

Correlation of Acentric Factor and Critical Compressibility of Alkali Metals

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Abstract

The Corresponding States Principle (CSP) manifests the existence of a universal relation between the dimensionless parameters of fluids. The original two-parameter CSP can be applied only to spherical molecules. Introduction of a third parameter in the original two-parameter CSP enhances the scope of CSP to include fluids whose fields deviate from spherical symmetry. The central problem in the use of CSP lies in the choice of the physically realistic characteristic parameters of substances. To extend the CSP to molecular fluids, the nonspherical nature of molecules is taken into account through the acentric factor of substances. The CSP may also be augmented with the critical compressibility of substances. In this respect, CSP based correlations between the critical compressibility and the acentric factor are relevant. Alkali metals exhibit considerable uniformity when their thermodynamic properties are expressed in a suitable dimensionless form. Microscopically, it implies that the form of the intermolecular potential is the same. Hence, the CSP based study of alkali metals is significant. This work deals with a CSP based study on the correlations of the critical compressibility and the acentric factor of cesium, rubidium and potassium. These correlations are established through a generalized van der Waals equation of state. This three-parameter equation differs from the known van der Waals equation of state by the modified expression for molecular pressure. It has been established that the critical compressibility factor has a parabolic dependence on the acentric factor of alkali metals. Moreover, cesium, rubidium and potassium are found to obey the single-parameter law of corresponding states, with the critical compressibility or the acentric factor as the thermodynamic similarity parameter.

Keywords

Acentric Factor, Alkali Metals, Corresponding States Principle, Critical Compressibility Factor, Molecular Pressure, Fluid Phase Equilibrium

1. Introduction

Alkali metals are typical metals. Hence, the study of their thermodynamic properties is of scientific interest. Moreover, the technological developments such as cooling systems for fast-neutron nuclear reactors, magneto-hydrodynamic energy conversion etc. employ fluid alkali metals. In recent years, an increased theoretical and technological interest has stimulated [1-19] extensive research on alkali metals.

As a characteristic parameter of substances, the acentric factor represents the acentricity or non-sphericity of molecules. Originally, the acentric factor was introduced as a measure of the amount by which the thermodynamic properties of a substance differ from those predicted by the principle of corresponding states. To take into account the

effects of molecular geometry, the acentric factor is widely employed [20] as a parameter in the principle of corresponding states. Moreover, the acentric factor is also employed in determining the thermodynamic properties of substances such as compressibility factor [21], fluid-phase equilibrium [22], virial coefficients [23], vapor pressure [24], enthalpy of vaporization [25], vapor-liquid interfacial tension [26], thermal conductivity [27], viscosity [28] and the alpha function of equation of state [29]. Besides, the knowledge of acentric factor is also required in the technological applications such as separation technology [30], extraction processes in petroleum technology [31] etc. Owing to these facts, the study of acentric factor of substances acquires scientific and technological significance. On the other hand,

the vapor-liquid critical point of substances is a fundamental characteristic point on the phase diagram. The knowledge of critical-point parameters makes it possible to predict the high-temperature properties of fluids on the basis of the law of corresponding states. Hence, the critical compressibility factor is used [32] as a parameter in the corresponding-states-principle. Moreover, both the critical compressibility factor and the acentric factor are simultaneously used [33] as parameters in the corresponding-states-principle. Considering these facts, a correlation between the acentric factor and the critical compressibility factor of substances, in particular, the one for alkali metals acquires significance.

The present work deals with the study of a corresponding-states-based correlation between the acentric factor and the critical compressibility factor of cesium, rubidium and potassium. Such a correlation is significant as the acentric factor and the critical compressibility factor are characteristic parameters of substances determined by the intermolecular forces.

2. Generalized Van Der Waals Equation of State

To improve the accuracy in the description of the thermodynamic properties of fluids, the known two-parameter van der Waals equation of state was generalized [34] by introducing a third parameter n in the expression for molecular pressure. Such a generalized van der Waals equation of state for one mole of substance is:

$$P = \frac{RT}{V-b} - \frac{a}{V^n} \quad (1)$$

where P is the pressure, V is the molar volume, T is the temperature and R is the universal gas constant; a , b and n are substance-specific constants, calculated through experimental data. The parameter n takes into account the specificity of attractive forces of various substances.

At the critical point, we have:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad (2)$$

$$T^* \left[\frac{(n^2-1)(V_2^* - V_1^*)}{[(n+1)V_1^* - (n-1)][(n+1)V_2^* - (n-1)]} + \ln \left[\frac{(n+1)V_2^* - (n-1)}{(n+1)V_1^* - (n-1)} \right] - \frac{(n+1)^2}{4(n-1)} \left(\frac{1}{V_1^{*n-1}} - \frac{1}{V_2^{*n-1}} \right) \right] = 0 \quad (7)$$

$$\frac{4n(V_2^* - V_1^*)T^*}{[(n+1)V_1^* - (n-1)][(n+1)V_2^* - (n-1)]} - \left(\frac{1}{V_1^{*n}} - \frac{1}{V_2^{*n}} \right) = 0 \quad (8)$$

$$(V_2^* - V_1^*)P^* - \frac{(n+1)}{(n-1)} \left(\frac{1}{V_1^{*n-1}} - \frac{1}{V_2^{*n-1}} \right) + \left(\frac{1}{V_1^{*n}} - \frac{1}{V_2^{*n}} \right) = 0 \quad (9)$$

It has been established [35-50] that the generalized van der

Waals equation of state is suitable for studying the high-

Application of these conditions to the equation of state given by Eq. (1) gives the critical compressibility factor as:

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{n^2 - 1}{4n} \quad (3)$$

Where P_c is the critical pressure, V_c is the critical volume and T_c is the critical temperature. Eq. (3) correlates the critical compressibility factor Z_c and the thermodynamic similarity parameter n . It manifests the fact that the critical compressibility factor is determined by the intermolecular forces, of which n is a measure.

Moreover, we may write Eq. (1) in terms of the reduced variables

$$P^* = P/P_c, V^* = V/V_c, T^* = T/T_c \text{ as:}$$

$$P^* = \frac{1}{(n-1)} \left(\frac{4nT^*}{(n+1)V^* - (n-1)} - \frac{n+1}{V^{*n}} \right) \quad (4)$$

The reduced equation of state given by Eq. (4) expresses the single-parameter law of corresponding states with the thermodynamic similarity parameter n . That is,

$$f(P^*, V^*, T^*, n) = 0 \quad (5)$$

Thus, the substances obeying the generalized van der Waals equation of state, with the same values of parameter n , are thermodynamically similar.

3. Fluid Phase Equilibrium and Acentric Factor

The fluid phase equilibrium is defined by the equalities of the Gibbs free energy, the pressure and the temperature of liquid and vapor phases:-

$$G_1 = G_2, P_1 = P_2, T_1 = T_2 \quad (6)$$

Where the indices 1 and 2 refer to liquid and vapor phases, respectively.

Application of the fluid phase equilibrium conditions given by Eq. (6) to Eq. (4) produces two equations in V^* , T^* coordinates and one equation in P^* , V^* coordinates:-

Waals equation of state is suitable for studying the high-

temperature properties of fluid alkali metals. Hence, Eqs. (7)-(9) can be considered to be valid for fluid alkali metals.

The acentric factor of a substance is defined [51] as:

$$\omega = -\log P_{vp}^* \text{ at } T^* = 0.7 - 1 \quad (10)$$

To obtain the values of acentric factor, therefore, the reduced vapor pressure at $T^*=0.7$ is required.

4. Calculations and Analysis

The parameter n of the generalized van der Waals equation of state was determined [35] through experimental data on liquid density [52], heat of evaporation at melting point [53]

Table 1. Acentric factor and critical compressibility factor of alkali metals.

Metal	n	Z_c Eq. (3)	ω Eqs. (7)-(10)	Z_c Expt. [43]	ω Expt. [43, 44]
Cesium	1.511±0.0325	0.212±0.0137	0.193±0.0042	0.202	-0.195
Rubidium	1.523±0.0328	0.217±0.0140	0.201±0.0043	0.219	-0.198
Potassium	1.515±0.0326	0.214±0.0138	0.185±0.0040	0.175	-0.184

The relative errors in the estimation of the acentric factor ω for cesium, rubidium and potassium are 2.176%, 2.139% and 2.162%, respectively. The critical compressibility factor of cesium, rubidium and potassium is determined by Eq. (3) with the values of the parameter n presented in Table 1. The errors in the estimation of n lead Z_c to have the relative errors of 6.453%, 6.462% and 6.456% for cesium, rubidium and potassium, respectively. Moreover, the results of our calculations were found to agree [37] with the values of acentric factor of cesium, rubidium and potassium estimated through experimental data on vapor pressure [54] and on critical-point parameters [55].

5. Acentric Factor-Critical Compressibility Correlation

The plot of the thermodynamic similarity parameter versus the acentric factor of cesium, rubidium and potassium, determined by the generalized van der Waals equation of state, reveals that a parabola can be drawn through these three points. The equation of the parabola passing through these three points is algebraically found [36] to be:

$$n = 125\omega^2 + 47.750\omega + 6.071 \quad (11)$$

Eq. (11) gives the correlation between the thermodynamic similarity parameter n and the acentric factor of cesium, rubidium and potassium. In general, the acentric factor is calculated through experimental data on the critical point and the vapor pressure of substances in the critical region which are seldom reliably determined due to severe experimental difficulties. On the other hand, Eq. (11) enables one to determine the acentric factor of cesium, rubidium and potassium through the thermodynamic similarity parameter n which can be reliably determined. Moreover, it follows from Eqs. (4) and (11) that the acentric factor can also be used as the thermodynamic similarity parameter instead of the

and on critical temperature [54] for cesium, rubidium and potassium. The values of the parameter n are presented in Table 1. As seen, the values of the thermodynamic similarity parameter n for cesium, rubidium and potassium differ only slightly. The relative errors in the estimation of the parameter n for cesium, rubidium and potassium are 2.151%, 2.154% and 2.152%, respectively. For cesium, rubidium and potassium, the reduced pressures at $T^*=0.7$ were determined [37] by solving Eqs. (7)-(9) with the values of the parameter n presented in Table 1. Then, the acentric factor ω of cesium, rubidium and potassium was determined [37] by Eq. (10), using the obtained values of vapor pressures at $T^*=0.7$. The obtained values of acentric factor ω are presented in Table 1.

parameter n , as the parameter ω is expressed in terms of the parameter n . That is,

$$f(P^*, V^*, T^*, \omega) = 0 \quad (12)$$

This means that the substances obeying the generalized van der Waals equation of state, with the same values of the acentric factor, are thermodynamically similar.

On the other hand, Eq. (3) is a quadratic equation in terms of n . That is,

$$n^2 - 4Z_c n - 1 = 0 \quad (13)$$

One of the solutions of Eq. (13), with the physical consideration i.e. $n > 0$ taken into account, gives

$$n = 2Z_c + \sqrt{4Z_c^2 + 1} \quad (14)$$

It follows from Eqs. (4) and (14) that the critical compressibility factor Z_c can also be used as the thermodynamic similarity parameter instead of the parameter n , as the parameter Z_c is expressed in terms of the parameter n . That is,

$$f(P^*, V^*, T^*, Z_c) = 0 \quad (15)$$

On the other hand, Eqs. (11) and (14) give the correlation of the acentric factor and the critical compressibility factor as

$$Z_c + \sqrt{Z_c^2 + 0.250} = 62.500\omega^2 + 23.875\omega + 3.036 \quad (16)$$

Eq. (16) correlates the measures of the intermolecular forces and that of nonsphericity of molecules. The corresponding-states-based correlation given by Eq. (16) is significant in the study of cesium, rubidium and potassium since the corresponding states principle plays an important role in evaluating and correlating the physiochemical

properties of substances. Moreover, the corresponding-states-based correlations between the properties that depend primarily on intermolecular forces are significant in practical applications.

A few other linear correlations between the acentric factor and the critical compressibility factor have been reported [20, 56] for various substances. However, those correlations do not fit the experimental data for the acentric factor and the critical compressibility factor of cesium, rubidium and potassium. On the other hand, the correlation given by Eq. (16) is found to fit the experimental data for the acentric factor and the critical compressibility factor of cesium, rubidium and potassium. Moreover, Eq. (16) shows that the acentric factor of cesium, rubidium and potassium is not linear with the critical compressibility factor.

6. Conclusion

This work has established the correlations between the critical compressibility factor and the acentric factor for cesium, rubidium and potassium on the basis of the generalized van der Waals equation of state. The generalized van der Waals equation of state accurately describes the thermodynamic properties of fluid alkali metals in a wide range of temperatures from the melting point to the critical point. Hence, the obtained correlations between the critical compressibility factor and the acentric factor of alkali metals are precise within the accuracy of the used experimental data. Moreover, it has been established that the critical compressibility factor and the acentric factor of alkali metals are the thermodynamic similarity parameters in the corresponding states principle. It has been established that the critical compressibility factor has a parabolic dependence on the acentric factor of alkali metals. The alkali metals are typical metals which have numerous high-temperature applications. In this respect, the obtained correlations are theoretically and technologically significant as the critical compressibility factor and the acentric factor are characteristic thermodynamic parameters of alkali metals.

References

- [1] W. C. Pilgrim, S. Hosokawa, C. Morkel, *Contrib. Plasma Phys.* 41 (2001) 283-286.
- [2] A. A. Likal'ter, H. Hess, H. Schneidenbach, *Physica Scripta* 66 (2002) 89-93.
- [3] F. Hensel, W. C. Pilgrim, *Contrib. Plasma Phys.* 43 (2003) 306-310.
- [4] L. Maftoon-Azad, A. Boushehri, *Int. J. Thermophys.* 25 (2004) 893-899.
- [5] V. Rogankov, T. Bedrova, *VysnykLviv Univ. Ser. Physica*, 38 (2005) 197-202.
- [6] E. K. Goharshadi, A. R. Berenji, *J. Nucl. Mat.* 348 (2006) 40-44.
- [7] O. M. Krasilnikov, *Fizika Metalovi Metalovedenie* 103 (2007) 306-310.
- [8] L. A. Blagonravov, *Teplofiz. Vys. Temp.* 46 (2008) 680-684.
- [9] J. Amoros, S. Ravi, *Physics and Chemistry of Liquids* 49 (2011) 9-20.
- [10] M. Moosavi, S. Sabzevari, *J. Mol. Liq.* 174 (2012) 117-123.
- [11] N. Mehdipour, *Fluid Phase Equilib.* 355 (2013) 8-11.
- [12] T. Bouazza, L. Baggami, M. Bouledroua, *Int. J. Thermophys.* 35, 327-335 (2014).
- [13] L. Biolsi, *Int. J. Thermophys.* 35, 1785-1802 (2014).
- [14] L. Biolsi, M. Biolsi, *Int. J. Thermophys.* 37, 42 (2016).
- [15] Q. Liu, *Int. J. Thermophys.* 37, 65 (2016).
- [16] X. Li, S. Li, H. Ren, J. Yang, Y. Tang, *Nanomaterials*, 7, 184 (2017)/
- [17] H. Nikoofard, F. Bakhtiar, *Physics and Chemistry of Liquids*, (2018)/
- [18] V. P. Stepanov, *Russian J. Physical Chemistry A*, 93, 799-803 (2019).
- [19] T. V. Gordeychuk, M. V. Kazachek, *Russian J. Physical Chemistry A*, 93, 1000-1003 (2019).
- [20] L. P. Filippov, *Prediction of Thermophysical Properties of Liquids and Gases*, Energoatomizdat, Moscow, 1988.
- [21] A. J. Queimada, J. A. P. Coutinho, I. M. Marrucho, J. L. Daridon, *Int. J. Thermophys.* 27 (2006) 1095-1109.
- [22] J. K. Singh, J. Adhikari, S. K. Kwak, *Fluid Phase Equilib.* 248 (2006) 1-6.
- [23] D. X. Liu, H. W. Xiang, *Int. J. Thermophys.* 24 (2003) 1667-1680.
- [24] H. W. Xiang, *J. Phys. Chem. Ref. Data* 33 (2004) 1005-1011.
- [25] A. Mulero, I. Cachadina, M. I. Para, *Ind. Eng. Chem. Res.* 47 (2008) 7903-7916.
- [26] A. J. Queimada, E. H. Stenby, I. M. Marrucho, J. A. P. Coutinho, *Fluid Phase Equilib.* 212 (2003) 303-314.
- [27] F. Paradela, A. J. Queimada, I. M. Marrucho, C. P. Netto, J. A. P. Coutinho, *Int. J. Thermophys.* 26 (2005) 1461-1475.
- [28] A. J. Queimada, I. M. Marrucho, J. A. P. Coutinho, *Fluid Phase Equilib.* 183-184 (2001) 229- 238.
- [29] N. A. Darwish, S. A. Al-Muhtaseb, *Thermochim. Acta* 287 (1996) 43-52.
- [30] J. Shi, M. Khatri, S. J. Xue, G. S. Mittal, Y. Ma, D. Li, *Separation and Purification Technology* 66 (2009) 322-328.
- [31] A. Leon, M. Parra, J. Grosso, *CT&F-Ciencia Tecnologia Futuro* 3 (2008) 129-142.
- [32] J. O. Valderrama, L. A. Cisternas, *Fluid Phase Equilib.* 29 (1986) 431-438.
- [33] H. Tang, *Int. Chem. Eng.* 27 (1987) 148-157.
- [34] M. M. Martynyuk, *Zh. Fiz. Khim.* 65 (1991) 1716-1717.

- [35] M. M. Martynyuk, R. Balasubramanian, *Int. J. Thermophys.*, 16 (2) (1995) 533–543.
- [36] R. Balasubramanian, *High Temp. –High Press.*, 34 (2002) 335.
- [37] R. Balasubramanian, *Int. J. Thermophys.*, 24 (2003) 201-206.
- [38] R. Balasubramanian, *J. Chem. Eng. Jpn.*, 37 (2004) 1415.
- [39] R. Balasubramanian, *Physica B*, 381 (2006) 128.
- [40] R. Balasubramanian, *Int. J. Thermophys.*, 27 (2006) 1494-1500.
- [41] R. Balasubramanian, *J. Nucl. Mat.*, 366 (2007) 272.
- [42] R. Balasubramanian, *Asia-Pacific J. Chem. Eng.*, 3 (2008) 90.
- [43] R. Balasubramanian, *J. of Molecular Liquids*, 151 (2010) 130-133.
- [44] R. Balasubramanian, *Thermochemica Acta*, 566 (2013) 233-237.
- [45] R. Balasubramanian, *Open J. Chem. Eng. Sci.*, 1 (2014) 61-66.
- [46] R. Balasubramanian, Kowsarbanu A, Ramesh A, *Open Sci. J. Modern Phys.* 5 (2) (2018) 24-31.
- [47] R. Balasubramanian, Ramesh A, Kowsarbanu A, *American J. Chem. Mat. Sci.*, 5 (6) (2018) 91-98.
- [48] R. Balasubramanian, and Sakthivel M, *AmericanJ. Chem. Mat. Sci.* 6 (2) (2019) 36-43.
- [49] R. Balasubramanian, and Ruba K, *AmericanJ. Chem. Mat. Sci.* 6 (2) (2019) 44-51.
- [50] R. Balasubramanian, and Anupriya S, *AmericanJ. Chem. Mat. Sci.* 6 (2) (2019) 52-57.
- [51] R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, Singapore (1988).
- [52] P. Browning, P. E. Potter, in: R. W. Ohse (Ed.), *Handbook of Thermodynamic and Transport Properties of Alkali*.
- [53] *Metals*, Blackwell Scientific, Oxford (1985) 349-358.
- [54] K. Hornung, in: R. W. Ohse (Ed.), *Handbook of Thermodynamic and Transport Properties of Alkali Metals*.
- [55] Blackwell Scientific, Oxford (1985) 487-524.
- [56] F. Hensel, H. Uchtmann, *Annu. Rev. Phys. Chem.* 40 (1989) 61-83.
- [57] R. W. Ohse, J. F. Babelot, J. Magill, M. Tatenbaum, in: R. W. Ohse (Ed.), *Handbook of Thermodynamic and*.
- [58] *Transport Properties of Alkali Metals*, Blackwell Scientific, Oxford (1985) 329-347.
- [59] D. R. Schreiber, K. S. Pitzer, *Fluid Phase Equilib.* 46 (1989) 113-130.