$\partial T)_P$ is shown in Figs. 1 and 2. a_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
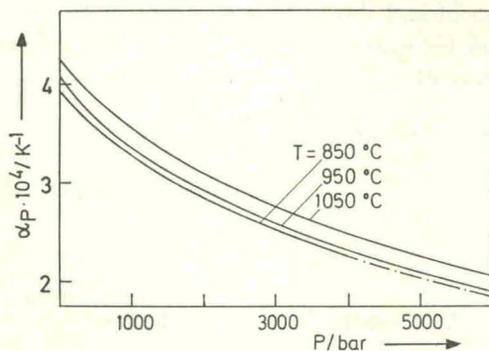
Fig. 1. Thermal expansion coefficient versus pressure. —·—·— extrapolation beyond stability range of liquid phase.
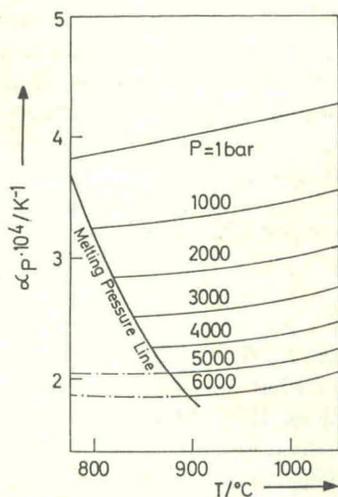
Fig. 2. Thermal expansion coefficient versus temperature. —·—·— extrapolation beyond stability range of liquid phase.

for all the liquids he investigated [25-27]. 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 $\varkappa_T = -(1/V)(\partial V/\partial P)_T$ 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 Richards [28] 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.
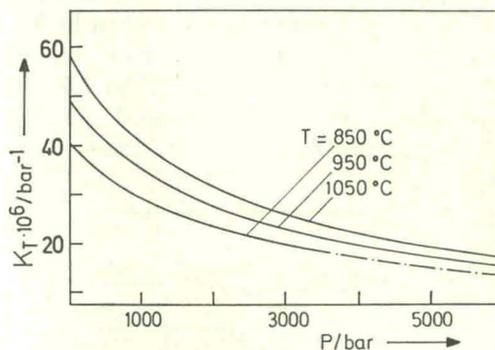
Fig. 3. Isothermal compressibility versus pressure. —·—·— extrapolation beyond stability range of liquid phase.
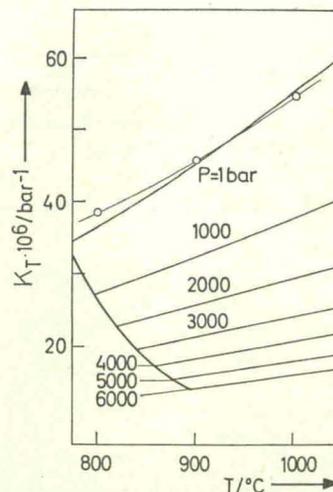
Fig. 4. Isothermal compressibility versus temperature. ◯—◯ compressibility from velocity of sound measurements [28].

The thermal pressure coefficient $\beta_V = \alpha_P/\varkappa_T = (\partial P/\partial T)_V$ 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 salts [3], 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 –
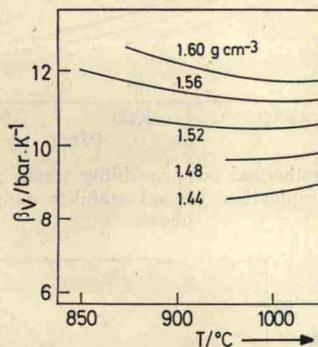
Fig. 5. Thermal pressure coefficient versus temperature for various constant densities.
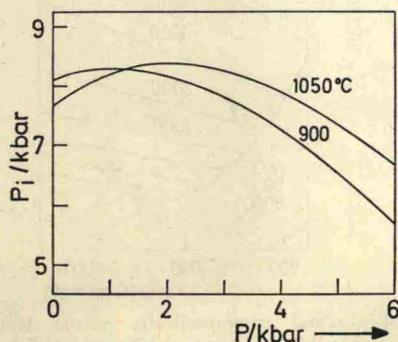
Fig. 6. Internal pressure versus pressure.

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 Pandele [30] or may be calculated from the respective thermodynamic function of potassium chloride vapor and the heat of vaporization [31].

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

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

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 fluorides [35] or sodium and potassium nitrate [36] 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 Richards [28]

$$w = 2275 - 0.878\,t \pm 6 \tag{6}$$

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

$$\gamma = C_p/C_V = \varkappa_T w^2 M/V \quad \text{and} \tag{7}$$