

measurements are made. For this purpose the volume of the volumeters is calibrated as a function of the displacement of its upper end using density values obtained by isochoric measurements. It turns out that for volume changes smaller than about $\pm 15\%$ even under these extreme conditions the volume-displacement relation is reproducible although not linear, as was also observed by Babb et al.⁹ at room temperature. If the volume change of the bellows caused by melting of the salt at 1 bar exceeds about 15% it may be partly irreversible. In this case a redetermination of the zero point volume of the bellows and of its crosssection is necessary with the aid of density values determined with volumeters of type 1. This leads to an additional uncertainty in the final density values of about 0.15% (see also Sect. 2.4 and Table 1).

2.4 Determination of Density

The density of molten KCl corresponding to a measured pair of temperature and pressure is calculated from

$$\rho(P, T) = m/V_0(P, T) = m/[V_0(1 \text{ bar}, 20^\circ\text{C}) + \Delta V_{T,C} + \Delta V_{T,B} + \Delta V_P] \quad (1)$$

where m is the amount of salt in the volumeter, $V_0(P, T)$ the volume of the volumeter at P and T and zero displacement, $V_0(1 \text{ bar}, 20^\circ\text{C})$ the calibrated volume at 1 bar and 20°C , $\Delta V_{T,C}$ the volume correction of the total volumeter due to thermal expansion as if it were totally made from the material of the rigid part, $\Delta V_{T,B}$ a correction to $\Delta V_{T,C}$ taking into account, that the bellows and the rigid part are made from different materials, ΔV_P the correction due to compression of the volumeter. All the corrections are temperature and pressure dependent.

The corrections due to thermal expansion are calculated according to

$$\Delta V_{T,C} = 3 V_0(1 \text{ bar}, 20^\circ\text{C}) \alpha_C [t - 20], \quad (2)$$

$$\Delta V_{T,B} = -2 V_{0,B}(1 \text{ bar}, 20^\circ\text{C}) \Delta \alpha_{C-B} [t - 20], \quad (3)$$

where α is the average linear thermal expansion coefficient between 20°C and the measuring temperature, $\Delta \alpha_{C-B} = \alpha_C - \alpha_B$ is the difference between the coefficients for cell and bellows materials, t is the measuring temperature in degrees centigrade, and $V_{0,B}(1 \text{ bar}, 20^\circ\text{C})$ is the volume of the bellows at 1 bar, 20°C , and zero displacement. Equation (3) is taking into account that the correction for the

difference in thermal expansion between the cell and bellows materials in axial direction is already included in the displacement measurement.

The values used for the different thermal expansion coefficients in the range between 800 and 1050°C are.

$$\alpha_C = (16.4 + 0.003 t \pm 0.3) \cdot 10^{-6} \text{ (see }^{10}\text{)},$$

$$\alpha_B = (12.9 + 0.004 t) \cdot 10^{-6} \text{ (see }^{11}\text{)},$$

$$\Delta \alpha_{C-B} = (3.5 - 0.001 t) \cdot 10^{-6}.$$

The relative uncertainty of α_C amounts to 1.6%, that of $\Delta \alpha_{C-B}$ is estimated to be 8%. The corresponding errors in $V_0(P, T)$ are 0.09% and 0.02%, respectively. The pressure dependence of the thermal expansion coefficient is small and can therefore be neglected in the thermal expansion correction.

Since the overall correction for the compression of the volumeter is of the order 0.5% in $V_0(P, T)$, it is not necessary to distinguish between the compressibilities of the two different materials and to take into account the pressure dependence of the compressibility when calculating the correction which can then be written as

$$\Delta V_P = -\beta(T) P [V_0(1 \text{ bar}, 20^\circ\text{C}) + \Delta V_{T,C} + \Delta V_{T,B}] \quad (4)$$

The compressibility $\beta(T)$ may be calculated from

$$\beta(T) = \frac{3[1 - 2\nu(T)]}{E(T)} \quad (5)$$

with data for Young's modulus $E(T)$ ¹² and Poisson's ratio $\nu(T)$ ¹³ extrapolated beyond 820°C . It turns out that ν does not show a systematic variation with temperature. It thus has its usual value $\nu = 0.3$ over the whole temperature range. For $E(T)$ the following relation holds:

$$E(T) = 22860 - 11.6 t \text{ (in } \text{kp mm}^{-2}\text{)}.$$

The value for β at room temperature obtained from Eq. (5) is $6.02 \cdot 10^{-7} \text{ bar}^{-1}$. It is in good agreement with data for the constituent pure metals obtained by Bridgman¹⁴ from high-pressure experiments. He also demonstrated that the pressure dependence of the compressibility may be expressed as a linear function of pressure and that the pressure dependent term is contributing less than 5% below 6 kbar. Hence it is justified to neglect it here.

The estimated error of the compressibility is about 10% below 2 kbar and about 20% for the highest pressures. This leads to errors in $V_0(P, T)$ of 0.025% and 0.13%, respectively.

2.4 Uncertainties in Density

The uncertainties in the final density values caused by various experimental errors may be obtained from

$$\begin{aligned} \Delta \rho / \rho = & \Delta m / m + [\Delta V_0(1 \text{ bar}, 20^\circ \text{C}) + \Delta V_0(P, T) \\ & + q_0(\Delta l - \Delta l_0) + \Delta V_{\text{cal}}] / V_0(P, T) \quad (6) \\ & + \alpha \Delta T + \beta \Delta P \end{aligned}$$

where the symbols appearing for the first time have the following significance: Δm : error in the amount of salt in the volumeter, $\Delta V_0(1 \text{ bar}, 20^\circ \text{C})$: error in volume calibration; $\Delta V_0(P, T)$: error due to inaccuracies of the corrections $\Delta V_{T,C}$, $\Delta V_{T,B}$, and ΔV_P ; Δl : uncertainty in displacement measurement; Δl_0 : reduction of Δl by fixing the zero point of displacement for type 2 volumeters by calibration (see Sect. 2.2); ΔV_{cal} : uncertainty in calibration of $V_0(P, T)$ and q_0 of type 2 volumeters after an irreversible volume change (see Sect. 2.3); $\Delta T, \Delta P$: errors in temperature and pressure measurement, respectively (see Sect. 2.1); α, β : thermal expansion coefficient and isothermal compressibility of the salt, respectively.

The numerical values of the uncertainties for the two different types of volumeters are given in Table 1 for various pressures.

Table 1. Relative uncertainties of final density value due to various experimental errors.

Volumeters Pressure	Type 1		Type 2
	1 bar	2000 bar	6000 bar
$\Delta m/m$	0.017	0.017	0.008
$\Delta V_0(1 \text{ bar}, 20^\circ \text{C})/V_0(P, T)$	0.035	0.035	0.042
$\Delta V_0(P, T)/V_0(P, T)$	0.090	0.115	0.240
$q_0 \Delta l / V_0(P, T)$	0.050	0.080	0.250
$q_0 \Delta l_0 / V_0(P, T)$	—	—	-0.150
$\Delta V_{\text{cal}} / V_0(P, T)$	—	—	0.150
$\alpha \Delta T$	0.085	0.062	0.041
$\beta \Delta P$	0.006	0.009	0.012
total $\Delta \rho / \rho$	0.28	0.32	0.59
$\Delta \rho / \rho$ when based on values at 1 bar	0.1	0.14	0.41

3. Results

Following the procedure described above twenty quasi-isochores with 431 experimental points and nine isotherms with 87 points are measured covering

the temperature, pressure, and density ranges from 770 to 1050 °C, from 1 to 6000 bar, and from 1.36 to 1.67 g cm⁻³, respectively. The uncorrected points of some of the quasi-isochores are shown in Fig. 4, where the points obtained upon heating and cooling in different cycles are marked by different symbols. As may be seen from the figure, the scatter of the experimental points is very small and statistical, thus indicating that there is neither hysteresis nor any time-dependent effect.

All unsmoothed experimental points corrected for the effects described in Sects. 2.2 and 2.4 are collected in Table 2.

Since PVT data for molten KCl at high pressures have not been published previously, a comparison with data from other sources is not feasible. Density values at normal pressure obtained by fitting a second order polynomial to the quasi-isochores shown in Fig. 4, subsequent numerical extrapolation of $T(P)$ to normal pressure and calculating the corresponding density values from Eq. (1) are shown

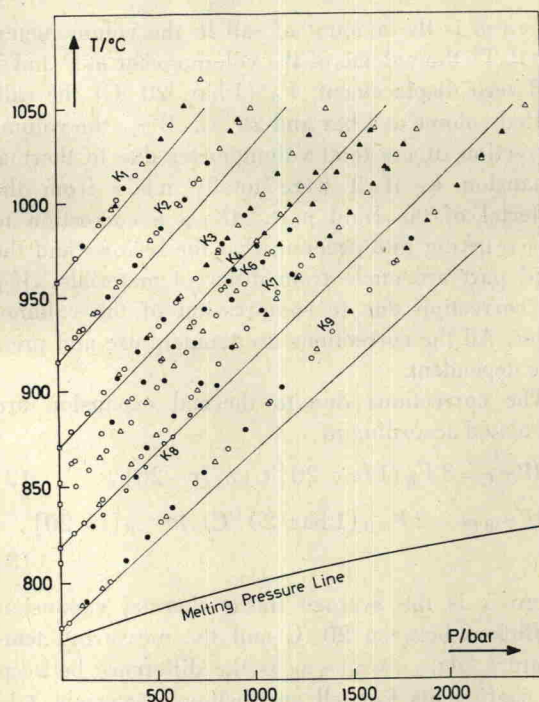


Fig. 4. Uncorrected experimental points on quasi-isochores and isochores (full lines) corresponding to quasi-isochores $K_1, K_2, K_3, K_7,$ and K_9 . ● heating first run, ○ cooling first run, △ heating second run, ▲ cooling second run, □ extrapolated points at 1 bar (see text).