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# Densities of NaOH(aq) at Temperatures from (323 to 573) K and 10 MPa Pressure

**Lubomír Hnědkovský,[†] Erich Königsberger,* Ivan Cibulka,[†] Lan-Chi Königsberger, Simon Schrödle,[‡] Peter M. May, and Glenn Hefter***

School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150, Australia

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Densities of sodium hydroxide solutions at concentrations of $0.1 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 8$ have been measured by vibrating-tube densimetry over the temperature range $323 \le T/\text{K} \le 573$ at a pressure of 10 MPa. The purpose-built densimeter, which is capable of measuring densities of corrosive fluids at temperatures up to 573 K and pressures up to 30 MPa, has a platinum−rhodium vibrating tube with inlet/outlet tubes of platinum and an optical detection system. Calibrations were carried out with water and aqueous solutions of sodium chloride at temperatures up to 523 K. At higher temperatures, nitrogen was substituted as the auxiliary density reference because of uncertainties in the NaCl(aq) densities. The apparent molar volumes of NaOH(aq) calculated from the measured densities were fitted with an extended Redlich−Meyer equation. The present results are in good agreement with literature data but are more precise. The current global accuracy in the densities of NaOH(aq) appears to be about 0.1 %, being significantly better at lower concentrations and temperatures but slightly worse at higher concentrations and temperatures. More accurate knowledge of the densities of the reference materials (other than water) used for calibrating vibrating-tube densimeters under extreme conditions is probably required to improve the accuracy of such data.

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## 1. Introduction

In the Bayer process, hot concentrated sodium hydroxide solutions are used to extract aluminum-containing minerals, chiefly gibbsite and boehmite, from bauxitic ores. Purified aluminum hydroxide (gibbsite) is then precipitated by cooling. Because the solubilities and rates of dissolution of gibbsite and boehmite increase with increasing temperature, the digestion stage of the modern industrial Bayer process is being carried out at increasingly high temperatures. As density is an important parameter for both process control and engineering design purposes, accurate models of NaOH(aq) densities are needed as a basis for the quantitative description of the volumetric properties of the more complex Bayer plant liquors. Solution densities are also required to calculate other thermodynamic quantities at the elevated temperatures and pressures used in such hydrometallurgical processes.

Despite an abundance of data at temperatures up to ∼373 K,[1,2] the volumetric properties of NaOH(aq) at higher temperatures have not been studied extensively. Most published models[1,3,4] use the experimental density data of Dibrov et al.,[5] obtained by a pycnometric method with a claimed accuracy of ∼0.3 %, at concentrations in the range $0.8 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 23.8$ and at temperatures up to 623 K at saturation pressure. In attempting to correlate their enthalpy and heat capacity data for NaOH(aq), Simonson et al.[3] discovered major inaccuracies in the widely used correlation of Pabalan and Pitzer[1] and gave a revised Pitzer representation of the volumetric properties of NaOH(aq). However, at temperatures above 353 K, their formulation was again based solely on the densities of Dibrov et al.[5] They commented[3] that high-quality measurements of the density of NaOH(aq) above 348 K were needed to resolve the problems.

Subsequently, Corti et al.[6] determined NaOH(aq) densities with a vibrating-tube densimeter, but their experiments were limited to a rather small number of solutions of relatively low concentrations ($m \le 3$ mol·kg$^{-1}$) at temperatures below 523 K. During the course of the present study, which commenced in 2003, two further studies have appeared, both using vibrating-tube densimeters. Thus, Corti and Simonson[7] reported NaOH(aq) densities to $T = 623$ K, $P = 30$ MPa, and $m = 6$ mol·kg$^{-1}$ NaOH , whereas Trevani et al.[8] determined densities at $T =$ (523.15 and 573.15) K, $P = 14$ MPa, and $0.2 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 2.5$. Corti and Simonson correlated their data using a Pitzer model with two parameters ($\beta^{(0)V}$ and $C^V$) at constant $T$ and $P$ but found it necessary to include a NaOH$^0$(aq) ion pair in their model at $T > 523.15$ K. While evidence for weak ion pairing in NaOH(aq) solutions exists,[9−12] other researchers did not find it necessary to include a NaOH$^0$(aq) ion pair in their model even at 573 K.[8] It is also noteworthy that there are still significant differences between Corti and Simonson's latest model[7] and the existing experimental data at high temperatures[8] and concentrations.[7] Given the difficulties of working with concentrated NaOH(aq), particularly with respect to its contamination with carbonate, and its importance as a major industrial reagent, further experimental investigation of the densities of sodium hydroxide solutions is appropriate.

As a continuation of our previous investigations of NaOH(aq) at $298.15 \le T/\text{K} \le 363.15$ at atmospheric pressure,[13,14] the present paper deals with the measurement of the densities of NaOH(aq) over the temperature range $323.15 \le T/\text{K} \le 573.15$ at a pressure of (mostly) 10 MPa and at solute concentrations of $0.1 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 8$, using a purpose-built

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* To whom correspondence should be addressed. E-mail: e.koenigsberger@murdoch.edu.au.

[†] Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic.

[‡] Present address: Richmond Lab, University of Oregon, Eugene, OR 97403, USA.

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vibrating-tube densimeter. This extends the concentration range to cover both the bauxite digestion and the gibbsite precipitation stages of the Bayer process.

## 2. Construction and Operation of the Densimeter

***2.1 Assembly and Commissioning.*** The present vibrating-tube densimeter is capable of measurements up to 573 K and pressures up to 30 MPa. Its design, while based on that of Hynek et al.,[15] including various later modifications,[16] also has a number of new features. To cope with the corrosive nature of the present caustic solutions, the vibrating tube was made from platinum−10 % rhodium alloy, and the inlet and outlet tubing for the densimeter are pure platinum. The sample loops and all other ancillary items, which are kept at room temperature, are made of stainless steel. Most of the parts of the densimeter system, such as the vibrating tube, transport tubes, block (cell), and heated components (cylinders and lids), were constructed and tested in Prague, where the electronics were also built. All components were then air-freighted to Australia, where the densimeter was assembled, commissioned, and tested.

***2.2 Design and Operation.*** As the present densimeter is similar to previous designs,[15,16] only its particular features will be discussed here. The vibrating tube is an electrical lead in a magnetic field, with the tube being driven directly by an alternating current passing through it. The period of vibration of the tube is sensed by an optical system, with the light from a photodiode passing through optical leads (quartz rods) to a photodetector. This ensures high sensitivity, no "ballast" mass, and stable oscillation. Four active independent heating units and one passive unit (a counter-current heat exchanger made by twisting together the Pt inlet and outlet tubes plus a preheater) ensure a temperature stability of ± 2 mK during individual experiments and ± 10 mK over long periods (∼12 h). The temperature of the inner block was measured using a calibrated (NIST traceable, uncertainty ± 6 mK) Pt resistance thermometer (Burns Engineering, Minnetonka, MN, model 12001-A-15-10-1-A). Pressure was measured with an accuracy of 0.1 % by means of a calibrated (National Standards (NMI) traceable) Druck (Leicester, UK, model PDCR 4071) pressure transducer. The densimeter works in the flow regime, which ensures good accuracy and a precision of better than 0.2 % in the measurement of the density difference between the solution and water, high throughput (∼30 min per sample), low sample consumption (∼20 mL per measurement), and short residence time (1 min) in the hot zone.

The high-pressure fluid delivery system is similar to the one described by Jedelsky et al.[16] It comprises an HPLC pump (Alltech, Deerfield, IL, model 626), which delivers degassed, pure water direct to the densimeter or via two sample loops. The two sample loops can be used singly or in series, thereby allowing sodium aluminate samples (which will be the subject of a future publication) to be preceded by, and flushed out with, NaOH solution to prevent precipitation of $Al(OH)_3$. A back-pressure regulator (Dresser Grove Mity-Mite, Salt Lake City, UT, model 91XW) and two double-ended stainless-steel cylinders (Swagelok, Solon, OH) were connected in series to maintain constant pressure. The cylinders, each of 500 mL capacity, in which nitrogen at the target pressure is gradually replaced by solution, acted as passive pressure buffers, dampening the inevitable pulses of the pump/regulator system and protecting the backpressure regulator from the corrosive samples. Their capacity was suitable for several days of operation, after which they could be emptied of waste and repressurized with $N_2$.

***2.3 Data Acquisition and Evaluation.*** All important experimental parameters, such as temperature, pressure, and period of vibration, are continuously monitored, stored, and displayed on a computer.

Density measurements for a given sample with a vibrating-tube densimeter typically involve at least three measurements. For a vibrating tube at constant temperature and pressure, the square of the (harmonic) oscillation period of the tube depends on the density of the fluid contained within it. Thus, the density of the solution, $\rho$, is calculated according to

$$\rho - \rho_w = k(\tau^2 - \tau^2_w) \qquad (1)$$

where $\tau$ and $\tau_w$ represent the periods of oscillation of the densimeter tube containing the solution and pure water, respectively; $\rho_w$ represents the density of water at the conditions at which the measurement is made; and $k$ is a constant characteristic of the mechanical properties of the tube.

The behavior of real vibrating tubes cannot be satisfactorily described in purely theoretical terms because of the complicated mutual dependence of the driving force, natural frequency, damping force, and amplitude.[17] It is thus customary to determine the densimeter constant $k$ at each desired temperature and pressure by the measurement of $\tau^2$ for two reference substances of accurately known density (one of which is invariably water)

$$k = (\rho_w - \rho_{ref})/(\tau^2_w - \tau^2_{ref}) \qquad (2)$$

The other reference substance is usually nitrogen gas with $\rho_{ref}$ being calculated from an appropriate equation of state.[18] The disadvantage of this approach for the measurement of densities of concentrated aqueous solutions of electrolytes, which is the focus here, is that $\rho \gtrsim \rho_w \gg \rho_{ref}$, and thus measurements are almost always made *outside* the calibration range. This demands that the calibration constant be applicable at densities outside the calibration range, i.e., that the vibrating tube acts as a strictly harmonic oscillator under all conditions. While this assumption appears to be reasonable under near-ambient conditions, it may not be so under the more extreme conditions of interest here, as has been recognized by previous workers in this area.[17] Unfortunately, there is no substance denser than water, even including $D_2O$, whose density is known with sufficient accuracy, particularly at high temperatures and pressures, to act as a reliable second reference material. For these reasons, calibrations in this study were carried out using water (with densities calculated from IAPWS-95)[19] with appropriate aqueous solutions of sodium chloride as the other reference substance. The densities of the latter were calculated using the extended Pitzer formulation of Archer[20] which was based on the NaCl(aq) data then available.

This method of calibration is satisfactory up to about 523 K. Unfortunately, above this temperature, the density of NaCl(aq) starts to change considerably, the available database becomes less satisfactory, and the Archer formulation becomes less certain. For these reasons, nitrogen was used as the second reference substance at 573.15 K. This did not lead to any apparent discontinuity in the data, but it did mean that the true uncertainties in the observed densities at this temperature were higher than those at lower temperatures. These issues are further discussed below.

***2.4 Solution Preparation.*** Sodium chloride solutions for calibration were prepared by weight (Univar analytical reagent, assay 99.90 % min., Ajax Finechem, Australia, dried overnight at 383 K) using buoyancy corrections.

**Table 1. Experimental Densities, $\rho$, Apparent Molar Volumes, $V_\phi$, and Differences in Apparent Molar Volumes, $\Delta V_\phi = V_\phi(\text{exptl}) - V_\phi(\text{calcd})$, of NaOH(aq)**

| $m / \text{mol·kg}^{-1}$ | $\rho / \text{g·cm}^{-3}$ | $V_\phi / \text{cm}^3\text{·mol}^{-1}$ | $\Delta V_\phi / \text{cm}^3\text{·mol}^{-1}$ | $m / \text{mol·kg}^{-1}$ | $\rho / \text{g·cm}^{-3}$ | $V_\phi / \text{cm}^3\text{·mol}^{-1}$ | $\Delta V_\phi / \text{cm}^3\text{·mol}^{-1}$ |
|---|---|---|---|---|---|---|---|
| $T = 323.15$ K, $P = 2$ MPa, $\rho_w = 0.988872$ g·cm$^{-3}$ | | | | | | | |
| 0.09892 | 0.993042 | −2.651 | 0.210 | 2.9939 | 1.102250 | 1.543 | −0.002 |
| 0.09892 | 0.993087 | −3.114 | −0.253 | 2.9939 | 1.102232 | 1.549 | 0.004 |
| 0.09892 | 0.993057 | −2.805 | 0.056 | 4.0003 | 1.135593 | 2.560 | 0.008 |
| 0.09892 | 0.993080 | −3.042 | −0.181 | 4.0003 | 1.135562 | 2.567 | 0.015 |
| 0.1999 | 0.997265 | −2.468 | 0.048 | 4.9272 | 1.164362 | 3.418 | 0.020 |
| 0.1999 | 0.997265 | −2.468 | 0.048 | 4.9272 | 1.164372 | 3.416 | 0.018 |
| 0.4998 | 1.009532 | −1.788 | 0.013 | 5.9632 | 1.194983 | 4.221 | −0.050 |
| 0.4998 | 1.009517 | −1.758 | 0.043 | 5.9632 | 1.194979 | 4.222 | −0.049 |
| 1.0064 | 1.029586 | −0.887 | 0.031 | 6.8866 | 1.219572 | 5.018 | 0.025 |
| 1.0064 | 1.029575 | −0.876 | 0.042 | 6.8866 | 1.219573 | 5.018 | 0.025 |
| 2.0058 | 1.067144 | 0.501 | 0.069 | 8.0000 | 1.248119 | 5.790 | −0.012 |
| 2.0058 | 1.067144 | 0.501 | 0.069 | | | | |
| $T = 323.15$ K, $P = 10$ MPa, $\rho_w = 0.992309$ g·cm$^{-3}$ | | | | | | | |
| 0.1004 | 0.996538 | −2.459 | −0.072 | 1.9979 | 1.069815 | 0.844 | −0.007 |
| 0.1004 | 0.996527 | −2.349 | 0.039 | 2.9989 | 1.104904 | 1.955 | 0.001 |
| 0.1011 | 0.996561 | −2.395 | −0.010 | 4.0003 | 1.137820 | 2.935 | 0.009 |
| 0.1011 | 0.996552 | −2.305 | 0.080 | 5.0015 | 1.168707 | 3.812 | 0.008 |
| 0.2008 | 1.000684 | −2.033 | 0.017 | 5.9845 | 1.197209 | 4.588 | −0.001 |
| 0.2008 | 1.000691 | −2.068 | −0.018 | 6.9982 | 1.224731 | 5.330 | −0.002 |
| 0.4993 | 1.012820 | −1.383 | −0.037 | 8.1915 | 1.254929 | 6.127 | −0.001 |
| 1.0021 | 1.032587 | −0.492 | −0.014 | | | | |
| $T = 373.15$ K, $P = 10$ MPa, $\rho_w = 0.962932$ g·cm$^{-3}$ | | | | | | | |
| 0.1071 | 0.967434 | −3.780 | 0.010 | 3.9683 | 1.105877 | 2.341 | −0.001 |
| 0.1071 | 0.967432 | −3.760 | 0.030 | 4.9873 | 1.137017 | 3.296 | −0.005 |
| 0.2063 | 0.971522 | −3.339 | −0.011 | 5.9945 | 1.165762 | 4.168 | 0.004 |
| 0.5006 | 0.983362 | −2.425 | −0.003 | 7.0000 | 1.192662 | 4.960 | 0.007 |
| 1.0066 | 1.003097 | −1.436 | −0.066 | 7.0000 | 1.192782 | 4.944 | −0.009 |
| 1.9979 | 1.039602 | 0.139 | 0.015 | 8.1915 | 1.222532 | 5.796 | −0.008 |
| 3.0003 | 1.074352 | 1.332 | 0.004 | | | | |
| $T = 423.15$ K, $P = 10$ MPa, $\rho_w = 0.922319$ g·cm$^{-3}$ | | | | | | | |
| 0.1020 | 0.926887 | −9.234 | −0.011 | 4.0067 | 1.070869 | −0.188 | 0.005 |
| 0.1020 | 0.926893 | −9.303 | −0.080 | 5.0132 | 1.101939 | 1.044 | 0.014 |
| 0.2019 | 0.931217 | −8.361 | 0.073 | 5.0132 | 1.101999 | 1.032 | 0.002 |
| 0.4993 | 0.943749 | −6.928 | 0.034 | 5.9826 | 1.129994 | 2.089 | 0.006 |
| 1.0041 | 0.964154 | −5.369 | −0.002 | 6.9942 | 1.157329 | 3.082 | 0.009 |
| 2.0023 | 1.002152 | −3.225 | −0.007 | 7.9972 | 1.182779 | 3.961 | 0.007 |
| 3.0053 | 1.037713 | −1.574 | 0.001 | | | | |
| $T = 473.15$ K, $P = 10$ MPa, $\rho_w = 0.870946$ g·cm$^{-3}$ | | | | | | | |
| 0.1008 | 0.875988 | −19.90 | 0.131 | 1.9957 | 0.956451 | −9.615 | −0.014 |
| 0.1008 | 0.876005 | −20.12 | −0.089 | 3.0012 | 0.993727 | −7.020 | 0.019 |
| 0.1008 | 0.876003 | −20.10 | −0.063 | 3.9793 | 1.027361 | −4.998 | 0.014 |
| 0.1998 | 0.880725 | −18.39 | 0.174 | 4.9905 | 1.059697 | −3.236 | −0.012 |
| 0.4980 | 0.894456 | −15.88 | −0.002 | 5.9814 | 1.089057 | −1.718 | −0.018 |
| 0.4980 | 0.894426 | −15.81 | 0.075 | 6.9658 | 1.116247 | −0.391 | −0.017 |
| 1.0002 | 0.916262 | −13.12 | 0.001 | 6.9658 | 1.116267 | −0.394 | −0.020 |
| 1.9957 | 0.956424 | −9.599 | 0.002 | 7.9825 | 1.142397 | 0.834 | 0.013 |
| $T = 523.15$ K, $P = 10$ MPa, $\rho_w = 0.805701$ g·cm$^{-3}$ | | | | | | | |
| 0.1000 | 0.811722 | −42.79 | −0.154 | 2.0054 | 0.902001 | −21.73 | −0.014 |
| 0.1000 | 0.811722 | −42.79 | −0.154 | 3.0052 | 0.942171 | −17.37 | −0.090 |
| 0.1000 | 0.811711 | −42.62 | 0.013 | 3.9990 | 0.977951 | −13.77 | 0.082 |
| 0.2004 | 0.817364 | −39.44 | −0.014 | 5.0028 | 1.011551 | −10.95 | 0.049 |
| 0.4995 | 0.833124 | −33.78 | 0.025 | 6.0055 | 1.042561 | −8.589 | 0.001 |
| 0.4995 | 0.833124 | −33.78 | 0.025 | 6.0055 | 1.042641 | −8.604 | −0.014 |
| 0.4995 | 0.833104 | −33.72 | 0.083 | 7.0016 | 1.071151 | −6.590 | −0.030 |
| 1.0025 | 0.857633 | −28.33 | −0.015 | 7.0016 | 1.071041 | −6.572 | −0.013 |
| 1.0025 | 0.857680 | −28.40 | −0.081 | 7.9991 | 1.097711 | −4.839 | 0.004 |
| 2.0054 | 0.902001 | −21.73 | −0.014 | 7.9991 | 1.097551 | −4.817 | 0.025 |
| $T = 573.15$ K, $P = 10$ MPa, $\rho_w = 0.715290$ g·cm$^{-3}$ | | | | | | | |
| 0.1122 | 0.724654 | −105.82 | −0.329 | 1.9962 | 0.832976 | −50.93 | 0.035 |
| 0.1122 | 0.724632 | −105.44 | 0.046 | 1.9962 | 0.833161 | −51.08 | −0.109 |
| 0.2173 | 0.732398 | −95.67 | 0.388 | 3.0042 | 0.878767 | −41.06 | 0.096 |
| 0.2173 | 0.732406 | −95.74 | 0.319 | 3.9984 | 0.918890 | −33.94 | 0.148 |
| 0.5495 | 0.754575 | −79.45 | −0.058 | 4.9993 | 0.955585 | −28.46 | 0.036 |
| 0.5495 | 0.754588 | −79.49 | −0.101 | 6.0040 | 0.989120 | −24.03 | −0.071 |
| 1.1053 | 0.787201 | −64.73 | −0.177 | 6.9992 | 1.019780 | −20.42 | −0.114 |
| 1.1053 | 0.787190 | −64.72 | −0.160 | 7.9972 | 1.047992 | −17.33 | 0.075 |

Sodium hydroxide stock solutions (∼10 mol·kg$^{-1}$) were prepared as outlined previously[21] with solid NaOH pellets (Univar analytical reagent, assay 97.0 % min., Ajax Finechem, Australia). To minimize carbonate contamination, which is invariably present (often to quite high levels) even in analytical quality NaOH,[21] the stock solutions were equilibrated with calcium oxide then filtered (0.45 $\mu$m) under high-purity nitrogen. Concentrations were determined to ± 0.2 % relative by titration against standard hydrochloric acid (NIST traceable). Carbonate levels, as determined by titration and confirmed by Raman spectroscopy, were always found to be < 0.1 % of the total alkalinity. Working solutions were prepared from the stock solutions by weight dilution without buoyancy corrections using degassed, $CO_2$-free Millipore Milli-Q water. All solutions were stored under high-purity nitrogen prior to the density measurements.

## 3. Results and Discussion

***3.1 Calibration.*** At temperatures up to 523.15 K, the calibration constant of the densimeter (eq 2), determined with water and up to six (but typically two or three) independently prepared NaCl(aq) solutions at concentrations of $0.5 \lesssim m/\mathrm{mol{\cdot}kg^{-1}} \lesssim 3.3$, was found to be reproducible to within 0.1 %, which is consistent with the mechanical properties of the tube. There was a systematic difference (of about 0.3 % on average) between the water−nitrogen and the (always larger) water−NaCl calibration constants. This probably resulted from the slightly nonlinear dependence of $\rho$ on $\tau^2$ (i.e., the tube is not a perfect harmonic oscillator). Thus, for the density measurements of the NaOH solutions (with densities higher than those of pure water) at $323 \leq T/\mathrm{K} \leq 523$, the water−NaCl(aq) calibration was employed. However, as already noted, at higher temperatures the reliability of Archer's model[20] for the density of NaCl(aq) is not as well established,[15] and thus a water−nitrogen calibration was used instead. It is worth noting here that the $\Delta\rho$ (= $\rho - \rho_w$) values predicted from Archer's model under conditions similar to the present ones agree with the measurements of Majer et al.[22] to only ± 1 kg·m$^{-3}$ (i.e., ca. ± 0.1 %), even though the data of Majer et al. were used for the parametrization of Archer's model! In fairness, it must also be recognized that this discrepancy is close to the experimental error estimated by Majer et al.[22] for NaCl(aq) densities under these conditions.

Corti and Simonson[7] also used a water−NaCl(aq) calibration. However, rather than using Archer's formulation,[20] they employed a new correlation of NaCl(aq) densities at a single concentration, $m = 5.972$ mol·kg$^{-1}$, which was based about 50 % on unpublished data[23] and 50 % on various published sources (not all of which were available to Archer). This correlation[7] gives $\Delta\rho$ values that are lower than Archer's values by (2.4 to 3.3) kg·m$^{-3}$ between (523 and 573) K. Trevani et al.[8] on the other hand used an average of calibration constants determined from water and 1.078 mol·kg$^{-1}$ NaCl(aq) (calculated from Archer's model) or $D_2O$. Clearly, there is a need for further investigation of the calibration procedures for vibrating-tube densimeters in general and especially of reference materials with densities higher than those of water. This would need to be done by an independent method such as a magnetic float or buoyancy balance[24] and is obviously outside the scope of the present work.

As already noted, the switch from water−NaCl(aq) to water−$N_2$ calibrations at $T > 523.15$ K in the present study did not produce any detectable discontinuity in the NaOH(aq) densities. However, because $\Delta\rho$ (the measured quantity) increases markedly with concentration, the precision of its measurement starts to have an impact on the accuracy of $\rho$ itself, especially at higher temperatures. Taking this and other factors into consideration, the overall *accuracy* in the NaOH(aq) densities at 573.15 K is probably not better than ± 0.1 %, being rather better at lower concentrations (where the solution density approaches that of pure water) and lower temperatures (where the experimental and calibration uncertainties are lower) but, correspondingly, slightly worse at higher concentrations and temperatures.

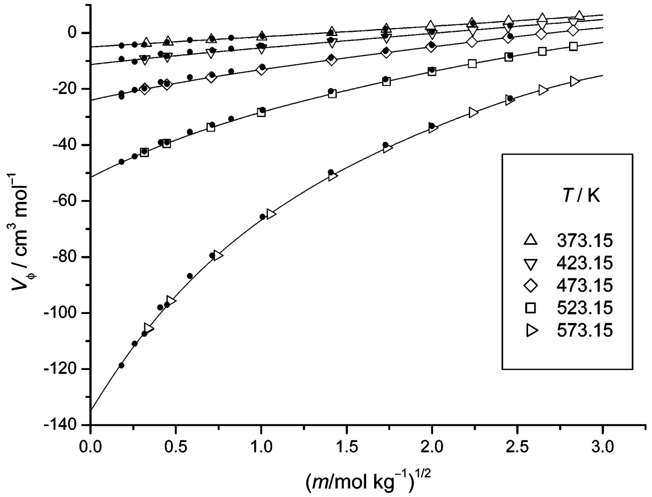

**Figure 1.** Apparent molar volumes of NaOH(aq): open symbols, this work at $P = 10$ MPa; filled circles, Corti and Simonson data[7] interpolated to $P = 10$ MPa. Lines were calculated from eq 4 using the parameters from Table 3. Data at $T = 323.15$ K omitted for representational clarity.

***3.2 Densities of Sodium Hydroxide Solutions.*** The experimental densities of NaOH(aq) solutions obtained in the present work are collected in Table 1. Multiple entries for the same concentration are repeat measurements (using the same calibration) of the same solution to establish measurement precision. The actual experimental conditions were always within ± 0.05 K and generally within ± 0.05 MPa (± 0.15 MPa at 323.15 K) of the temperatures and pressures reported in Table 1. Because the $\Delta\rho$ values are essentially constant over these small temperature and pressure ranges (in the worst case, the variation was calculated to be $6{\cdot}10^{-5}$ g·cm$^{-3}$ or ∼0.006 %), densities are reported for the rounded conditions given in Table 1. As our modeling software[25] incorporates the IAPWS-IF97 "industrial formulation"[26] to calculate the thermodynamic properties of water, the NaOH(aq) densities are based on $\rho_w$ calculated from this formulation. For convenience, these values are also given in Table 1. It should be noted that the measured quantity $\Delta\rho$ is independent of the model selected for $\rho_w$. The values of $\Delta\rho$ can be calculated readily by subtraction using the data in Table 1.

***3.3 Molar Volumes of Sodium Hydroxide Solutions.*** Apparent molar volumes ($V_\phi$) were calculated from the experimental densities (Table 1) using the usual relationship

$$V_\phi = (M_s/\rho) - \{(\rho - \rho_w)/(m\rho\rho_w)\} \qquad (3)$$

where $M_s$ is the molar mass of NaOH and SI units are assumed. The values so obtained are plotted in Figures 1 and 2 along with selected literature data.

A variety of equations have been used to fit density and/or apparent molar volume data as a function of concentration, temperature, and pressure.[27,28] The relative merits of these equations, all of which involve numerous adjustable parameters, have been discussed on several occasions.[28,29] The Pitzer formalism[30] is probably the most favored at present, especially among chemical engineers. However, there are difficulties in fitting NaOH(aq) data at high temperatures and concentrations to the Pitzer model as has been noted by a number of workers.[3,7,8] We defer consideration of such models for now

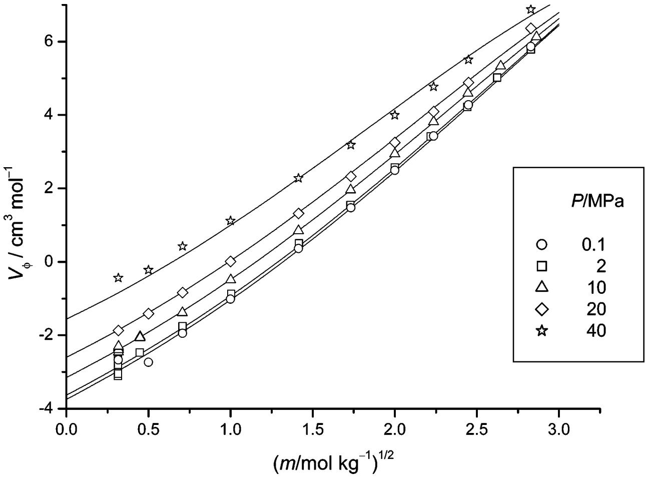

**Figure 2.** Apparent molar volumes of NaOH(aq) at $T = 323.15$ K as a function of pressure: $P = (2$ and $10)$ MPa (this work); $P = (0.1, 20,$ and $40)$ MPa.[2] Lines were calculated from eqs 4 to 8 using the parameters from Table 2 (see text).

and, for convenience, fit the present $V_\phi$ values (Table 1) with an extended Redlich−Meyer equation,[27] similar to that employed by Trevani et al.[8]

$$V_\phi = V^{\rm o} + A_{\rm V} m^{0.5} + B_{\rm V} m + C_{\rm V} m^{1.5} + D_{\rm V} m^2 \qquad (4)$$

where $V^{\rm o}$/cm$^3$·mol$^{-1}$ represents the partial molar volume of NaOH(aq) at infinite dilution; $A_{\rm V}$/cm$^3$·mol$^{-1}$ (kg·mol$^{-1}$)$^{0.5}$ is the theoretical Debye−Hückel slope for volumes;[29−31] and the other $X_{\rm V}$ are empirical parameters. The Debye−Hückel slopes were calculated using the correlation of Archer and Wang[31] for the dielectric constant of water and the equation of state of Hill[32] for the other required properties of water. The values of $A_{\rm V}$ so obtained are broadly consistent with other recent estimations.[33] The ability of this equation to fit the data over a wide range of concentrations, temperatures, and even pressures (see below) is illustrated in Figures 1 and 2.

The expression for the standard (infinite dilution) partial molar volume $V^{\rm o}$ took the form

$$V^{\rm o} = 10^6 M_{\rm s}/\rho_{\rm w} - \kappa_{\rm w} RT(M_{\rm s}/M_{\rm w} - 1) + \kappa_{\rm w} T \rho_{\rm w}{}^2 \ln T(\upsilon_1 T^2 \ln \rho_{\rm w} + \upsilon_2 \rho_{\rm w} + \upsilon_3 \rho_{\rm w} \ln \rho_{\rm w} \ln T) \qquad (5)$$

where $M_{\rm w}$/kg·mol$^{-1}$ is the molar mass of water; $\rho_{\rm w}$/kg·m$^{-3}$ and $\kappa_{\rm w}$/MPa$^{-1}$ are the density and isothermal compressibility of water, calculated from Hill's equation of state;[32] $R$/J·K$^{-1}$·mol$^{-1}$ is the gas constant; $T$/K is the thermodynamic temperature; and $\upsilon_i$ are adjustable parameters. Because the variation in $V_\phi$ depends almost exclusively on the measured quantity ($\rho - \rho_{\rm w}$), slightly different formulations for $\rho_{\rm w}$ (IAPWS-IF97 and Hill) in eqs 3 and 5 do not result in significant inconsistencies in the fitting of the data. The form of eq 5 is loosely based on the well-known dependence of partial molar volumes on compressibility (as, for example, in scaled particle theory) but otherwise has no special significance.

The empirical parameters in eq 4, $B_{\rm V}$, $C_{\rm V}$, and $D_{\rm V}$, were found to correlate strongly with $A_{\rm V}$, and hence the following relationships were selected as providing a good fit to the rather complex temperature dependence with a reasonable number of adjustable parameters. Equations 6 to 8 take into account the rapid change in the apparent molar volumes of aqueous electrolyte solutions close to the critical point of water at 647 K.

$$B_{\rm V} = b_1 \frac{1}{(647 - T)T^4} + b_2 \frac{A_{\rm V}}{(647 - T)T^4 \ln T} + b_3 \frac{A_{\rm V} T^2}{(647 - T) \ln T} + b_4 A_{\rm V} T^3 \qquad (6)$$

$$C_{\rm V} = c_1 \frac{\ln T}{T^3} + c_2 T \ln T + c_3 \frac{A_{\rm V}}{(647 - T)T^4 \ln T} \qquad (7)$$

$$D_{\rm V} = d_1 \frac{T^2}{647 - T} + d_2 \frac{A_{\rm V}}{(647 - T)T^3} + d_3 \frac{A_{\rm V} T^2}{647 - T} \qquad (8)$$

Thus, the overall equation used to fit the $V_\phi(m,T)$ values at $P = 10$ MPa contained 13 adjustable parameters ($\upsilon_i$, $b_i$, $c_i$, and $d_i$), all of which were statistically significant and independent of temperature and pressure. This equation describes the experimental density differences $\Delta\rho$ ($= \rho - \rho_{\rm w}$) to within ± 0.1 % at $T < 523$ K and to within ± 0.2 % at higher temperatures (Figure 3), with an overall root mean square deviation of $\sigma((\Delta\rho_{\rm exptl} - \Delta\rho_{\rm calcd})/\Delta\rho_{\rm calcd}) = 0.00122$ g·cm$^{-3}$. The corresponding apparent molar volumes (Figure 4) are described to within ± 0.2 cm$^3$·mol$^{-1}$ (again significantly better at $T < 523$ K) with $\sigma(V_\phi) = 0.083$ cm$^3$·mol$^{-1}$ overall. It should be noted that these $\sigma$ values are averages of quantities that vary strongly (by more than an order of magnitude) and therefore must be interpreted with care. The limited data measured at $P = 2$ MPa (Table 1) were not included in the fit.

The values of the adjustable parameters $\upsilon_i$, $b_i$, $c_i$, and $d_i$ obtained from fitting the apparent molar volume data are given in Table 2, and the resulting values of the parameters $V^{\rm o}$, $B_{\rm V}$, $C_{\rm V}$, and $D_{\rm V}$ at each experimental temperature and $P = 10$ MPa are summarized in Table 3, along with the calculated values of the Debye−Hückel slope $A_{\rm V}$. It should be noted that the present $V^{\rm o}$ values are broadly consistent with those obtained by Corti and Simonson, with a reported standard error of fit of ∼1 cm$^3$·mol$^{-1}$, from their isothermal/isobaric Pitzer fits of the experimental data given in their Table 5.[7]

Because the parameters of the present fitting equation were derived using only the data at $P = 10$ MPa, their values hold strictly for that pressure only. However, at low temperatures, where the compressibilities of water and aqueous solutions change only slightly with pressure, eqs 4 to 8 can be used with the parameters in Table 2 along with the appropriate values of $\kappa_{\rm w}$ and $A_{\rm V}$, for the prediction of $\Delta\rho$ and $V_\phi$ at other pressures with reasonable accuracy. This is illustrated in Figure 2 which plots the present $V_\phi$ values at $T = 323.15$ K and $P = (2$ and $10)$ MPa, along with values at $P = (0.1, 20,$ and $40)$ MPa at the same temperature, taken from the literature survey of Simonson and Ryther.[2] Even at $P = 40$ MPa, where failure might be expected, eq 4 fits the data reasonably well.

***3.4 Comparisons with Literature Data.*** The most recent data for NaOH(aq) densities[8] were obtained at $T = (523$ and $573)$ K and $0.2 \lesssim m/\text{mol·kg}^{-1} \lesssim 2.5$ but at only one pressure ($P = 14$ MPa) and thus cannot be directly compared with the present results. However, it is noted that Trevani et al.[8] found differences of up to ± 2.5 cm$^3$·mol$^{-1}$ in $V_\phi$ and $V^\circ$ between their data and the model of Corti and Simonson.[7]

The comparison of most interest is therefore with the data of Corti and Simonson (C&S) because they cover ranges of temperature and concentration similar to the present study, and they were measured over a range of pressures. However, exact comparison of the present data with those of C&S is not straightforward. In addition to the need to interpolate with respect to pressure, it can be shown that even relatively minor

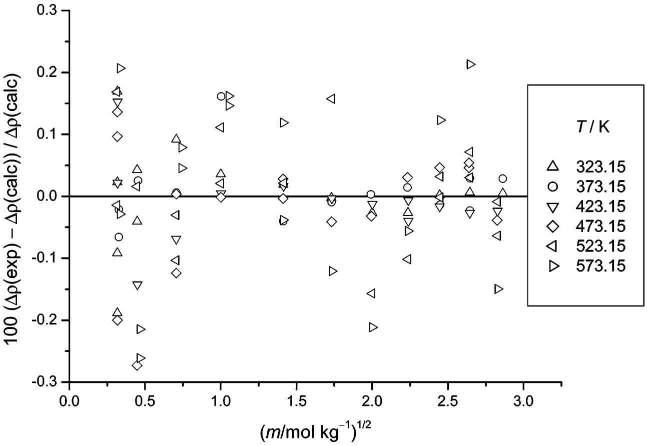

**Figure 3.** Relative density differences for NaOH(aq) measured in this work at $P = 10$ MPa (points) compared with the values calculated from eq 4 using the parameters from Table 3 (line).

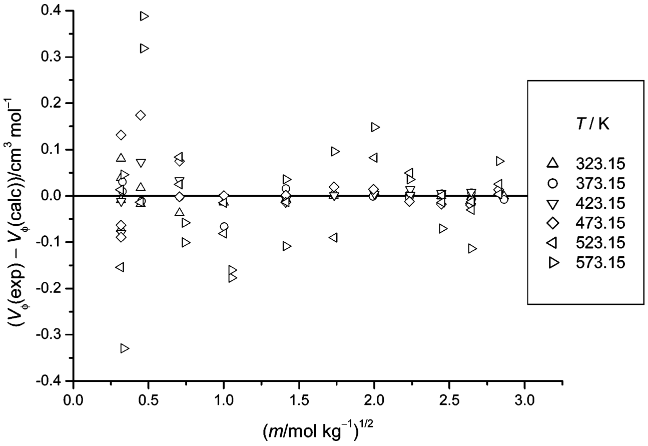

**Figure 4.** Present apparent molar volumes ($V_\phi$) of NaOH(aq) at $P = 10$ MPa (points) compared with the values calculated from eq 4 using the parameters from Table 3 (line).

**Table 2. Empirical Parameters for Equations 5 to 8**

| $i$ | $v_i$ | $b_i$ | $c_i$ | $d_i$ |
|---|---|---|---|---|
| 1 | −1.242796E−12 | 6.293613E+12 | −3.310092E+06 | −1.890253E−04 |
| 2 | −3.486583E−07 | −1.217307E+13 | −2.294140E−05 | 1.875988E+08 |
| 3 | 7.424377E−09 | 3.769641E−05 | 6.063174E+12 | −4.255494E−06 |
| 4 | | −1.201656E−09 | | |

**Table 3. Parameters for Equation 4 Valid at a Pressure of 10 MPa and at Concentrations of $m \leq 8$ mol·kg$^{-1}$**

| $T$/K | $V^{oa}$ | $A_V{}^a$ | $B_V$ | $C_V$ | $D_V$ |
|---|---|---|---|---|---|
| 323.15 | −3.150 | 2.297 | 0.3235 | 0.0729 | −0.02467 |
| 373.15 | −5.029 | 3.942 | −0.5742 | 0.3322 | −0.05267 |
| 423.15 | −11.342 | 7.123 | −1.7338 | 0.6721 | −0.09666 |
| 473.15 | −24.080 | 13.917 | −4.0960 | 1.3130 | −0.17790 |
| 523.15 | −51.594 | 31.490 | −10.9211 | 3.0679 | −0.38069 |
| 573.15 | −135.028 | 101.625 | −43.9597 | 11.9785 | −1.39338 |

[a] Units: $V^o$/cm$^3$·mol$^{-1}$; $A_V$/cm$^3$·mol$^{-1}$ (kg·mol$^{-1}$)$^{0.5}$.

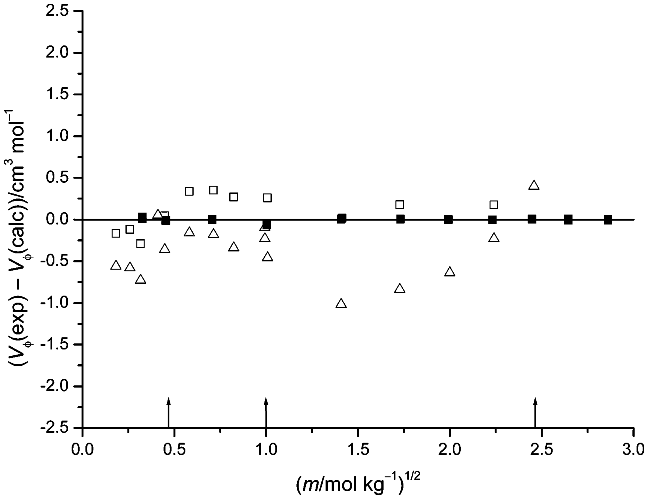

**Figure 5.** Deviations of apparent molar volumes of NaOH(aq) from the present model (eq 4) at $T = 373.15$ K and $P = 10$ MPa (line): filled squares, this work; open squares, Corti and Simonson[7] interpolated to $P = 10$ MPa; and open triangles, deviations between the data and model of Corti and Simonson at $P \approx 7$ MPa[7] taken from their Table 4. The arrows indicate the concentrations of Corti and Simonson's stock solutions (see text).

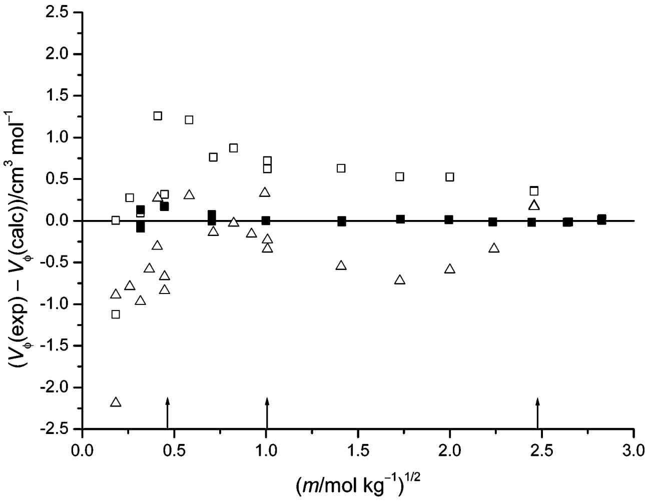

**Figure 6.** Deviations of apparent molar volumes of NaOH(aq) from the present model (eq 4) at $T = 473.15$ K and $P = 10$ MPa (line): filled squares, this work; open squares, Corti and Simonson[7] interpolated to $P = 10$ MPa; and open triangles, deviations between the data and model of Corti and Simonson at $P \approx 7$ MPa[7] taken from their Table 4. The arrows indicate the concentrations of Corti and Simonson's stock solutions (see text).

differences in temperature and concentration produce significant uncertainties in the interpolated volumes, especially at higher temperatures.

Keeping these limitations in mind, Figures 5 to 7 compare the present data with those of C&S at three representative temperatures ($T$/K = 373.15, 473.15, and 573.15, respectively). In each of these figures, which are plotted to the same scale for ease of comparison, the zero line represents eq 4, with the parameters from Table 3. The filled squares are the present experimental values at $P = 10$ MPa (as shown at higher sensitivity in Figure 4). The open squares are the values of C&S at their experimental temperatures (which are close, but not exactly equal, to the present temperatures) inter- or extrapolated (depending on the temperature) to $P = 10$ MPa. Such values could be obtained only where C&S reported data at two pressures at (nearly) the same concentration, hence the gaps in Figures 5 to 7. Also shown in Figures 5 to 7 (open triangles) are the deviations reported by C&S (their Table 4) between their experimental data (at ca. (7 or 11) MPa, depending on the temperature) and their Pitzer model (with 14 adjustable parameters in total) at the same temperature and pressure. Note that no deviations were reported by C&S for $m > 1$ mol·kg$^{-1}$ NaOH at $T = 573$ K (Figure 7, see also below).

A number of conclusions can be drawn from the comparisons in Figures 5 to 7. First, (as can also be seen from Figure 1) the present results are in broad agreement with those of C&S but are more precise (less scattered). Second, the present eq 4 fits the data of C&S to about the same level of precision as their

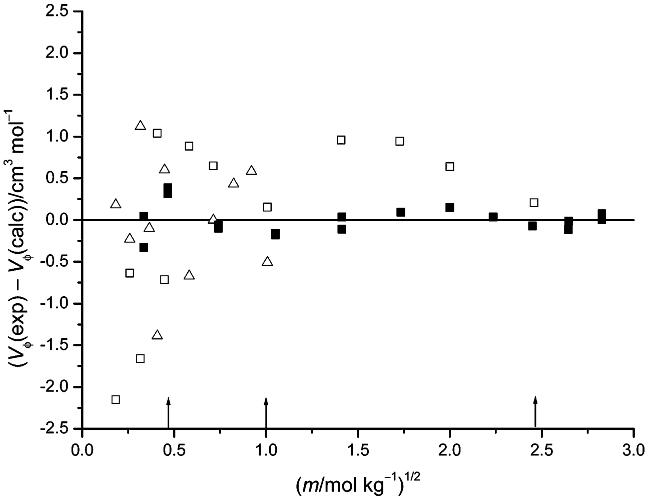

**Figure 7.** Deviations of apparent molar volumes of NaOH(aq) from the present model (eq 4) at $T = 573.15$ K and $P = 10$ MPa (line): filled squares, this work; open squares, Corti and Simonson[7] extrapolated to $P = 10$ MPa; and open triangles, deviations between the data and model of Corti and Simonson at $P \approx 11$ MPa[7] taken from their Table 4. The arrows indicate the concentrations of Corti and Simonson's stock solutions (see text).

Pitzer model at all temperatures. Third, as might be expected, the quality of all fits decreases with increasing temperature. This reflects the very real difficulties in measurement, along with the rapid changes in density and the fitting parameters with temperature and pressure, at these temperatures. Corti and Simonson also noted difficulties in modeling their data at $T > 523$ K. At such temperatures, even with the inclusion of an ion pair in their Pitzer model, C&S could represent their experimental data satisfactorily only up to $m \approx 1$ mol·kg$^{-1}$ NaOH.[7]

Figures 5 to 7 also reveal recurring irregularities in the C&S data at particular concentrations (indicated by the arrows on the *x*-axes). These concentrations correspond to those of the stock solutions employed by C&S for the in situ preparation of their diluted solutions, which was achieved with a twin-barreled proportioning pump.[7] These discontinuities suggest that some experimental difficulties may have been encountered with this device or, at least, that its use lowered the precision of their measurements.

It should be noted that as all the results being compared in Figures 3 to 7 were obtained with vibrating-tube densimeters, which measure $\Delta\rho$ ($= \rho - \rho_w$) directly, they are largely independent of the values chosen for $\rho_w$ (nevertheless, the value of $\rho_w$ selected for the calculation of both $\Delta\rho$ and $V_\phi$ for each data set was that used by the original authors). On the other hand, the results *are* dependent on the calibration constant of the densimeter and hence on $\rho_{ref}$ (strictly, eq 2, on $|\rho_w - \rho_{ref}|$). This suggests that some of the differences between the present data and those of C&S (Figures 5 to 7) are due to the uncertainties in $\rho_{ref}$ and the calibration procedure, i.e., the performance of vibrating tubes as harmonic oscillators under these extreme conditions.

None of the above comments are intended, or should be seen, as criticism of the work of Corti and Simonson.[7] Reliable measurement of the densities of these chemically aggressive solutions at high temperatures and pressures is not a trivial exercise. Although the present results are more precise, their accuracy seems to be similar to those of C&S, with the differences probably mostly reflecting the uncertainties in calibration. It is also apparent, from the present study and the work of C&S[7] and Trevani et al.,[8] that in addition to the experimental problems the modeling of densities (and other thermodynamic properties) of NaOH(aq) to the limits of experimental precision needs further examination. In the meantime, the present data have been incorporated into our ten-component synthetic Bayer liquor model,[14,25,34] which aims at improved modeling capabilities for predicting the thermodynamic properties of Bayer process solutions employed in alumina production.

## 4. Conclusions

The present set of experimental NaOH(aq) densities complement those of Corti and Simonson[7] and the more restricted values of Trevani et al.[8] They provide a sound basis for the calculation of the densities and related thermodynamic quantities for NaOH(aq) over the ranges of concentration, temperature, and pressure of industrial interest. All three data sets are adequately represented by the various models developed by their respective authors, but significant (absolute) uncertainties exist, especially at higher temperatures.

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