

# Corresponding States Correlations of Supercritical-Point Parameters and Acentric Factor of Alkali Metals

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## Abstract

The Corresponding States Principle (CSP) has a significant role in the estimation of thermophysical properties of fluids. It 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 supercritical-point parameters. In this respect, CSP based correlations between the supercritical-point parameters 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 supercritical-point parameters 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. Moreover, cesium, rubidium and potassium are found to obey the single-parameter law of corresponding states, with the reduced supercritical parameters or the acentric factor as the thermodynamic similarity parameter.

## Keywords

Acentric Factor, Alkali Metals, Corresponding States Principle, Quasispinodal, Supercritical Parameters

## 1. Introduction

The Corresponding States Principle (CSP) has a significant role in the estimation of thermophysical properties of fluids. It 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 supercritical-point parameters. In this respect, CSP based correlations between the supercritical-point parameters 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. In recent years, there has been a spurt of research activity involving the use of CSP for predicting the thermophysical properties of fluids. However, the CSP based study of metallic fluids is scarce. The supercritical parameters of substances determine the upper

limits of temperature, pressure and volume of the phase characterized by the anomalies in the thermodynamic stability. That is, in the interval from the critical point to the supercritical point on the phase diagram, the supercritical fluids exhibit anomalies in their thermodynamic stability. The supercritical fluids, owing to their unique properties, are employed [1-4] in numerous technological applications. Considering these facts, in recent years, numerous studies [5-13] on the supercritical fluids have been made.

On the other hand, the acentric factor, as a characteristic parameter of substances, represents the nonsphericity of molecules. The acentric factor is widely employed [14] as a parameter in the corresponding states principle. Moreover, the acentric factor is employed in determining the thermodynamic properties of substances such as compressibility factor [15], fluid-phase equilibrium [16], virial coefficients [17], vapor pressure [18], enthalpy of vaporization [19], vapor-liquid interfacial tension [20], thermal conductivity [21], viscosity [22] and the alpha function of equation of state [23]. The knowledge of acentric factor is also required in the technological applications such as separation technology [1], extraction processes in petroleum technology [24] etc. Considering these facts, in recent years, numerous studies [25-28] on the acentric factor of substances have been made.

In this respect, the study of the correlations between the supercritical parameters and the acentric factor of substances, particularly for alkali metals, acquires significance. The study of the thermodynamic properties of the alkali metals is of scientific and technological interest. This is underscored by the fact that the alkali metals are typical metals employed in the technological developments such as cooling systems for fast-neutron nuclear reactors, magnetohydrodynamic energy conversion etc. Considering these facts, in recent years, numerous studies [29-36] on the thermophysical properties of alkali metals have been made.

The present work, based on a three-parameter generalized van der Waals equation of state, deals with the thermodynamic study of correlations between the supercritical parameters and the acentric factor of cesium, rubidium and potassium. Such correlations are significant as the supercritical parameters and the acentric factor are characteristic thermodynamic parameters of substances determined by the intermolecular forces.

## 2. Generalized Van Der Waals Equation of State

The known van der Waals equation of state does not lend itself to the precise description of the thermodynamic properties of fluids. Hence, an improvement of this equation was proposed [37] 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. The substance-specific constants  $a$ ,  $b$  and  $n$  are calculated through experimental data. The parameter  $n$  takes into account the specificity of attractive forces of various substances.

The critical point conditions are

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

Applying these conditions, we may write Eq. (1) in terms of the reduced variables  $P^* = P/P_c$ ,  $V^* = V/V_c$ ,  $T^* = T/T_c$  as

$$P^* = \frac{1}{(n-1)} \left( \frac{4nT^*}{(n+1)V^* - (n-1)} - \frac{n+1}{V^{*n}} \right) \quad (3)$$

Where  $P_c$  is the critical pressure,  $V_c$  is the critical volume and  $T_c$  is the critical temperature.

The reduced equation of state given by Eq. (3) expresses the single-parameter law of corresponding states with the thermodynamic similarity parameter  $n$ . That is, the substances with the same value of parameter  $n$  are thermodynamically similar. Such substances have similar intermolecular force characteristics.

## 3. Quasispinodal and Supercritical Point

The locus of the points of inflection on the supercritical isotherms on the phase diagram of substances is known as the quasispinodal. This is a characteristic curve on the phase diagram. The quasispinodal is defined [38] by the conditions:

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0, \quad -\left(\frac{\partial P}{\partial V}\right)_T > 0 \quad (4)$$

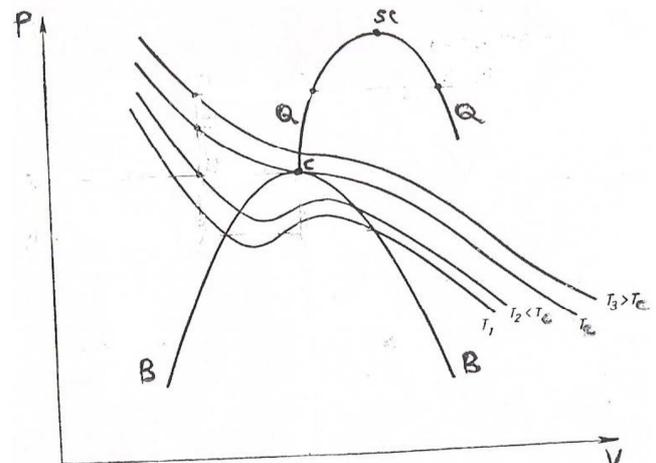


Figure 1. A typical phase diagram of substances.

B-Binodal (liquid-vapor equilibrium curve); Q-Quasispinodal; C-Critical point; SC-Supercritical point; Other curves-Isotherms

The quasispinodal on the phase diagram has two branches (Figure 1). One branch, corresponding to the minimum values of the isothermal elasticity, defines the supercritical states of decreased thermodynamic stability and increased fluctuations. The other branch, corresponding to the maximum values of the isothermal elasticity, defines the supercritical states of increased thermodynamic stability and decreased fluctuations. These branches of the quasispinodal merge at the supercritical point which is a characteristic point on the phase diagram. The supercritical point is defined by the conditions:

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0, \quad \left(\frac{\partial^3 P}{\partial V^3}\right)_T = 0, \quad -\left(\frac{\partial P}{\partial V}\right)_T > 0 \quad (5)$$

Application of the conditions given by Eq. (5) to Eq. (3) gives the reduced supercritical volume  $V_{sc}^*$ , the reduced supercritical temperature  $T_{sc}^*$  and the reduced supercritical pressure  $P_{sc}^*$  as

$$V_{sc}^* \equiv \frac{V_{sc}}{V_c} = \frac{n+2}{n+1} \quad (6)$$

$$T_{sc}^* \equiv \frac{T_{sc}}{T_c} = \frac{27}{8} \left(\frac{n+1}{n+2}\right)^{n+2} \quad (7)$$

$$T^* \left[ \frac{(n^2-1)(V_2^* - V_1^*)}{[(n+1)V_1^* - (n-1)][(n+1)V_2^* - (n-1)]} + \ln \left[ \frac{(n+1)V_2^* - (n-1)}{(n+1)V_1^* - (n-1)} \right] - \frac{(n+1)^2}{4(n-1)} \left( \frac{1}{V_1^{*n-1}} - \frac{1}{V_2^{*n-1}} \right) \right] = 0 \quad (10)$$

$$\frac{4n(V_2^* - V_1^*)T^*}{[(n+1)V_1^* - (n-1)][(n+1)V_2^* - (n-1)]} - \left( \frac{1}{V_1^{*n}} - \frac{1}{V_2^{*n}} \right) = 0 \quad (11)$$

$$(V_2^* - V_1^*)P^* - \frac{(n+1)}{(n-1)} \left( \frac{1}{V_1^{*n-1}} - \frac{1}{V_2^{*n-1}} \right) + \left( \frac{1}{V_1^{*n}} - \frac{1}{V_2^{*n}} \right) = 0 \quad (12)$$

The acentric factor of a substance is defined [14] as

$$\omega = -\log P_{vp}^* \text{ at } T^* = 0.7 - 1 \quad (13)$$

### 5. Correlations Between Supercritical Parameters and Acentric Factor

Analysis of the values of the thermodynamic similarity parameter and the acentric factor of cesium, rubidium and potassium, determined by the generalized van der Waals equation of state, reveals the correlation between the thermodynamic similarity parameter  $n$  and the acentric factor  $\omega$  as

$$P_{sc}^* \equiv \frac{P_{sc}}{P_c} = \frac{(7n+8)}{n(n+2)} \left( \frac{n+1}{n+2} \right)^{n+1} \quad (8)$$

As seen, the reduced supercritical parameters are determined by the thermodynamic similarity parameter  $n$ . Moreover, it follows from Eq. (3) and Eqs. (6)-(8) that any of the reduced supercritical parameters  $V_{sc}^*$ ,  $T_{sc}^*$  and  $P_{sc}^*$  can also be used as the thermodynamic similarity parameter instead of the parameter  $n$ . The Eqs. (6)-(8) Manifest the fact that the reduced supercritical parameters  $V_{sc}^*$ ,  $T_{sc}^*$  and  $P_{sc}^*$  are determined by the intermolecular forces of which  $n$  is a measure.

### 4. 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:-

$$G_1 = G_2, P_1 = P_2, T_1 = T_2 \quad (9)$$

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

Application of the fluid phase equilibrium conditions given by Eq. (9) to Eq. (3) produces two equations in  $V^*$ ,  $T^*$  coordinates and one equation in  $P^*$ ,  $V^*$  coordinates:

$$n = 125\omega^2 + 47.750\omega + 6.071 \quad (14)$$

Eq. (14) 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. (3) and (14) that the acentric factor can also be used as the thermodynamic similarity parameter instead of the parameter  $n$ , as the parameter  $\omega$  is expressed in terms of the parameter  $n$ . 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.

From Eqs. (6) and (14), we get the reduced supercritical volume correlated to the acentric factor for cesium, rubidium and potassium as

$$V_{sc}^* = \frac{125\omega^2 + 47.750\omega + 8.071}{125\omega^2 + 47.750\omega + 7.071} \quad (15)$$

From Eqs. (7) and (14), we get the reduced supercritical temperature correlated to the acentric factor for cesium, rubidium and potassium as

$$P_{sc}^* = \frac{875\omega^2 + 334.250\omega + 50.497}{2(125\omega^2 + 47.750\omega + 8.071)} \left( \frac{125\omega^2 + 47.750\omega + 7.071}{125\omega^2 + 47.750\omega + 8.071} \right)^{125\omega^2 + 47.750\omega + 8.071} \quad (17)$$

Eqs. (15)-(17) are significant as these correlate the measures of the intermolecular forces and that of nonsphericity of molecules.

## 6. Calculations and Analysis

As seen from Eqs. (6)-(8), the knowledge of the value of the parameter  $n$  enables one to determine the supercritical parameters of substances. It has been established [39-48] that the generalized van der Waals equation of state given by Eq. (1) is suitable for studying the high-temperature properties of fluid alkali metals. The parameter  $n$  of the generalized van der Waals equation of state was determined [--] through experimental data on liquid density, heat of evaporation at

$$T_{sc}^* = \frac{27}{8} \left( \frac{125\omega^2 + 47.750\omega + 7.071}{125\omega^2 + 47.750\omega + 8.071} \right)^{125\omega^2 + 47.750\omega + 8.071} \quad (16)$$

From Eqs. (8) and (14), we get the reduced supercritical pressure correlated to the acentric factor for cesium, rubidium and potassium as

melting point and on critical temperature of cesium, rubidium and potassium. The obtained 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 do not differ much. 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 supercritical parameters are determined by Eqs. (6)-(8) with the values the parameter  $n$  presented in Table 1. The obtained values of the reduced supercritical parameters for cesium, rubidium and potassium are presented in Table 1. For cesium, rubidium and potassium, the reduced supercritical parameters are found to be about  $T_{sc}^* = 1.04$ ,  $P_{sc}^* = 1.14 P_c$  and  $V_{sc}^* = 1.40 V_c$ .

Table 1. Reduced supercritical parameters and acentric factor of alkali metals.

Metal	$n$	$V_{sc}^*$ Eq. (6)	$T_{sc}^*$ Eq. (7)	$P_{sc}^*$ Eq. (8)	Eqs. (10)-(13)
Cesium	1.511	1.398	1.040	1.140	- 0.193
Rubidium	1.523	1.396	1.041	1.141	- 0.201
Potassium	1.515	1.398	1.041	1.140	- 0.185

For cesium, rubidium and potassium, the acentric factor was determined [---] by Eqs. (10)-(13) with the values of the parameter  $n$  presented in Table 1. The obtained values of acentric factor  $\omega$  are presented in Table 1. The results of our calculations were found to agree [--] with the values of acentric factor of cesium, rubidium and potassium estimated through experimental data on vapor pressure and on critical-point parameters.

## 7. Conclusion

This work has established the correlations between the supercritical parameters 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 supercritical parameters and the acentric factor of alkali metals are precise within the accuracy of the used experimental data. Moreover, it has been established that the supercritical parameters and the acentric factor of alkali metals are the thermodynamic similarity parameters in the corresponding states principle. 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 supercritical parameters and the acentric factor are characteristic thermodynamic parameters of alkali metals.

## References

- [1] J. Shi, M. Khatri, S. J. Xue, G. S. Mittal, Y. Ma and D. Li, Separation and Purification Techn. Vol. 66, pp. 322-328, 2009.
- [2] G. Brunner, Chem. Biomol. Eng. Vol. 1, pp. 321-342, 2010.
- [3] J. Liu, E. L. Regalado, I. Mergelsberg and C. J. Welch, Org. Biomol. Chem. vol. 11, pp. 4925-4929, 2013.
- [4] G. A. Leeke, T. Lu, R. H. Bridson and J. P. K. Seville, The J. Supercritical Fluids, vol. 91, pp. 7-14, 2014.
- [5] M. k. Hrnica, D. Cor, M. T. Verboten, Z. Knez, Food quality and Safety, 2, 59-67 (2018).
- [6] S. Clercq, A. Mouahid, P. Gerard, E. Badens, The Journal of Supercritical Fluids, 141, 29-38 (2018).
- [7] J. Lang, L. Matejova, Z. Matej, L. Capek, L. Svoboda, The Journal of Supercritical Fluids, 141, 39-48 (2018).
- [8] M. Akizuki, Y. Oshima, The Journal of Supercritical Fluids, 141, 173-181 (2018).

- [9] G. Seong, T. Aida, Y. Nakagawa, T. Nanba, O. Okada, A. Yoko, T. Tomai, S. Takami, T. Adschiri, *The Journal of Supercritical Fluids*, 147, 302-309 (2019).
- [10] B. Zezere, J. Cordeiro, J. Leite, A. L. Magalhaes, I. Portugal, C. M. Silva, *The Journal of Supercritical Fluids*, 143, 259-267 (2019).
- [11] D. M. Heyes, L. V. Woodcock, *Fluid Phase Equilibria*, 536, 301-308 (2013).
- [12] H. Magnier, R. Curtis, L. Woodcock, *Natural Science*, 6, 797-807 (2014).
- [13] J. L. Finney, L. V. Woodcock, *J. Phys: Condens. Mat.* 26, 1-19 (2014).
- [14] L. P. Filippov, *Prediction of Thermophysical Properties of Liquids and Gases*, Energoatomizdat, Moscow, 1988.
- [15] A. J. Queimada, J. A. P. Coutinho, I. M. Marrucho and J. L. Daridon, *Int. J. Thermophys.* vol. 27, pp. 1095-1109, 2006.
- [16] J. K. Singh, J. Adhikari and S. K. Kwak, *Fluid Phase Equilib.* Vol. 248, pp. 1-6, 2006.
- [17] D. X. Liu and H. W. Xiang, *Int. J. Thermophys.*, vol. 24, pp. 1667-1680, 2003.
- [18] H. W. Xiang, *J. Phys. Chem. Ref. Data*, vol. 33, pp. 1005-1011, 2004.
- [19] A. Mulero, I. Cachadina and M. I. Para, *Ind. Eng. Chem. Res.* vol 47, pp. 7903-7916, 2008.
- [20] A. J. Queimada, E. H. Stenby, I. M. Marrucho and J. A. P. Coutinho, *Fluid Phase Equilib.*, vol. 212, pp. 303-314, 2003.
- [21] F. Paradela, A. J. Queimada, I. M. Marrucho, C. P. Netto and J. A. P. Coutinho, *Int. J. Thermophys.*, vol. 26, pp. 1461-1475, 2005.
- [22] A. J. Queimada, I. M. Marrucho and J. A. P. Coutinho, *Fluid Phase Equilib.*, vol. 183-184, pp. 229- 238, 2001.
- [23] N. A. Darwish and S. A. Al-Muhtaseb, "A comparison between four cubic equations of state in predicting the inversion curve and spinodal curve loci of methane", *Thermochim. Acta*, vol. 287, pp. 43-52, 1996.
- [24] A. Leon, M. Parra and J. Grosso, "Estimation of critical properties of typically columbian vacuum residue sara fractions", *CT&F-Ciencia Tecnologia Futuro*, vol. 3, pp. 129-142, 2008.
- [25] E. Ghasemian, R. Zobeydi, *Fluid Phase Equilibria*, 358, 40-43 (2013).
- [26] S. Tahami, H. Ghasemitabar, K. Movagharnjad, *Fluid Phase Equilibria*, In Press (2019).
- [27] I. Machin, C. Olivera\_Fuentes, *J. Computational Methods in Sciences and Engineering*, 17, 161-175 (2017).
- [28] W. H. Carande, A. F. Kazakov, C. D. Muzny, M. D. Frenkel, *J. Chem Eng. Data*, 60, 1377-1387 (2015).
- [29] M. T. Bouazza, L. Baggami, M. Bouledroua, *Int. J. Thermophys.*, 35, 327-335 (2014).
- [30] L. Biolsi, *Int. J. Thermophys.*, 35, 1785-1802 (2014).
- [31] L. Biolsi, M. Biolsi, *Int. J. Thermophys.*, 37, 42 (2016).
- [32] Q. Liu, *Int. J. Thermophys.*, 37, 65 (2016).
- [33] X. Li, S. Li, H. Ren, J. Yang, Y. Tang, *Nanomaterials*, 7, 184 (2017).
- [34] H. Nikoofard, F. Bakhtiar, *Physics and Chemistry of Liquids*, ----- (2018).
- [35] V. P. Stepanov, *Russian J. Physical Chemistry A*, 93, 799-803 (2019).
- [36] T. V. Gordeychuk, M. V. Kazachek, *Russian J. Physical Chemistry A*, 93, 1000-1003 (2019).
- [37] M. M. Martynyuk, "Generalized van der Waals equation of state for liquids and gases", *Zh. Fiz. Khim.*, vol. 65, pp. 1716-1717, 1991.
- [38] V. K. Semenchenko, *Selected Topics of Theoretical Physics*, Prosveshenie Publication, Moscow 1966.
- [39] M. M. Martynyuk and R. Balasubramanian, "Equation of state for fluid alkali metals: binodal", *Int. J. Thermophys.*, vol. 16, pp. 533-543, 1995.
- [40] R. Balasubramanian, "Acentric factor of alkali metals", *Int. J. Thermophys.*, vol. 24, pp. 201-206, 2003.
- [41] R. Balasubramanian, "A correlation of maximum attainable superheat and acentric factor of alkali metals", *Thermochim. Acta*, vol. 566, pp. 233-237, 2013.
- [42] R. Balasubramanian, "Correlations of characteristic thermodynamic parameters of alkali metals", *Open J. Chem. Eng. Sci.*, vol. 1, pp. 51-60, 2014.
- [43] R. Balasubramanian, Kowsarbanu A and Ramesh A, *Open Sci. J. Modern Phys.*, vol. 5, No. 2, 24-31, (2018).
- [44] R. Balasubramanian, Ramesh A, and Kowsarbanu A, *American J. Chem. Mat. Sci.*, vol. 5, No. 6, 91-98, (2018).
- [45] R. Balasubramanian, and Sakthivel M, *American J. Chem. Mat. Sci.*, vol. 6, No. 2, 36-43, (2019).
- [46] R. Balasubramanian, and Ruba K, *American J. Chem. Mat. Sci.*, vol. 6, No. 2, 44-51, (2019).
- [47] R. Balasubramanian, and Anupriya S, *American J. Chem. Mat. Sci.*, vol. 6, No. 2, 52-57, (2019).
- [48] R. Balasubramanian, "A study on the supercritical parameters of alkali metals", *Open J. Chem. Eng. Sci.*, vol. 1, pp. 61-66, 2014.