrigerants using fundamental equations of state and calculate the uncertainty in the wide range of temperature and pressure to evaluate the applicability of these equations in the prediction of thermodynamic properties of these refrigerants. Using a developed computer code based on fundamental equations of state, thermodynamic properties of Helium and Neon including density, internal energy, enthalpy, entropy, isobaric specific heat capacity, and isochoric heat capacity are calculated. By comparing the results of predictions with the valid reference data is (Jacobsen, Penoncello & Lemmon, 1997), the scope of this equation to predict the thermodynamic properties of Helium and Neon are offered. In earlier work, not only the prediction of the thermodynamic properties of cryogenic refrigerants such as Helium and Neon not considered, but also providing a diagram that easily presents the applicability of fundamental equation of state in different ranges of temperature and pressure has been neglected. In the following section, a brief description is provided of the types of equations of state. Then the fundamental equations and how to obtain thermodynamic properties have been obtained. Finally, the results of comparing the reference data and predicted thermodynamic properties using fundamental equations of state are presented.

2. Theory of fundamental equation of state

The most common thermodynamic properties that are measured and used in the equations of state are pressure, temperature and specific volume (or its reverse, the density). Primary types of the equation of state make a correlation between the thermodynamic properties in which the pressure is expressed as a function of temperature and density (or specific volume). The general form of the pressure-explicit equation of state is (Jacobsen, Penoncello & Lemmon, 1997):

$$P = P(\rho, T) \quad (1)$$

Virial equation of state (equation 2), cubic equations of state (equation 3) such as Van der Waals and Peng-Robinson and Lee-Kesler equations of state are the most common pressure explicit equations of state. The typical pressure explicit equation of state must be integrated for the calculation of enthalpy and entropy (Jacobsen, Penoncello & Lemmon, 1997).

$$\frac{P}{\rho RT} = 1 + B\rho + C\rho^2 + D\rho^3 + \dots \quad (2)$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + ubv + wb^2} \quad (3)$$

In the secondary form of the equation of state, Helmholtz energy is used as a dependent variable (Jacobsen, Penoncello & Lemmon, 1997):

$$A = A(\rho, T) \quad (4)$$

This form of the equation of state is named the *fundamental equation of state*. Therefore, on this basis, equations of state are divided into two general categories:

1. Pressure-explicit equations of state
2. Fundamental equations of state

As mentioned, the fundamental form of the equation of state is implicit in the Helmholtz energy. This form of the equation has some advantages over other forms of the equation of state. An inherent advantage in fundamental equations of state is that all thermodynamic properties can be derived with relatively simple differentiation.

Schmidt and Wagner developed a 32-term fundamental equation in 1985 (Jacobsen, Penoncello, & Lemmon, 1997). Although this form was developed for oxygen, it has been used by other investigators for correlating properties of other fluids. The equation is explicit in dimensionless Helmholtz energy. Jacobsen et al. developed a general form of the fundamental equation similar to that of Schmidt and Wagner which has been used for correlating thermodynamic properties of several cryogenics. The functional form of this equation is (Jacobsen, Penoncello & Lemmon, 1997):

$$\frac{A(\rho, T)}{RT} = \alpha(\delta, \tau) = \alpha^0(\delta, \tau) + \bar{\alpha}(\delta, \tau) \quad (5)$$

where $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$, and T_c and ρ_c are critical temperature and critical density respectively. The Helmholtz energy consists of two parts: the ideal gas contribution part ($\alpha^0(\delta, \tau)$), and the residual part of the Helmholtz energy $\bar{\alpha}(\delta, \tau)$.

The ideal gas portion is given by (Jacobsen, Penoncello & Lemmon, 1997):

$$\alpha^0(\delta, \tau) = \frac{h_0^0 \tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{C_p^0}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{C_p^0}{\tau} d\tau \quad (6)$$

where τ_0 and δ_0 are as defined below. Also, h_0^0 and s_0^0 are arbitrary values for enthalpy and entropy at standard temperature (T_0) and pressure (P_0).

$$\tau_0 = \frac{T_c}{T_0} \quad (7)$$

$$\delta_0 = \frac{P_0}{RT_0 \rho_c} \quad (8)$$

The residual part of the Helmholtz energy is given by (Jacobsen, Penoncello & Lemmon, 1997)

$$\bar{\alpha}(\delta, \tau) = \sum_{k=1}^m N_k \delta^{i_k} \tau^{j_k} \exp(-\gamma \delta^{l_k}) \quad (9)$$

where $\gamma = 0$ for terms with $l_k = 0$ and $\gamma = 1$ for terms where $l_k \neq 0$. It is generally expected that the i_k and l_k are positive integers and the j_k are real numbers (positive or negative).

3. Prediction of thermodynamic properties using fundamental equation of state

As mentioned, the fundamental equation of states allows computing other thermodynamic properties with differentiation of Helmholtz energy. Table 1 shows examples of functions for obtaining the thermodynamic properties from Helmholtz energy. These functions can be used easily in computer programs.

4. Prediction of thermodynamic properties of Helium and Neon

To calculate the thermodynamic properties of Helium and Neon, coefficients and parameters reported by Jacobsen et al. were used (Jacobsen, Penoncello, & Lemmon, 1997). Thermodynamic properties were calculated at pressures 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, and 100 MPa with temperature step of 10 °C at low temperatures and 100 °C at high temperatures from saturated point up to 1500 °C for Helium and 650 °C for Neon, using a developed computer code in MATLAB software. Since in the fundamental equations of state, Helmholtz energy has been explicit in terms of temperature and density, the equation should be solved numerically to obtain thermodynamic properties at a given temperature and pressure. Therefore, at a given temperature, the Newton-Raphson method was used to achieve the corresponding density to the desired pressure with an approximation of 0.000001 MPa.

Table 1. functions for calculation of thermodynamic properties from Helmholtz (Jacobsen, Penoncello, & Lemmon, 1997)

Property	Relation
Pressure	$\frac{P}{P_c} = \frac{\delta}{\tau Z_c} \left[1 + \delta \left(\frac{\partial \bar{\alpha}}{\partial \delta} \right) \right]$
Internal energy	$\frac{U}{RT} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right) + \left(\frac{\partial \bar{\alpha}}{\partial \tau} \right) \right]$

Entropy		$\frac{S}{R} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right) + \left(\frac{\partial \bar{\alpha}}{\partial \tau} \right) \right] - \alpha^0 - \bar{\alpha}$
Enthalpy		$\frac{H}{RT} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right) + \left(\frac{\partial \bar{\alpha}}{\partial \tau} \right) \right] + \delta \left(\frac{\partial \bar{\alpha}}{\partial \delta} \right) + 1$
Isochoric capacity	heat	$\frac{C_V}{R} = -\tau^2 \left[\left(\frac{\partial^2 \alpha^0}{\partial \tau^2} \right) + \left(\frac{\partial^2 \bar{\alpha}}{\partial \tau^2} \right) \right]$
Isobaric capacity	heat	$\frac{C_P}{R} = \frac{C_V}{R} + \frac{\left[1 + \delta \left(\frac{\partial \bar{\alpha}}{\partial \delta} \right) - \delta_\tau \left(\frac{\partial^2 \bar{\alpha}}{\partial \delta \partial \tau} \right) \right]^2}{\left[1 + 2\delta \left(\frac{\partial \bar{\alpha}}{\partial \delta} \right) + \delta^2 \left(\frac{\partial^2 \bar{\alpha}}{\partial \delta^2} \right) \right]}$

5. Result and discussion

Using a developed computational code based on fundamental equation of state, thermodynamic properties of gases Helium and Neon were calculated as two cryogenic refrigerants. By comparison, these calculated properties with reference (Jacobsen, Penoncello & Lemmon, 1997), the applicability diagrams of the fundamental equation of state were provided for these two refrigerants. Also, forecast errors of thermodynamic properties inside the applicability region are presented. The thermodynamic properties were calculated for pressures up to 100 MPa and in the temperature range 10 to 1500 K and 30 to 650 K, respectively for Helium and Neon. A standard reverse-Brayton

cryocooler cycle for long-length High-Temperature Superconducting cable systems is one of the most application of the range studied in this investigation (Hou, Zhao, Chen, & Xiong, 2006) and (Maboudi & Zia Bashrhagh, 2015).

5.1 Thermodynamic properties of Helium

As an example, Table 2 shows a part of the thermodynamic property table obtained for Helium using the fundamental equation of state. Figure 1 shows a comparison between the entropy of Helium gas calculated using the fundamental equations of state and reference data (Jacobsen, Penoncello & Lemmon, 1997) in various temperatures and pressures. As can be seen in this figure, the difference between the results obtained from the fundamental equations of state and the reference data is negligible, which indicates the capability of the fundamental equations of states in the calculation of the thermodynamic properties of gases. These comparisons were done about other thermodynamic properties of Helium and adaptation of results with reference data was investigated. In Figure 2, the applicability region of the fundamental equation of state for predicting the thermodynamic properties of Helium can be seen on the temperature-entropy graph for different pressures. Forecast errors of thermodynamic properties of Helium in high accuracy region are presented in Table 3.

Table 2. Thermodynamic properties of Helium

Temp. (K)	Density (kg/m ³)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg - K)	C _v (kJ/kg - K)	C _p (kJ/kg - K)
P=0.1 MPa						
4.2163	16.41700	24.55547	30.61263	8.520723	3.240029	8.988085
10	4.920719	45.08910	65.29761	13.84447	3.114800	5.425187
20	2.394672	76.84773	118.3734	17.52999	3.120772	5.249881
30	1.592025	108.2165	170.6781	19.65120	3.119743	5.217455
60	0.796100	201.9026	326.8120	23.25939	3.117620	5.198080
100	0.478019	326.6140	534.6401	25.91357	3.116729	5.194345
150	0.318834	482.4395	794.3275	28.01946	3.116338	5.193378
200	0.239187	638.2455	1053.989	29.51346	3.116168	5.193115
300	0.159500	949.8399	1573.292	31.61906	3.116021	5.192992
400	0.119640	1261.427	2092.590	33.11299	3.115958	5.192979
800	0.059831	2507.762	4169.788	36.71249	3.115883	5.193010
1200	0.039889	3754.095	6246.996	38.81808	3.115864	5.193030
1500	0.031912	4688.845	7804.906	39.97687	3.115857	5.193038

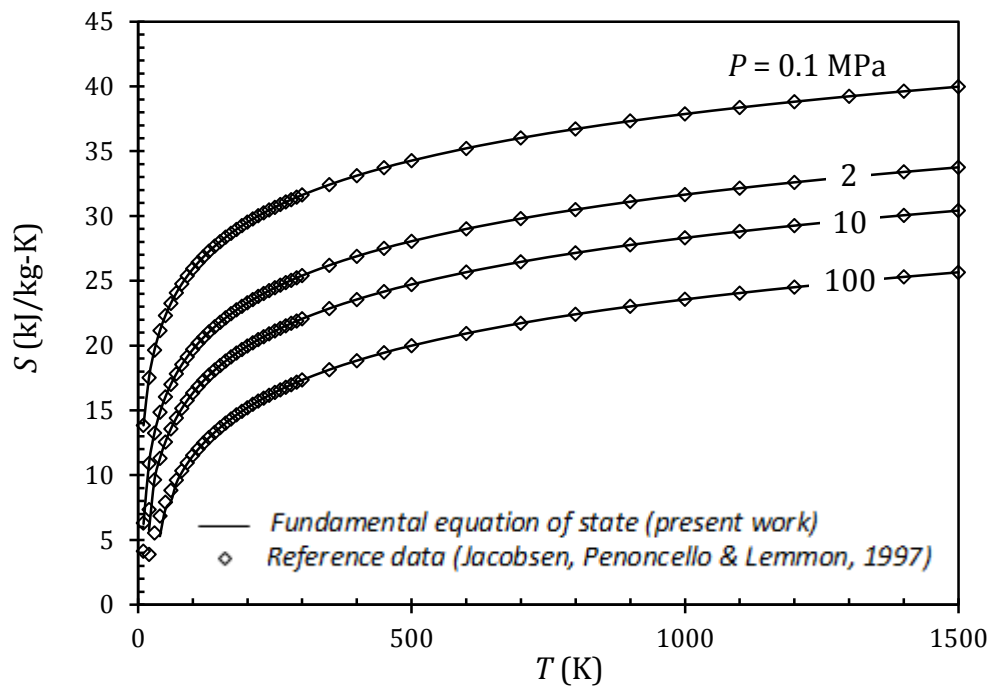


Figure 1. Entropy of Helium vs temperature in different pressures

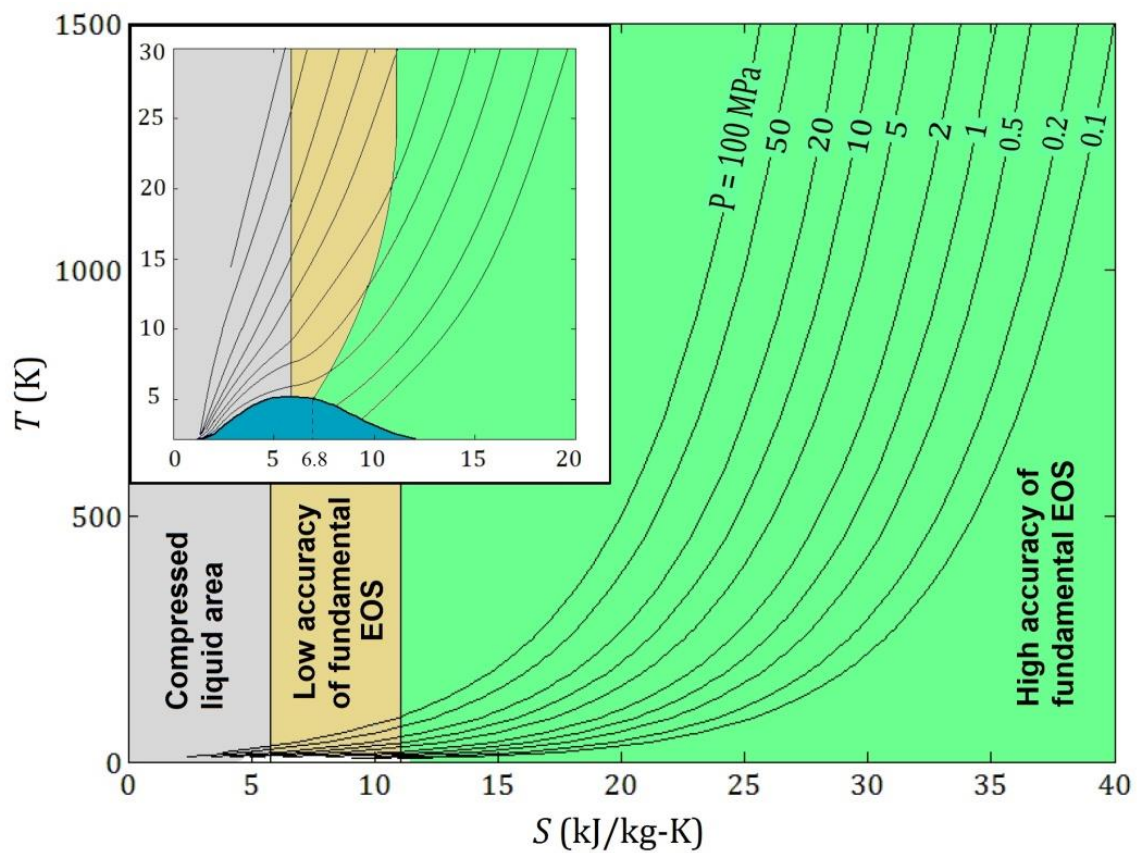


Figure 2. Applicability area of fundamental equation of state in predicting the thermodynamic properties of Helium.

Table 3. Relative error of predicting thermodynamic properties of Helium in high accuracy area shown in figure 2

Property	Minimum error%	Maximum error%	Average error%
Density	0.11	0.57	0.54
Internal energy	0.00	0.31	0.00
Enthalpy	0.00	0.39	0.01
Entropy	0.03	0.10	0.05
Isochoric heat capacity	0.00	0.64	0.01
Isobaric heat capacity	0.00	3.37	0.03

Figure 3 shows the relative error percentage of the results on the boundary of the applicability area of the fundamental equation of states (the line between the green and brown areas in Figure 2) in predicting the thermodynamic properties of Helium. According to the graph, it is shown that relative error of density, unlike other thermodynamic properties, decreases

with increasing pressure. The maximum error is related to the isobaric heat capacity and isochoric heat capacity which is 3.37% and 0.94% respectively. The relative error of other thermodynamic properties on the boundary between high and low accuracy areas does not exceed 0.6%. The relative error in the low accuracy area shown in Figure 2, is above 5%.

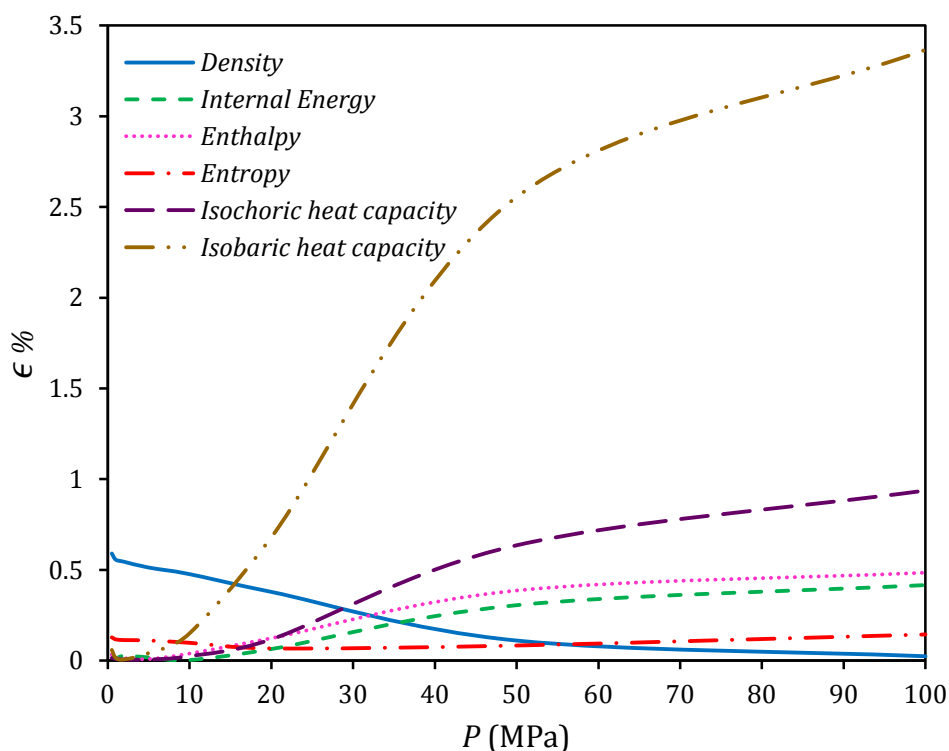


Figure 3. Relative error of thermodynamic properties of Helium using fundamental equation of states on the boundary between high and low accuracy areas shown in figure 2

5.2 Thermodynamic properties of Neon

Table 4 shows a selection of thermodynamic properties of Neon that were calculated using the fundamental equation of state. Figure 4 compares the entropy of Neon gas calculated using the fundamental equations of state with entropy obtained from reference data (Jacobsen, Penoncello & Lemmon, 1997) in various temperatures and pressures. As can be seen in this figure, the difference between the results calculated using the fundamental equations of state and the reference data is negligible. These

comparisons were done for other thermodynamic properties of Neon and adaptation of results with reference data was investigated. Figure 5 shows the areas with acceptable and high accuracy of the fundamental equations of state to predict the thermodynamic properties of Neon gas. The relative error of calculating the thermodynamic properties in the area with high accuracy can be seen in Table 5. For Neon in the acceptable accuracy area of the fundamental equations of state, the maximum error in the calculation of the thermodynamic properties was

5.42 %, which is related to the isobaric heat capacity.

Figure 6 shows the relative error percentage of the results on the boundary of the applicability area of the fundamental equation of states (the line between the green and yellow areas shown in Figure 5) in predicting the thermodynamic properties of Neon. According to the graph, the relative error percentage of thermodynamic properties on the boundary between high and acceptable accuracy areas of the

fundamental equation of states does not exceed 1% except density that its relative error percentage is little more than 1 %. The relative error of all thermodynamic properties in acceptable accuracy area in figure 5 is in the range of 1% to 5%, except isobaric heat capacity that its relative error percentage is little more than 5 %. The relative error in the low accuracy area, shown in Figure 5, is above 5%.

Table 4. Thermodynamic properties of Helium

Temp. (K)	Density (kg/m ³)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)	C _v (kJ/kg-K)	C _p (kJ/kg-K)
P= 0.1 MPa						
27.061	8.891836	18.11989	29.35858	4.831906	0.576348	0.906184
30	8.100149	19.43684	31.77397	4.916676	0.477713	0.832618
35	6.984547	21.94122	36.2489	5.054416	0.550370	0.944077
40	6.114363	24.76466	41.10857	5.184128	0.583875	0.992979
50	4.880505	30.75937	51.23525	5.409971	0.607413	1.024568
60	4.058377	36.90119	61.52498	5.597556	0.614104	1.031705
80	3.036388	49.27353	82.18520	5.894725	0.617392	1.033313
100	2.426494	61.66107	102.8450	6.125233	0.618015	1.032623
120	2.021051	74.04470	123.4906	6.313441	0.618165	1.031963
160	1.515216	98.79836	164.7511	6.610195	0.618201	1.031158
200	1.212067	123.5403	205.9884	6.840242	0.618182	1.030751
300	0.808079	185.3721	309.0389	7.258082	0.618136	1.030341
400	0.606111	247.1899	412.0651	7.554470	0.618110	1.030203
600	0.404122	370.8112	618.0944	7.972160	0.618083	1.030111
650	0.373044	401.7152	669.5997	8.054613	0.618079	1.030101

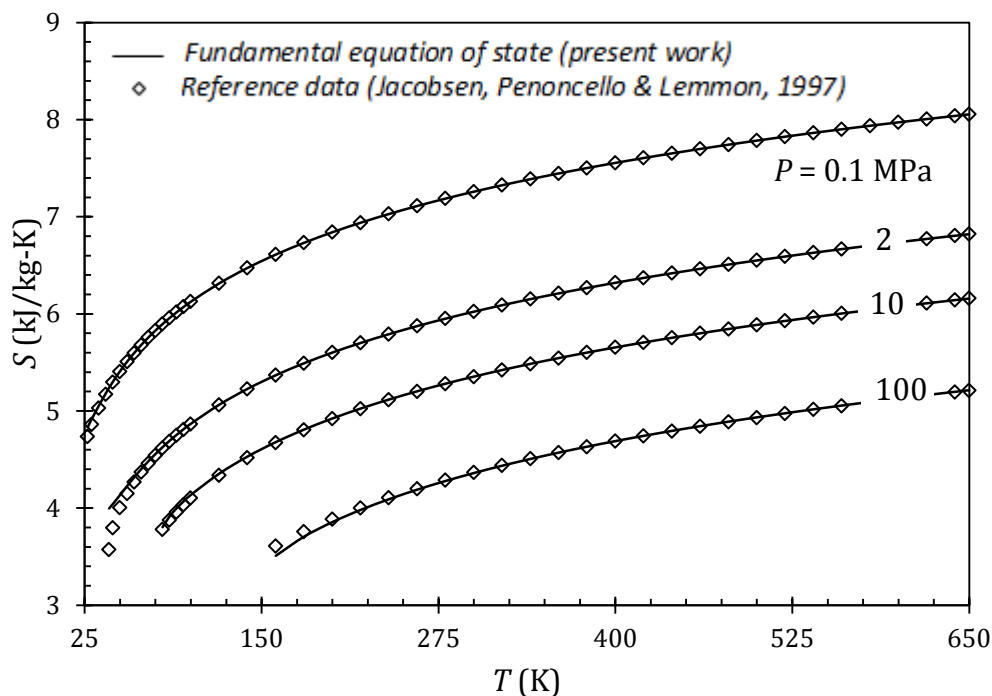


Figure 4. Entropy of Neon vs temperature in different pressures

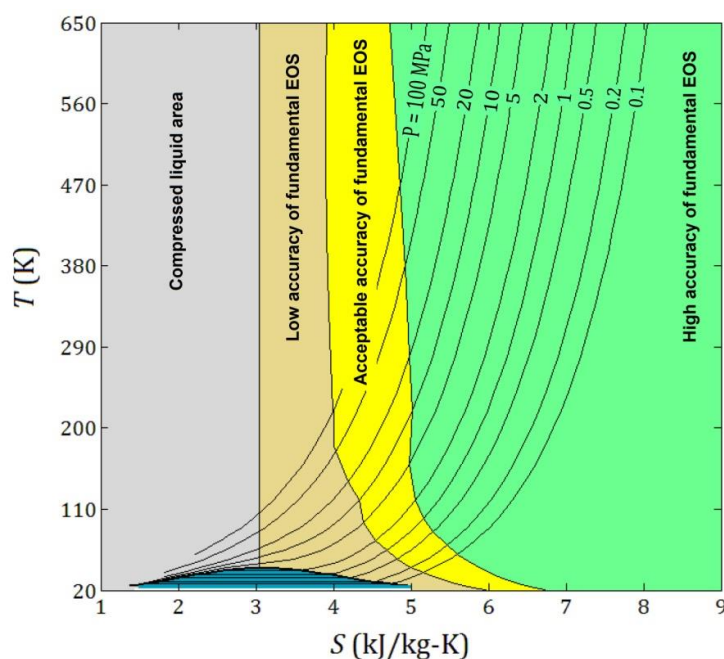


Figure 5. Applicability area of fundamental equation of state in predicting the thermodynamic properties of Neon

Table 5. Relative error of predicting thermodynamic properties of Neon in high accuracy area shown in figure 5

Property	Minimum error%	Maximum error%	Average error%
Density	0.06	0.99	0.24
Internal energy	0.00	0.86	0.13
Enthalpy	0.00	0.79	0.15
Entropy	0.00	0.10	0.02
Isochoric heat capacity	0.00	0.57	0.03
Isobaric heat capacity	0.00	1.10	0.17

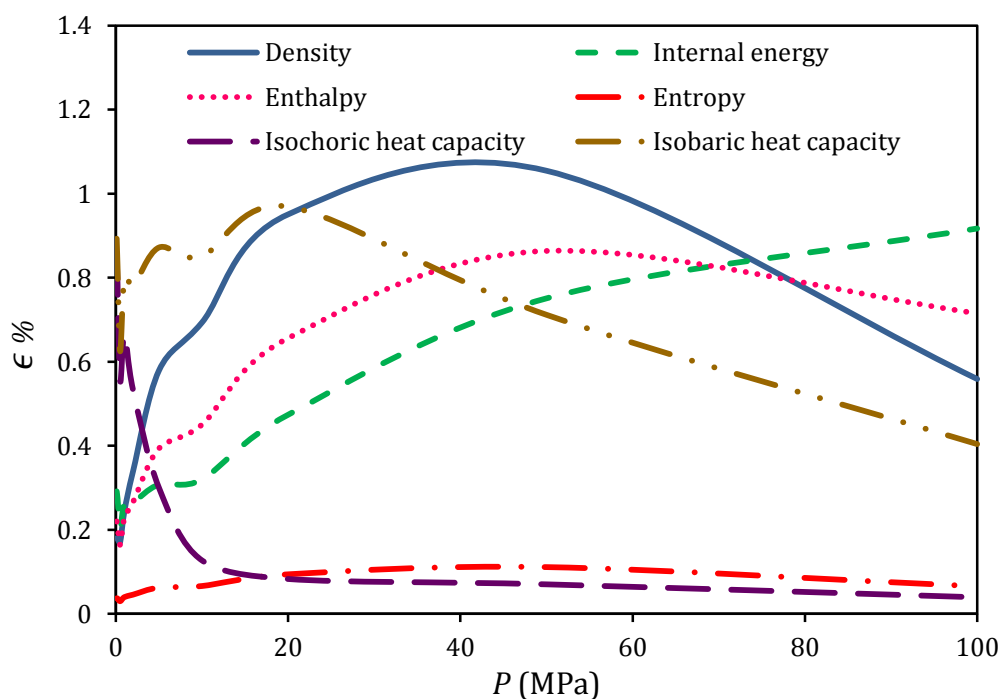


Figure 6. Relative error of thermodynamic properties of Neon on the boundary between high and acceptable accuracy areas of fundamental equation of states

6. Conclusion

Using a developed computational code based on the fundamental equation of state, the thermodynamic properties of two refrigerants Helium and Neon were predicted. By comparison, the results with reference data (Jacobsen, Penoncello & Lemmon, 1997), the pressure and temperature area in which the fundamental equation of state can be applied with high accuracy, were presented. Due to error of computation the thermodynamic properties in these areas, the accuracy of equations to predict thermodynamic properties of the cryogenic refrigerants in a wide range of temperature and pressure were approved. Most of the equations are effective only for certain areas of temperature and pressure however the fundamental equations of state can meet this problem greatly. In the applicability area of the fundamental equations of state with high accuracy area, the average relative errors of predicting thermodynamic properties of Helium is about 0.54, 0.01, and 0.05 percent respectively for density, enthalpy, and entropy. These errors for Neon are about 0.24, 0.15, and 0.02 percent respectively for density, enthalpy, and entropy. Due to the small amount of error in the calculation of the thermodynamic properties, these equations can be used for computer simulation of thermodynamic cycles in the gaseous phase.

7. References

- Bücker, D., & Wagner, W. (2006). A reference equation of state for the thermodynamic properties of ethane for temperatures from the melting line to 675 K and pressures up to 900 MPa. *Journal of Physical and Chemical Reference Data*, 35(1), 205-266.
- Dillon, H., & Penoncello, S. (2004). A fundamental equation for calculation of the thermodynamic properties of ethanol. *International Journal of Thermophysics*, 25(2), 321-335.
- Estela-Urbe, J. F. (2013a). An improved Helmholtz energy model for non-polar fluids and their mixtures. Part 1: Application to non-polar pure fluids. *Fluid Phase Equilibria*, 350, 1-12.
- Estela-Urbe, J. F. (2013b). An improved Helmholtz energy model for non-polar fluids and their mixtures. Part 2: Application to mixtures of non-polar fluids. *Fluid Phase Equilibria*, 354, 326-343.
- Estela-Urbe, J. F. (2013c). An improved Helmholtz energy model for non-polar fluids and their mixtures. Part 3: Application to natural gases and related systems. *Fluid Phase Equilibria*, 356, 229-245.
- Estela-Urbe, J. F. (2014). Helmholtz energy and extended corresponding states model for the prediction of thermodynamic properties of refrigerants. *Fluid Phase Equilibria*, 369, 13-32.
- Gernert, J., & Span, R. (2016). EOS-CG: A Helmholtz energy mixture model for humid gases and CCS mixtures. *The Journal of Chemical Thermodynamics*, 93, 274-293.
- Grigoriev, B., Alexandrov, A. & Gerasimov, A. (2018). Application of multiparameter fundamental equations of state to predict the thermodynamic properties and phase equilibria of technological oil fractions. *Fuel*, 215, 80-89.
- Hou, Y., Zhao, H. L., Chen, C. Z., & Xiong, L. Y. (2006). Developments in reverse Brayton cycle cryocooler in China. *Cryogenics*, 46(5), 403-407. doi: <https://doi.org/10.1016/j.cryogenics.2005.11.021>
- Jacobsen, R., Stewart, R., & Jahangiri, M. (1986). A thermodynamic property formulation for nitrogen from the freezing line to 2000 K at pressures to 1000 MPa. *International Journal of Thermophysics*, 7(3), 503-511.
- Jacobsen, R. T., Penoncello, S. G., & Lemmon, E. W. (1997). *Thermodynamic properties of cryogenic fluids*: Springer.
- Kunz, O., & Wagner, W. (2012). The GERG-2008 wide-range equation of state for natural gases and other mixtures: an expansion of GERG-2004. *Journal of chemical & engineering data*, 57(11), 3032-3091.
- Leachman, J. W., Jacobsen, R. T., Penoncello, S., & Lemmon, E. (2009). Fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen. *Journal of Physical and Chemical Reference Data*, 38(3), 721-748.
- Maboudi, M., & Zia Bashrhagh, M. (2015). Applicability of fundamental equations of state in Simulation of Cryogenic Systems; Case Study: Reverse Brayton cryocooler for HTS cable. *Modares Mechanical Engineering*, 14(15), 103-110.
- Thol, M., Dubberke, F., Rutkai, G., Windmann, T., Köster, A., Span, R., & Vrabec, J. (2015). Fundamental equation of state correlation for hexamethyldisiloxane based on experimental and molecular simulation data. *Fluid Phase Equilibria*.
- Thol, M., Rutkai, G., Köster, A., Kortmann, M., Span, R., & Vrabec, J. (2015). Fundamental equation of state for ethylene oxide based on a hybrid dataset. *Chemical Engineering Science*, 121, 87-99.

