

# Equation of State and Thermodynamic Properties of Molten Potassium Chloride to 1320 K and 6 kbar

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From the Tait equation an equation of state containing five adjustable parameters was developed which fits experimental density data of molten potassium chloride to 1320 K and 6 kbar with a standard deviation of 0.04%. The thermal expansion coefficient, isothermal compressibility, internal pressure, and molar heat capacities at constant pressure and constant volume were calculated as functions of pressure and temperature from the equation of state and were compared with computer simulation results. A method for an estimate of high-pressure PVT data for molten salts is suggested which yields results superior to the best computed data presently available.

## 1. Introduction

PVT measurements on molten salts reported in the literature are restricted to low-melting salts, e. g. the alkali nitrates or organic salts. Furthermore, they are either limited to relatively narrow pressure ranges (Barton et al.<sup>1</sup>, Bannard<sup>2</sup>, Barton and Speedy<sup>3</sup>) or suffer from considerable experimental error (Owens<sup>4</sup>, alkali nitrates up to 9 kbar in a piston-cylinder apparatus; Treiber and Tödheide<sup>5</sup>, BiCl<sub>3</sub> up to supercritical temperatures and 3.5 kbar).

In a recent paper<sup>6</sup> we reported on PVT measurements on molten potassium chloride up to 1320 K and 6 kbar which provide density values accurate to 0.15% below 2 kbar and to 0.41% at higher pressures. The purpose of that study was to investigate for the first time the PVT behavior of a typical molten salt with only two spherical ions as constituents over an appreciable density range. The accuracy of the results is sufficient to derive an equation of state for a melt with long range forces between the constituent particles and to calculate some thermodynamic properties of molten KCl from this equation for comparison with the properties of other types of liquids. The experimental data also enable a test of the high-pressure results of computer simulations using the Monte Carlo<sup>7</sup> and the molecular dynamics<sup>8</sup> methods.

## 2. Equation of State

Most equations of state for liquids are based on more or less empirical relations. In general the number of adjustable parameters in an equation of

state is strongly dependent on the required accuracy and also on the range in which the equation is valid.

For moderate precision (a few percent) an equation of state containing only two adjustable parameters may be sufficient. Among those equations the equation of Redlich and Kwong<sup>9</sup> proved to be particularly well suited to describe the PVT behavior of liquids in the high-temperature high-pressure range<sup>5, 10</sup>. On the other hand, Burnham et al.<sup>11</sup> needed a ninth degree polynomial in temperature and pressure containing 55 adjustable parameters to fit their experimental PVT data for water to 0.1% in the range between 20 and 900 °C and 2 and 10 kbar.

Besides the equations of state a number of equations have been proposed which accurately describe the variation of state along an isotherm using only a small number of adjustable parameters, e. g. the equations of Tait<sup>12</sup>, Hayward<sup>13</sup>, Hudleston<sup>14</sup>, and Chaudhuri<sup>15</sup>. Comparisons<sup>16-18</sup> of the quality of various of these equations for a number of liquids showed a slight superiority of the Tait equation over the other equations, although it yields a meaningless result in the limit of infinite pressure. Nevertheless, it was also successfully applied to solids<sup>19</sup> and the dependence of its constants upon the intermolecular pair potential was investigated<sup>20</sup>.

The Tait equation reads in its integrated form

$$\begin{aligned} [\varrho(P) - \varrho(P_0)]/\varrho(P) &= [V(P_0) - V(P)]/V(P_0) \\ &= A \ln \{ (B+P)/(B+P_0) \} \quad (1) \end{aligned}$$

where  $\varrho$  is the density,  $V$  the specific or molar volume,  $P$  the pressure,  $A$  and  $B$  are constants, and the subscript 0 denotes a reference point, usually at  $P_0=1$  bar. The values for  $A$  vary only from 0.089 for liquid hydrocarbons to 0.149 for water.

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The  $B$  parameter is usually of the order of  $10^2$  to  $10^3$  bar. Consequently,  $P_0$  in Eq. (1) may be neglected in most cases.

The most obvious way to obtain an equation of state from the Tait equation is to determine the parameters  $A$  and  $B$  by fitting the experimental data for various temperatures and to express  $A$  and  $B$  as functions of temperature. Unfortunately, even for highly accurate experimental results this procedure does not lead to steady functions of temperature since the fitted values of  $A$  and  $B$  are sensitively dependent on accidental errors in the experimental data. It is thus necessary, to proceed in the opposite direction, that is, to express  $A$  and  $B$  a priori as temperature functions in Eq. (1) and to fit the resulting equation of state to the complete set of PVT data rather than to isothermal data in order to determine the new parameters. This can be done by a multidimensional fit using the method of the "steepest descent"<sup>21</sup>.

The problem is to find suitable functions  $A(T)$  and  $B(T)$  which provide an excellent fit of the experimental data over the whole temperature and pressure ranges. Actually, from an arbitrarily chosen set of functions those functions are selected by trial and error which lead to the smallest mean squared deviation and to a statistical distribution of the deviations between the experimental and the calculated values not only in the entire measuring range but also in arbitrarily chosen subranges.

Since  $A$  has been found to depend only slightly on temperature<sup>16, 18</sup>,  $A(T)$  was chosen to be a constant or a linear function of temperature, whereas  $B(T)$  was assumed to be a linear, quadratic, hyperbolic, or exponential function of temperature. Of all possible combinations of these analytic expressions for  $A(T)$  and  $B(T)$  the set

$$\begin{aligned} A(T) &= A_0 + A_1 \vartheta, \\ B(T) &= B_0 + B_1 \vartheta + B_2 \vartheta^2 \end{aligned} \quad (2)$$

with  $\vartheta = T - T_F$  ( $T_F$  = melting temperature at  $P_0 = 1$  bar) proved to be the best. In combination with Eq. (1) and neglecting  $P_0$  it leads to

$$\begin{aligned} \varrho(P, T) &= \varrho(P_0, T) / [1 - (A_0 + A_1 \vartheta) \\ &\cdot \ln \{ (B_0 + B_1 \vartheta + B_2 \vartheta^2 + P) / (B_0 + B_1 \vartheta + B_2 \vartheta^2) \}] \end{aligned} \quad (3)$$

where  $\varrho(P_0, T)$  is the density of molten potassium chloride at the reference pressure  $P_0 = 1$  bar. It can be obtained from measurements of Van Artsdalen and Yaffe<sup>22, 23</sup>, which are in good agreement with

our own data<sup>6</sup> and may be expressed as

$$\varrho(1 \text{ bar}, T) = 1.9767 - 0.5831 \cdot 10^{-3} t \quad (4)$$

where  $t$  is the temperature in degree centigrade and  $\varrho$  is in  $\text{g cm}^{-3}$ .

The values determined for the five constants  $A_0$ ,  $A_1$ ,  $B_0$ ,  $B_1$ , and  $B_2$  in Eq. (3) are given in Table 1. The standard deviation of the experimental points from Eq. (3) is 0.04% in density and is thus one

Table 1. Parameters for equation of state (3).

Parameter	Unit	Value
$A_0$		0.093619
$A_1 \cdot 10^5$	K <sup>-1</sup>	7.2495
$B_0$	bar	2750.5
$B_1$	bar K <sup>-1</sup>	-3.8324
$B_2 \cdot 10^3$	bar K <sup>-2</sup>	3.4383
Standard Deviation		
$s \cdot 10^4$	$\text{g cm}^{-3}$	6.23
$s$	% of density	0.04
Experimental limit of error <sup>6</sup>	% of density	0.41

order of magnitude smaller than the experimental limits of error<sup>6</sup>. Since the deviations are also found to be statistically distributed, Eq. (3) with the parameters of Table 1 provides an equation of state suited for the calculation of thermodynamic properties of molten KCl.

Recently, Witt<sup>17, 24</sup> published an equation of state with seven adjustable parameters which he also derived from the Tait equation with the additional assumption of straight density isobars. Witt found that his equation yielded good results in fitting the PVT data of various organic liquids in the temperature range between 25 and 80 °C. For KCl Witt's equation was found to be inadequate, since the standard deviation is twice as high as for Eq. (3) and the deviations are not statistical in the sense described above. This is mainly due to the non-linearity of the density isobars in the broader temperature interval in the case of KCl.

### 3. Thermodynamic Properties

From the equation of state (3) several thermodynamic quantities have been calculated as functions of pressure and temperature for comparison with the properties of other types of liquids. The result for the thermal expansion coefficient  $\alpha_P = (1/V)(\partial V /$