

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

G. Goldmann and K. Tödheide

Institut für Physikalische Chemie und Elektrochemie, Universität Karlsruhe, Karlsruhe, Germany

(Z. Naturforsch. 31 a, 769-776 [1976]; received April 23, 1976)

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.¹, Bannard², Barton and Speedy³) or suffer from considerable experimental error (Owens⁴, alkali nitrates up to 9 kbar in a piston-cylinder apparatus; Treiber and Tödheide⁵, BiCl₃ up to supercritical temperatures and 3.5 kbar).

In a recent paper⁶ 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 Carlo⁷ and the molecular dynamics⁸ 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 Kwong⁹ proved to be particularly well suited to describe the PVT behavior of liquids in the high-temperature high-pressure range^{5, 10}. On the other hand, Burnham et al.¹¹ 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 Tait¹², Hayward¹³, Hudleston¹⁴, and Chaudhuri¹⁵. Comparisons¹⁶⁻¹⁸ 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 solids¹⁹ and the dependence of its constants upon the intermolecular pair potential was investigated²⁰.

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 ϱ 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.

Reprints requests to Dr. K. Tödheide, Institut für Physikalische Chemie und Elektrochemie, Universität Karlsruhe, Kaiserstr. 12, D-7500 Karlsruhe 1.

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"²¹.

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^{16, 18}, $A(T)$ 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^{22, 23}, which are in good agreement with

our own data⁶ 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 ϱ is in 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 ⁻¹	7.2495
B_0	bar	2750.5
B_1	bar K ⁻¹	-3.8324
$B_2 \cdot 10^3$	bar K ⁻²	3.4383
Standard Deviation		
$s \cdot 10^4$	g cm^{-3}	6.23
s	% of density	0.04
Experimental limit of error ⁶	% of density	0.41

order of magnitude smaller than the experimental limits of error⁶. 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^{17, 24} 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 $\alpha_P = (1/V) (\partial V /$

$\partial T)_P$ is shown in Figs. 1 and 2. α_P decreases to about half its low-pressure value in the pressure range to 6 kbar. The isobars in Fig. 2 show a slight curvature which is getting more pronounced at higher pressures. However, there is no minimum on the isobars in the stability range of liquid KCl as was found by Bridgman at pressures below 4 kbar

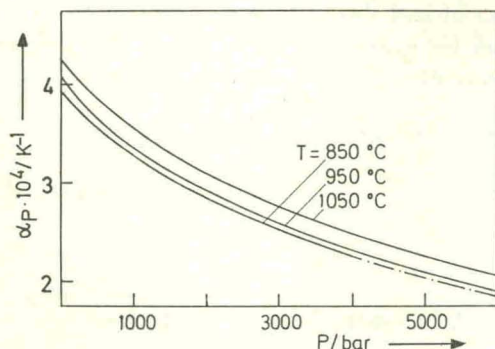


Fig. 1. Thermal expansion coefficient versus pressure. --- extrapolation beyond stability range of liquid phase.

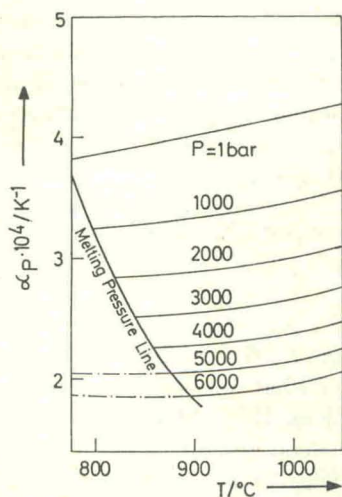


Fig. 2. Thermal expansion coefficient versus temperature. --- extrapolation beyond stability range of liquid phase.

for all the liquids he investigated²⁵⁻²⁷. Extrapolation of the thermal expansion coefficient beyond the stability range of the liquid phase indicates that a minimum may exist in the range of the supercooled liquid at high pressures.

The compressibility $\kappa_T = -(1/V) (\partial V / \partial P)_T$ is plotted as a function of pressure and temperature in Figs. 3 and 4, respectively. The compressibility of

KCl which is considerably smaller than for ordinary molecular liquids at ordinary pressure becomes comparable with those at high pressures, thus indicating that the individual differences in the intermolecular pair potentials become less important at high pressures where the compressibility of a substance is almost exclusively influenced by the size and shape of the particles. The temperature dependence of the compressibility is strongly reduced at high pressures. The compressibility values calculated at ordinary pressure are in good agreement with those of Bockris and Richards²⁸ obtained from velocity of sound measurements, which are also shown in Fig. 4. Most probably the small discrepancies are due to uncertainties in the molar heat capacities which enter the calculation of compressibilities from velocity of sound data.

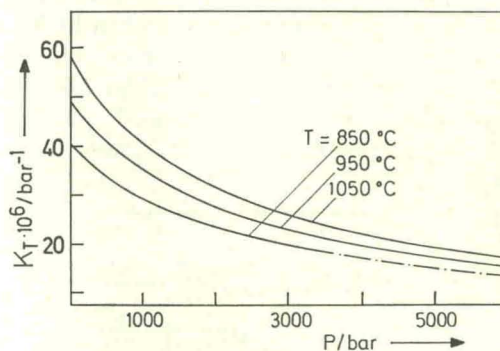


Fig. 3. Isothermal compressibility versus pressure. --- extrapolation beyond stability range of liquid phase.

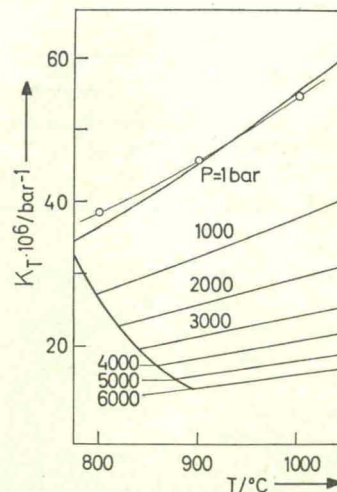


Fig. 4. Isothermal compressibility versus temperature. ○—○ compressibility from velocity of sound measurements²⁸.

The thermal pressure coefficient $\beta_V = \alpha_P/\alpha_T = (\partial P/\partial T)_V$ which is shown in Fig. 5 as a function of temperature for various constant densities is almost independent of temperature for low densities. At higher densities, however, a distinct temperature dependence is observed. Thus, the isochores are straight lines only in the low pressure range (up to about 2000 bar) as has also been found for the alkali metal nitrates^{1,2} and for organic salts³, but they exhibit some curvature at higher pressures. Therefore, the assumption of straight isochores frequently made for extrapolations of PVT data to higher pressures is not justified for KCl and probably not for other molten salts.

The internal pressure $P_i = (\partial U/\partial V)_T = T(\partial P/\partial T)_V - P = T\beta_V - P$ is readily calculated from the thermal pressure coefficient. It is plotted as a function of pressure in Figure 6. The zero pressure values of the internal pressure of molten KCl range around 8 kbar. As was expected these values are higher than for organic liquids (2.5 to 3.5 kbar)²⁴ but are clearly lower than for the alkali nitrates (10 to 12 kbar)²⁹. Contrary to sodium nitrate at 400 –

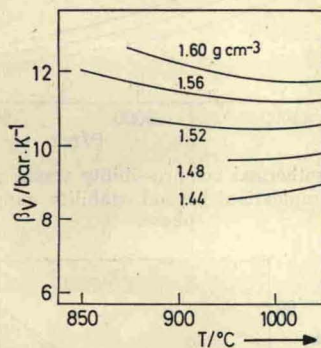


Fig. 5. Thermal pressure coefficient versus temperature for various constant densities.

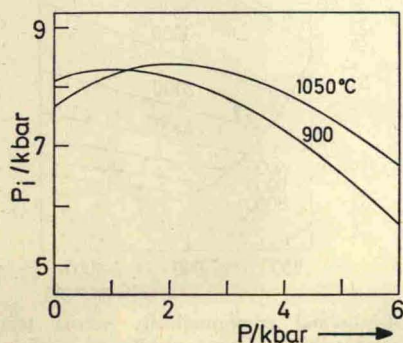


Fig. 6. Internal pressure versus pressure.

500 °C for KCl a maximum of the internal pressure is observed at intermediate pressures (Figure 6). Extrapolation to higher pressures at 1000 °C yields the result that the internal pressure goes through zero at about 11.5 kbar or at a corresponding density of 1.76 g cm⁻³.

The PVT data and their analytical representation by Eq. (3) are accurate enough to enable the calculation of enthalpy, entropy, and Gibbs free energy values for molten KCl up to 6 kbar with reasonable uncertainties from the following relations:

$$H(P, T) = H(P_0, T) + \int_{P_0}^P [V(P, T) - T(\partial V(P, T)/\partial T)_P] dP,$$

$$S(P, T) = S(P_0, T) - \int_{P_0}^P (\partial V(P, T)/\partial T)_P dP,$$

$$G(P, T) = G(P_0, T) + \int_{P_0}^P V(P, T) dP.$$

The reference values at a reference pressure P_0 (1 bar or some other low pressure) may be obtained directly from the literature as, for example, for $H(P_0, T)$ from drop calorimetric measurements of Marchidan and Pandele³⁰ or may be calculated from the respective thermodynamic function of potassium chloride vapor and the heat of vaporization³¹.

The molar heat capacity at constant pressure $C_p(P, T)$ calculated from

$$C_p(P, T) = C_p(P_0, T) - T \int_{P_0}^P (\partial^2 V(P, T)/\partial T^2)_P dP \quad (5)$$

is plotted as a function of temperature and pressure in Figs. 7 and 8. The reference molar heat capacity values at $P_0 = 1$ bar reported in the literature^{30, 32-34} scatter by about 10% and are found to be temperature independent. As was expected, however, recent precise enthalpy measurements on molten salts, e. g. the alkali fluorides³⁵ or sodium and potassium nitrate³⁶ led to temperature dependent molar heat capacities. In order to use temperature dependent reference values also for KCl, $C_p(P_0, T)$ was derived from velocity of sound measurements of Bockris and Richards²⁸

$$w = 2275 - 0.878 t \pm 6 \quad (6)$$

where the velocity of sound is in m sec⁻¹ and the temperature t in degree centigrade, by means of the thermodynamic relations

$$\gamma = C_p/C_V = \alpha_T w^2 M/V \quad \text{and} \quad (7)$$

$$C_p = w^2 \alpha_p^2 T M / (\gamma - 1)$$

$$= w^2 \alpha_p^2 T M / (\alpha_T w^2 M / V - 1) \quad (8)$$

where M is the molar mass. The values for α_p , α_T , and V were calculated from Equation (3). The estimated error of the heat capacities at normal pressure calculated from Eqs. (6) to (8) is about 15%. In spite of such a large uncertainty a decrease of $C_p(P_0, T)$ with increasing temperature can be established from Fig. 7, although it may not be as pronounced as shown in the figure. A negative temperature dependence of the molar heat capacity, although somewhat exceptional, was also evaluated from Monte Carlo calculations for molten KCl⁷ (see also Section 4 and Table 3) and from molecular dynamics calculations for molten NaCl³⁷. It was also found experimentally for fused NaNO₃ and KNO₃³⁶ as well as for some other liquids, e.g. water³⁸ and mercury³⁹. For higher pressures the sign of the temperature dependence of the heat

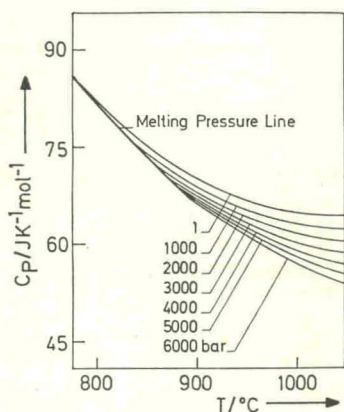


Fig. 7. Molar heat capacity at constant pressure versus temperature.

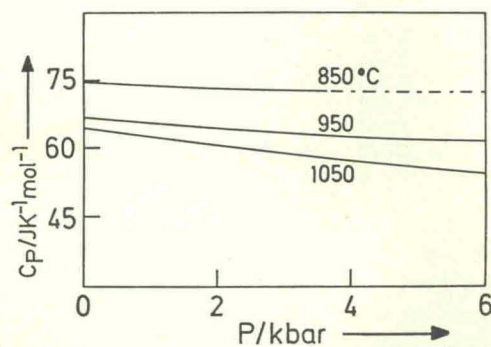


Fig. 8. Molar heat capacity at constant pressure versus pressure. - - - - extrapolation beyond stability range of liquid phase.

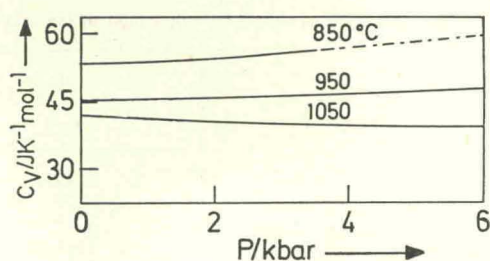


Fig. 9. Molar heat capacity at constant volume versus pressure. - - - - extrapolation beyond stability range of liquid phase.

capacity remains the same, but it appears from Fig. 7 that the molar heat capacity probably passes a minimum at temperatures above 1100 °C.

The temperature independent heat capacity values at 1 bar reported in the literature^{30, 32-34} ranging from 67.0 to 74.2 J mol⁻¹ K⁻¹ correspond to some intermediate values in the temperature interval covered by the PVT experiments.

The molar heat capacity C_p also decreases slightly with increasing pressure (Figure 8).

Figure 9 shows the molar heat capacity at constant volume C_V calculated from

$$C_p - C_V = \alpha_p^2 T \cdot V / \alpha_T \quad (9)$$

as a function of pressure. Since the uncertainties in C_V are considerable, the change in sign of its pressure dependence may or may not be real. C_V also decreases with increasing temperature for constant density as well as for constant pressure.

4. Comparison with Computer Simulations

The first and most extensive computer simulation experiments for molten salts have been performed on potassium chloride. Woodcock and Singer⁷ employed the Monte Carlo method to calculate the macroscopic properties of KCl using the Huggins-Mayer pair potential with constants determined by Fumi and Tosi⁴⁰ from the properties of the crystal at 298 K. Five of their calculated PVT points fall into the density range of the experiments. They are compiled in Table 2. The maximum difference between experimental and calculated densities amounts to 2%, corresponding to a pressure difference of 850 bar. MC computations by Larsen, Førlund, and Singer⁴¹ gave PVT data with density values which are low by about 4%. Preliminary density values obtained by Lewis⁴² from molecular dynamics cal-

Table 2. Comparison of computer simulation results with experimental data.

Reference	T_{cal}	ρ_{cal}	P_{cal}	ρ_{exp} ($T_{\text{cal}}, P_{\text{cal}}$)	$100(\rho_{\text{cal}} - \rho_{\text{exp}})/$ ρ_{exp}	P_{exp} ($T_{\text{cal}}, \rho_{\text{cal}}$)	$P_{\text{cal}} - P_{\text{exp}}$
	[°C]	[g cm ⁻³]	[bar]	[g cm ⁻³]	[%]	[bar]	[bar]
Woodcock and Singer ⁷	772	1.608	2820	1.635	-1.7	1967	853
	772	1.528	670	1.558	-2.0	29	641
	1033	1.528	3710	1.560	-2.0	2856	854
	1033	1.455	1440	1.465	-0.7	1260	180
	1033	1.389	(-30)	1.372	+1.3	195	-225
Larsen et al. ⁴¹	810	1.439	1	1.504	-4.3		
	810	1.491	810	1.544	-3.4		

Table 3. Comparison of computer simulation results⁷ with experimental data.

T [°C]	P [bar]	$10^4 \alpha_p$ [K ⁻¹]		$10^6 \kappa_T$ [bar ⁻¹]		β_V [bar K ⁻¹]		P_i [kbar]		C_p [J K ⁻¹ m ⁻¹]	
		cal	exp	cal	exp	cal	exp	cal	exp	cal	exp
772	2820	2.33	2.56	19.2	18.2	12.1	14.1	12.6	8.6	60.9	84.2
772	670	3.04	3.41	30.6	24.0	9.92	12.1	10.4	8.6	67.3	85.7
1033	3710	0.35	2.52	4.04	23.0	8.66	11.1	11.3	7.7	45.3	58.1
1033	1440	2.19	3.24	30.2	34.3	7.24	9.5	9.45	8.2	56.0	61.1
1033	(-30)	3.37	4.24	52.5	57.0	6.42	7.1	8.38	7.6	61.5	64.1

Table 4. Comparison of estimated (Eq. (11)) with measured densities.

Salt	$10^6 \kappa_T$ (1 bar, T) [bar ⁻¹]	B Eq. (10) [bar]	T [°C]	P [bar]	ρ_{est} [g cm ⁻³]	ρ_{exp} [g cm ⁻³]	$100(\rho_{\text{est}} - \rho_{\text{exp}})/$ ρ_{exp} [%]
	KCl	38.4 ²⁸	2358	800	1000	1.566	1.558 ⁶
45.7		1987	900	1000	1.514	1.508	0.4
			900	5000	1.661	1.647	0.8
			1000	1000	1.462	1.458	0.3
54.7		1667	1000	5000	1.618	1.613	0.3
KNO ₃	23.4 ²⁸	3769	400	1000	1.869	1.864 ²	0.3
			400	5000	1.992	1.978 ⁴	0.7
			400	10000	2.095	2.091 ⁴	0.2
	29.4	3008	500	1000	1.804	1.796 ²	0.4
			500	5000	1.941	1.938 ⁴	0.2
			500	10000	2.051	2.047 ⁴	0.2
NaNO ₃	21.6 ²⁸	4080	400	1000	1.894	1.886 ²	0.4
			400	5000	2.014	2.022 ⁴	-0.4
			400	10000	2.115	2.157 ⁴	-1.9
	26.8	3296	500	1000	1.832	1.818 ²	0.8
			500	5000	1.964	1.966 ⁴	-0.1
			500	10000	2.072	2.106 ⁴	-1.6

culations with the same pair potential as has been used by Woodcock and Singer fall about 7% below the experimental results. Recent MC calculations on molten potassium chloride using the Pauling potential⁴³ or including ionic polarization effects⁴⁴ yielded even less satisfactory results. The calculated

density values at the melting temperature at 1 bar are low by 15.8 and 12.8%, respectively. MC computations on other molten salts by Lewis, Singer, and Woodcock (see⁴³) also using the Huggins-Mayer potential led in most cases to larger discrepancies with experimental data than for KCl.

Table 3 shows a comparison of the best set of computed values for some derived properties⁷ with experimental data. Obviously, the temperature and pressure dependences of the quantities compiled in the table from the computer experiments are qualitatively correct. The numerical values, however, normally fall outside the experimental limits of error. The best agreement is achieved for the molar heat capacity, but this quantity, unfortunately, can only be derived from the experiments with poor accuracy. Thus it appears that computer simulation methods cannot produce *PVT* data and related quantities at high pressure with an accuracy comparable to that of precise experimental studies.

5. Estimate of High-pressure *PVT* Data for Molten Salts

Since precise measurements of high-pressure *PVT* data for molten salts are difficult and time consuming and since computer simulations in spite of long computing times cannot produce sufficiently accurate results at present, a method for satisfactory estimates of *PVT* data for other molten salts is highly desirable for the interpretation of experimental results obtained at high pressures, e.g. specific electrical conductivities of the alkali metal chlorides⁴⁵. The Tait equation has proven to be an excellent equation of state for various types of liquids, if the parameters *A* and *B* are allowed to vary with temperature. It was also noticed that *A* varies only slightly with temperature and has similar values for quite different liquids. Kuss and Taslimi¹⁷ found that the *PVT* data of many organic liquids could be well described by the Tait equation, when

A was held constant and the temperature dependence of *B* was expressed as

$$B(T) = 0.089/\kappa_T(1 \text{ bar}, T) + 40/\text{bar} \quad (10)$$

where $\kappa_T(1 \text{ bar}, T)$ is the isothermal compressibility of the liquid at 1 bar. Equation (10) and Eq. (1) yield the equation of state

$$\rho(P, T) = \rho(1 \text{ bar}, T) / [1 - 0.1 \cdot \ln \{ (0.089/\kappa_T(1 \text{ bar}, T) + 40 + P) : (0.089/\kappa_T(1 \text{ bar}, T) + 40) \}] \quad (11)$$

For *A* the value 0.1 has been introduced which seems to be the best choice for molten salts. Equation (11) enables the calculation of the density of a liquid at high pressure when its density and isothermal compressibility are known as functions of temperature at ordinary pressure. In Table 4 densities which were estimated with the aid of Eq. (11) are compared with experimental values for KCl, KNO₃, and NaNO₃. Up to 5 kbar the discrepancies are well below 1%. The *PVT* measurements for the nitrates above 1 kbar are performed in a piston-cylinder apparatus with an error limit which is comparable to the differences between the estimated and measured values listed in Table 4.

It appears that Eq. (11) enables an estimate of high-pressure densities for molten salts which is superior to the best results of computer simulations presently available.

Acknowledgement

Financial support of this work by the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF) from Funds of the Bundesministerium für Wirtschaft is gratefully acknowledged.

- ¹ A. F. M. Barton, G. J. Hills, D. J. Fray, and J. W. Tomlinson, *High Temperatures-High Pressures* **2**, 437 [1970].
- ² J. E. Bannard, Thesis, University of Southampton, 1969.
- ³ A. F. M. Barton and R. J. Speedy, *J. Chem. Soc. Faraday Trans. I* **70**, 506 [1974].
- ⁴ B. B. Owens, *J. Chem. Phys.* **44**, 3918 [1966].
- ⁵ G. Treiber and K. Tödheide, *Ber. Bunsenges. physik. Chem.* **77**, 1079 [1973].
- ⁶ G. Goldmann and K. Tödheide, *Z. Naturforsch.* **31a**, 656 [1976].
- ⁷ L. V. Woodcock and K. Singer, *Trans. Faraday Soc.* **67**, 12 [1971].
- ⁸ L. V. Woodcock, *Chem. Phys. Lett.* **10**, 257 [1971].
- ⁹ O. Redlich and J. N. S. Kwong, *Chem. Reviews* **44**, 233 [1949].
- ¹⁰ K. Mangold and E. U. Franck, *Ber. Bunsenges. physik. Chem.* **66**, 260 [1962].
- ¹¹ C. W. Burnham, J. R. Holloway, and N. F. Davis, *Am. J. Sci.* **267A**, 70 [1969].
- ¹² P. G. Tait, *Scientific Papers*, Vol. 2, Cambridge University Press, 1898, p. 334.
- ¹³ A. T. J. Hayward, *Brit. J. Appl. Phys.* **18**, 965 [1967].
- ¹⁴ L. J. Hudleston, *Trans. Faraday Soc.* **33**, 97 [1937].
- ¹⁵ P. M. Chaudhuri, G. P. Mathur, and R. A. Stager, *Canad. J. Chem. Eng.* **46**, 132 [1968].
- ¹⁶ E. Kuss and M. Taslimi, *Chem. Ing. Techn.* **42**, 1073 [1970].
- ¹⁷ K. Witt, *Antriebstechnik* **12**, 137 [1973].
- ¹⁸ F. Hötte, *Chem. Ing. Techn.* **46**, 762 [1974].
- ¹⁹ R. Ginell and Th. J. Quigley, *J. Phys. Chem. Solids* **26**, 1157 [1965].
- ²⁰ G. A. Neece and D. R. Squire, *J. Phys. Chem.* **72**, 128 [1968].
- ²¹ U. Hoffmann and H. Hofmann, *Einführung in die Optimierung*, Verlag Chemie, Weinheim 1971.
- ²² E. R. Van Artsdalen and I. S. Yaffe, *J. Phys. Chem.* **59**, 118 [1955].
- ²³ I. S. Yaffe and E. R. Van Artsdalen, *J. Phys. Chem.* **60**, 1125 [1956].

- ²⁴ K. Witt, Thesis, University of Eindhoven, 1973.
- ²⁵ P. W. Bridgman, Proc. Amer. Acad. Arts Sci. **49**, 3 [1913].
- ²⁶ P. W. Bridgman, Proc. Amer. Acad. Arts Sci. **66**, 185 [1931].
- ²⁷ P. W. Bridgman, Proc. Amer. Acad. Arts Sci. **67**, 1 [1932].
- ²⁸ J. O'M. Bokris and N. E. Richards, Proc. Roy. Soc. A **241**, 44 [1957].
- ²⁹ B. Cleaver and B. C. J. Neil, Trans. Faraday Soc. **65**, 2860 [1969].
- ³⁰ D. I. Marchidan and L. Pandeale, Rev. Rom. Chim. **20**, 299 [1975].
- ³¹ S. H. Bauer and R. F. Porter, in M. Blander ed., Molten Salt Chemistry, Interscience Publishers, New York 1964, pp. 607-680.
- ³² K. K. Kelly, U.S. Bur. Mines, Bull. No. 476 [1949].
- ³³ A. S. Dworkin and M. A. Bredig, quoted by S. J. Yosim and B. B. Owens, J. Chem. Phys. **41**, 2032 [1964].
- ³⁴ B. F. Markov and T. A. Tishura, Ukrain. Khim. Zhur. **39**, 757 [1973].
- ³⁵ A. C. Macleod, J. Chem. Soc. Faraday Trans. I **69**, 2026 [1973].
- ³⁶ E. W. Dewing, J. Chem. Eng. Data **20**, 221 [1975].
- ³⁷ J. W. E. Lewis and K. Singer, J. Chem. Soc. Faraday Trans. II **71**, 41 [1975].
- ³⁸ G. S. Kell, in: F. Franks ed., Water: A Comprehensive Treatise, Vol. 1, Plenum Press, New York 1972, pp. 363-412.
- ³⁹ Th. B. Douglas, A. F. Ball, and D. C. Ginnings, J. Res. Natl. Bur. Stdrds. **46**, 334 [1951].
- ⁴⁰ F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **25**, 31 [1964].
- ⁴¹ B. Larsen, F. Førland, and K. Singer, Mol. Phys. **26**, 1521 [1973].
- ⁴² J. W. E. Lewis, Atlas Computer Laboratory, Chilton, Didcot, Berkshire, private communication, 1974.
- ⁴³ S. Romano and I. R. McDonald, Physica **67**, 625 [1973].
- ⁴⁴ S. Romano and C. Margheritis, Physica **77**, 557 [1974].
- ⁴⁵ R. Schamm and K. Tödheide, to be published.