

# **Heat Capacity Difference of Alkali Metals**

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#### Abstract

The heat capacity difference of liquid alkali metals has been the determined on the basis of a generalized van der Waals equation of state over a wide range of temperatures from the boiling point to the critical point. With the increase in temperature, the heat capacity difference of liquid alkali metals is found to increase. In the temperature range from the boiling point to 0.8Tc, the heat capacity difference of liquid alkali metals has a parabolic dependence on temperature. In the temperature range from  $0.8T_c$  to  $T_c$ , heat capacity difference of liquid alkali metals has a linear dependence on temperature with a large positive slope. As the generalized van der Waals equation of the state accurately determines the thermophysical properties of alkali metals in wide range of temperature from the boiling point to the critical point, the obtained data on the heat capacity difference of liquid alkali metals has metals has metals has a point to the critical point.

### **Keywords**

Alkali Metals, Heat Capacity, Equation of State

## **1. Introduction**

Alkali metals have high electrical and thermal conductivities, small densities and viscosities, low melting temperature and work function, wide temperature range of liquid state, large heat of evaporation. Hence, they are widely used in nuclear energetics, emission electronics, power-intensive chemical current sources, medicine, and other fields. The liquid alkali metals act as coolants in nuclear power plants. The construction of high energy electrochemical cells, thermionic and magneto-hydrodynamic converters is possible using these metals. They are effectively used in extraction metallurgy. Due to the scientific and technological significance of the alkali metals, numerous studies on the thermodynamic properties of alkali metals have been made [1-29].

The heat capacity difference is a characteristic thermodynamic property of liquids. The knowledge of heat capacity difference is essential in understanding the thermodynamic behavior of liquid alkali metals and also in several technological applications. In recent years, several studies have been made [30-38] on the heat capacity of liquids. Although, the thermodynamic properties of liquid alkali metals are widely investigated, there are temperature regions

where accurate information does not exist. The measurement of thermophysical properties of liquid alkali metals especially at high temperature is very difficult as these metals are reactive at high temperature. Prediction of these properties using accurate equation of state is an alternative to the experimental difficulties associated with their measurement.

The given work, based on the three- parameter generalized van der Waals equation of state, deals with the determination of heat capacity difference of liquid alkali metals. The generalized van der Waals equation of state differs from the known van der Waals equation of state by the modified expression for internal pressure. It has been established [39-50] that the generalized equation state satisfactorily describes the thermodynamic properties of alkali metals over a wide range of temperature from the boiling point to the critical point. Therefore, the data on the heat capacity difference of alkali metals, obtained in the given work, may be considered to be reliable.

# 2. Generalized van der Waals Equation of State

To improve the accuracy in determining the thermodynamic properties of substances the known two-parameter van der Waals equation of state is modified [39] by introducing the third parameters n in the expression for internal pressure. The three-parameter generalized van der Waals equation of state for one mole of substance has the form

$$P = \frac{RT}{V-b} - \frac{a}{V^n} \tag{1}$$

Where R is the gas constant, P is the pressure, V is the molar volume, T is the temperature; a, b and n are substance-specific parameters to be determined through experimental data.

The vapor-liquid critical point conditions are

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

Application of the vapor-liquid critical point conditions to the generalized van der Waals equation of state given by Eq. (1) gives the critical volume  $V_c$ , the critical temperature  $T_c$  and the critical pressure  $P_c$  as

$$V_c = \left(\frac{n+1}{n-1}\right)b\tag{3}$$

$$T_c = \frac{4na}{RN^{n+1}b^{n-1}(n-1)^2}$$
(4)

$$P_c = \frac{a}{N^n b^n} \left(\frac{1}{N}\right) \tag{5}$$

Where,

$$N = (n+1)/(n-1)$$

The critical compressibility factor is given by.

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{n^2 - 1}{4n} \tag{6}$$

Then, the generalized van der Waals equation of state given by Eq. (1) may be rewritten in the reduced form as

$$P^* = \frac{1}{(n-1)} \left[ \frac{4nT^*}{(n+1)V^* - (n-1)} - \frac{n+1}{V^{*^n}} \right]$$
(7)

Where  $P^* = P/P_c$  is the reduced pressure,  $V^* = V/V_c$  is the reduced volume,  $T^* = T/T_c$  is the reduced temperature. The reduced equation of state given by Eq. (7) 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. That is, such substances have similar intermolecular force characteristics.

For alkali metals, the parameters a, b and n of the generalized van der Waals equation of state have been determined [39] through experimental data on critical

parameters. The parameters a, b and n of the generalized van der Waals equation of state given by Eq. (1) may be determined using the parameters of any characteristic point on the phase diagram of substances. However, the use of vapor-liquid critical-point parameters for determining equation-of-state parameters enhances the ability of the equation of state in determining the thermodynamic properties of alkali metals at high temperatures. The algorithm of such a method is as follows:

Eq. (6) correlates the parameter n to the critical compressibility factor. Hence, the parameter n is determined through Eq. (6) which is a quadratic equation with respect to the parameter n That is,

$$n^2 - 4nZ_c - 1 = 0 \tag{8}$$

Eq. (8) has two solutions for *n* such as

$$n = 2Z_c + \sqrt{4Z_c^2 + 1}$$
 (9)

$$n = 2Z_c - \sqrt{4Z_c^2 + 1}$$
 (10)

As seen, Eq. (9) gives a positive value for n while Eq. (10) gives a negative value for n. Due to physical consideration (i.e. the generalization parameter in the internal pressure term of the equation of state should have a positive value), only Eq. (9) can be used for determining the parameter n while Eq. (10) is to be neglected. Thus, Eq. (9) enables one to determine the parameter n through the critical compressibility factor of substances.

Eq. (4) may be used for determining the parameter a of the van der Waals equation of state. Eq. (4) gives

$$a = \frac{T_c R N^{n+1} b^{n-1} (n-1)^2}{4n}$$
(11)

Substitution of Eq.(3) into Eq.(11) gives

$$a = \frac{T_c R N^{n+1} \left(\frac{V_c}{N}\right)^{n-1} (n-1)^2}{4n}$$
$$a = \frac{T_c R N^{n+1} \frac{V_c^{n-1}}{N^{n-1}} (n-1)^2}{4n}$$
$$a = \frac{T_c R N^{n+1} N^{-n+1} V_c^{n-1} (n-1)^2}{4n}$$
$$a = \frac{R T_c V_c^{n-1} N^2 (n-1)^2}{4n}$$
$$a = \frac{R T_c V_c^{n-1} (n-1)^2 \frac{(n+1)^2}{(n-1)^2}}{4n}$$

Hence, the parameter a is correlated to the critical-point

parameters as

$$a = \frac{RT_c V_c^{n-1} (n+1)^2}{4n}$$
(12)

Eq. (12) enables one to determine the parameter a of the generalized van der Waals equation of state through the parameter n and the critical-point parameters of substances.

Eq. (3) may be used for determining the parameter b. Eq. (3) gives

$$b = \frac{V_c}{N} \tag{13}$$

Eq. (13) may be rewritten as

$$b = \left(\frac{n-1}{n+1}\right) V_c \tag{14}$$

Eq. (14) enables one to determine the parameter b of the generalized van der Waals equation of state through the parameter n and the critical-volume of the substances.

Thus, with the use of the experimental data on the critical temperature, critical volume and critical pressure of alkali metals, the values of all the three parameters of the generalized van der Waals equation of state can be determined. The obtained values of the parameters a, b and n are presented in Table 1. As seen, the values of the thermodynamic similarity parameter n for cesium, potassium and sodium are the same if confined to the accuracy of the experimental data used.

Table 1.	Equation	of state	parameters	[39]	1
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METAL	$a \frac{J}{mol} \left(\frac{m^3}{mol}\right)^{n-1}$	$b10^{-5}\left(\frac{\mathrm{m}^{3}}{\mathrm{mol}}\right)$	n	
Cesium	279.2	6.756	1.511	
Potassium	256.0	4.429	1.515	
Sodium	415.5	2.315	1.440	

# 3. Heat Capacity Difference by Generalized van der Waals Equation of State

The Heat Capacity difference is given by

$$C_{p} - C_{v} = T \left(\frac{\partial P}{\partial V}\right)_{V} \left(\frac{\partial V}{\partial T}\right)_{P}$$
(15)

Where, Cp – Isobaric heat capacity and Cv - Isochoric heat capacity

Differentiate Eq. (1) with respect to temperature T we get,

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \frac{R}{V-b}$$
(16)

Eq. (1) may be rewritten as

$$\frac{RT}{V-b} = P + \frac{a}{V^n}$$

$$T = \frac{(V-b)}{R} \left( P + \frac{a}{V^n} \right)$$

$$T = \frac{(V-b)P}{R} + \frac{(V-b)a}{RV^n}$$

$$T = \frac{(V-b)P}{R} + \frac{a}{R} (V-b)V^{-n}$$
(17)

Differentiating the Eq. (17) with respect to molar volume V, we get

$$\left(\frac{\partial T}{\partial V}\right)_{p} = \frac{P}{R} + \frac{a}{R}(V-b) - nV^{-n-1}$$

$$\left(\frac{\partial T}{\partial V}\right)_{p} = \frac{P}{R} + \frac{a}{R}\left[V^{-n} + (V-b) - nV^{-n+1}\right]$$

$$\frac{\partial T}{\partial V}\right)_{p} = \frac{P}{R} + \frac{a}{R}\left[\frac{1}{V^{-n}} - \frac{n\left(V-b\right)}{V^{-n+1}}\right]$$

$$\left(\frac{\partial V}{\partial T}\right)_{p} = \frac{1}{R}\left[P + a\left(\frac{1}{V^{-n}} - \frac{n(V-b)}{V^{-n+1}}\right)\right]$$

$$\left(\frac{\partial V}{\partial T}\right)_{p} = \frac{1}{\frac{1}{R}\left[P + a\left(\frac{1}{V^{-n}} - \frac{n(V-b)}{V^{-n+1}}\right)\right]}$$

$$\left(\frac{\partial V}{\partial T}\right)_{p} = \frac{R}{P + a\left(\frac{1}{V^{-n}} - \frac{n(V-b)}{V^{-n+1}}\right)}$$
(18)

Substituting Eq. (16) and (18) in (15) we get

$$C_{p} - C_{v} = T\left(\frac{R}{V-b}\right) \left(\frac{R}{P + a\left(\frac{1}{V^{n}} - \frac{n(V-b)}{V^{n+1}}\right)}\right)$$
$$C_{p} - C_{v} = \frac{TR^{2}}{(V-b)\left[P + a\left(\frac{1}{V^{n}} - \frac{n(V-b)}{V^{n+1}}\right)\right]}$$
(19)

The molar volume V and molar density related by

$$V = \frac{\mu}{\rho} \tag{20}$$

Where  $\mu$  – molar mass  $\rho$  – density. Substitute Eq. (20) in Eq. (19) we get.

$$C_{P} - C_{V} = \frac{TR^{2}}{\left(\frac{\mu}{\rho} - b\right)\left[P + a\left(\frac{1}{\frac{\mu}{\rho^{n}}} - \frac{n\left(\frac{\mu}{\rho} - b\right)}{\left(\frac{\mu}{\rho}\right)^{n+1}}\right)\right]}$$
(21)

$$C_{p} - C_{v} = \frac{\rho T R^{2}}{\left(\frac{\mu - b\rho}{\rho}\right) \left[P + a \left(\frac{\rho^{n}}{\mu^{n}} - \frac{n\left(\frac{\mu - b\rho}{\rho}\right)}{\frac{\mu^{n+1}}{\rho^{n+1}}}\right)\right]}$$
(22)

$$C_{p} - C_{v} = \frac{\rho T R^{2}}{\left(\mu - b\rho\right) \left[P + a \left(\frac{\rho^{n}}{\mu^{n}} - \frac{n(\mu - b\rho)(\rho^{n+1})}{\rho\mu^{n+1}}\right)\right]}$$

$$C_{p} - C_{v} = \frac{\rho T R^{2}}{\left(\mu - b\rho\right) \left[P + a \left(\frac{\rho^{n}}{\mu^{n}} - \frac{n(\mu - b\rho)\rho^{n}}{\mu^{n+1}}\right)\right]}$$

$$C_{p} - C_{v} = \frac{\rho T R^{2}}{\left(\mu - b\rho\right) \left[P + a \left(\frac{\rho^{n}\mu}{\mu^{n+1}} - \frac{n(\mu - b\rho)\rho^{n}}{\mu^{n+1}}\right)\right]}$$

$$C_{p} - C_{v} = \frac{\rho T R^{2}}{\left(\mu - b\rho\right) \left[P + a \left(\frac{\rho^{n}\mu - n(\mu - b\rho)\rho^{n}}{\mu^{n+1}}\right)\right]}$$
(23)

# 4. Determination of Heat Capacity Difference of Liquid Alkali Metals

As seen from Eq. (23), for the determination of heat capacity difference of alkali metals, the knowledge of vapor and liquid density at saturation is required. These properties of liquid alkali metals have been determined [51] through the generalized van der Waals equation of state. Using the data on the vapor and liquid density at saturation and the values of the parameters [39]. a and n for alkali metals, heat capacity difference is determined through Eq.(23). The obtained values are presented in Tables 2-4. Moreover, the obtained temperature dependence of the heat capacity difference for liquid alkali metals has been plotted in Figures 1-3.

Table 2. Heat capacity	, difference a	of liquid	cesium.
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T,K	$C_p - C_{v \text{ J/K.mol}}$
302	9.1298
400	9.6541
600	10.6404
800	11.8015
942	12.9876
1000	13.5467
1200	16.2078
1300	18.1637
1400	20.9550
1500	24.4721

Table 3. Heat capacity difference of liquid potassium.

<i>Т</i> ,К	$C_p - C_{v \text{ J/K.mol}}$
2108	63.8385
2129	65.9719

T,K	$C_p - C_{v \text{ J/K.mol}}$
2175	89.0136
2186	98.5605
2197	111.6655

Table 4. Heat capacity difference of liquid sodium.

<i>т</i> ,К	$C_p - C_{v \text{ J/K.mol}}$
400	9.3131
500	9.9484
700	10.3325
800	10.3124
900	10.8466
1000	11.6999
1100	12.2904
1200	12.936
1300	13.684
1400	14.626
1500	15.662
1600	16.957
1700	18.295
1800	20.789
1900	23.833
2000	27.698
2100	37.279
2194	41.417
2244	47.399



Figure 1. Heat capacity difference of liquid cesium.



Figure 2. Heat capacity difference of liquid potassium.



Figure 3. Heat capacity difference of liquid sodium.

### 5. Results and Discussion

The heat capacity difference of liquid alkali metals has been determined, on the basis of a generalized van der Waals equation of state, over a wide range of temperature from the boiling point to the critical point. With the increase in temperature, the heat capacity difference of liquid alkali metals is found to increase. In the temperature range from the boiling point to 0.8Tc, the heat capacity difference of liquid alkali metals has a parabolic dependence on temperature. In the temperature range from  $0.8T_{\rm C}$  to  $T_{\rm C}$ , the heat capacity difference of liquid alkali metals has a linear dependence on temperature with a large positive slope. As the generalized van der Waals equation of state accurately determines the thermophysical properties of alkali metals in a wide range of temperature from the boiling point to critical point, the obtained data on the heat capacity difference of liquid alkali metals may be considered to be reliable.

### 6. Conclusion

This work has determined the heat capacity difference of liquid alkali metals, on the basis of the generalized van der Walls equation of state which accurately determines the thermophysical properties of alkali metals in a wide range of temperature from the boiling point to the critical point. Hence, the obtained data on the heat capacity difference of liquid alkali metals may be considered to be reliable. Moreover, due to the peculiar nature of the critical state of substances, reliable experimental data on the heat capacity difference of liquid alkali metals in the vicinity of critical point are not available. Owing to this fact, the data on the heat capacity difference liquid alkali metals obtained in this work may be considered to be the recommended data.

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