Densities and Apparent Molar Volumes of Atmospherically Important Electrolyte Solutions. 1. The Solutes H_2SO_4 , HNO_3 , HCl, Na_2SO_4 , $NaNO_3$, NaCl, $(NH_4)_2SO_4$, NH_4NO_3 , and NH_4Cl from 0 to 50 °C, Including Extrapolations to Very Low Temperature and to the Pure Liquid State, and $NaHSO_4$, NaOH, and NH_3 at 25 °C

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Supporting Information

ABSTRACT: Calculations of the size and density of atmospheric aerosols are complicated by the fact that they can exist at concentrations highly supersaturated with respect to dissolved salts and supercooled with respect to ice. Densities and apparent molar volumes of solutes in aqueous solutions containing the solutes H₂SO₄, HNO₃, HCl, Na₂SO₄, NaNO₃, NaCl, (NH₄)₂SO₄, NH₄-NO₃, and NH₄Cl have been critically evaluated and represented using fitted equations from 0 to 50 °C or greater and from infinite dilution to concentrations saturated or supersaturated with respect to the dissolved salts. Using extrapolated densities of high-temperature



solutions and melts, the relationship between density and concentration is extended to the hypothetical pure liquid solutes. Above a given reference concentration of a few mol kg⁻¹, it is observed that density increases almost linearly with decreasing temperature, and comparisons with available data below 0 °C suggest that the fitted equations for density can be extrapolated to very low temperatures. As concentration is decreased below the reference concentration, the variation of density with temperature tends to that of water (which decreases as temperature is reduced below 3.98 °C). In this region below the reference concentration, and below 0 °C, densities are calculated using extrapolated apparent molar volumes which are constrained to agree at the reference concentrations with an equation for the directly fitted density. Calculated volume properties agree well with available data at low temperatures, for both concentrated and dilute solutions. Comparisons are made with literature data for temperatures of maximum density. Apparent molar volumes at infinite dilution are consistent, on a single ion basis, to better than $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ from 0 to 50 °C. Volume properties of aqueous NaHSO₄, NaOH, and NH₃ have also been evaluated, at 25 °C only. In part 2 of this work (ref 1) an ion interaction (Pitzer) model has been used to calculate apparent molar volumes from -20 to 50 °C, and from 0 to 100 wt % of solute, are tabulated for the electrolytes listed in the title and have also been incorporated into the extended aerosol inorganics model (*E-AIM*, http://www.aim.env.uea.ac.uk/aim/aim.php) together with densities of the solid salts and hydrates.

1. INTRODUCTION

Densities of pure aqueous solutions and mixtures are required to convert concentrations between mass and volume units. For common and industrially important electrolytes, a number of compilations of density exist, based upon data from studies carried out over more than a century.^{2–4} New measurements have continued to be made, focusing for example on the components of seawater and brines^{5–7} or on extreme conditions such as very low or very high temperature.^{8–14} Recent studies of the densities of aqueous solutions, presenting fitted equations from which densities can be calculated as functions of concentration and temperature, include the work of Krungalz et al.¹⁵ and Laliberté and Cooper.¹⁶ Krungalz et al.¹⁵ use the Pitzer¹⁷ ion

interaction model and apply it to data up to saturation (with respect to the dissolved salts) for temperatures from about 15 to 95 °C. Monnin¹⁸ also uses the Pitzer model, for a treatment of brine components at 25 °C only. Laliberté and Cooper¹⁶ treat 59 electrolytes from 0 to 100 °C (depending on the available data) using an empirical equation for apparent specific volume that does not include a Debye—Hückel term (and which will therefore not accurately represent apparent molar volumes in the limit of infinite dilution). These studies, and most other compilations

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and correlations of solution densities, are of limited use for atmospheric calculations because they cannot be applied either to solutions supersaturated with respect to the dissolved solutes or to solutions at temperatures below 0 °C.

In the field of atmospheric chemistry, the densities of aqueous and solid forms of common atmospheric constituents such as H_2SO_4 , $(NH_4)_2SO_4$, and the components of sea salt and windblown dust are needed to calculate aerosol particle and droplet size from a knowledge of molar or mass composition. Partial molar volumes of water and solutes in aqueous solutions are required in calculations of the formation of nanoparticles in the atmosphere, gas-particle partitioning to these particles (influenced by the Kelvin effect), and their growth into fog and cloud droplets. A unique feature of the behavior of atmospheric aerosol droplets is their ability to exist as liquids at concentrations that are greatly supersaturated with respect to solid salts and/or supercooled with respect to the formation of ice.¹⁹⁻²¹ For example, studies using an electrodynamic balance have shown that single aqueous aerosol droplets of NaCl can be concentrated to a molality of about 15 mol kg⁻¹ at room temperature before crystallization,^{22–24} compared to saturation in a bulk solution at about 6 mol kg⁻¹. Similar experiments have been carried out for many other salts^{24–29} and have shown that NH_4NO_3 and NaNO₃, for example, can exist as liquid droplets up to concentrations approaching the pure melt at room temperature.^{25,29,30}

Substantial supercooling with respect to ice has also been demonstrated. Experiments using both electrodynamic balances and emulsions in which small droplets of aqueous solution exist in a liquid carrier phase have demonstrated supercooling with respect to ice of up to 30 K for dilute solutions^{31,32} and about 60 K for 3.4 mol kg⁻¹ H₂SO₄ which has a normal (bulk solution) freezing temperature of 252 K.³³

In the atmosphere, the range of temperatures of interest is approximately 180-323 K for studies of tropospheric and stratospheric aerosols and cloud droplets. These liquid particles exist at equilibrium, or close to equilibrium, with the atmospheric relative humidity which is therefore equivalent to their water activity. Relative humidity ranges from close to 100% to less than 10% in dry environments, leading to aerosols ranging from very dilute to extremely concentrated or supersaturated with respect to dissolved solids. A very few measurements of densities of aqueous aerosol droplets at supersaturated concentrations have been made at room temperature, 25,30,34 and some densities of bulk solutions and small volumes held in capillaries that have been measured at low temperatures include concentrations that are supersaturated with respect to ice or other solids.^{8,35} No systematic studies of the densities of supersaturated and supercooled aqueous solutions have been made over wide ranges of temperature and composition, and the tabulations of solution densities and apparent molar volumes that exist^{2,3,36} are restricted to subsaturated concentrations and temperatures mostly greater than 0 °C. Densities of the atmospherically important system H₂SO₄-(NH₄)₂SO₄-H₂O system have been studied (for supersaturated concentrations) at compositions corresponding to $NH_4HSO_4-H_2O$ and $(NH_4)_3H(SO_4)_2-H_2O$,^{25,35} and no complete treatment of the density of the mixture over the whole composition range yet exists even at 25 °C.

In this work we critically assess the available density data for aqueous solutions of 12 atmospherically important solutes and combine the results with literature measurements for supersaturated solutions and for (extrapolated) high temperature melts to yield fitted equations for apparent molar volumes and densities from infinite dilution to the hypothetical pure liquid solutes. The treatment extrapolates to very low temperature, tending to values for pure liquid water and the extrapolated melt at the two extremes of concentration, and is consistent with known behavior and/or data at intermediate concentrations. The estimation of the densities of mixtures is briefly discussed, as is the incorporation of the results (for practical use) in the extended aerosol inorganics model (*E-AIM*) of Clegg, Brimblecombe, and Wexler.^{37–39} In a companion paper,¹ hereafter referred to as part 2, we use a Pitzer ion interaction model to describe volume properties of 0–3 mol kg⁻¹ aqueous H₂SO₄ as a function of temperature and 0–6 mol kg⁻¹ H₂SO₄–(NH₄)₂SO₄–H₂O at 25 °C.

2. THEORY

The apparent molar volume $(V^{\phi}/\mathrm{cm}^3 \,\mathrm{mol}^{-1})$ of a solute "s" in a pure aqueous solution is related to the density of the solution $(\rho/\mathrm{g} \ \mathrm{cm}^{-3})$ and that of pure water $(\rho_\mathrm{w}/\mathrm{g} \ \mathrm{cm}^{-3})$ by the equations¹⁵

$$V^{\phi} = (M_{\rm S}/\rho) - [(1-x_{\rm s})/x_{\rm s}] 18.0152 [(\rho - \rho_{\rm w})/(\rho \rho_{\rm w})] \quad (1a)$$

$$V^{\phi} = (M_{\rm S}/\rho) - (1000/m)(\rho - \rho_{\rm w})/(\rho \rho_{\rm w})$$
(1b)

where $M_{\rm S}$ (g mol⁻¹) is the molar mass of the solute, $x_{\rm s}$ is its mole fraction in solution, m (mol kg⁻¹) is the molality of the solute, and 18.0152 g is the molar mass of pure water. The mole fraction $x_{\rm s}$ is equal to $n_{\rm s}/(n_{\rm s} + n_{\rm w})$ where n is the number of moles of solute or water (w). The apparent molar volume of the solute in a pure aqueous solution is related to the total volume of the solution ($V/\rm cm^3$) by

$$V^{\phi} = (V - n_{\rm w} V^{\circ}_{\rm w})/n_{\rm s} \tag{2}$$

where $V_{\rm w}^{\circ}$ (cm³ mol⁻¹) is the molar volume of pure water at the temperature of interest.

Apparent molar volumes of electrolytes at infinite dilution in water (i.e., at zero concentration) are additive in terms of the individual ions so that, for electrolyte $M_{\nu+}X_{\nu-}$

$$V^{\phi\infty}(\mathbf{M}_{v+}\mathbf{X}_{v-}) = v_+ V^{\phi\infty}(\mathbf{M}^{z+}) + v_- V^{\phi\infty}(\mathbf{X}^{z-}) \qquad (3)$$

where $V^{\phi^{\infty}}$ is the infinite dilution apparent molar volume of the solute or ion, z^+ and z^- are the magnitudes of the charges on the ions, and v_+ and v_- are the numbers of cations and anions in one formula weight of the electrolyte. By convention $V^{\phi^{\infty}}(H^+)$ is set equal to zero at all temperatures, thus allowing other individual ionic values to be determined from those of the electrolytes. In practical studies of the volume properties of solutions, the variation of $V^{\phi}(M_{v+}X_{v-})$ with concentration is typically represented as the sum of the value of the apparent molar volume at infinite dilution, a Debye–Hückel term that yields the approach to this value in very dilute solutions, and a polynomial in molality that represents $V^{\phi}(M_{v+}X_{v-})$ at higher concentrations.

Noting that the partial molar volume of the solute at infinite dilution in the solvent is equivalent to $V^{\phi \circ \circ}$, the total volume of the solution in eq 2 can be written as

$$V = n_{\rm w} V_{\rm w}^{\rm o} + n_{\rm s} V^{\phi \infty} + \Delta V^{\rm ex} \tag{4}$$

where ΔV^{ex} (cm³) is the excess volume of the solution which is equal to the differential of the excess Gibbs energy of the solution with respect to pressure (*P*)¹⁵

$$\Delta V^{\rm ex} = \left(\partial G^{\rm ex} / \partial P\right)_{T, n_{\rm w}} \tag{5}$$



Figure 1. Phase diagram of an arbitrary solute in water, showing both the normal liquid region (unshaded) and the solid region (shaded). The plot is divided into three areas, (I), (II), and (III). Line (a) marks the reference concentration for this solute (described in the text), and line (b) denotes the concentration of the pure solute (100 wt %). The curved boundary in area (III) indicates saturation of the liquid phase with respect to the solid solute, and the boundary that is mostly in area (II) indicates saturation with respect to ice. The closeness of line (a) to the eutectic point (the intersection of the two lines showing saturation) has no significance.

where temperature (T/K) and the number of moles of the solvent are kept constant. By substitution into eq 2 it is then found that

$$V^{\phi} = V^{\phi \infty} + (1/n_s) (\partial G^{\text{ex}} / \partial P)_{T, n_{\text{ex}}}$$
(6)

This equation relates the apparent molar volume of the solute to the differentials of the mean activity coefficient of the solute and the osmotic coefficient of the solution with respect to pressure. We make use of this relationship in the treatment of densities of aqueous H_2SO_4 and acid sulfate solutions in part 2 of this work. The equations used to represent the density of pure water and the apparent molar volumes of the electrolytes as functions of temperature and concentration are described in the following sections.

3. OUR APPROACH

Our overall aims are (i) to represent measured apparent molar volumes over the normal liquid range (from infinite dilution to saturation and from 0 to 50 $^{\circ}$ C or greater) to within experimental uncertainty, (ii) to provide estimates of densities of supersaturated solutions extending to the hypothetical pure liquid electrolyte, and (iii) to provide extrapolations of densities of all concentrations to very low temperature. To do this, it is necessary to use different equations and methods, according to the temperature and concentration range of interest.

The phase diagram of a typical, arbitrary, electrolyte solution is shown in Figure 1. In the limit of infinite dilution the calculated densities tend to those for pure water, and in the limit of zero water content they tend to those for the pure liquid solute or melt (line b in Figure 1), usually extrapolated from data for high temperatures. An effort is made to ensure that apparent molar volumes of the different electrolytes at infinite dilution ($V^{\phi\infty}(M_{\nu+}X_{\nu-})$) are additive in terms of the individual ions, as far as possible (although it has not been possible to resolve all inconsistencies in data for dilute solutions).

The (*t*, wt %) region shown in Figure 1 is divided into three. Area I above 0 °C and the liquid part of area III are where most density measurements of aqueous solutions are made. There are relatively few systematic studies of densities in the liquid part of the phase diagram below 0 °C (in area II). Of the solutes considered here, there are comprehensive data only for aqueous $NaCl^8$ and $H_2SO_4^{-14}$ although there are a number of measurements for electrolytes at single, or just a few, concentrations.^{9,35,43,44} Most of area III, above the reference concentration (line a) in Figure 1, consists of concentrations at which the solution is supersaturated with respect to the solid solute. The reference concentration for each solute is one for which the available data suggest that densities extrapolate linearly, or close to linearly, to very low temperature. The phase diagram is bounded at 0 wt % by liquid and supercooled water and at 100 wt % by the hypothetical pure liquid electrolyte. Although droplets containing most solutes will effloresce at some concentration <100 wt %²¹, some can retain water close to zero relative humidity (and 100 wt % solute concentration).^{30,45} In the subsections below we discuss the basis for the divisions in Figure 1 and the different approaches used to represent densities and apparent molar volumes in each area or combinations of areas.

3.1. Densities of Subsaturated Solutions above 0 °C. It is for these solutions, area I and the lower part of III in Figure 1, for which most data exist and for which tabulations or fitted equations for densities are available in many compilations. In this work we fit measured densities as apparent molar volumes for both areas, for temperatures between 0 °C and at least 50 °C. For a number of solutes there are also data for supersaturated solutions, and the fit is extended into area III in the figure to the pure liquid melt (100 wt %). The equations used, presented in section 4, include a Debye-Hückel term so that the value of the apparent molar volume is correctly represented as infinite dilution is approached. We have re-evaluated the apparent molar volume at infinite dilution, $V^{\phi\infty}$, for many of the solutes to yield more accurate and consistent values than available hitherto. Densities of aqueous solutions in area III, which includes supersaturated solutions, are also represented using fitted equations in order to provide consistent extrapolations of density to very low temperature (which was found not to be possible using the expressions for apparent molar volume). The equations for density can be used for all temperatures in area III of Figure 1.

3.2. Densities of Aqueous Solutions below 0 °C. The density of pure water peaks at 3.98 °C and declines steeply at lower temperatures.⁴⁶ Measurements of the densities of dilute aqueous solutions at temperatures below 0 °C show that similar maxima occur (see Kaulgud and Pokale⁴⁷ and references therein)— the more concentrated the solution, the lower the temperature of the maximum, and the broader and more indistinct it becomes. This behavior is apparent in densities of aqueous NaCl, for example.³¹ The relationship between solute molality and the temperature of maximum density can be represented for dilute solutions by equations such as⁴⁷

$$\Delta \theta = K_{\rm m} m \tag{7}$$

where $\Delta \theta$ (K) is the difference between the temperature of maximum density of the solution and that of water, *m* (mol kg⁻¹) is molality, and $K_{\rm m}$ is a constant. Values of $K_{\rm m}$ have been determined for several electrolytes, and the relationship appears to hold to maximum molalities of a few mol kg⁻¹ (above which deviations

occur). As concentration is further increased, the peak in the density becomes less distinct and eventually disappears. For aqueous NaCl, for example, a maximum in the density is still apparent for a 1.487 mol kg⁻¹ solution at about 260 K but has not been measured for higher molalities.³¹

Densities of concentrated solutions of electrolytes including $HCl_{2}^{9}H_{2}SO_{4}^{9,14}$ and several others measured to temperatures as low as $-70 \degree C^{9,48,49}$ show no relationship to that of pure water below 0 °C and increase almost linearly with temperature from close to 100 °C to as low as -40 to -70 °C (the limit of the available data). This behavior is analogous to that found for the molar heat capacities of low temperature (including supercooled) aqueous NaCl and NaNO3 solutions.31,32 The heat capacity of pure water rises as temperature is lowered, increasing steeply to an apparent limit at about 227 K (-46 °C).⁵⁰ This phenomenon has been studied for several decades, and it had been suggested that a singularity in the properties of pure water occurred at this temperature.^{51,52} Heat capacities of aqueous NaCl and NaNO3 below 0 °C, determined by Archer and Carter,^{31,32} show a similar rise as temperature is lowered, although of smaller magnitude than that for water and shifted to lower temperatures. At concentrations above 4 mol kg⁻¹ NaNO₃ (see Figure 2 of Carter and Archer³²), and 4.5 mol kg⁻¹ of NaCl (Figure 4 of Archer and Carter³¹) no increase in heat capacity is observed even for temperatures approaching 230 K.

It is unclear whether this behavior—and the concentration above which no density maximum and rise in heat capacity are observed—is related more closely to solute molality or solution ionic strength. The latter might be expected, for both heat capacity and density, if it is caused by the disruption of the different structural configurations of water molecules that are thought to exist in the pure solvent and in dilute aqueous solutions.^{53–55} In this study we define two concentration ranges over which densities are treated: first, concentrations greater than or equal to a reference concentration for which densities have an almost linear relationship temperature even below 0 °C. Second, concentrations below the reference concentration for which densities are calculated using apparent molar volumes of the solute and the density of pure water. As the solutions become more dilute, their densities approach that of pure water.

3.2.1. Concentrated Solutions. At moderate to high concentrations the densities of many aqueous solutions have been shown to vary with temperature in a linear or near-linear way, as noted above. This leads us to select, for each electrolyte studied, a "reference" concentration for which we represent the dependence of density on temperature using a simple expression that is approximately linear in T and fitted to the available data (including measurements below 0 °C where available). This equation is assumed to extrapolate accurately to very low temperature. Area III in Figure 1 is bounded by this reference concentration and the melt (100 wt %). In this area the measured densities of subsaturated solutions (and of supersaturated solutions where data are available) are represented as functions of temperature and solute weight fraction by equations that yield the correct densities for the melt and the reference concentration, and which extrapolate to very low temperature-typically 150 K—yielding simple monotonic increases in density.

3.2.2. Dilute Solutions. Studies of the maximum supercooling of small droplets of aqueous solutions of a wide range of electrolytes⁵⁶ show that the degree of supersaturation with respect to ice that can be obtained is related, to a first-order approximation, to the water activity of the solution. For aqueous

H₂SO₄, which is the main inorganic constituent of liquid aerosol droplets in the stratosphere, Figures 6 and 7 of Koop and Molina³³ show that a droplet of about 3.75 mol kg⁻¹ molality can remain liquid to about 170 K, much less than the 247 K which is the temperature at which this concentration is in equilibrium with solid ice. As will be discussed in section 3.4, measurements of liquid water and D₂O densities are available to temperatures below 150 K.53,57 In order that calculated solution densities in area II of Figure 1 approach these values as $x_s \rightarrow 0$, we combine the molar volume of water at the temperature of interest with extrapolated values of the apparent molar volume of the solute from higher temperatures to yield an estimate of the density. Constraints are applied so that calculated densities at 0 °C agree, first, with the treatment of subsaturated solutions described in section 3.1 and, second, with densities of the reference concentration at all temperatures.

3.3. Densities of Melts. Densities of five pure liquid electrolytes (melts) at 25 °C have been measured by Zelenyuk et al.³⁰ using an electrodynamic balance and compared with densities of the solid salts and with extrapolations of the equations of Tang^{25,26} for densities of the supersaturated aqueous solutions. The results are included in Table 1, in which comparisons are made in terms of molar volumes. Predictions from Tang's equations for the additional salts NaCl, Na₂SO₄, and (NH₄)₂SO₄ have been added. We note that there is a fitted equation for aqueous NH₄NO₃ in Table 1 of Tang.²⁶ No reference is given to the source of information on which this is based, but it appears that the equation has been fitted only to densities of subsaturated solutions.

Differences between the molar volumes of the melts and the solids for the salts in Table 1 range from 1% to 9%. It seemed to us that comparisons over a wider range of electrolytes might enable reasonable estimates of melt densities, and their variation with temperature, to be made for the salts of interest here. For cases where the melt is not attainable in practice, even in small aerosol particles, the information should be of use in estimating the densities of supersaturated aqueous mixtures, as described in the Appendix.

Densities of a wide range of molten salts and their mixtures have been reviewed by Janz⁵⁸ who presents a fitted equation, of the form $\rho = a + bT$, for each salt. Table 1 lists coefficients of the equation for 20 salts, together with the melting points of the solids and the range of temperatures over which the melt densities have been fitted. It is clear, first of all, that the slopes $\partial \rho / \partial T$ are quite similar, varying only by about a factor of 2. Also, for the chloride, nitrate, and sulfate salts of the higher alkali metals (Li, Na, and K) the slopes are smaller in magnitude than those of Rb and Cs. We have compared values of melt densities at 25 °C calculated using the equations of Janz⁵⁸ with those measured by Zelenyuk et al.³⁰ and also calculated using the equations of Tang and Munkelwitz.^{25,26} The percentage differences between solid and liquid densities were much larger than those determined experimentally at 25 °C, no doubt because of the large extrapolation-several hundred kelvin. We therefore did the following: first, we assumed that the density of the solid salt at 25 °C provides an upper limit for a hypothetical melt density at 0 K. Second, using the equations of Janz we generated values of density at 10 K intervals over their range of validity and then refitted these values constraining the equation to yield the density of the solid at 0 K. The coefficients of these new equations (see the notes to Table 1), some with terms in T^2 as well as T, are given in Table 1. Differences between the calculated molar volumes of

| | | | | | melt density ^c (eq 1) | | T range d (K) | melt density ^e (eq 2) | | |
|--|--------------------------------|---------|---|--------------------------|----------------------------------|----------|----------------------|----------------------------------|----------|----------|
| salt | $M_{\rm S}\left({\rm g} ight)$ | mp (°C) | $V^{\circ}(\mathrm{solid})^a (\mathrm{cm}^3 \mathrm{mol}^{-1})$ | $\Delta V^{\circ b}$ (%) | a | b | - | a | b | с |
| LiCl | 42.39 | 610 | 20.478 | 9.84 | 1.8842 | -4.328 | 894-1054 | 2.07 | -6.2205 | |
| NaCl | 58.44 | 801 | 26.931 | 8.64 | 2.1389 | -5.526 | 1080-1300 | 2.17 | -5.7854 | |
| NaCl ^f | 58.44 | 801 | 26.931 | (39.47) | | | | | | |
| KCl | 74.55 | 771 | 37.500 | 7.29 | 2.1359 | -5.831 | 1053-1212 | 1.988 | -4.5281 | |
| RbCl | 120.92 | 715 | 43.812 | 3.52 | 3.121 | -8.832 | 996-1196 | 2.760 | -2.2613 | -2.9800 |
| CsCl | 168.36 | 645 | 42.217 | 10.49 | 3.7692 | -10.65 | 945-1179 | 3.988 | -12.695 | |
| LiNO ₃ | 68.95 | 253 | 28.971 | 14.95 | 2.068 | -5.46 | 545-714 | 2.380 | -10.379 | |
| NaNO ₃ | 84.99 | 307 | 37.606 | 8.88 | 2.32 | -7.15 | 583-643 | 2.26 | -6.1805 | |
| NaNO3 ^g | 84.99 | 307 | 37.606 | 7.6 | | | | | | |
| NaNO ₃ ^f | 84.99 | 307 | 37.606 | (8.1) | | | | | | |
| KNO3 | 101.1 | 337 | 47.915 | 6.56 | 2.3063 | -7.235 | 620-730 | 2.11 | -4.3569 | |
| RbNO3 | 147.5 | 305 | 47.428 | 10.66 | 3.1366 | -10.687 | 590-690 | 3.11 | -9.8608 | -0.63977 |
| CsNO ₃ | 194.9 | 414 | 53.251 | 11.12 | 3.6206 | -11.6605 | 545-714 | 3.66 | -12.282 | |
| NH_4NO_3 | 80.04 | 169.6 | 46.535 | 10.61 | 1.759 | -6.675 | 453-463 | 1.72 | -4.9899 | -1.8196 |
| NH ₄ NO ₃ ^g | 80.04 | 169.6 | 46.535 | 8.1 | | | | | | |
| NH ₄ NO ₃ ^h | 80.04 | 169.6 | 46.535 | 13.0 | 1.69721 | -5.99 | 443-473 | 1.72 | -7.20421 | 1.325343 |
| Li_2SO_4 | 109.95 | 859 | 49.751 | 0.85 | 2.464 | -4.07 | 1133-1487 | 2.21 | -0.18581 | -1.4752 |
| Na_2SO_4 | 142.04 | 884 | 52.607 | 6.34 | 2.628 | -4.83 | 1173-1350 | 2.70 | -5.3990 | |
| Na ₂ SO ₄ ^f | 142.04 | 884 | 52.607 | (12.2) | | | | | | |
| K ₂ SO ₄ | 174.26 | 1069 | 65.511 | 7.02 | 2.4697 | -4.473 | 1348-1411 | 2.66 | -5.8486 | |
| Rb ₂ SO ₄ | 267 | 1050 | 74.167 | 6.75 | 3.442 | -6.65 | 1359-1818 | 3.60 | -7.6371 | |
| Cs_2SO_4 | 361.88 | 1005 | 85.349 | 6.61 | 4.300 | -9.515 | 1309-1803 | 4.24 | -8.7412 | -0.24728 |
| $(NH_4)_2SO_4^{f}$ | 132.14 | i | 74.70 | (14.9) | | | | | | |
| NaHSO ₄ | 120.06 | 315 | 49.407 | 3.55 | 2.6587 | -9.259 | 473-512 | 2.43 | 0 | -9.3637 |
| NaHSO4 ^g | 120.6 | 315 | 49.407 | 11.0 | | | | | | |
| NaHSO4 ^f | 120.6 | 315 | 49.407 | (9.5) | | | | | | |
| KHSO4 | 136.17 | 200 | 58.694 | 2.75 | 2.579 | -8.646 | 489-528 | 2.32 | 0 | -6.9886 |
| NH4HSO4 | 115.11 | 147 | 64.669 | 2.29 | 1.9352 | -5.381 | 453-509 | 1.78 | 0 | -4.4878 |
| NH4HSO4g | 115.11 | 147 | 64.669 | 1.1 | | | | | | |
| NH₄HSO₄ ^f | 115.11 | 147 | 64.669 | (2.9) | | | | | | |

^{*a*}Molar volume of the solid at 25 °C. ^{*b*} The percentage difference at 25 °C between the molar volume of the melt, calculated from eq 2 in this table, from the molar volume of the solid at the same temperature: $100(V^{\circ}(\text{melt}) - V^{\circ}(\text{solid}))/V^{\circ}(\text{solid})$. ^{*c*} Parameters for the following equation for the density of the pure melt, taken from Janz:⁵⁸ $\rho = a + 10^{-4}bT$ (eq 1). ^{*d*} The temperature range of the density data to which eq 1 in this table was fitted. ^{*e*} Parameters for the following equation for the density of the pure melt: $\rho = a + 10^{-4}bT + 10^{-7}cT^2$ (eq 2). This expression was fitted to densities generated using eq 1 (over its range of validity) and constrained to yield at 0 K the density of the pure solid at 25 °C. ^{*f*} The value of ΔV° was calculated by extrapolating the equations of Tang and Munkelwitz^{25,26} to obtain molar volumes of the melt. The maximum solute wt % of the density data are (NH₄)₂SO₄, 80%; Na₂SO₄, 68%; NaNO₃, 98%; NaCl, 45%; NH₄HSO₄, 78%; and NaHSO₄, 95%. The equation of Tang²⁶ for aqueous NH₄NO₃ appears to have been fitted to data for subsaturated solutions only and is not used here. ^{*g*} Molar volumes of the melts are measurements of Zelenyuk et al.^{30 *h*} The equations were fitted to the data of Shirai and Ishibashi.^{103 *i*} Decomposes at 235 °C.¹⁰²

the (hypothetical) melts and each solid at 25 °C are listed in Table 1 and shown in Figure 2. Values for the nitrate salts are broadly comparable with those obtained experimentally by Zelenyuk et al.,³⁰ and there is a similar level of agreement for NH₄HSO₄. For NaHSO₄ both Zelenyuk et al.'s measurement and Tang and Munkelwitz's²⁵ extrapolated equation yield percentage differences of 10–11% compared with about 4.5% for the modified equation based upon the high temperature melt densities. Figure 2 shows that for the salts of the atmospherically important ions Na⁺, K⁺, and NH₄⁺ the percentage differences are mostly 6–11%, with the exception of NH₄HSO₄ for which the percentage differences based upon both measured and estimated melt densities are 2–3%, and NaHSO₄ for which the percentage difference based upon the estimated melt density is

about 3.5% (compared to 9–11% based on the measured melt density, and the value predicted from the equation of Tang and Munkelwitz). Percentage differences for NaCl and Na₂SO₄ based upon the extrapolated equations of Tang²⁶ and Tang and Munkelwitz²⁵ yield markedly larger percentage differences, but we attribute this to the fact that the data on which the equations are based extend only to 68 wt % (Na₂SO₄) and 45 wt % (NaCl).

It is worth noting here that the densities of solid salts also vary with temperature. Data for $(NH_4)_2SO_{4(s)}$ from 0 to 100 °C yield an average slope of about -1.59×10^{-4} g cm $^{-3}$ K $^{-1}.^{59}$ and measurements for four sulfuric acid hydrates below -78 °C yield slopes ranging from -0.965×10^{-4} to -1.33×10^{-4} g cm $^{-3}$ K $^{-1}.^{60}$ This implies that the actual densities of solids at extreme



Figure 2. Percentage differences between the molar volumes of melts of alkali metal and ammonium salts at 25 °C and those of the solids (column ΔV° in Table 1), plotted against the cation in the salt. Key: open circle and dotted line, nitrate salts; dot and solid line, chloride salts; plus and dashed line, sulfate salts; cross and dash-dot line, bisulfate salts. The values joined by the lines are based upon measured (high temperature) molar volumes extrapolated to 25 °C. The individual annotated points were calculated mostly from measured molar volumes of melts at 25 °C or extrapolations of densities for supersaturated aqueous solutions. Key: (T), equations of Tang and Munkelwitz^{25,26} (25 °C); (Z), measurements of Zelenyuk et al.³⁰ (25 °C); (Sh), equation fitted to high temperature melt data of Shirai and Ishibashi.¹⁰³

low temperature will be higher than we have assumed in the calculations described above. For $(NH_4)_2SO_4$ the assumed hypothetical molar volume at 0 K is about 15-30% higher than the probable value for the solid.

We do not claim that the supercooled melt densities obtained using the equations in Table 1 are accurate. However, it is likely that (i) slopes of ρ with respect to *T* from these expressions are satisfactory first-order approximations, and (ii) the equations also provide guidance for establishing melt densities at room temperature for those salts of interest here which have not been studied experimentally (NaCl, Na₂SO₄, NH₄Cl, and (NH₄)₂SO₄). When developing fits of the melt densities of the aqueous salt solutions, including extrapolations into the supersaturated area (III) in Figure 1, we have used the results in Table 1 and Figure 2 to assign hypothetical melt densities at 25 °C, and their variation with temperature.

3.4. Density of Pure Water. In this study densities of pure water as a function of temperature are calculated using eq 16 of Kell⁴⁶ for all temperatures greater than -30 °C. Recently, the temperature dependence of the density of supercooled water has been studied by optical scattering over the temperature range 30 < T < 373 K covering three regions: the stable liquid phase, the metastable supercooled liquid phase, and the amorphous solid phase.⁵³ The experiments were conducted using water confined in hydrophobic nanoporous material to prevent nucleation.

In order to calculate densities of low temperature aqueous solutions from apparent molar volumes—area II of Figure 1— densities of supercooled water are needed. We have combined the experimental results of Mallamace et al.,⁵³ their Figure 2, with values from the equation of Kell⁴⁶ to obtain a best fit representation of the density of water from 373.15 to <100 K. This reproduces values given by the equation of Kell for temperatures



Figure 3. Densities (ρ) of liquid and supercooled water plotted against temperature (*T*). Key: dots, data from Figure 2 of Mallamace et al.;⁵³ line, fitted cubic spline with knots and coefficients listed in Table S1. At temperatures greater than or equal to 243.15 K, the fitted spline reproduces values calculated using eq 16 of Kell.⁴⁶ (see notes to Table S1 for details).

 \geq 243.15 K to within $\pm 1 \times 10^{-7}$ g cm⁻³. The results are shown in Figure 3, and the coefficients and knots of the normalized cubic B-spline fitting equation are listed in Table S1 of the Supporting Information.

4. EQUATIONS

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Several different fitting equations are used in this study to represent apparent molar volumes and density, depending on the aqueous concentration range of interest and also on the chemical system. The basic equations used for most systems are described in this section.

4.1. Pitzer Model. Sodium sulfate is the least soluble of the electrolytes considered in this study, and a Pitzer ion-interaction model was used to represent V^{ϕ} as a function of T below the reference concentration for the aqueous salt. The expression for an electrolyte $M_{v+}X_{v-}$ of any charge type, incorporating the ionic strength dependent virial term of Archer,^{17,61,62} is given below

$$V^{\phi} = V^{\phi \infty} + v_{MX} z_M z_X (A_V/2b) \ln(1+bI^{1/2})$$

2RT $v_M v_X m [\beta^{0V} + \beta^{1V} g(\alpha I^{1/2}) + m v_M z_M (C^{0V} + C^{1V} h(\omega I^{1/2}))]$
(8)

where functions g(x) and h(x) are given by

$$g(x) = 2[1 - (1 + x) \exp(-x)]/x^2$$
(9a)

$$h(x) = (6 - (6 + x(6 + 3x + x^2)) \exp(-x))/x^4$$
(9b)

In eq 8 A_V (cm³ kg^{1/2} mol^{-3/2}) is the molal Debye–Hückel constant for volume, ^{17,63} *b* is equal to 1.2, and *I* is the molal ionic strength which is given by $(\sum_i m_i z_i^2)/2$ where the summation is over the molalities of all ions *i*. In this work we use a value of A_V at a reference pressure of 0.1 MPa from the evaluation of Archer

and Wang.⁶³ The total number of ions in the formula of the electrolyte is $v_{\rm MX\prime}$ and $v_{\rm M}$ and $v_{\rm X}$ are the numbers of cations M and anions X (thus $v_{MX} = v_M + v_X$). The magnitudes of the charges on the ions are $z_{\rm M}$ and $z_{\rm X}$. For a 1:1 electrolyte such as NaCl v_{MX} is equal to 2, and v_{M} , v_{X} , z_{M} , and z_{X} are all equal to unity. The gas constant, R, has a value of 83.1447 cm³ bar⁻¹ K⁻¹ mol⁻¹ (or 82.0575 cm³ atm⁻¹ K⁻¹ mol⁻¹), T (K) is temperature, and $m \pmod{\text{kg}^{-1}}$ is the molality of the electrolyte in solution. The fitted parameters in the model are β^{0V} , β^{1V} , C^{0V} , and C^{1V} . Finally, α and ω are constants for each electrolyte, which are typically assigned values of 1.2 or 1.4 (α), and 2.5 (ω). Each fitted parameter p^{V} is equal to the differential with respect to pressure of the same parameter p in the Pitzer model equations for activity and osmotic coefficients, so that $p^{V} = (\partial p / \partial P)_{T}$. See Pitzer¹⁷ for a full description of the model and Clegg et al.⁶² for the model equations incorporating the additional virial term noted above.

Values of the parameters, which vary with temperature, are determined by fitting eq 8 to data for apparent molar volumes over a range of molalities (typically up to about 6 mol kg⁻¹). In most older applications of the Pitzer equation, without the C^1 term, the C^0 parameter will simply be given as "C". Sometimes the alternative C^{ϕ} is used, which is related to C by $C = C^{\phi}/2(z_M z_X)^{1/2.17}$

4.2. Empirical Equation. Work by Tang^{25,26,34} has shown that densities of aqueous solutions can be represented from pure water to concentrations approaching the pure liquid electrolyte by simple polynomial expressions in the weight percentage or weight fraction of the solute. Our own tests showed that the latter variable was preferable to mole fraction because, for a given concentration, weight fraction is closer to unity than mole fraction (for solutes with molar masses greater than that of water, which is true in most cases here). The result was better fits at the highest concentrations combined with more plausible extrapolations to the melt.

In order to represent V^{ϕ} over the entire concentration range, we have used an equation that combines a mole fraction based Debye—Hückel term with a polynomial in the weight fraction of solute (*wf*)

$$V^{\phi} = V^{\phi \infty} + v_{MX} z_M z_X (A_{V,x}/2\rho) \ln(1+\rho I_x^{1/2}) + w f^{0.5} C_1(T) + w f^{0.75} C_2(T) + w f C_3(T) + w f^{1.5} C_4(T) + w f^2 C_5(T) + w f^{2.5} C_6(T) + w f^3 C_7(T) + w f^{3.5} C_8(T)$$
(10)

where ρ (the equivalent of *b* in eq 8, and not density) is a constant with a value of 13.0, $A_{V,x}$ is the mole fraction Debye–Hückel volume constant and is equal to $A_V(1000/M_w)^{1/2}$ where M_w (18.0152 g) is the molar mass of water. Symbol I_x represents the mole fraction ionic strength of the solution, equal to $(\sum_i x_i z_i^2)/2$ where x_i is the mole fraction of ion *i*

$$x_i = n_i / (\sum_j n_j + n_w) \tag{11}$$

where n_i is the moles of ion *i*, the summation is over all ions *j* (including *i*), and n_w is the number of moles of the solvent. In eq 10 the fitted quantities are $V^{\phi^{\infty}}$ and the coefficients $C_{1-n}(T)$. In cases where the equation is being fitted to data over a range of temperatures, each parameter $C_i(T)$ can be the following function of *T*

$$C_{i}(T) = c_{i,0} + (T - T_{r})(c_{i,1} - T_{r}c_{i,2} + 0.5c_{i,3}T_{r}^{2}) + 0.5(T^{2} - T_{r}^{2})(c_{i,2} - c_{i,3}T_{r}) + (T^{3} - T_{r}^{3})c_{i,3}/6$$
(12)

where the reference temperature T_r is equal to 298.15 K and $c_{i,j}$ are fitted coefficients.

4.3. Equation for the Reference Concentration. The expression used to represent the densities of aqueous solutions at the reference concentration of each solute (ρ^* , corresponding to line a in Figure 1) is a simple polynomial in temperature

$$\rho^* = D_0 + D_1 T + D_2 T^{1.5} + D_3 T^2 + D_4 T^{2.5} + D_5 T^{2.75} + D_6 T^3$$
(13)

where D_{1-6} are the fitted coefficients and ρ^* is in units of g cm⁻³. Generally only one or two of the temperature-dependent terms is required for each electrolyte.

4.4. Concentrated Solutions. Volume properties of these solutions (above the reference concentration) are constrained by the density of the melt at a weight fraction of unity, by the density of the reference concentration, and by measured densities for some of the more soluble salts and those for which densities of supersaturated solutions have been determined. In this work the principal equations used to represent densities as functions of both temperature and concentration are given below.

$$\rho = P_0 + P_1 T^{s(1)} + P_2 T^{s(2)} + P_3 T^{s(3)}$$
(14)

where each parameter P_i is given by

$$P_{i} = p_{i,100} + p_{i,1}v^{t(i,1)} + p_{i,2}v^{t(i,2)} + p_{i,3}v^{t(i,3)} + p_{i,4}v^{t(i,4)} + p_{i,5}v^{t(i,5)} + p_{i,6}v^{t(i,6)}$$
(15a)

and $p_{i,j}$ are fitted coefficients, except for $p_{i,3}$ which is given by

$$p_{i,3} = (p_{i,\text{ref}} - p_{i,100} - p_{i,1}v^{*t(i,1)} - p_{i,2}v^{*t(i,2)} - p_{i,4}v^{*t(i,4)} - p_{i,5}v^{*t(i,5)} - p_{i,6}v^{*t(i,6)})/v^{t(i,3)}$$
(15b)

The quantity *v* in eq 15a is equal to (1 - wf) for the electrolyte of interest, and v^* in eq 15b is $(1 - wf^*)$ where wf^* is the weight fraction of electrolyte at the reference concentration. Coefficients $p_{i,ref}$ and $p_{i,100}$ have the same values as the corresponding terms in the equations for the densities of solutions of the reference concentration and of the melt, respectively. For each coefficient $p_{i,i}$ the multiplier v is raised to the power t(i,j). The form of eqs 14 and 15 ensures that the calculated densities of both the melt and the solution at the reference concentration are the same as those given by equations fitted to data for these two concentrations only. For a few electrolytes (those for which very few data are available for concentrations greater than the reference concentration) simpler equations were used. Both sets of exponents in eq 14 and eq 15 were chosen so that the equations yield selfconsistent, and close to linear extrapolations of densities to very low temperatures.

4.5. Extrapolation to T < 273.15 K. For concentrations greater than the reference concentration, the equations in section 4.4 are used. However, for dilute solutions (area II in Figure 1) densities are calculated from apparent molar volumes extrapolated from values at higher temperatures and the density of pure water. This is done as follows. First, an apparent molar volume for the temperature (T) and molality (m) of interest is predicted using values of V^{ϕ} , $\partial V^{\phi}/\partial T$, and $\partial^2 V^{\phi}/\partial T^2$ for the same concentration at a reference temperature T_r which is greater than 273.15 K

$$V^{\phi}(\text{extr.},m, T) = V^{\phi}(m,T_{r}) + (T-T_{r})(\partial V^{\phi}(m,T_{r})/\partial T) -T_{r}\partial^{2}V^{\phi}(m,T_{r})/\partial T^{2}) + \partial^{2}V^{\phi}(m,T_{r})/\partial T^{2}(T^{2}-T_{r}^{2})/2$$
(16)

Table 2. Sources of Data for Aqueous HCl

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
|----------------|---------------------------|---------------|---------------------------|-----------------------|------|-------------|-----------------------------------|
| 1-30 | wt % | -5 to 80 | ρ | $g m L^{-1}$ (old) | yes | b, c | 2 |
| 100 | wt % | -104 to -83 | $ ho(t, 4^\circ)$ | | no | d | 2 |
| 100 | wt % | -109 to -81 | $ ho(t, 4^\circ)$ | | no | е | 161 |
| 100 | wt % | -87.5 to -100 | ρ | $\rm g~cm^{-3}$ | yes | f | 71 |
| 100 | wt % | -114 to -33.2 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | <i>f,</i> g | 72 |
| 100 | wt % | 0-47.8 | ρ | $g \text{ cm}^{-3}$ | no | h | 74 |
| 0.00348-0.189 | $mol L^{-1}$ | 25 | $\Delta ho(\text{rel.})$ | | yes | i | 162 |
| 0.02426-0.2030 | $mol L^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 163 |
| 0.0402-4.002 | $mol \ L^{-1}$ | 25 | Δho | $\rm g~cm^{-3}$ | yes | j | 164 |
| 0.608-8.447 | $mol kg^{-1}$ | 25 | ρ | $\rm g~cm^{-3}$ | no | | 126 |
| 0.580-10.744 | ${ m mol}~{ m L}^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | k | 85 |
| 0.1409-1.407 | ${ m mol}~{ m L}^{-1}$ | 25 | $\rho(t,t)$ | | no | | 165 |
| 0.125-12.186 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 83 |
| 0.582-16.37 | $mol kg^{-1}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 84 |
| 2.2218-0.5542 | $mol kg^{-1}$ | 25 | ρ | see note | no | 1 | 166 |
| 6.94-31.61 | wt % | 25 | $\rho(t, 4^{\circ})$ | | yes | | 78 |
| 1.52-39.15 | wt % | 15 | $\rho(t, 4^\circ)$ | | yes | | 79 |
| 1.356-36 | wt % | 19.5 | $ ho(t, 4^\circ)$ | | yes | | 80 |
| 15.63-100 | wt % | 20 | $ ho(t, 20^\circ)$ | | yes | | 77 |
| 0.002-0.1 | ${\rm mol}~{\rm dm}^{-3}$ | 35 | ρ | $\rm g~cm^{-3}$ | no | | 167 |
| 0.0927-1.276 | $mol kg^{-1}$ | 5-45 | Δho | $\rm g~cm^{-3}$ | yes | | 65 |
| 5.129-16.071 | $mol kg^{-1}$ | 0-80 | V^{ϕ} | $\rm cm^3~mol^{-1}$ | yes | с | 82 |
| 0.0049-1.0337 | $mol kg^{-1}$ | 0-50 | V^{ϕ} | $\rm cm^3 mol^{-1}$ | yes | | 68 |
| 1.2031-2.9574 | $mol kg^{-1}$ | 25-75 | ρ | $g \text{ cm}^{-3}$ | yes | | 75 |
| 0.0224-0.39197 | $mol kg^{-1}$ | 10-40 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 76 |
| 0.1013-6.017 | $mol kg^{-1}$ | 25-250 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | т | 12 |
| 23.3-27.6 | wt % | -73 to 20 | ρ | $g mL^{-1}$ (old) | yes | п | 9 |
| 0.01992-0.1428 | $mol L^{-1}$ | 12.5-42.5 | $\rho(t,t)$ | | no | | 168 |
| 2.43-12.77 | $mol kg^{-1}$ | 0-100 | V (rel.) | | yes | | 81 |
| 3.65-31.61 | wt % | -6 to 26 | $ ho(t, 4^\circ)$ | | no | 0 | 78 |
| 0-14.52 | wt % | -28.84 to 0 | $\rho(t, 4^{\circ})$ | | no | 0 | 44 (Roloff, 1895) |
| 7.5-14.6 | wt % | -38 to -1 | V (rel.) | | no | 0 | 44 (Tamman and Schwarzkopf, 1928) |
| 61.65-67.65 | wt % | -20 to 50 | $\rho(t, 4^\circ)$ | | no | 0 | 44 (Rupert, 1909) |

 ${}^{a} \rho(t,u)$ is the density of the solution at t °C relative to that at u °C, $\Delta \rho$ is a density difference (usually relative to that of pure water at the same temperature), $\Delta \rho$ (rel.) is the density difference (from pure water) divided by the density of pure water, and V(rel.) is the volume of the solution relative to that at a fixed temperature. b Values are listed to 38 wt % at 20 °C. c See text for explanation of how the data were adjusted before fitting. d Other original data were used, see text. e Original data upon which the International Critical Tables equation is based. f See text for an explanation of how these low temperature data were used. g The apparent molar volume is for the saturation vapor pressure of the liquid, which varies from 13.8 to 964.1 kPa. h The data are for pressures up to 80.8 atm, and units of g cm⁻³ assumed. i The tabulated quantity is $10^{7}(\rho - \rho_{w})/\rho_{W}$ (apparent molar volumes in mL (old) mol⁻¹ are also given). i The tabulated quantity is $1000(\rho - \rho_{w})$. k Data attributed to Hedestrand. l These data were inadvertently omitted from fitting, and it is unclear whether the unit of density is g mL⁻¹ (old) or g cm⁻³. m Measurements are at high pressure (10–28 MPa) and were not used. n See text regarding an apparent error in one of the concentrations. o Used for comparisons only.

where $V^{\phi}(\text{extr., }m, T)$ is the extrapolated apparent molar volume. The reference temperature that is used for each solute is generally equal to or greater than 298.15 K, because the differentials of V^{ϕ} with respect to T that are obtained using the equations in sections 4.1 and 4.2 are likely to be less reliable at temperatures close to the lower limit of the fit at 273.15 K. Apparent molar volumes extrapolated using eq 16 (and eq 10 for V^{ϕ}) could be used to obtain the solution density, but there are two further factors to consider: first, values from eq 16 are unlikely to agree exactly at 273.15 K with V^{ϕ} calculated using the directly fitted equation (eq 10). Second, for the molality equal to the reference concentration, the calculated solution density must be equal to the value given by eq 13 for all T below 273.15 K.

In order to obtain continuity in V^{ϕ} between directly calculated values at 273.15 K and values extrapolated from eq 16, we first calculate a function Y(m) for molalities from zero to the molality of the reference concentration, m^*

$$Y(m) = (V^{\phi}(m, 273.15 \text{ K}) - V^{\phi}(\text{extr.}, m, 273.15 \text{ K})) / (V^{\phi}(m^*, 273.15 \text{ K}) - V^{\phi}(\text{extr.}, m^*, 273.15 \text{ K}))$$
(17)

where apparent molar volumes for the reference molality m^* in the denominator are obtained using either the fitted model for the low concentration region (the equations in sections 4.1 and 4.2) or eq 13 for ρ^* . Values of Y(m) for each electrolyte are represented by the fitted equation

$$Y(m) = E_1 + E_2(m/m^*) + E_3(m/m^*)^{1.5} + E_4(m/m^*)^2 + E_5(m/m^*)^{0.5} + E_6(m/m^*)^{2.5} + E_7(m/m^*)^3 + E_8(m/m^*)^{3.5} + E_9(m/m^*)^4$$
(18)

Values of Y(m) have been determined for all solutes in this study for which densities below 0 °C are calculated and the fitted coefficients $E_{1.9}$ are tabulated. In the case where eq 13 is used to calculate values for m^* the value of $Y(m^*)$ will not be exactly equal to unity, due to differences between the fitted and extrapolated V^{ϕ} obtained using eq 13 and those used to represent V^{ϕ} in the numerator of eq 17. We therefore normalize Y(m) by dividing by the value of $Y(m^*)$ obtained using eq 17, so that $Y_N(m) = Y(m)/Y(m^*)$.

Next, it is assumed that the values of $Y_N(m)$ are invariant with temperature and we write an equation for estimated apparent molar volumes of the solute for $T \le 273.15$ K and $0 \le m \le m^*$ that meets the requirement for agreement with eq 13 for the reference concentration

$$V^{\phi}(m, T) = V^{\phi}(\text{extr., } m, T) + Y_{N}(m)(V^{\phi}(\text{extr., } m^{*}, T, \rho^{*} \text{ eq})$$

$$V^{\phi}(\text{extr.}, m^*, T)) \tag{19}$$

where $V^{\phi}(\text{extr.}, m^*, T, \rho^* \text{ eq})$ is calculated using eq 16 but with apparent molar volumes and their differentials obtained from eq 13 for ρ^* , and the other apparent molar volumes are obtained using the fitted models for the low concentration region.

5. SOURCES OF DATA

Densities of common electrolyte solutions have been measured for over 150 years. Many early data are tabulated by Timmermans⁴⁴ (up to about 1959), and sources of measurements are also listed in the International Critical Tables.² These tables, compiled over the period up to 1926-1933, contain densities as functions of weight percent and temperature that are the result of a critical evaluation of the data available at the time. The sources of data given particular weight in the evaluation for each solute are noted. These tabulated densities are still widely used and are reproduced elsewhere.³⁶ Values of densities from the International Critical Tables are used in this study for most of the solutes as representing measurements up to about 1930. In some cases, where values disagree with modern measurements, the original data on which the International Critical Tables values are based have been re-evaluated, or adjustments made. Details are given in the individual sections for each solute.

Densities of aqueous solutions listed in the more recent compilations of Zaytsev⁴ and Sohnel and Novotny³ were obtained by fitting standard equations to available measurements and are not the product of critical evaluations for each solute. We have found that the densities in these compilations, particularly that of Zaytsev,⁴ do not represent available density measurements within experimental uncertainty. They are not further considered.

The literature was searched for measurements of densities and apparent molar volumes from about 1920 onward, mainly using *Chemical Abstracts*. We have attempted to be comprehensive. Many studies are listed in the compilation of Lobo⁶⁴ and also in recent evaluations of solution densities including those of Krumgalz et al.¹⁵ and Laliberté and Cooper.¹⁶ Millero and co-workers have carried out extensive measurements of densities of aqueous solutions containing the major components of sea salt.^{57,65–69} Data from numerous older studies are tabulated in the compilations of Timmermans,⁴⁴ and some have been used in this work. They are



Figure 4. Measured and fitted molar volumes (V°) of pure liquid HCl as a function of temperature (*T*). Key: dot, Shapiro and Sadoway;⁷¹ circle, da Ponte and Staveley;⁷² star, data of Ansdell⁷⁴ at high pressures adjusted to hypothetical values at 1 atm pressure; line, eq 20. The vertical lines indicate the magnitude of the increase in the molar volume needed to account for the change in pressure (data of Ansdell).

referred to by author and year (and Timmermans is cited as the reference) in the tables of data sources.

Measured densities are presented in a variety of units, and also as specific gravities (relative to water at the same temperature or at a reference temperature), or as $\Delta \rho$ relative to the density of water at the same temperature. It is not always clear what form of specific gravity is intended. Unless the authors state otherwise, specific gravity is taken to mean $\rho(t)/\rho(\text{water, 4 °C})$ (denoted $\rho(t, 4^{\circ})$) where $\rho(t)$ is the density of the aqueous solution at t° C. Densities tabulated in the International Critical Tables are given in units of $g m L^{-1}$. The 12th General Conference on Weights and Measures (1964) defined the liter to be the same as the cubic decimeter (1000 cm³). Previously, from 1901, the liter had been defined as the volume occupied by 1 kg of water at the temperature of its maximum density (3.98 °C) at 1 atm pressure. This implies the following relationship between the pre-1964 mL and the cubic centimeter:⁷⁰ 1.0 mL (old) = 1.000028 cm³. All densities given in g mL⁻¹ in studies before 1964 have been converted to g cm⁻³ using this equation unless otherwise stated. Densities given in g mL $^{-1}$ (old) are equivalent to specific gravities $\rho(t, 4^{\circ})$. While the effect of the conversion on solution concentrations can be considered negligible (and we have not adjusted any tabulated concentrations), the effect on apparent molar volumes is significant for very low molalities. We note that prior to 1901 the liter was effectively the same as it is currently defined.

All sources of data used in this study, their concentration and temperature ranges and the units used, are listed in tables for each solute in the sections below.

6. RESULTS

The evaluations of the data for each solute are described in this section, together with the results of the fits for each composition region in Figure 1. Calculated densities over the entire composition range and for temperatures up to 50 $^{\circ}$ C (including predictions for supercooled and supersaturated solutions) are also shown.



Figure 5. Measured and fitted apparent molar volumes and densities of aqueous HCl at 25 °C. (a) Apparent molar volumes of HCl (V^{ϕ}) plotted against HCl concentration $(\sqrt{\text{wt }}\%)$. Key: solid triangle, Herrington et al.;⁷⁵ cross, Hershey et al.;⁶⁵ circle, Millero et al.;⁶⁸ plus, Rizzo et al.;⁸³ square, Redlich and Bigeleisen;¹⁶² inverted solid triangle, Dunn;¹⁶³ star, Wirth;¹⁶⁴ solid square, Allred and Woolley;⁷⁶ triangle, Torok and Berecz;⁸⁴ solid square, eq 20 for liquid HCl; line, the fitted model. The inset shows the difference $(\Delta V^{\phi}, \text{observed } - \text{calculated})$ between apparent molar volumes calculated using the fitted model, and values listed in the International Critical Tables. (b) The difference between measured and fitted apparent molar volumes $(\Delta V^{\phi}, \text{observed } - \text{calculated})$, plotted against HCl concentration $(\sqrt{\text{wt }}\%)$. Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in a measured density. (c) Measured and calculated densities (ρ) of aqueous HCl, plotted against HCl concentration (wt %). Key: the symbols have the same meanings as in (a); line, the fitted model.

Data were first compared visually, as apparent molar volumes. Measurements at very low concentrations were also checked to determine that they approached the Debye—Hückel limiting slope. Data with a high degree of scatter, or which showed large deviations from measurements from other sources, were rejected. Other data that showed more scatter than the most precise measurements, or for which small systematic deviations from the general trend were apparent, were given reduced weights. For most solutes, the data at 25 °C were fitted first, to serve as a fixed reference in the temperature-dependent fits and to establish $V^{\phi\infty}(25 \text{ °C})$. The variation of $V^{\phi\infty}$ with *T* was then determined and the fit of apparent molar volumes extended to other temperatures. Finally, equations for extrapolations to low temperature were obtained using densities for region III of Figure 1 and based upon apparent molar volumes in region II.

The coefficients of many of the fitted equations are listed in tables in the Supporting Information to this work (identified by



Figure 6. Densities of 23.3 wt % HCl (the reference concentration). (a) Measured and fitted densities (ρ) plotted against temperature (*T*). Key: circle, International Critical Tables (adjusted); dot, Garrett and Woodruff;⁹ plus, Akerlof and Teare⁸² (adjusted); triangle, Lunge and Marchlewski;⁷⁹ square, Haase et al.;⁸⁷ solid triangle, model (eq 10); line, the fitted equation. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated). Key: the symbols have the same meanings as in (a).

the prefix S in each table number). Note that in order to avoid the inadvertent introduction of errors, most coefficients are given to more significant figures than are necessary. In order to assess uncertainties, readers should refer to the figures in which fitted and measured apparent molar volumes and densities are compared and to the table in which statistics for the principal solutes are listed.

Volume data are sometimes fitted as specific volumes of the solution rather than apparent molar volumes of the solute,⁵

because small errors in measured densities of dilute solutions result in very large errors in apparent molar volume (see eq 1a). We have fitted apparent molar volumes, but weight to zero those values at low concentrations that show large deviations from other data and/or the expected limiting law extrapolation to infinite dilution. For some solutes the weights given to data at the lowest concentrations were also reduced. In the figures that compare measured and fitted apparent molar volumes and densities only data that were given nonzero weights are shown.

6.1. HCl. Sources of densities are listed in Table 2. There are data at low temperatures for three concentrations of aqueous acid⁹ and for pure liquid HCl.^{71,72} The critical point of HCl is at only about 50 °C, and the acid has a normal boiling point of 188.18 K.⁷² Because of this, densities of the aqueous solutions have only been determined experimentally to about 16 mol kg⁻¹, for which the equilibrium partial pressure of the acid is about 0.2 atm.⁷³ Ansdell⁷⁴ has measured densities of the liquid acid from 0 to 47.8 °C, but at pressures of about 28–81 atm, and Rupert⁴⁴ has measured densities of 61.65 wt % to 67.65 wt % acid from -20 to 50 °C at unspecified high pressures. With the exception of the studies of Herrington,⁷⁵ Allred and Woolley,⁷⁶ and Millero and co-workers,^{65,68} most of the modern measurements of densities are for single temperatures, particularly 25 °C.

Table 2 includes four of the studies⁷⁷⁻⁸⁰ listed as sources for the evaluated densities in the International Critical Tables and given "some weight", and also the study of Kremers⁸¹ which is one of the three listed as being given "more weight". These sources are examined in this work because the evaluated densities in the International Critical Tables differ systematically from the comprehensive later work by Akerlof and Teare.⁸²

6.1.1. Aqueous Solutions at 25 °C. Densities and apparent molar volumes at this temperature have been studied by at least 20 groups following the International Critical Tables evaluation. The three most precise studies are those of Rizzo et al.,⁸³ Torok and Berecz,⁸⁴ and Geffken.⁸⁵ The data are compared in Figure 4 of Rizzo et al.⁸³ Densities measured by Torok and Berecz⁸⁴ are higher than those of Rizzo et al. above 3 mol dm^{-3} by up to about $0.00025 \text{ g cm}^{-3}$ (at 11 mol dm⁻³), while those from Geffken's⁸⁵ much earlier study-which are also shown in Figure 4 of Rizzo et al.-are lower at all concentrations (by up to a maximum of about 0.0004 g cm⁻³ at 11 mol dm⁻³). We have accepted the results of Rizzo et al. and of Torok and Berecz, and rejected those of Geffken. A comparison of the densities listed in the International Critical Tables with values from Rizzo et al. shows that the former yield apparent molar volumes that are lower, by as much as $0.1 \text{ cm}^3 \text{ mol}^{-1}$, at molalities above 4 mol kg⁻¹

Millero et al.⁶⁸ list 10 estimates of $V^{\phi \circ \circ}$ at 25 °C (see their Table 4), ranging from 17.4 to 18.2 cm⁻³ mol⁻¹, and their own fitted value is 17.82 cm⁻³ mol⁻¹. Several of the other studies listed in Table 2 provide measurements of dilute solutions, and in this work we have redetermined $V^{\phi \circ \circ}$ as a function of temperature.

Apparent molar volumes of aqueous HCl above the upper concentration limit of available data are needed in order to make estimates of densities of mixtures of which HCl is a component. This is because predictive models typically require densities of pure aqueous solutions at the total ionic strength, or total mass concentration, of the mixture.^{35,86} Shapiro and Sadoway⁷¹ have measured the densities of pure liquid HCl, at atmospheric pressure, from 163.15 to 185.65 K. Measurements have also been made by da Ponte et al.⁷² from 188.29 to 243.49 K at higher pressures and by Ansdell⁷⁴ from 0 to 47.8 °C at pressures from



Figure 7. Comparison of apparent molar volumes (V^{ϕ}) of HCl from different sources, plotted against the square root of HCl molality (\sqrt{m}): (a) 0 °C; (b) 19.5 °C; (c) 40 °C; (d) 60 °C. Key: circles, International Critical Tables; plus, Akerlof and Teare;⁸² solid square, calculated from the densities of Barnes and Scott⁸⁰ and relative volumes determined by Kremers.⁸¹

about 28 to 80.8 atm. At these high temperatures (above about 0 °C) the molar volume of the acid rises steeply with temperature as the critical point is reached. This is quite unlike the behavior of the acids H_2SO_4 and HNO_3 (which are liquids at 25 °C), and for the purposes of this study—to be able to estimate the densities of very concentrated mixtures in which HCl is a component—we have assumed a simple linear relationship of the density of the liquid with temperature. This was obtained by fitting the data of Shapiro:⁷¹

$$\rho(100\%) = 1.649687 - 0.0024687T \tag{20}$$

where T(K) is temperature. Equation 20 is assumed to apply at all temperatures and is compared in Figure 4 with the data of Shapiro and with measurements at higher temperatures (and pressures).

Next, measured densities at 25 °C over the entire concentration range (including the pure liquid, from eq 20) were fitted as apparent molar volumes using eq 10. The results are shown in Figure 5, and the coefficients $c_{i,0}$ for the parameters $C_i(T)$ in eq 12 are listed in Table S3 in the Supporting Information. The fitted value of $V^{\phi\infty}$ (HCl) is 17.84 cm³ mol⁻¹, which differs by only 0.02 cm³ mol⁻¹ from that obtained by Millero et al.⁶⁸ (a difference that is similar in magnitude to the scatter in the fitted data shown in Figure 5c). Our equation yields apparent molar volumes that differ from the equation of Rizzo et al.⁸³ by an average of only ±0.014 cm³ mol⁻¹ up to 16.5 mol kg⁻¹. Comparisons of the fitted model with the available data, shown in the inset to Figure 5a, show clearly the deviation of the International Critical Tables densities from recent measurements (and from the model).



Figure 8. Apparent molar volumes (V^{ϕ}) of HCl from 0 to 80 °C, plotted against the square root of HCl molality (\sqrt{m}) . Key: circles, values from the International Critical Tables adjusted by a fixed ΔV^{ϕ} (at all *T*) to agree with our best fit equation at 25 °C; plus, values from Akerlof and Teare⁸² (similarly adjusted). The temperature (°C) of each set of data is marked on the plot.



Figure 9. Apparent molar volumes of HCl at infinite dilution ($V^{\phi\infty}$), as a function of temperature (*t*). Key: diamond, this work; solid square, Allred and Woolley;⁷⁶ plus, Hershey et al.⁶⁵ (refitted); circle, Millero et al.⁶⁸ (refitted); triangle, Herrington et al.;⁷⁵ square, Barnes and Scott⁸⁰ (refitted); star, Lunge and Marchlewski⁷⁹ (refitted); dot, International Critical Tables (refitted); solid line, this work; dashed line, equation of Hershey et al.;⁶⁵ dotted line, equation of Sharygin and Wood.¹² Values from those sources noted as refitted, above, were determined in this work from the original density or apparent molar volume data.

6.1.2. The Reference Concentration. A concentration of 23.3 wt % (8.332 mol kg⁻¹) was chosen because measurements



Figure 10. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of HCl from 0 to 60 °C, plotted against the square root of HCl molality (\sqrt{m}). All apparent molar volumes are offset by an amount ($t/t^{\circ} - 25$)/2.5 cm³ mol⁻¹, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure at 10 °C intervals, and unmarked data are for temperatures half way between (i.e., at 5, 15, 35 °C, etc.) unless otherwise indicated. Key: dot, International Critical Tables (adjusted); cross, Hershey et al.;⁶⁵ plus, Akerlof and Teare⁸² (adjusted); star, Millero et al.;⁶⁸ solid triangle, Herrington et al.;⁷⁵ circle, Allred and Woolley;⁷⁶ square, Garrett and Woodruff;⁹ triangle, Lunge and Marchlewski;⁷⁹ diamond, Barnes and Scott;⁸⁰ inverted triangle, Schwers;⁷⁷ lines, the fitted model. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated). Key: the symbols have the same meanings as in (a), and the dotted lines show the effect of a ±0.00005 g cm⁻³ error in the measured density (at 25 °C).

have been made at this concentration by Garrett and Woodruff⁹ to 200 K. Values of densities interpolated from the International

Table 3. Comparison of Densities of Aqueous HCl^a

| | $\Delta ho \ (10^{-3} { m g \ cm^{-3}})$ | | | | | | | | | |
|------|--|----------------------|---------|---------|--|--|--|--|--|--|
| wt % | 0 °C | 20 °C | 40 °C | 60 °C | | | | | | |
| | | Akerlof and Tea | re | | | | | | | |
| 2 | -0.0439 | -0.323 | -0.127 | -0.0959 | | | | | | |
| 4 | -0.0969 | -0.216 | -0.164 | -0.240 | | | | | | |
| 6 | -0.108 | -0.202 | -0.205 | -0.361 | | | | | | |
| 8 | -0.0688 | -0.202 | -0.248 | -0.458 | | | | | | |
| 12 | 0.131 | -0.211 | -0.368 | -0.636 | | | | | | |
| 16 | 0.411 | -0.318 | -0.572 | -0.803 | | | | | | |
| 20 | 0.539 | -0.589 | -0.862 | -1.02 | | | | | | |
| 24 | 0.319 | -1.01 | -1.19 | -1.29 | | | | | | |
| 28 | -0.443 | -1.59 | -1.47 | -1.60 | | | | | | |
| 32 | -1.88 | -2.24 | -1.53 | -1.82 | | | | | | |
| 36 | -3.57 | -8.29 | -0.631 | -1.29 | | | | | | |
| | In | ternational Critical | Tables | | | | | | | |
| 2 | -0.0222 | 0.0486 | -0.0051 | 0.0063 | | | | | | |
| 4 | 0.0146 | 0.146 | 0.188 | 0.0316 | | | | | | |
| 6 | 0.0027 | 0.159 | 0.206 | 0.0205 | | | | | | |
| 8 | -0.168 | 0.0585 | 0.114 | -0.0562 | | | | | | |
| 12 | -0.149 | 0.149 | 0.233 | 0.135 | | | | | | |
| 16 | 0.211 | 0.422 | 0.478 | 0.427 | | | | | | |
| 20 | 0.628 | 0.630 | 0.658 | 0.691 | | | | | | |
| 24 | 0.837 | 0.887 | 0.847 | 0.956 | | | | | | |
| 28 | 0.324 | 0.774 | 0.898 | 0.823 | | | | | | |
| 32 | | 0.260 | | | | | | | | |
| 36 | | -0.486 | | | | | | | | |

^{*a*} Values of $\Delta \rho$ are equal to $10^3(\rho_i - \rho)$ where ρ_i are densities either from Table II of Akerlof and Teare⁸² or from the International Critical Tables (converted to units of g cm⁻³), and ρ are densities calculated using the model developed in this work.

Critical Tables and the work of Akerlof and Teare⁸² were added (after their adjustment, as described in the next section), and also results of studies by Lunge,⁷⁹ Barnes and Scott,⁸⁰ and Haase et al.⁸⁷ The densities were fitted as a linear function of temperature using eq 13, and the coefficients are listed in Table S2 in the Supporting Information. The data and fitted equation are compared in Figure 6.

6.1.3. Aqueous Solutions above 0 °C. The densities in the International Critical Tables and the measurements of Akerlof and Teare⁸² are the two most comprehensive data sets. However, they disagree by a consistent amount (in terms of apparent molar volume) from about 5 to 12 mol kg⁻¹ at all temperatures. As noted earlier, the principal data used in the International Critical Tables evaluation are relative volumes (referenced to 19.5 °C) determined by Kremers⁸¹ for 2.43-12.77 mol kg⁻¹ HCl from 0 to 100 °C. Also cited is the work of Barnes and Scott⁸⁰ who measured densities of 1.356-36 wt % HCl at 19.5 °C. Figure 7 shows apparent molar volumes at four temperatures calculated from the data of Barnes and Scott⁸⁰ and of Kremers,⁸¹ and from interpolated densities from the International Critical Tables and the work of Akerlof and Teare.⁸² It is evident from the agreement between the International Critical Tables values and those based upon the measurements of Barnes and Scott that the latter have been used as a reference to calculate densities at other temperatures using the measurements of Kremers. It is also clear that the



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Figure 11. (a) Measured and fitted densities (ρ) of aqueous HCl at high concentrations, plotted against temperature (t). Key: dot, International Critical Tables (adjusted); plus, Akerlof and Teare⁸² (adjusted); square, Garrett and Woodruff;⁹ triangle, Lunge and Marchlewski;⁷⁹ diamond, the extrapolations of Haase et al.⁸⁷ below 0 °C; lines, the fitted model. For each set of data the wt % concentration of HCl is noted on the plot. (b) The difference between measured and fitted densities ($\Delta \rho$, observed calculated). Key: the symbols have the same meanings as in (a).

differences between the calculated molar volumes and those from Akerlof and Teare are similar at all temperatures.

These results suggest that the apparent molar volumes from the International Critical Tables can be corrected at all temperatures by the addition of a small ΔV^{ϕ} , equivalent to the difference between the value from our best fit equation at 25 °C and that from the International Critical Tables evaluation at the same concentration (and also at 25 $^{\circ}$ C). In the case of the Akerlof and Teare measurements, a small systematic error seems the most likely explanation for the consistency of the offset from the International Critical Tables values at all temperatures (Figure 7) and from our best fit equation at 25 $^{\circ}$ C (Figure 6). Accordingly, both data sets have been corrected for use in this study in the manner noted above. They are compared in Figure 8 for temperatures from 0 to 80 $^{\circ}$ C and agree very well in view of



Figure 12. Calculated densities of aqueous HCl from 1.0 to 10.0 wt % concentration (marked on the plot), as a function of temperature (t). The intermediate dotted lines are densities at 2, 4, 6, and 8 wt % of acid. Key: dot, temperature of maximum density of 0–10 wt % acid listed in the International Critical Tables; dash-dot line, temperatures of maximum density obtained in this work.

the fact that, apart from being referenced to the same best fit apparent molar volumes at 25 $^{\circ}$ C, the two sets of data are independent of one another.

Apparent molar volumes of dilute aqueous HCl have been measured by Millero et al.⁶⁸ at 0, 25, and 50 °C and by Hershey et al.⁶⁵ at five intermediate temperatures (also including 25 °C). Values of the apparent molar volume at infinite dilution $(V^{\phi\infty})$ were evaluated individually at each temperature, combined with results at high temperatures obtained by Helgeson and Kirkham,⁸⁸ and then fitted to yield an equation for $V^{\phi\infty}$ from 0 to 200 °C.⁶⁵ Note that Hershey et al.⁶⁵ combined their data with those of Akerlof and Teare⁸² (without correction or adjustment) in order to fit apparent molar volumes and relative densities as functions of molality and temperature. It seems unlikely that this affected their evaluation of $V^{\phi\infty}$, which appears to have been done separately, because their Figure 1 of $\hat{V}^{\hat{\phi}^{\infty}}$ against temperature shows only data points from their own measurements and from the work of Helgeson and Kirkham.⁸⁸ Later, Sharygin and Wood¹² measured volumetric and thermal properties of aqueous HCl to high temperature and pressure. They combined their results with measurements for normal temperatures and pressures from 11 other sources and fitted a Pitzer model to the data. This model includes an expression for $V^{\phi\infty}$ at 0.1 MPa for temperatures below 100 °C.

In Figure 9 $V^{\phi\infty}$ from the equations of Hershey et al.⁶⁵ and Sharygin and Wood¹² are compared with values obtained here by fitting to measurements (from various sources) at individual temperatures. The equations agree closely below 25 °C, and the measured $V^{\phi\infty}$ plotted on the graph suggest that above about 40 °C the best values of $V^{\phi\infty}$ may lie in the region between the predictions of the two equations. Accordingly we have refitted $V^{\phi\infty}$ calculated from the two equations. A weight of unity was assigned to the results of Hershey et al. below 38 °C (and zero to those of Sharygin and Wood), and at higher temperatures both sets of values were given equal weight. Our estimate of $V^{\phi\infty}$ at 25 °C (17.84 cm³ mol⁻¹) was included in the data set and given a



Figure 13. Measured and calculated densities (ρ) of aqueous HCl at low temperatures. (a) Densities for fixed concentrations (in wt %, indicated on the plot) as a function of temperature (t). Key: dot, Schuncke;⁴⁴ plus, Tamman and Schwarzkopf;⁴⁴ lines, the model developed in this study. For clarity, not all of the data of Schuncke are shown. (b) Densities along the freezing curve with respect to ice, as a function of HCl concentration (wt%). Key: solid square, Roloff;⁴⁴ line, the model developed in this study. Temperatures (in °C) of individual measurements are shown on the plot.



Figure 14. Calculated densities of 0 to 100 wt % HCl as a function of temperature (t). (a) From 0 to 60 wt %. Dotted lines show calculated densities at intermediate wt % of HCl (10, 30, and 50 wt %). (b) From 60 to 100 wt %. Dotted lines show calculated densities at intermediate wt % of HCl.

weight of 5.0. The fitted equation, which is plotted in Figure 9, is given below

$$V^{\phi\infty}(\text{HCl}) = 16.3404 + 0.0917139t + 0.0101881t^{1.5}$$

-0.00550034t² + 0.000531252t^{2.5} - (0.183640 × 10⁻⁴)t³
(21)

where t (°C) is temperature.

Next, apparent molar volumes from sources listed in Table 2, including the corrected values from the International Critical Tables and the work of Akerlof and Teare,⁸² were fitted as

functions of temperature and concentration from 0 to 60 °C and from 0 to 38 wt % using eq 10. Apparent molar volumes from eq 13 for the reference concentration were included in the fit, and values of the coefficients $c_{i,j}$ for the parameters $C_i(T)$ are listed in Table S3. Calculated values of V^{ϕ} are compared with the data in Figure 10. Densities from the International Critical Tables and Akerlof and Teare⁸² are compared with the fitted equation in Table 3. Note that the equations of both Hershey et al.⁶⁵ and Sharygin and Wood¹² were fitted to the uncorrected V^{ϕ} of Akerlof and Teare.⁸²

We now address the estimation of densities and apparent molar volumes of very concentrated aqueous solutions up to and including the hypothetical liquid HCl. Only a simple approach seems justified given the limited data and the fact that liquid HCl does not exist at atmospheric pressure above 188 K. An examination of the data for high concentrations (30–38 wt %), the desirability of continuity in the first and second differentials of density with respect to temperature, and the need to constrain $\partial \rho / \partial T$ for the liquid to eq 20, suggested an equation of the form

$$\rho(T) = \rho(T_{\rm r}) + (T - T_{\rm r})(q_1 - q_2 T_{\rm r}) + q_2(T^2 - T_{\rm r}^2)/2 \quad (22)$$

where

$$q_1 = r_1 + r_2 \, w f^{r_3} \tag{23a}$$

$$q_2 = r_4 + r_5\sqrt{wf} + r_6wf \tag{23b}$$

where r_1 to r_6 are fitted coefficients, *wf* is the acid weight fraction in solution, *T* (K) is temperature, and T_r is equal to 298.15 K. Values of the coefficients were determined by fitting to densities measured by Garrett and Woodruff⁹ (all temperatures) and the adjusted densities from the International Critical Tables and the study of Akerlof and Teare⁸² (0–80 °C) for concentrations greater than 22 wt %. Equation 22, although equivalent to eq 20 for the pure liquid, is not constrained to agree exactly with eq 13 for the reference concentration in order to represent better the other available data. At the reference concentration there is agreement in the predicted density to within 3.5 × 10⁻⁴ g cm⁻³ from -50 to 50 °C. The results of the fit are shown in Figure 11, and the fitted coefficients are listed in Table S4 in the Supporting Information.

6.1.4. Aqueous Solutions below 0 °C. Equation 22 above can be used to estimate densities of aqueous solutions for concentrations >23.3 wt % at all temperatures. For more dilute solutions we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to T are calculated from eq 16 and eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. Fitted coefficients E_i in eq 18 for Y(m) are listed in Table S5 in the Supporting Information. Figure 12 shows calculated densities of 1-10 wt % HCl to -30 °C, together with temperatures of maximum density listed in the International Critical Tables. There is good agreement up to 5 wt % HCl, but a consistent negative deviation at higher concentrations for which the reason is unclear. However, we note that comparisons of temperatures of maximum density for all solutes (see section 8) show generally good agreement between predictions and measurements.

In Figure 13a we compare model predictions with low temperature densities from two sources. The data of Schunke⁷⁸ at the two highest concentrations do not agree with the model (or other data), but there is otherwise reasonable agreement.

| Table 4. | Sources | of Data | for | Aqueous | NaCl |
|----------|---------|---------|-----|---------|------|
|----------|---------|---------|-----|---------|------|

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
|---------------|---------------|--------------|-----------------------|-----------------------|------|-------------|-----------|
| 1-26 | wt % | 0-100 | ρ | $g m L^{-1}$ (old) | no | Ь | 2 |
| 0-45 | wt % | 25 | ρ | $\rm g~cm^{-3}$ | yes | с | 26 |
| 6.2-11.0 | $mol kg^{-1}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | d | 91 |
| 0-6.0 | $mol kg^{-1}$ | -23 to 327 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | е | 61 |
| 0-5.5 | $mol kg^{-1}$ | 0-300 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | <i>f,</i> g | 90 |
| 0.371-5.997 | $mol kg^{-1}$ | 5-45 | Δho | $\rm g~cm^{-3}$ | no | h | 7 |
| 0.00858-6.014 | $mol kg^{-1}$ | -20 to 20 | ρ | $\rm g~cm^{-3}$ | no | i | 8 |

 ${}^{a}\Delta\rho$ is a density difference relative to that of pure water at the same temperature ($\rho - \rho_{w}$). b The International Critical Tables evaluation also includes a few densities for <1 wt % concentration and for temperatures greater than 100 °C. c Tang²⁶ presents a fitted equation to densities that include measurements for solutions supersaturated with respect to the salt. In this work densities for concentrations from 27 to 43 wt % were used in the fit to data at 25 °C. d Estimated by Teng et al. from data for mixtures with four other solutes. ${}^{e}A$ critical evaluation of the available data, for molalities up to saturation and for pressures up to 100 MPa. ${}^{f}A$ critical evaluation of the available data, for molalities up to saturation and pressures to 300 bar. g This study combines new measurements with earlier data and presents fitted models of relative density and apparent molar volume from 0 to 6 mol kg⁻¹ and 0 to 100 °C. h This study combines new measurements with earlier data and presents fitted models of relative density and apparent molar volume from 0.1 mol kg⁻¹ to saturation and from 0 to 50 °C. i Data below 0 °C were used to test extrapolations of the model.

The measurements of densities of saturated solutions by Roloff,⁸⁹ shown in Figure 13b, are likely to be in error because densities of solutions for which concentration is increasing and temperature decreasing are almost certain to show a superlinear increase (as calculated by the model).

6.1.5. All Concentrations and Temperatures. By combining the results described above it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and for molalities up to about 16 mol kg⁻¹ from equations fitted to the available data and to estimate the volume properties for lower temperatures and for highly concentrated solutions. Values of densities of aqueous HCl are shown in Figure 14 for 0–100% acid and for temperatures from 50 to -173 °C.

To what concentrations are the calculated densities likely to be accurate, given that the variation of the molar volume of pure liquid HCl has been treated as varying almost linearly with temperature (Figure 4)? First, above 250 K predicted densities for concentrations approaching that of the pure liquid will be too high. Second, caculated densities up to about 16 mol kg (36.6 wt %) closely represent available measurements, as shown in the sections above, and are likely to be accurate. The only measurements that appear to exist at intermediate concentrations are those of Rupert⁴⁴ for 61.65 to 67.65 wt % acid at greater than atmospheric pressure. Calculated densities for these concentrations for temperatures from -20 to 20 °C are higher than those measured by about 0.03 g cm^{-3} (neglecting the effect of pressure). On the basis of these comparisons it is likely that the model yields densities that are too high for concentrations significantly above 35-40 wt % acid. However, in most cases it is likely that densities for very high wt % of acid will only be required for calculations involving highly concentrated mixtures, for which estimation methods typically require volume properties of individual components at the total concentration of the mixture. In the atmosphere the concentration of HCl in liquid aerosols and droplets will usually be small, and so the influence of errors in the density of aqueous HCl on that of the mixture is unlikely to be significant.

6.2. NaCl. Sources of densities used in this work are listed in Table 4. Densities have been extensively studied over the normal liquid range (including as a function of pressure) and for this region we have listed only the International Critical Tables, the evaluations of Archer⁶¹ and Rogers and Pitzer,⁹⁰ and the

combined experimental and modeling studies of Lo Surdo et al.⁷ and Connaughton et al.⁵ We have chosen the work of Archer⁶¹ to calculate densities in the subsaturated range. The relevant equation for the calculation of apparent molar volume is eq 19 in that work, with model coefficients listed in Archer's Table 2 and the volume interaction parameters obtained by differentiation. See ref 61 for corrections to typographical errors in Archer's paper. Sources of original density data are listed by Archer and in other studies.^{5,7,15,16}

6.2.1. Reference Concentration. A reference concentration of 6.0 mol kg⁻¹ was chosen for NaCl. Archer and Carter's³¹ measurements of specific heats (c_p) of supercooled aqueous NaCl show that, for molalities above about 5 mol kg⁻¹, c_p decreases smoothly with temperature and there is no sign of the peak that occurs in the 240–260 K region for more dilute solutions and especially for pure water (see section 3.3 above). We therefore assume that densities of 6.0 mol kg⁻¹ NaCl can be extrapolated nearly linearly below 0 °C in common with other electrolytes of similar concentrations.⁹

Densities of 6.0 mol kg⁻¹ NaCl were generated using Archer's⁶¹ model from 0 to 100 °C and were fitted as a function of temperature using eq 13. The fitted coefficients are listed in Table S2 (Supporting Information) and the densities shown in Figure 15 together with values calculated using equations presented by Connaughton et al.⁵ and Lo Surdo et al.⁷ There is satisfactory agreement. The equation extrapolates to very low temperature to yield a continuously rising density to 0 K and has a slope at 25 °C (-5.86×10^{-4} g cm⁻³ K⁻¹) that is quite close to that of the melt (-5.78×10^{-4} g cm⁻³ K⁻¹).⁵⁸ 6.2.2. Aqueous Solutions Above 0 °C. Teng et al.⁹¹ have

6.2.2. Aqueous Solutions Above 0 °C. Teng et al.⁹¹ have estimated densities of aqueous NaCl to 11.0 mol kg⁻¹, at 25 °C, from data for solution mixtures at the same temperature using two different mixing rules (see their Figure 5 and Table 5). Tang²⁶ presents an equation for densities of aqueous NaCl at 25 °C, based in part upon electrodynamic balance measurements to supersaturated concentrations, that is valid to 45 wt % NaCl (14 mol kg⁻¹). This extrapolates to give a maximum density of about 1.66 g cm⁻³ close to 80 wt % NaCl and a density of 1.556 g cm⁻³ for the melt. This is equivalent to an apparent molar volume of 37.56 cm³ mol⁻¹, which is 39% higher than that of the solid salt (see Table 1). The comparisons shown in Figure 2 for a number of salts strongly suggest that this figure is unrealistically high and



Figure 15. Densities (ρ) of 6.0 mol kg⁻¹ NaCl (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: dot, generated using the equation of state of Archer;⁶¹ line, fitted equation including extrapolation to very low temperature. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated). Key: dot, generated using the equation of state of Archer;⁶¹ plus, equation of Lo Surdo et al.⁷ (for comparison only); circle, relative density equation of Connaughton et al.⁵ (for comparison only); cross, Pitzer equation ("fix" method) of Connaughton et al.⁵ (for comparison only).

that the density of the hypothetical NaCl melt should be greater than predicted by Tang's extrapolated equation. Our equation for melt densities as a function of temperature in Table 1, based on the equation of Janz⁵⁸ but modified to yield a density at 0 K the same as that of the solid, predicts a hypothetical melt density of 2.006 g cm⁻³ at 25 °C (a molar volume of 29.13 cm³ mol⁻¹). This is 8.6% greater than the density of the solid, similar to that of the other melts. However, a comparison with the behavior of other solutes for which data are available up to the melt (NaHSO₄, NH₄HSO₄, and NaNO₃) suggested that this molar volume is still too high. Some tests using the BET equation for excess molar volume (eq 16 of Abraham⁹²) together with the isotherm for water activity of Ally et al.⁹³ suggested a lower molar volume of $27-28 \text{ cm}^3 \text{ mol}^{-1}$ would be more reasonable, and a value of 28.0 cm³ mol⁻¹ was selected. We adopted this value as a best estimate of the melt density, to which densities of super-saturated solutions must extrapolate.

Equation 10 was used to fit densities of aqueous NaCl at 25 °C generated by the model of Archer⁶¹ and the value for the melt noted above. At molalities close to 6 mol kg⁻¹ the equation of Tang²⁶ does not accurately reproduce the trend in apparent molar volume with concentration (though the error is quite small) and values generated from this equation were given a low weight. Densities listed by Teng et al.,⁹¹ which are estimated from data for mixtures, were given the same weight as those of Tang, as were some values generated using the BET equation. Results are shown in Figure 16 as apparent molar volumes and as densities, and the fitted coefficients are listed in Table S3 in the Supporting Information. There are only small differences between densities calculated by our equation, that of Tang over its range of validity, and the densities of Teng et al.

At concentrations below saturation with respect to solid NaCl (about 6 mol kg⁻¹, which varies very little with temperature) apparent molar volumes of NaCl and solution densities can be calculated directly from the equations of Archer.⁶¹ At higher concentrations—up to the melt—there are no data except those for 25 °C described above. Accordingly, we estimate densities for solutions at temperatures other than 25 °C, and for molalities above the reference concentration, from the following expression

$$\rho(T) = \rho(T_{\rm r}) + q_1(T - T_{\rm r})(q_1 - q_2 T_{\rm r}) + q_2(T^2 - T_{\rm r}^2)/2 \quad (24)$$

where $\rho(T_r)$ is the density at the reference temperature of 298.15 K and the weight fraction of NaCl of interest (given by eq 10). The quantities q_1 and q_2 were obtained simply by linearly interpolating (as a function of weight fraction) between the values for the reference concentration and the melt. This yields the following two expressions for weight fractions greater than or equal to 0.25962 (6 mol kg⁻¹)

 $q_1 = -5.2816566 \times 10^{-4} - (2.443434 \times 10^{-5}) \textit{wf} \quad (25a)$

$$q_2 = -2.421396 \times 10^{-6} + (2.421396 \times 10^{-6}) wf \qquad (25b)$$

6.2.3. Aqueous Solutions below 0 °C. Mironenko et al.⁹⁴ describe the development of a Pitzer ion-interaction model for densities of aqueous mixtures at low temperatures, including NaCl as a component. They determined model parameters for aqueous NaCl at -6.66, -12.22, and -17.78 °C based upon data in the ASHRAE Handbook.⁹⁵ The parameters are valid over quite limited ranges of molality and are listed in their Table 5. Later, Mironenko et al.⁸ measured densities of aqueous NaCl at molalities from 0.00858 to 6.0141 mol kg⁻¹ and 293 to 258 K (with two additional points at 253 K). The results agree well with densities calculated using the Archer model.³¹ The authors developed a revised Pitzer model for density, for individual temperatures at 5 K intervals from 258 to 298 K. (Their parameters for 298 K—presumably 298.15 K—were taken from the study of Krumgalz et al.⁹⁶)



Figure 16. Measured and fitted apparent molar volumes of NaCl in aqueous solution at 25 °C. (a) Apparent molar volumes (V^{ϕ}) plotted against the square root of the weight percent of NaCl ($\sqrt{wt }$ %). Key: dot, equation of state of Archer;⁶¹ circle, equation of Tang;²⁶ plus, from Table 5 of Teng et al.;⁹¹ line, the fitted model. The solid vertical arrow indicates a solution saturated with respect to NaCl_(s), and the arrow indicates the limit of concentration attainable in small droplets at this temperature (the nucleation concentration). (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against NaCl concentration ($\sqrt{wt }$ %). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in the measured density. (c) Measured and calculated densities (ρ) of aqueous NaCl, plotted against NaCl concentration ($\sqrt{wt }$ %). Key: solid square, value for the melt (estimated in this study); the other symbols have the same meanings as in (a); line, the fitted model. The inset shows the difference between densities calculated using the fitted model and the equation of Tang²⁶ (model – Tang values).

Akinfiev et al.^{97,98} used the data of Mironenko et al.,⁸ together with heat capacities determined by Archer and Carter³¹ to develop a Pitzer model of activities, thermal properties, and volumetric properties which was able to reproduce the measured phase diagram to -20 °C. Volumetric (density) parameters are given to -15 °C, and the authors examine the variation of $V^{\phi\infty}$ with respect to temperature in terms of the Helgeson–Kirkham– Flowers model. The later paper by Akinfiev et al.⁹⁸ is essentially the same as that by Akinfiev et al.⁹⁷ Apparent molar volumes of NaCl in solutions below 0 °C and for concentrations less than the reference molality (m^*) of 6.0 mol kg⁻¹ are estimated in this work using eq 19. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to *T* are calculated using Archer's model,⁶¹ and densities and apparent molar volumes for the reference molality itself were calculated using eq 13 and coefficients listed in Table S2 (Supporting Information). Coefficients of the function for Y(m) are listed in Table S5 (Supporting Information).



Figure 17. Comparison of calculated densities (ρ) of aqueous NaCl with measurements of Mironenko et al.⁸ (their Table 1) at low temperatures. (a) Results for dilute solutions, shown as a function of temperature (*t*). Key: circle, 0.00858 mol kg⁻¹; dot, 0.01717 mol kg⁻¹; square, 0.03430 mol kg⁻¹; solid square, 0.05156 mol kg⁻¹; triangle, 0.06907 mol kg⁻¹; solid triangle, 0.08590 mol kg⁻¹; lines, predicted using the model developed in this work. Densities calculated using the equation of state of Archer⁶¹ for temperatures less than 0 °C are very close to the calculated values shown (and would be indistinguishable from them on this plot). (b) Results for concentrated solutions, shown as a function of temperature (*t*). Key: dot, measured densities at the NaCl molalities indicated on the plot; solid line, the model developed in this work; dotted line, the equation of state of Archer.⁶¹

We compare predicted densities with the measurements of Mironenko et al.⁸ in Figure 17. At low concentrations (0.00858 to 0.0859 mol kg⁻¹, Figure 17a) for which densities show a peak and then decline as temperature is lowered, the model agrees very well with the measurements. At the higher molalities shown in Figure 17b a gradual transition can be seen between concentrations for which there is a peak in density (0.3484 and, perhaps, 1.4871 mol kg⁻¹) and those higher concentrations for which density appears to increase continuously as temperature falls. The predictions agree very well with the data and also Archer's model.

6.2.4. All Concentrations and Temperatures. By combining the results described above, it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and for subsaturated solutions and to estimate them for lower temperatures and for supersaturated solutions, see Figure 18.

6.3. NH₄Cl. Sources of data are listed in Table 5 and include some studies carried out prior to the evaluation in the International Critical Tables. Sharygin and Wood¹³ tabulate modern sources of density measurements, as do Laliberté and Cooper,¹⁶ and these sources are included in the table. Fifty sources of density data were considered by the International Critical Tables, but only two studies are listed as being given "more weight", and one "some weight". The densities of Gerlach, as listed by Timmermans,⁴⁴ are included in this work as are several other early studies for which data are listed in the same compilation.

Densities of supersaturated aqueous NH_4Cl have not been measured, mainly because a relatively rapid method would be needed in an electrodynamic balance experiment to minimize the effects of particle evaporation (as HCl and NH_3).

6.3.1. Aqueous Solutions at 25 °C. Apparent molar volumes at infinite dilution ($V^{\phi\infty}(NH_4Cl)$) at this temperature have been determined by Allred and Woolley⁹⁹ (35.83 cm³ mol⁻¹), Leduc



Figure 18. Calculated densities from 0 to 100 wt % NaCl as a function of temperature (t). Dotted lines show calculated densities at intermediate wt % of NaCl (10, 30, 50, 70, and 90 wt %).

et al.¹⁰⁰ (35.79 cm³ mol⁻¹) and Roux et al.⁴¹ (36.2 cm³ mol⁻¹). Adding values for the individual ions from Millero's¹⁰¹ Table 1 yields 35.69 cm³ mol⁻¹ and the single ion $V^{\phi\infty}$ of Roux et al.⁴¹ yield 36.0 cm³ mol⁻¹. Our own fits to the available data yield 35.85 \pm 0.02 cm³ mol⁻¹ at 25 °C, and we have adopted this value.

Table 5. Sources of Data for Aqueous NH₄Cl

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
|-----------------|------------------------|--------------|-----------------------|-----------------------|------|------|----------------------------------|
| 1-24 | wt % | 0-60 | ρ | $g mL^{-1}$ (old) | yes | Ь | 2 |
| 0.002-0.200 | ${ m mol}~{ m L}^{-1}$ | 25 | ρ | $g mL^{-1}$ (old) | no | | 169 |
| 0.10-7.30 | $mol kg^{-1}$ | 25 | ρ | $g mL^{-1}$ (old) | yes | | 170 |
| 0.2003-1.0008 | $mol kg^{-1}$ | 25 | Δho | $g \text{ cm}^{-3}$ | yes | | 69 |
| 0.4437-4.437 | $mol kg^{-1}$ | 25 | $\rho(t, 4^\circ)$ | | no | | 44 (Getman, 1908) |
| 1.268-5.071 | $mol L^{-1}$ | 25 | ρ | $g mL^{-1}$ (old) | no | | 171 |
| 0.0497-5.0611 | $ m mol~dm^{-3}$ | 25 | ρ | $g \text{ cm}^{-3}$ | yes | | 127 |
| 0.00614-2.186 | $ m mol~dm^{-3}$ | 25 | ρ | $cm^3 mol^{-1}$ | yes | | 172 |
| 0.03671-0.2164 | $mol kg^{-1}$ | 25 | ρ | $\rm cm^3 \ mol^{-1}$ | no | с | 41 |
| 3.480-21.03 | wt % | 0 | $\rho(t, 4^\circ)$ | | yes | | 44 (Charpy, 1893) |
| 1.0-26.0 | wt % | 15 | ρ | $g m L^{-1}$ (old) | yes | | 44 (Gerlach, 1859) |
| 10.62, 17.42 | wt % | 18 | rel. vol. | | no | d | 44 (De Heen, 1881) |
| 0.999-24.8 | wt % | 18 | $ ho(t, 4^\circ)$ | | no | | 44 (Jessen-Hansen, 1927) |
| 5.13-24.25 | wt % | 19 | $ ho(t, 4^\circ)$ | | no | | 44 (Cheneveau, 1907) |
| 10.69-26.47 | wt % | 20 | $ ho(t, 4^\circ)$ | | no | | 44 (Spacu and Popper, 1934) |
| 2.65-24.2 | wt % | 11.5 | $\rho(t, 4^\circ)$ | | no | | 44 (de Block, 1925) |
| 12.54, 19.54 | wt % | 0 | $ ho(t, 4^\circ)$ | | no | | 44 (Anderson and Asmussen, 1932) |
| 0.0005-0.258 | $mol \ dm^{-3}$ | 35 | $\rho(t, t)$ | | no | | 173 |
| 0.08459-0.01705 | ${ m mol}~{ m L}^{-1}$ | 35 | ρ | $g mL^{-1}$ (old) | no | | 174 |
| 9.11-24.71 | wt % | 10 - 30 | $\rho(t, 4^{\circ})$ | | no | | 44 (Grabowsky, 1904) |
| 0.001-0.6008 | $mol \ dm^{-3}$ | 12.5-42.5 | $\rho(t, t)$ | | no | | 175 |
| 0.25-1.0 | $mol kg^{-1} soln.$ | 30-73.5 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | | 176 |
| 3.043-10.516 | $mol kg^{-1}$ | 50-65 | ρ | $\rm g~cm^{-3}$ | yes | | 104 |
| 0.0625-1.00 | $mol kg^{-1}$ | 35-50 | V^{ϕ} | $\rm cm^3 mol^{-1}$ | no | | 177 |
| 0.03906-0.04036 | $mol kg^{-1}$ | 10-40 | V^{ϕ} | $\rm cm^3 mol^{-1}$ | yes | | 99 |
| 1.588-6.750 | $mol kg^{-1}$ | 25-45 | $\rho(t, 4^{\circ})$ | | yes | | 44 (Shibata and Holemann, 1931) |
| 0.0503-0.4566 | $mol kg^{-1}$ | 35-50 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | | 178 |
| 0.0697 | $mol kg^{-1}$ | 20-40 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 66 |
| 0.05-5.00 | $mol kg^{-1}$ | 15-55 | ρ | $kg m^{-3}$ | yes | | 179 |
| 0.0995-5.981 | $mol kg^{-1}$ | 25-325 | Δho | $kg m^{-3}$ | no | е | 13 |

 ${}^{a}\rho(t, u)$ is the density of the solution at t °C relative to that at u °C, and $\Delta\rho$ is a density difference (usually relative to that of pure water at the same temperature). b There are also values for $\rho(20.004^{\circ}, 4^{\circ})$ for 0.01-0.05 wt %, and $\rho(t, 4^{\circ})$ from 0 to 50 °C for 5.2733 wt % solutions. c Deposited Supporting Information. d The volume of the solution at temperature t, divided by the volume at 10 °C. e Measurements were at pressures from 9.95 to 28.2 MPa.

Solid NH₄Cl sublimes at a temperature of 340 °C,¹⁰² and so there are no measurements of the density of the pure melt. The relationship between $V^{\phi\infty}(NH_4Cl)$ and $\sqrt{wt \%}$ of aqueous solutions at 25°C is roughly linear, suggesting a hypothetical molar volume of the melt equal to at least 42 $\text{cm}^3 \text{ mol}^{-1}$. Shirai and Ishibashi¹⁰³ have measured specific volumes of $\rm NH_4NO_3 +$ NH₄Cl mixtures, containing 2.5 to 10 wt % NH₄Cl, from 170 to 190 °C. If it is assumed that the total volume of the melt is related to the sum of the molar volume of NH₄NO₃ at the experimental temperature (also measured by Shirai and Ishibashi) plus an apparent molar volume of NH₄Cl (V^{ϕ} (NH₄Cl)^{*}), the latter can be determined from the measured densities. Figure 19 shows values of $V^{\phi}(NH_4Cl)^*$ plotted against the mole fraction of NH₄Cl in the mixture. Although the experimental range of mole fraction is quite small, the data suggest a hypothetical pure molar volume $V^{\circ}(NH_4Cl)$ of at least 47 cm³ mol⁻¹ in this temperature range, and probably higher. We have assumed a linear relationship of hypothetical melt density with temperature for all the electrolytes considered here. Adopting a slope of $-6 \times$ 10^{-4} g cm⁻³ K⁻¹ for NH₄Cl (typical of those of the other chlorides in Table 1) and assuming a molar volume of the melt of 48 cm³ mol⁻¹ at 170 °C yields a value of 42.4 cm³ mol⁻¹ at 25 °C which is consistent with the data for aqueous solutions. We have therefore retained this value of the slope and set the hypothetical molar volume of the melt at 25 °C to a round 42.0 cm³ mol⁻¹, to obtain the following equation for the melt density:

$$\rho(100\%) = 1.45246 - (6.4 \times 10^{-4})T \tag{26}$$

where T (K) is temperature. The intercept at 0 K (1.45246 g cm⁻³) is lower than that of the solid at 25 °C (1.52 g cm⁻³) by only 0.07 g cm⁻³; thus the relationship given by the equation is quite consistent with those for the other salts for which there are more data.

Nonzero weights were given to data at 25 °C from seven of the sources listed in Table 5, and apparent molar volumes were fitted from 0 to 100 wt % using eq 10. The results are plotted in Figure 20, and the fitted coefficients are listed in Table S3 (Supporting Information). The modern data and densities from the International Critical Tables agree well at this temperature.

6.3.2. The Reference Concentration. A value of 24 wt % $(5.90371 \text{ mol kg}^{-1})$ was chosen, which is at the upper limit of the listed densities in the International Critical Tables. Densities



Figure 19. Apparent molar volumes $(V^{\phi}(NH_4Cl)^*)$ of NH_4Cl in NH_4NO_3 solvent at temperatures of 170-190 °C, plotted against the mole fraction of NH_4Cl in the mixture. Key: circles, Shirai and Ishibashi;¹⁰³ line, fitted (as a visual guide only).

for this concentration were also interpolated from the work of Rashkovskaya and Chernen'kaya¹⁰⁴ (for 70-100 °C, and extrapolated for 50-60 °C), Shibata and Holemann,⁴⁴ and from Gerlach.⁴⁴ We note that densities in the work of Rashkovskaya and Chernen'kaya for concentrations below 30 wt % are taken from earlier evaluations. The cited works do not include the International Critical Tables, but it is possible that this is still a source. Densities for the reference concentration are shown in Figure 21 and are represented by eq 13 and fitted coefficients listed in Table S2 (Supporting Information).

6.3.3. Aqueous Solutions above 0 °C. Apparent molar volumes at infinite dilution from a number of sources, including our own estimates obtained from fits at individual temperatures, are plotted in Figure 22. The values estimated by Fajans and Johnson¹⁰⁵ were obtained by assuming a simple proportionality between $V^{\phi\infty}(NH_4Cl)$ and the square root of molality, without a Debye-Hückel term, and this may explain why the values in the figure are high relative to the others. Values of $V^{\phi\infty}(NH_4Cl)$ calculated as $(0.5V^{\phi\infty}((NH_4)_2SO_4) - 0.5V^{\phi\infty}(Na_2SO_4) + V^{\phi\infty}$ (NaCl)), using our fitted equations for these quantities, agree satisfactorily with the individual determinations of $V^{\phi\infty}(NH_4Cl)$ shown in the figure, although at high temperatures the uncertainty is greatest (of the order of $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$). We note that the individual ionic volumes tabulated by Millero¹⁰¹ yield $37.2 \text{ cm}^3 \text{ mol}^{-1}$ at 50 °C, which seems to be about 0.8 $\text{cm}^3 \text{ mol}^{-1}$ too high. Also, using $V^{\phi\infty}(\text{NaCl})$ of Connaughton et al.⁵ in place of those of Archer⁶¹ in the relationship above yields $V^{\phi\infty}(NH_4Cl)$ which differ by about $-0.2 \text{ cm}^3 \text{ mol}^{-1}$ at 50 °C from those shown in Figure 22. We have based $V^{\phi\infty}(\mathrm{NH}_4\mathrm{Cl})$ in this study on $V^{\phi\infty}(\mathrm{NH}_4\mathrm{Cl})$, 25 °C) equal to 35.85 cm³ mol⁻¹ and then fitted the calculated values of $(0.5V^{\phi\infty})((NH_4)_2SO_4) - 0.5V^{\phi\infty}(Na_2SO_4) + V^{\phi\infty}$. (NaCl)) at other temperatures to obtain the following equation

$$V^{\phi\infty}(\text{NH}_{4}\text{Cl}) = 35.85 - (1.3521157 \times 10^{5})(1/T - 1/T_{\text{r}}) - 671.00884 \ln(T/T_{\text{r}}) + 0.7692039(T - T_{\text{r}})$$
(27)

where T (K) is temperature and T_r is the reference temperature of 298.15 K. Calculated $V^{\phi \infty}$ (NH₄Cl) are shown in Figure 22.

Comparisons of apparent molar volumes from the sources of data listed in Table 5 led to the rejection of all but seven of the studies. Measured apparent molar volumes were combined with molar volumes of the melt generated by eq 26, and apparent molar volumes for the reference concentration (from eq 13), and fitted using eq 10 from 0 to 60 °C. The results are shown in Figure 23, and the fitted parameters are listed in Table S3 (Supporting Information). The data that were accepted for inclusion in the fit are represented mostly to within ± 0.1 cm³ mol⁻¹. Apparent molar volumes calculated from the densities in the International Critical Tables are generally too high at 1 and 2 wt % below 25 °C, but this systematic error seems to extend to higher concentrations at 50 and 50 °C and some data were rejected.

6.3.4. Aqueous Solutions below 0 °C. There are no measured densities for temperatures below 0 °C. For concentrations greater than or equal to the reference concentration, we fitted measured densities and values generated from the results of the fit above, using eq 14. The expression yields the same densities as the equations fitted previously for the melt and for the reference concentrations, and extrapolates monotonically increasing densities for temperatures below 0 °C. The results are shown in Figure 24, and the fitted coefficients of eq 14 are listed in Table S6 (Supporting Information). It can be seen in the figure that $\Delta \rho$ ranges between about -0.001 and 0.002 g cm⁻³. The measured and fitted apparent molar volumes shown in Figure 24a suggest that the 0-60 °C fit described in section 6.3.3 above may overestimate densities of (supersaturated) 30-80 wt % solutions close to 0 °C. The fit of the densities directly yields a more linear relationship between ρ and temperature.

For concentrations below the reference concentration, we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to *T* in eq 16 are calculated using eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. The value of m^* is 5.90371 mol kg⁻¹, and the coefficients of eq 18 for Y(m) are given in Table S5 (Supporting Information).

6.3.5. All Concentrations and Temperatures. By combining the results described above it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and for subsaturated solutions and to estimate them for lower temperatures and for supersaturated solutions; see Figure 25.

6.4. H₂SO₄. Sources of densities are listed in Table 6 and include some measurements to very low temperature. A number of other studies focus on dilute solutions because of interest in the effect of the dissociation of the HSO₄⁻ ion on the apparent molar volume of the acid, and the values of the two infinite dilution apparent molar volumes $V^{\phi\infty}(2H^+, SO_4^{-2})$ and $V^{\phi\infty}(H^+, HSO_4^{-1})$.

Densities of aqueous H_2SO_4 have been studied for very many years because of the acid's industrial importance. Timmermans,⁴⁴ writing in 1960, tabulates data from 19 studies. Of these the work of Domke and Bein¹⁰⁸—which covers the ranges 0–100 wt % acid and 0–60 °C—is recommended as the standard work. Timmermans cites a further 34 studies covering the period 1826 to 1953 and dismisses them as insufficiently accurate. (Of these, only the study of Campbell et al.¹⁰⁹ is listed in Table 6.) The evaluated densities in the International Critical Tables are based chiefly upon the work of Domke and Bein and studies of Kremers^{110,111} that include thermal expansivity information. We have adopted the densities listed in the International Critical Tables as our primary



Figure 20. Measured and fitted apparent molar volumes of NH₄Cl in aqueous solution at 25 °C. (a) Apparent molar volumes of NH₄Cl (V^{ϕ}) plotted against the square root of the NH₄Cl weight percent ($\sqrt{wt \%}$). Key: dot, International Critical Tables; solid square, hypothetical melt (this study); star, Pearce and Pumplin;¹⁷⁰ square, Millero et al.;⁶⁹ plus, Allred and Woolley;⁹⁹ diamond, Albright et al.;¹²⁷ circle, Isono;¹⁷⁹ inverted solid triangle, Stokes;¹⁷² solid triangle, Shibata and Holemann;⁴⁴ line, the fitted model. The solid vertical arrow indicates a solution saturated with respect to NH₄Cl(_s), and the arrow indicates the limit of concentration attainable in small droplets at this temperature (the nucleation concentration). (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against NH₄Cl concentration ($\sqrt{wt \%}$) and excluding the melt. Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous NH₄Cl, plotted against NH₄Cl concentration ($\sqrt{wt \%}$). Key: the symbols and vertical arrows have the same meanings as in (a); line, the fitted model.

source for this study, supplemented with more recent measurements at low concentrations and for low temperatures.

6.4.1. Dilute Aqueous Solutions above 0 °C. Apparent molar volumes of H₂SO₄ vary very steeply with molality in dilute solutions because of the effect of the varying dissociation of the HSO₄⁻ ion (e.g., see Figure 7 of Clegg et al.⁶²). At 25 °C, the degree of dissociation (α) is approximately 0.2 from 1.0 to 0.25 mol kg⁻¹ but at lower molalities rises to unity at infinite dilution. This is reflected in a more than factor of 2 difference between $V^{\phi \infty}(2H^+, SO_4^{-2})$ and the value of the apparent molar

volume in a 0.25 mol kg⁻¹ solution.¹ Data are shown in Figure 26 for 25 °C and molalities up to 1.0 mol kg⁻¹.

Experimental apparent molar volumes $V^{\phi}(H_2SO_4)$ can be expressed as the sums of the apparent molar volumes of the two pairs of ions $(2H^+ + SO_4^{-2})$ and $(H^+ + HSO_4^{-1})$ present in solution¹¹²

$$V^{\phi}(H_2SO_4) = (1-\alpha)V^{\phi}(H^+, HSO_4^-) + \alpha V^{\phi}(2H^+, SO_4^{-2-})$$
(27)



Figure 21. Densities (ρ) of 24 wt % NH₄Cl (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: circle, International Critical Tables; plus, Rashkovskaya and Chernen'kaya;¹⁰⁴ square, Gerlach;⁴⁴ solid triangle, this work; line, the fitted model including extrapolation to very low temperature. (b) The difference between measured and fitted densities ($\Delta\rho$, observed – calculated). Key: the symbols have the same meanings as in (a).



Figure 22. Apparent molar volumes of NH₄Cl at infinite dilution $(V^{\phi\infty})$, as a function of temperature (*t*). Key: square, Allred and Woolley;⁹⁹ dot, Leduc and Desnoyers;¹⁰⁰ star, Fajans and Johnson;¹⁰⁵ circle, Millero;¹⁰¹ solid triangles, values from fits to the available data at each temperature (this work); line, the fitted model (eq 27).

where $V^{\phi}(H_2SO_4)$ is the stoichiometric apparent molar volume calculated from eq 1a and α is equal to $mSO_4^{2-}/(mSO_4^{2-} + mHSO_4^{-})$. Symbol $V^{\phi}(H^+, HSO_4^{-})$ (cm³ mol⁻¹) is the apparent molar volume contribution of the (H⁺ + HSO_4^{-}) ions in solution and $V^{\phi}(2H^+, SO_4^{2-})$ (cm³ mol⁻¹) is the contribution of the (2H⁺ + SO_4^{2-}) present. In part 2 of this work¹ we develop a Pitzer ion interaction model of dilute aqueous sulphuric acid, from 0 to 3 mol kg⁻¹ and from 0 to 55 °C, with which the two separate contributions can be calculated. For concentrations below a few wt % of acid this model is believed to yield significantly more accurate apparent molar volumes and densities than can be obtained by interpolation of the densities in the International Critical Tables. Our results are listed in Tables 2 and 3 of part 2.

6.4.2. Reference Concentration. The reference concentration must lie below the maximum 3 mol kg⁻¹ of the Pitzer model referred to above, and above the lower limit of 6 wt % (0.65 mol kg⁻¹) of the fitted density equation described in the next section. A value of 2.1 mol kg⁻¹ was chosen, because at this molality the Pitzer model and fitted equation agree closely. Coefficients of the density equation (eq 13) were determined from the fitted model of density described in section 6.4.3 below and are listed in Table S2 (Supporting Information).

At 25 °C the ionic strength of 2.1 mol kg⁻¹ H₂SO₄ is about 3.26 mol kg⁻¹ (see Table 8 of Clegg et al.⁶²), which is lower than that of the reference concentrations of most of the other solutes in this study. It is therefore possible that densities at very low temperatures should show some influence of supercooled water, the density of which decreases to about 200 K as shown in Figure 3. A bulk solution of 2.1 mol kg⁻¹ H_2SO_4 is saturated with respect to ice at 262.5 K,¹¹³ but small droplets can be supercooled to about 220 K.³³ Equation 13 above predicts a continuously rising density as T is decreased. Archer's model of NaCl (see Archer and Carter's³¹ Figure 7) suggests that for that salt there is no temperature of maximum density at ionic strength 4.011 mol kg^{-1} and that it may not exist at 2.033 mol kg^{-1} . If this behavior is more closely related to ionic strength than molality, then our equation is likely to be correct in not predicting a temperature of maximum density for the 2.1 mol kg⁻¹ acid. The Despretz constant, $K_{\rm m}$ in eq 7, given by Kaulgud and Pokale⁴⁷ for H₂SO₄, is about twice the magnitude of that for NaCl, which is qualitatively consistent with this conclusion.

6.4.3. Other Aqueous Solutions, and Pure Liquid H_2SO_4 , above 0 °C. It is clear from Table 6 that, with the exception of studies of densities at temperatures below 0 °C, most measurements carried out after the evaluation in the International Critical



Figure 23. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of NH₄Cl from 0 to 60 °C, plotted against the square root of NH₄Cl concentration $(\sqrt{\text{wt }}\%)$. All apparent molar volumes are offset by an amount $(t/t^{\circ} - 25)/2.5 \text{ cm}^3 \text{ mol}^{-1}$, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure. Key: dot, International Critical Tables; solid square, the melt (estimated in this work); star, Rashkovskaya and Chernen'kaya;¹⁰⁴ circle, Allred and Woolley;⁹⁹ square, Isono;¹⁷⁹ diamond, Charpy;⁴⁴ plus, Gerlach;⁴⁴ lines, the fitted model. (b) Measured and fitted apparent molar volumes (V^{ϕ}) of NH₄Cl at fixed concentrations, plotted against temperature (t). Key: solid triangle, generated using the fitted equation for the reference concentration (section 6.3.2); triangle, Millero and Drost-Hansen⁶⁶ for 0.0697 mol kg⁻¹; lines, the fitted model. (c) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated). Key: the symbols have the same meanings as in (a) and (b). (d) Densities (ρ) from 0 to 60 °C generated using the fitted model, as a function of NH₄Cl concentration ($\sqrt{\text{wt }}\%$). (Densities for 20 and 40 °C are shown as dotted lines.)

Tables are for dilute solutions. (Note that the extensive tabulations of Haase and co-workers for this¹¹⁴ and other acids are based on literature data and not new measurements.) Many of the dilute solution data were used in the fits of the Pitzer model described in part 2, and it can be seen in Figure 3 of that work that they agree well with the values from the International Critical Tables, at least above molalities of about 0.5 mol kg⁻¹ (4.7 wt % acid). Greenwood and Thompson,¹¹⁵ Gillespie and Wasif,¹¹⁶ Rhodes and Barbour,¹¹⁷ and Campbell et al.¹⁰⁹ have measured densities of concentrated solutions including the pure liquid acid. These are compared with values from the International Critical Tables in Figure 27. Except for the study of Campbell et al.¹⁰⁹ there is satisfactory agreement in all cases. We therefore adopt densities from the International Critical Tables for all temperatures and for all concentrations except for the dilute solutions modeled in part 2. Some adjustments of values were made very close to 100 wt % acid, using densities from the work of Greenwood.¹¹⁵



Figure 24. (a) Measured and fitted densities (ρ) of concentrated NH₄Cl as a function of temperature (t), for fixed wt % of NH₄Cl from 22 to 100 wt % (noted on the figure). Key: circle, generated using the fitted model for apparent molar volume; dot, International Critical Tables; solid triangle, Shibata and Holemann;⁴⁴ square, Grabowsky;⁴⁴ lines, the fitted model (dotted, 26.53 wt %; dash-dot, 24.71 wt %). (b) Measured and fitted densities (ρ) of NH₄Cl as a function of concentration ($\sqrt{wt \%}$), and at fixed temperatures (in °C, marked on the plot). Key: diamond, Gerlach;⁴⁴ inverted solid triangle, Jessen-Hansen;⁴⁴ star, Rashkovskaya and Chernen'kaya;¹⁰⁴ lines, the fitted model. (c) The difference between measured and fitted densities ($\Delta\rho$, observed – calculated). The symbols have the same meanings as in (a) and (b), with the addition of solid square, Cheneveau;⁴⁴ cross, Spacu and Popper;⁴⁴ plus, de Block.⁴⁴ These three sources contribute only a single point each and are not shown on plots (a) and (b).

Densities were fitted as functions of temperature and weight fraction using the following equation for acid concentrations from 0.06 to 1.0 weight fraction H_2SO_4 :

$$\rho(T, wf) = \rho(T_r, wf) + (T - T_r)(Q_1(T_r, wf) - T_rQ_2(T_r, wf)) + Q_2(T_r, wf)(T^2 - T_r^2)/2$$
(28)

where $\rho(T_r, wf)$ (g cm⁻³) is the density at the reference temperature T_r (298.15 K) and H₂SO₄ weight fraction wf, $Q_1(T_r, wf)$ (g cm⁻³ K⁻¹) is the first differential of $\rho(T_r, wf)$ with respect to temperature T (at T_r) and $Q_2(T_r, wf)$ is the second differential of $\rho(T_{rr}, wf)$ with respect to temperature. These differentials are assumed to vary continuously with weight fraction, *wf*. In order to develop an equation to reproduce the densities in the International Critical Tables, densities at each listed wt % of acid from 6 wt % to 100 wt % were first fitted individually as functions of temperature from 0 to 100 °C, resulting in an array of 95 values each of $\rho(T_r, wf)$, $Q_1(T_r, wf)$, and $Q_2(T_r, wf)$. The very close agreement between the tabulated and fitted densities suggests that the table of densities may have been prepared by assuming a similar relationship to eq 29 in the analysis of the original data. Values of $\rho(T_r, wf)$ were then fitted as a function of acid weight fraction using a normalized cubic b-spline (found to be superior to a polynomial), which reproduces the tabulated densities to within close to ± 0.0001 g cm⁻³ over the entire range. The knots and coefficients of the spline are listed in Table S7 (Supporting Information). Values of $Q_1(T_r, wf)$ were then fitted with a second cubic spline (see also Table 13), and finally $Q_2(T_r, wf)$ using the following polynomial

$$Q_{2}(T_{r},wf) = q_{1} + q_{2}wf^{0.5} + q_{3}wf + q_{4}wf^{2} + q_{5}wf^{3} + q_{6}wf^{4} + q_{7}wf^{5} + q_{8}wf^{6} + q_{9}wf^{7} + q_{10}/wf + q_{11}wf^{2.5} + q_{12}wf^{8} + q_{13}wf^{1.5}$$
(29)



Figure 25. Calculated densities of 0 to 100 wt % NH_4Cl as a function of temperature (*t*). Dotted lines show calculated densities at intermediate wt % of NH_4Cl (10, 30, 50, 70, and 90 wt %).

| able 0. Sources of Data for Aqueous 112504 | | | | | | | | | | |
|--|-----------------|---------------------|-----------------------|-----------------------|------|------|--|--|--|--|
| concn range | unit | <i>t</i> range (°C) | quantity ^a | unit | used | note | | | | |
| 1-100 | wt % | 0-100 | ρ | $g mL^{-1}$ (old) | yes | Ь | | | | |
| 0.0143-3.194 | $mol L^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | | | | |
| 0.001254-2.139 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | | | | |
| 0.052-0.5628 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | | | | |
| 98.91-99.94 | wt % | 25 | $\rho(t, 4^\circ)$ | | yes | | | | | |
| 0.0025-0.981 | $mol L^{-1}$ | 20 | $\rho(t, 4^\circ)$ | | yes | | | | | |
| 0.05-1.00 | $mol \ dm^{-3}$ | 19.85 | ρ | $g \text{ cm}^{-3}$ | yes | | | | | |
| 0.1781-1.013 | $mol kg^{-1}$ | 10-40 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | | | | |
| 12.3-76.5 | wt % | -40 to 33 | ρ | $g \text{ cm}^{-3}$ | no | с | | | | |
| 36 | wt % | -65 to 25 | ρ | $g mL^{-1}$ (old) | no | с | | | | |
| 100 | wt % | 7.5-70 | $ ho(t, 4^\circ)$ | | yes | | | | | |
| 10-100 | wt % | -40 to 149 | ρ | $lb ft^{-3}$ | no | c, d | | | | |
| 5-99.6 | wt % | 0-75 | ρ | $\rm g~cm^{-3}$ | yes | | | | | |
| 38.9-88.6 | wt % | -52.15 to 78.15 | ρ | $\rm g~cm^{-3}$ | no | с | | | | |

Table 6. Sources of Data for Aqueous H_3SO_4

wt %

mole fraction

50, 75

22.4

8.95-96.2

0.001 - 0.004

43

109

185

Values of the coefficients q_{1-13} are listed in Table S7 (Supporting Information). Combining the fitted $\rho(T_r, wf)$ and its differentials with respect to temperature in eq 29 allows densities to be calculated for concentrations above 6 wt % (0.65 mol kg⁻¹) and for temperatures up to 373.15 K, although in our work we only use eq 29 for calculations above the reference concentration of 2.1 mol kg⁻¹. Deviations only exceed 0.0002 g cm⁻³ for two tabulated densities between 80 and 85 wt % and for eight densities above 95 wt %.



Figure 26. Stoichiometric apparent molar volumes (V^{ϕ}) of H₂SO₄ in dilute solutions at 25 °C, as a function of the square root of molality (\sqrt{m} H₂SO₄). Key: dot, International Critical Tables; square, Hovey and Hepler;¹⁰⁷ circle, Lindstrom and Wirth;¹⁰⁶ star, Larson et al.;¹⁸¹ solid inverted triangle, Klotz and Eckert;¹⁸⁰ line, the fitted model from part 2 of this study.

^{*a*} $\rho(t, u)$ is the density of the solution at *t* °C relative to that at *u* °C. ^{*b*} Additional data are listed for $\rho(t, 4^{\circ})$ at 5.96, 13, and 18 °C. ^{*c*} The fitted model is compared with these data (see text). ^{*d*} Densities, including values below 0 °C (which are extrapolations), are largely based upon the International Critical Tables evaluation. ^{*c*} Densities are only given to three digits, and mole fractions to a single digit (possibly in error).

ρ

ρ

3419

 $g m L^{-1}$ (old)

 ${\rm kg}~{\rm m}^{-3}$

no

no



Figure 27. Densities (ρ) of concentrated H₂SO₄ solutions. (a) Density of 100 wt % acid, as function of temperature (*t*). Key: dot, International Critical Tables; plus, Greenwood and Thompson;¹¹⁵ circle, Gillespie and Wasif¹¹⁶ (99.94 wt %). (b) Densities of 85–100 wt % H₂SO₄ at 0, 25, and 50 °C (marked on the plot). Key: dot, International Critical Tables; diamond, Rhodes and Barbour;¹¹⁷ circle, Gillespie and Wasif;¹¹⁶ square, Campbell et al.;¹⁰⁹ plus, Greenwood and Thompson;¹¹⁵ Inset: detail close to 100 wt % at 25 °C.



Figure 28. (a) Measured and calculated densities of aqueous $H_2SO_4(\rho)$ to low temperatures (*T*). Key: dot, Garrett and Woodruff;⁹ circle, Myhre et al.;¹⁴ star, Beyer et al.;⁴³ line, eq 28. The concentrations of H_2SO_4 (in wt %) are indicated on the plot. (b) Comparison of densities (ρ) calculated using eq 28 (solid line) with those from the equation of Myhre et al.¹¹⁸ (dashed line) for 10–90 wt % acid (indicated on the plot) and from 150 to 273.15 K.

6.4.4. Aqueous Solutions above the Reference Concentration and below 0 °C. The bulk aqueous acid, undersaturated with respect to ice and H_2SO_4 hydrates, can exist to temperatures as low as 200 K.¹¹³ Measurements of the densities of the aqueous acid at low temperature have been made by Garrett,⁹ Myhre et al.,¹⁴ and Beyer et al.⁴³ The data are compared with predictions of eq 29 above in Figure 28a. It is clear that our representation of densities agrees well with the low temperature measurements overall, even though they were not included in the fit. We therefore adopt eq 29 for all temperatures below 0 °C and for concentrations above the reference concentration of 2.1 mol kg⁻¹. Myhre et al.^{14,118} have also fitted an equation to their data and densities from the International Critical Tables from 0 to 50 °C and 10 to 90 wt % acid. This is compared with our expression in Figure 28b. Myhre et al.¹¹⁸ state that their equation behaves consistently to 210 K, and the figure confirms quite close



Figure 29. Calculated densities of aqueous H_2SO_4 from 1.0 to 7.0 wt % concentration (marked on the plot), as a function of temperature (*t*). The intermediate dotted lines are densities at 2, 4, and 6 wt % of acid. Key: dot, temperature of maximum density of 0 to 7 wt % acid listed in the International Critical Tables; dash-dot line, temperatures of maximum density obtained in this work.



Figure 30. Calculated densities (ρ) of aqueous H₂SO₄ at low temperatures (t), including supercooled solutions. Key: solid lines, calculated densities from 0 to 40 wt % acid (indicated on the plot); bold solid line, the freezing curve of the acid with respect to ice; dotted line, densities at the nucleation concentration (at which homogeneous nucleation occurs in supercooled droplets⁵⁶).

agreement with the predictions of our model to this temperature, except for the 10 wt % acid (1.13 mol kg^{-1}). At this concentration below the reference concentration—our model uses the approach described in section 4.5 (see below for details) and the predicted density shows some of the decline at very



Figure 31. Calculated densities of 0 to 100 wt % H_2SO_4 as a function of temperature (*t*). Dotted lines show calculated densities at intermediate wt % of H_2SO_4 (10, 30, 50, 70, and 90 wt %).

low temperature that is characteristic of supercooled water. The polynomial equation used by Myhre et al. was fitted to densities of pure water only to 0 °C, which is likely to explain the difference.

6.4.5. Aqueous Solutions below the Reference Concentration, and below 0 °C. In order to estimate densities of aqueous solutions of H₂SO₄ below the reference molality (m^*) of 2.1 mol kg⁻¹, we have again used eq 19, though with some modifications to our approach. For aqueous sulfuric the variation of V^{ϕ} with molality and temperature at low concentrations is both larger and more complex than for other solutes because of the changing degree of dissociation (which is a function of both variables). Apparent molar volumes at very low temperature calculated using eq 19, which includes both first and second differentials of apparent molar volumes with respect to temperature, at first gave results that were not plausible even for several different choices of reference temperature in eq 16. The cause of this was investigated, beginning with the following equation for the stoichiometric apparent molar volume of H₂SO₄ (V^{ϕ} (H₂SO₄))

$$V^{\phi}(H_2SO_4) = (1 - mSO_4^{2^-}/m)V^{\phi}(H^+, HSO_4^-) + (mSO_4^{2^-}/m)V^{\phi}(2H^+, SO_4^{2^-})$$
(30)

where *m* is the stoichiometric or total molality of H₂SO₄. This equation is equivalent to eq 27. The quantities mSO_4^{2-} , $V^{\phi}(H^+, HSO_4^{-})$, and $V^{\phi}(2H^+, SO_4^{2-})$ all vary with temperature. Differentiation of eq 30 by parts enables expressions for $\partial V^{\phi}(H_2SO_4)/\partial T$ and $\partial^2 V^{\phi}(H_2SO_4)/\partial T^2$ to be obtained in terms of individual contributions of the quantities on the right-hand side of eq 30. It was found that the contribution of $\partial^2(mSO_4^{-2}/m)/\partial T^2 \cdot (V^{\phi}-(2H^+, SO_4^{-2}) - V^{\phi}(H^+, HSO_4^{-1}))$ to the extrapolated apparent molar volumes in eq 16 was the major cause of the problem, which is reasonable since the second differential of the degree of dissociation of HSO_4^{--} with respect to temperature is poorly constrained by data and unlikely to be accurately predicted by the model.

Table 7. Sources of Data for Aqueous Na₂SO₄

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | ref |
|---------------|--------------------------|--------------|-----------------------|-------------------------------|------|------|-----|
| 1-24 | wt % | 0-100 | ρ | $g mL^{-1}$ (old) | yes | Ь | 2 |
| 0-67 | wt % | 25 | ρ | see note | yes | с | 25 |
| 8.96-18.20 | wt % | 25 | $ ho(25,4^\circ)$ | | no | | 131 |
| 0.0239-0.196 | $mol L^{-1}$ | 25 | V^{ϕ} | $mL mol^{-1}$ | yes | | 163 |
| 0.88-21.8 | wt % | 25 | $ ho(25, 4^\circ)$ | | no | | 186 |
| 0.0005-0.0713 | $mol L^{-1}$ | 25 | rel dens | | no | d | 187 |
| 0.0-2.8757 | $mol kg^{-1}$ | 25 | ρ | $g mL^{-1}$ (old) | yes | е | 120 |
| 0.02-0.30 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | f | 188 |
| 0.10-1.9641 | $mol kg^{-1}$ | 25 | ρ | $g mL^{-1}$ (old) | no | g | 189 |
| 0.010-1.89 | $mol kg^{-1}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 190 |
| 0.00458-0.733 | $mol L^{-1}$ | 25 | see note | | yes | h | 191 |
| 0.0352-3.39 | $mol kg^{-1}$ | 40 | ρ | $\rm g~cm^{-3}$ | yes | | 192 |
| 0.80-5.37 | $mol L^{-1}$ | 25-60 | ρ | $g mL^{-1}$ (old) | yes | | 193 |
| 0.010-0.15 | $mol kg^{-1}$ | 25-175 | ρ | $\rm g~cm^{-3}$ | no | | 194 |
| 0.3316-3.477 | g/100 g H ₂ O | 0.7-101.9 | ρ | $\rm g~cm^{-3}$ | yes | i | 121 |
| 3.365-3.414 | g/100 g H ₂ O | 31.94-38.31 | ρ | $\rm g~cm^{-3}$ | yes | i | 122 |
| 1.3334 | $mol kg^{-1}$ | 0-45.26 | ρ | $\mathrm{g}~\mathrm{mL}^{-1}$ | no | | 195 |
| 0.00357-1.005 | $mol kg^{-1}$ | 0, 50 | Δho | $g mL^{-1}$ (old) | yes | j | 67 |
| 0.00259-0.720 | $mol kg^{-1}$ | 0-35 | Δho | $\rm g~cm^{-3}$ | yes | | 196 |
| 0.001-0.140 | $mol L^{-1}$ | 15-40 | rel. dens. | | no | k | 175 |
| 0.050-1.50 | $mol kg^{-1}$ | 15-55 | ρ | $kg m^{-3}$ | no | | 179 |
| 0.0333-1.2026 | $mol kg^{-1}$ | 25-150 | ρ | $\rm g~cm^{-3}$ | yes | | 197 |
| 1.0-28 | wt % | 27.5-37.5 | see note | | yes | 1 | 198 |
| 0.101-2.068 | $mol kg^{-1}$ | 35-85 | Δho | $\rm g~cm^{-3}$ | yes | т | 5 |
| 0.0996-1.00 | $mol kg^{-1}$ | 25 | Δho | $\rm g~cm^{-3}$ | yes | т | 69 |
| 0.052-1.625 | $mol kg^{-1}$ | 15-45 | Δho | $\rm g~cm^{-3}$ | yes | т | 7 |
| 0.1, 0.5, 1.0 | $mol kg^{-1}$ | 5-60 | ρ | $\rm g~cm^{-3}$ | no | | 199 |

^{*a*} $\rho(t, u)$ is the density of the solution at *t* °C relative to that at *u* °C, and $\Delta\rho$ is a density difference (usually relative to that of pure water at the same temperature). ^{*b*} $\rho(t, 4^{\circ})$ is also tabulated for 1.69 and 3.35 wt % solutions for temperatures of 110–140 °C. In this work values from the table of $\rho(t, 4^{\circ})$ attributed to source number 229.5 are given preference over densities in the main table at the same temperatures (25, 30, and 40 °C). Values listed for saturated solutions were also used (see also the note further below). ^c Tang and Munkelwitz²⁵ present only a fitted equation. The value of the density of pure water is given as 0.9971, suggesting units of g mL⁻¹ (old), although this seems unlikely given the date of publication. However, the equation is used here only to obtain densities of supersaturated solutions for which the molality is high enough that the unit used is not significant. ^{*d*} "rel dens" is ρ/ρ_w where ρ_w is the density of pure water at the same temperature. ^{*f*} Densities were generated from Rard and Miller's equation, which was fitted to data from nine sources, including three not listed above: Wendt,¹⁵¹ Urazov and Efimenko,²⁰⁰ and Lee.²⁰¹ From the value of the density of pure water used in Rard and Miller's equation (0.997072 g mL⁻¹) it appears that the older milliliter is used despite the date of their study (1979). ^{*f*} Values were generated from the equation given by the authors (fitted to their own measurements). ^{*s*} Apparent molar volumes also tabulated. ^{*h*} The tabulated quantity is 10⁶ ($\rho(t, 25^{\circ}) - 1$). ^{*i*} These studies of the densities of saturated solutions are the sources of the values listed in the International Critical Tables. ^{*i*} Values of V^{*d*} (in mL (old) mol⁻¹) are also tabulated the same temperature. ^{*i*} Table V of the author lists 10³ $\Delta V/V(25)$, where ΔV is the difference between the solution volume (in mL (old)) at temperature t^{*i*} C^{*i*} and the volume of the same mass of solution at 25

In the calculation of Y(m), for which a reference temperature of 298.15 K was used, we first subtracted the contribution of $\partial^2 (m SO_4^{2^-}/m)/\partial T^2$ above, and then assigned a constant value for all m (-0.991857161974848 \times 10⁻³, equal to the value of the differential at m equal to m^*). The revised function Y(m) was then represented by the following equation which further simplified its variation with molality

$$Y(m) = 1.947789 - 0.60059438m^{0.375}$$
(31)

When applying eq 19, and calculating $V^{\phi}(\text{extr.}, m, T)$ and $V^{\phi}(\text{extr.}, m^*, T)$ using eq 16, it is necessary to remove the effect of the term in $\partial^2(m\text{SO}_4^{-2r}/m)/\partial T^2$, denoted Z(m), by

subtracting the following from each value

$$(Z(m) + 0.9918572 \times 10^{-3})((T^2 + T_r^2)/2 - TT_r)$$
 (32)

where T_r is the reference temperature of 298.15 K. We have represented values of Z(m) for $0 \le m \le m^*$ by a cubic spline, for which the knots and coefficients are listed in Table S8 (Supporting Information). Finally, it is necessary that at 273.15 K the densities and apparent molar volumes calculated using the modified method of extrapolation described here be continuous with those calculated using the Pitzer ion interaction model in part 2 of this work. For this we add a small delta term $\Delta(\sqrt{m})$, which is the same at all temperatures, so that the extrapolated and



Figure 32. Measured and fitted apparent molar volumes of Na₂SO₄ in aqueous solution at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against Na₂SO₄ concentration ($\sqrt{wt \%}$). Key: dot, International Critical Tables; plus, Tang;²⁵ cross, Chen et al.;¹⁹⁶ circle, Gibson;¹⁹⁸ diamond, Korosi and Fabuss;¹⁹⁴ triangle, Millero et al.;⁶⁹ square, Magalhes et al.;²³³ solid inverted triangle, Rard and Miller;¹²⁰ star, Lo Surdo et al.;⁷ solid square, Geffken and Price;¹⁹¹ solid square, melt (this work). The solid vertical arrow indicates a solution saturated with respect to Na₂SO₄(s), and the arrow indicates the limit of concentration attainable in small droplets at this temperature (the nucleation concentration). (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against Na₂SO₄ concentration ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous Na₂SO₄, plotted against concentration ($\sqrt{wt \%}$). Key: the symbols and vertical arrows have the same meanings as in (a); line, the fitted model. The inset shows the difference between densities calculated using the fitted model and the equation of Tang and Munkelwitz²⁵ (model – Tang values).

adjusted apparent molar volume $V^{\phi}(\text{extr., } m, T)$ for aqueous H_2SO_4 is given by

$$V^{\phi}(\text{extr., } m, T)(\text{adj}) = V^{\phi}(\text{extr., } m, T) - (Z(m) + 0.9918572 \times 10^{-3})((T^2 + T_r^2)/2 - TT_r) + \Delta(m)$$
(33)

The same equation applies for $V^{\phi}(\text{extr.}, m^*, T)$. Values of $\Delta(\sqrt{m})$ have been fitted to a cubic spline, for which the knots and coefficients are listed in Table S8.

How well does this approach work? Figure 29 shows predicted densities of aqueous H_2SO_4 for 1-7 wt % acid, including the temperatures of maximum density listed in the International Critical Tables. There is excellent agreement with the model. Figure 30 extends these calculations to lower temperatures and shows both densities of solutions saturated with respect to ice (concentrations of these solutions were calculated using the model of Clegg and



Figure 33. Densities (ρ) of 22 wt % Na₂SO₄ (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: dot, average of best fit models at 25 °C; square, interpolations based on the measurements of Berkeley, ¹²¹ Dawson and Williams, ¹²² and the International Critical Tables (including the table of densities of saturated solutions); circle, International Critical Tables; solid square, interpolated from the measurements of Gibson; ¹⁹⁸ plus, from best fit Pitzer model section (6.5.2); line, the fitted equation. (b) The difference between measured and fitted densities ($\Delta\rho$, observed – calculated). Key: the symbols have the same meanings as in (a).



Figure 34. Apparent molar volumes of Na₂SO₄ at infinite dilution $(V^{\phi\infty})$, as a function of temperature (*t*). Key: square, determined in this work; solid line, fitted equation (eq 35); dashed line, equation of Krumgalz et al.;¹⁵ dash-dot line, equation of Lo Surdo et al.;⁷ dotted line, equation of Connaughton et al.⁵

Brimblecombe^{37,119}) and of supercooled solutions at the homogeneous nucleation limit for small droplets.⁵⁶ The predicted densities vary in a consistent way from water-like behavior at low concentrations to the nearly linear dependence upon temperature that has been measured in more concentrated solutions.



Figure 35. Molalities (m) and temperatures (t) for which measurements of apparent molar volumes or densities of aqueous Na₂SO₄ are available (excluding the data of Tang and Munkelwitz²⁵ for supersaturated solutions). Each circle represents a measurement. The horizontal dashed line marks the reference concentration.

6.4.6. All Concentrations and Temperatures. By combining the results described above with those from part 2 of this work, it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and to estimate them for lower temperatures including solutions supersaturated with respect to the solid hydrates; see Figure 31.



Figure 36. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of Na₂SO₄ from 0 to 35 °C, plotted against the square root of molality (\sqrt{m}). All apparent molar volumes are offset by an amount ($t/t^{\circ} - 25$)/2.5 cm³ mol⁻¹, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure. Key: dot, International Critical Tables; solid triangle, Dunn;¹⁶³ inverted triangle, Chen et al.;¹⁹⁶ star, Gibson;¹⁹⁸ solid square, Korosi and Fabuss;¹⁹⁷ plus, Millero et al.;⁶⁹ cross, Magalhes et al.;¹⁹⁰ diamond, Rard and Miller;¹²⁰ square, Lo Surdo et al.;⁷ solid diamond, Geffcken and Price;¹⁹¹ inverted solid triangle, Millero and Knox;⁶⁷ circle, Connaughton et al.;⁵ lines, the fitted model (the dotted lines are for 27 and 32.5 °C). (b) Measured and fitted apparent molar volumes (V^{ϕ}) of Na₂SO₄ from 37.5 to 75 °C, plotted against the square root of molality (\sqrt{m}). Values are offset as described for (a) above. Symbols and lines have the same meanings as in (a) with the exceptions of: plus, Fleischmann and Mersmann;¹⁹² bow tie, Ezrokhi.¹⁹³ (c) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against the square root of molality (\sqrt{m}). Key: the symbols have the same meanings as in (a) and (b); dotted lines, the effect of a ±0.00005 g cm⁻³ error in the measured density. (d) Densities (ρ) from 0 to 60 °C generated using the fitted model, plotted against the square root of molality (\sqrt{m}). (Densities for 20 and 40 °C are shown as dotted lines.)

6.5. Na₂SO₄. Sources of densities are listed in Table 7. The salt is quite insoluble (about 1.95 mol kg⁻¹ at 25 °C, as Na₂SO₄ · 10H₂O_(cr)) so that data are mostly limited to dilute solutions. Nonetheless, it is possible to obtain bulk aqueous solutions that are supersaturated with respect to the salt so that, for example, the fitted equation of Rard and Miller¹²⁰ is stated as being valid to 2.8757 mol kg⁻¹ at 25 °C and accurate to ±0.01% in ρ .

The International Critical Tables lists evaluated densities from 0 to 100 °C, and for maximum concentrations of 16–24 wt % salt. Additional values of $\rho(18.08^\circ, 4^\circ)$ and $\rho(25^\circ, 4^\circ)$ (densities relative to that of water at 4 °C) are also given, as well as densities of saturated aqueous solutions based on the work of Berkeley¹²¹ and Dawson and Williams¹²² (also listed in Table 7). Lo Surdo et al.⁷ have measured and fitted densities and apparent molar

volumes of aqueous Na_2SO_4 from 0 to 1.5 mol kg⁻¹ and from 0 to 50 °C. Later, Connaughton et al.⁵ made further measurements, extending to 95 °C, and fitted a Pitzer ion interaction model to the results. This model is valid from 0 to 100 °C and to



Figure 37. Differences between apparent molar volumes of Na₂SO₄ (ΔV^{ϕ}) calculated using the Pitzer model developed in this work and that of Connaughton et al.,⁵ as a function of the square root of molality (\sqrt{m}). Key: lines, differences (this study – values from the model of Connaughton et al.) at temperatures from 0 to 60 °C as indicated on the plot.

1.6 mol kg⁻¹. Tang and Munkelwitz²⁵ have determined densities of supersaturated aqueous Na₂SO₄ at 25 °C to a maximum concentration of 67 wt % (14.3 mol kg⁻¹). Finally, we note that Ellis¹²³ has measured densities of aqueous Na₂SO₄ from 50 to 200 °C at 20 atm pressure and calculated apparent molar volumes from the data.

6.5.1. Aqueous Solutions at 25 °C. Lo Surdo et al.⁷ quote values of the apparent molar volume of Na₂SO₄ at infinite dilution ($V^{\phi\infty}$ (Na₂SO₄)) ranging from 11.56 to 11.76 cm³ mol⁻¹ at 25 °C, and themselves obtained 11.72 cm³ mol⁻¹. The model of Connaughton et al.⁵ yields a value of $V^{\phi\infty}$ (Na₂SO₄) equal to 11.48 cm³ mol⁻¹ whereas Krumgalz et al.,¹⁵ who also used a Pitzer model, obtained 11.776 cm³ mol⁻¹. Taking Hovey and Hepler's¹⁰⁷ recommended $V^{\phi\infty}$ (2H⁺, SO₄²⁻) of 14.20 cm³ mol⁻¹ and a $V^{\phi\infty}$ (Na⁺) of -1.21 (ref 101) or -1.20 (ref 41) cm³ mol⁻¹ yields $V^{\phi\infty}$ (Na₂SO₄) equal to 11.8 or 11.78 cm³ mol⁻¹, respectively. In this study we have adopted $V^{\phi\infty}$ (Na₂SO₄) equal to 11.78 cm³ mol⁻¹.

The equation for extrapolated melt densities in Table 1 gives 2.539 g cm⁻³ at 25 °C. The equation of Tang and Munkelwitz,²⁵ when extrapolated from its upper limit of 67 to 100 wt % yields 2.4317 g cm⁻³. Given the large amount of extrapolation, and the absence of other information, we have adopted melt densities from the equation in Table 1 for use in this study:

$$\rho(100\%) = 2.70 - (5.399 \times 10^{-4})T \tag{34}$$

where T(K) is temperature.

Apparent molar volumes at 25 °C obtained from sources listed in Table 7 were fitted over the entire concentration range using eq 10. Values calculated from the equation of Rard and Miller¹²⁰ were included in the fit (at a reduced weight).



Figure 38. (a) Measured and fitted densities (ρ) of aqueous Na₂SO₄ at high concentrations, plotted against the square root of molality (\sqrt{m}). Key: solid square, saturated solutions (based on the measurements of Berkeley,¹²¹ Dawson and Williams,¹²² and the densities of saturated solutions listed in the International Critical Tables); circle and dot, International Critical Tables; other symbols, interpolated densities based upon the model of Connaughton et al.,⁵ the Pitzer model developed in this study, and data for saturated solutions noted above; lines, the fitted equation. The temperature (°C) corresponding to each set of data is indicated on the plot, which displays only a representative selection of the data fitted. (b) The difference between measured and fitted densities ($\Delta\rho$, observed – calculated). Key: solid square, saturated solutions (as in (a)); dot, International Critical Tables; plus, interpolated densities (all fitted data) based upon the model of Connaughton et al.,⁵ the Pitzer model developed in this study, and data for saturated solutions.

Results are shown in Figure 32, and the fitted parameters are listed in Table S3 (Supporting Information). The fitted equation represents most measured apparent molar volumes to within about ± 0.05 cm³ mol⁻¹ for concentrations below saturation and also agrees with the results of Tang and Munkelwitz²⁵ satisfactorily.

6.5.2. Reference Concentration. A reference concentration of 22 wt % was chosen, which is just below saturation at $25 \,^{\circ}$ C and at



Figure 39. Calculated densities from 0 to 100 wt % Na_2SO_4 as a function of temperature (*t*). Dotted lines show densities at intermediate concentrations (10, 30, 50, 70, and 90 wt %).

the upper concentration limit of the data at most other temperatures. Values of the density over a 0-100 °C range were obtained from several sources: from our own best fit Pitzer model described in the next section; by interpolation between densities of saturated solutions^{2,121,122} and model calculated values up to 1.6 mol kg⁻¹; and some values from other studies (also interpolated at 22 wt %). The data were fitted using eq 13 (see Figure 33), and the coefficients are listed in Table S2 (Supporting Information).

6.5.3. Aqueous Solutions above 0 °C. At 0 °C the equations of Lo Surdo et al.⁷ and of Connaughton et al.⁵ yield values of $V^{\phi\infty}(Na_2SO_4)$ that differ by 0.1 cm³ mol⁻¹, and at 50 °C the difference is 0.4 cm³ mol⁻¹. Krumgalz et al.¹⁵ obtained a value at 50 °C that is greater than that of Connaughton et al. by 0.59 cm³ mol⁻¹. Because of these disagreements we fitted apparent molar volumes from the studies listed in Table 7 using the Pitzer equation (eq 8) to obtain individual values of $V^{\phi\infty}(Na_2SO_4)$ at nine temperatures from 30 to 75 °C. These are compared with the other estimates noted above in the caption to Figure 34. For use in this study we fixed $V^{\phi\infty}(Na_2SO_4)$ at 25 °C to the previously selected value of 11.78 cm³ mol⁻¹ and then fitted our own values of $V^{\phi\infty}(Na_2SO_4)$ and those of Lo Surdo et al.⁷ and Connaughton et al.⁵ The following equation, valid from 0 to 75 °C, was obtained

$$V^{\phi \infty}(\text{Na}_2\text{SO}_4) = 28746.8530 + 6.802415T$$

- 4886.246974 ln(T) - (8.715969 × 10⁵)/T (35)

were *T* (K) is temperature. Fitted values are shown in Figure 34 and agree with the equation of Connaughton et al.⁵ to within (+0.15, -0.3) cm³ mol⁻¹. (Note that we have used their "Fix" equation, which is their preferred result.)

Figure 35 shows the (t, m) values of all the data for sources listed in Table 7, up to a maximum temperature of 80 °C. All

| | 1 | (1 /2- 1 | | | | | |
|---------------|------------------------------------|---------------------------------|-----------------------|-------------------------------|------|------|-----------------------------|
| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
| 1-50 | wt % | 0-100 | ρ | $g m L^{-1}$ (old) | yes | Ь | 2 |
| 0-78 | wt% | 25 | ρ | $\rm g~cm^{-3}$ | yes | с | 25 |
| 0.5-4.0 | $mol kg^{-1}$ | 25 | ρ | $\mathrm{g}~\mathrm{cm}^{-3}$ | yes | | 126 |
| 0.0296-4.0365 | mol dm ⁻³ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 127 |
| 1-50 | wt % | 15 | $ ho(t, 4^\circ)$ | | no | | 44 (Lunge and Kohler, 1912) |
| 10.215-38.825 | wt % | 15 | $ ho(t, 4^\circ)$ | | no | | 44 (Brummer, 1902) |
| 1-50 | wt % | 19 | $ ho(t, 4^\circ)$ | | no | | 44 (Schiff, 1860) |
| 6.46-28.64 | wt % | 19 | $\rho(t, 4^{\circ})$ | | no | | 44 (Cheveneau, 1907) |
| 0.3027-5.8906 | $mol kg^{-1}$ | 10-25 | ρ | $\rm g~cm^{-3}$ | yes | | 129 |
| 4.656 | $mol kg^{-1}$ | 20-40 | ρ | $\rm g~cm^{-3}$ | yes | | 128 |
| 4-50 | wt % | 0-90 | rel vol | | yes | d | 44 (de Lannoy, 1895) |
| 3.34-30.19 | $g\left(100~g~of~H_2O\right)^{-1}$ | 0-30 | rel vol | | yes | е | 124 |
| 20.03, 40.03 | wt % | -10.15 to 24.85 | ρ | $\mathrm{g}~\mathrm{cm}^{-3}$ | yes | | 35 |
| 0.05-5.0 | $mol kg^{-1}$ | 15-55 | ρ | $kg m^{-3}$ | no | f | 179 |
| | | | | | | | |

Table 8. Sources of Data for Aqueous (NH₄)₂SO₄

^{*a*} $\rho(t, u)$ is the density of the solution at t °C relative to that at u °C; see the notes further below regarding rel vol. ^{*b*} Tang and Munkelwitz²⁵ present only a fitted equation. The value of the density of pure water is given as 0.9971, suggesting units of g mL⁻¹ (old), although this seems unlikely given the date of publication. However, the equation is used here only to obtain densities of supersaturated solutions for which the molality is high enough that the unit used is not significant. ^{*c*} There is also a separate table of data for $\rho(16^\circ, 4^\circ)$ for concentrations of 1–5 wt % ^{*d*} Data are solution volumes relative those at 0 °C. We have fitted both the values listed in the compilation of Timmermans⁴⁴ at rounded temperatures and also the original unsmoothed values as described in the text. For the 4 wt % solutions the listed values of rel vol (at rounded temperatures) were replaced by our own estimates from the original data. ^{*c*} Data are solution volumes relative to those at 0 °C. ^{*f*} These data were at first inadvertently omitted. Comparisons with the fitted model for 25 °C, see main text, show large deviations and the data at all temperatures were therefore rejected.



Figure 40. Apparent molar volumes (V^{ϕ}) of $(NH_4)_2SO_4$ at 25 °C, as a function of the square root of molality (\sqrt{m}) . Key: dot, International Critical Tables; cross, Hervello and Sanchez;¹²⁹ solid diamond, Fang et al.;¹²⁸ circle, Albright et al.;¹²⁷ solid triangle, Goldsack and Franchetto;¹²⁶ star, Isono;¹⁷⁹ dotted lines, the effect of a ± 0.00005 g cm⁻³ error in measured density.

studies and data points are included, even those omitted from final fits. It is clear that there are relatively few data above the reference concentration of 22 wt %, and only the measurements of Tang and Munkelwitz²⁵ for concentrations greater than 30 wt %. Although the data are very limited, it is our aim to both represent measured densities for subsaturated solutions and provide estimated values for concentrations up to that of the melt. This was done in two stages. First, we used a Pitzer model (eq 8) to fit apparent molar volumes up to and including the reference concentration from 0 to 75 °C. Values calculated using eq 13 (for ρ^*) were included in the fit with an increased weight. We note that Connaughton et al.,⁵ fitting data from 0 to 95 °C, used a total of nine model coefficients (five for β^{0V} , three for β^{1V}). and one for $C^{0 V}$). Our fit uses the same number (three for $\beta^{0 V}$, four for β^{1V} and two for C^{0V}), but in our case C^{0V} varies with temperature. The equations for the Pitzer model parameters are listed in Table S9 (Supporting Information) and measured and fitted apparent molar volumes are shown in Figure 36. Agreement is satisfactory. The difference between our fitted equation and the "Fix" equation of Connaughton et al.⁵ is shown in Figure 37. For temperatures above 0 °C and molalities above 0.05 mol kg⁻¹ the two fitted equations agree to within ± 0.1 cm³ mol⁻¹ or better, similar to the uncertainty in the data.

Predictions of densities for concentrations above 22 wt % were based first of all on the equation for densities of 0-100 wt % Na₂SO₄ at 25 °C section (6.5.1). They were also constrained to yield eq 13 for the reference concentration and eq 34 for the melt. Densities obtained from the following sources were fitted: values for 22–30 wt % obtained by interpolation between our Pitzer model fit described above and densities of saturated solutions,^{2,121,122} measurements for the saturated solutions themselves, and values from our fitted Pitzer model and the International Critical Tables for concentrations from 17 to 22 wt %. The data for these relatively low concentrations were included in order to obtain a fit that reproduces the trends in the variation of density with respect to temperature close to the reference concentration. Our equation, which has just two fitted parameters (the others are derived from the equations for the melt and the reference concentration), is given below

$$\rho = \rho(T_{\rm r}) + (T - T_{\rm r})Q_1 + (T^3 - T_{\rm r}^3)Q_2 \qquad (36)$$

where T_r is equal to 298.15 K and

$$\begin{array}{l} Q_1 = -(5.399 \times 10^{-4}) + (0.80541318 \\ \times 10^{-3}) \sqrt{\nu} - 0.00041107238\nu^2 \end{array} \tag{37a}$$

$$Q_2 = -(0.27716993 \times 10^{-8})\nu + (1.3723983 \times 10^{-9})\nu^4 \qquad (37b)$$

In eq 37 the quantity v is equal to (1 - wf)/0.78, where wf is the weight fraction of Na₂SO₄ in solution. The value of the density at the reference temperature of 298.15 K in eq 36 is given by eq 10 with the coefficients listed in Table S3 (Supporting Information). The results of the fit, close to the reference concentration, are shown in Figure 38.

6.5.4. Aqueous Solutions below 0 °C. Equation 36 above can be used to estimate densities of aqueous solutions for concentrations >22 wt % at all temperatures. For more dilute solutions we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to *T* in eq 16 are calculated using eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. The value of m^* is 1.985675 mol kg⁻¹, and the coefficients of eq 18 for Y(m) are given in Table S5 (Supporting Information).

6.5.5. All Concentrations and Temperatures. By combining the results described above it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and for subsaturated solutions and to estimate them for lower temperatures and for supersaturated solutions; see Figure 39.

6.6. (NH₄)₂SO₄. Sources of densities are listed in Table 8. We have found only seven significant studies published after the evaluation in the International Critical Tables, which lists densities from 0 to 50 wt % salt and from 0 to 100 °C. We have included several earlier studies in Table 8, notably the measurements of relative volume by Tammann¹²⁴ and de Lannoy¹²⁵ which are the principal sources of data upon which the evaluation in the International Critical Tables is based. (Data from a total of 21 studies over the period 1860-1946, excluding that of Tammann are also listed in the compilation of Timmermans.⁴⁴) It will be shown below that apparent molar volumes calculated from the densities in the International Critical tables deviate systematically by a small amount from modern data, and have therefore been adjusted in this study. The deviation appears to be caused by the use of inaccurate absolute densities at one or more temperatures (such densities are required in order to use the relative volumes of Tammann and de Lannoy).

6.6.1. Aqueous Solutions at 25 °C. Densities have been measured at this temperature in six of the studies listed in Table 8 in addition to the values listed in the International Critical Tables. They are compared, as apparent molar volumes, in Figure 40 for all concentrations up to that of the saturated solution (approximately 5.8 mol kg⁻¹). It is clear that V^{ϕ} from the International Critical Tables are less than those from other studies, by up to about 0.5 cm³ mol⁻¹ at 1 mol kg⁻¹. Apparent molar volumes from the measurements of Isono¹⁷⁹ deviate systematically from those of other authors, except at the highest concentrations, and are not further considered.



Figure 41. Measured and fitted apparent molar volumes of $(NH_4)_2SO_4$ in aqueous solution at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of $(NH_4)_2SO_4$ weight percent in solution $(\sqrt{wt \%})$. Key: cross, Hervello and Sanchez;¹²⁹ solid diamond, Fang et al.;¹²⁸ circle, Albright et al.;¹²⁷ solid diamond, Goldsack and Franchetto;¹²⁶ plus, Tang and Munkelwitz;²⁵ square, estimated, see text; line, the fitted model. The solid vertical arrow indicates a solution saturated with respect to $(NH_4)_2SO_{4(s)}$, and the arrow indicates the limit of concentration attainable in small droplets at this temperature (the nucleation concentration). (b) The difference between measured and fitted apparent molar volumes $(\Delta V^{\phi}, \text{observed} - \text{calculated})$, plotted against the square root of $(NH_4)_2SO_4$ weight percent in solution $(\sqrt{wt \%})$. Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous $(NH_4)_2SO_4$, plotted against the square root of $(NH_4)_2SO_4$ weight percent in solution $(\sqrt{wt \%})$. Key: the same meanings as in (a); line, the fitted model. The inset shows the difference between densities calculated using the fitted model and the equation of Tang and Munkelwitz²⁵ (model – Tang values).

The apparent molar volume at infinite dilution, $V^{\phi\infty}$, is not well constrained by the data in Figure 40 which are increasingly

scattered in dilute solutions because the effects of errors in the measured density have a larger effect on V^{ϕ} . The value of $V^{\phi\infty}$



Figure 42. Densities (ρ) of 40 wt % (NH₄)₂SO₄ (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: circle, International Critical Tables; dot, Semmler et al.;³⁵ plus, calculated using the best fit model of apparent molar volumes developed in this work; line, the fitted equation. (b) The difference between measured and fitted densities ($\Delta\rho$, observed – calculated). Key: the symbols have the same meanings as in (a).

was therefore calculated as $(V^{\phi\infty}(Na_2SO_4) - 2V^{\phi\infty}(NaCl) + 2V^{\phi\infty}(NH_4Cl))$ and $(V^{\phi\infty}(Na_2SO_4) - 2V^{\phi\infty}(NaNO_3) + 2V^{\phi\infty}(NH_4NO_3))$. Connaughton et al.⁵ obtained 11.49 cm² mol⁻¹ for $V^{\phi\infty}(Na_2SO_4)$ at 25 °C, whereas Lo Surdo et al.⁷ had earlier found 11.72 cm³ mol⁻¹. Krumgalz et al.,¹⁵ fitting a wider range of data, determined $V^{\phi\infty}(Na_2SO_4)$ equal to 11.776 cm³ mol⁻¹. Both Connaughton et al. and Krumgalz et al. used Pitzer models (eqs 8 and 9a) to represent apparent molar volume data over a range of concentrations and temperatures. We adopted $V^{\phi\infty}(Na_2SO_4)$ equal to 11.72 cm³ mol⁻¹, as used in our fits to data for $Na_2SO_{4(aq)}$ above. A range of values of $V^{\phi\infty}$ for the other salts were taken from the literature ^{41,61} and from our own fits in this study. Estimated $V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4)$ from the two relationships noted above varied from 49.88 to 50.48 cm³ mol⁻¹ at 25 °C. These compare well with $50.0 \text{ cm}^3 \text{ mol}^{-1}$ based upon values for the individual ions cited by Hovey and Hepler¹⁰⁷ ($V^{\phi}(H_2SO_4)$) equal to 14.2 cm³ mol⁻¹) and recommended by Roux et al.⁴¹ $(V^{\phi\infty}(\text{NH}_4^+) \text{ equal to } 17.9 \text{ cm}^3 \text{ mol}^{-1})$. For use in this study we selected a value of 50.25 cm³ mol⁻¹ for $V^{\phi\infty}((\text{NH}_4)_2\text{SO}_4)$. Tang and Munkelwitz²⁵ have measured densities of super-

saturated solutions of $(NH_4)_2SO_4$ using an electrodynamic balance up to a maximum concentration of 78 wt % salt. Their fitted equation extrapolates to a molar volume of 85.3 cm³ mol⁻ at 100 wt %, about 14% higher than the molar volume of the solid. Density differences plotted in Figure 2 for the alkali metal sulfates (based upon the extrapolation of densities of high temperature melts) range from about 1% to 7%, suggesting that the hypothetical $(NH_4)_2SO_4$ melt may have a molar volume lower than 85.3 cm³ mol⁻¹ at 25 °C. Shirai and Ishibashi¹⁰³ have measured specific volumes of liquid NH₄NO₃, and NH₄NO₃ + $(NH_4)_2$ -SO₄ mixtures containing 2.5-7.5 wt % (NH₄)₂SO₄, from 180 to 200 °C. Assuming that the total liquid volume is simply the sum of the molar volumes of the two pure salts yields estimated molar volumes of $(NH_4)_2SO_4$ ranging from 82.5 to at least 85.0 cm³ mol⁻¹ at these temperatures. We compared apparent molar volumes of $(NH_4)_2SO_4$ with those of NH_4HSO_4 and $(NH_4)_2H(SO_4)_2$ for supersaturated solutions, and found that the two reciprocals $V^{\phi}((NH_4)_2SO_4)/$

 $V^{\phi}(\mathrm{NH_4HSO_4})$ and $V^{\phi}((\mathrm{NH_4})_2\mathrm{SO_4})/V^{\phi}((\mathrm{NH_4})_3\mathrm{H(SO_4)_2})$ varied approximately linearly with the square root of solute weight fractions. Extrapolating these relationships to 100 wt % of solute yielded estimates of the molar volume of the hypothetical liquid (NH₄)₂SO₄ of 85.5–85.9 cm³ mol⁻¹.

Measured apparent molar volumes at 25 °C were fitted over the entire concentration range using eq 10. Results are shown in Figure 41, and the fitted coefficients are listed in Table S3 (Supporting Information). The data of Goldsack and Franchetto,¹²⁶ Albright et al.,¹²⁷ Fang et al.,¹²⁸ Hervello and Sanchez,¹²⁹ and Tang and Munkelwitz²⁵ were given nonzero weights in the fits, as were values obtained using the empirical relationships with apparent molar volumes of NH₄HSO₄ and (NH₄)₃H(SO₄)₂ noted above.

In part 2 of this work we have fitted the same data, up to a maximum molality of 8 mol kg⁻¹, to the Pitzer expression given by eq 8 in order to create the model of apparent molar volumes of $H^+-NH_4^+-HSO_4^{--}-SO_4^{2-}$ aqueous solutions that is also described there.

6.6.2. Reference Concentration. A reference concentration of 5.04538 mol kg⁻¹ (40 wt %) was chosen for $(NH_4)_2SO_4$, because Semmler et al.³⁵ have measured densities for this concentration (actually 40.03 wt %) to 253 K. These data were combined with values from the International Critical Tables, which had been adjusted as described in section 6.6.3 and given a weight of 0.5, and densities from our own fitted model (see below). They are represented by eq 13, with coefficients listed in Table S2 (Supporting Information). The data and fitted equation are shown in Figure 42.

6.6.3. Aqueous Solutions above 0 °C. It was shown in Figure 40 that the densities listed in the International Critical Tables, which are based mainly upon relative volume data, yield lower apparent molar volumes than modern measurements at 25 °C. We have made comparisons at other temperatures by using our best fit apparent molar volumes at 25 °C together with the relative volumes of Tammann¹²⁴ and de Lannoy⁴⁴ to generate apparent molar volumes from 0 to 80 °C to compare with values in the International Critical Tables. As expected, the same deviations shown in Figure 40 for 25 °C are apparent at all



Figure 43. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of $(NH_4)_2SO_4$ from 0 to 60 °C, plotted against the square root of $(NH_4)_2SO_4$ concentration $(\sqrt{wt })$. All apparent molar volumes are offset by an amount $(t/t^{\circ} - 20)/5$ cm³ mol⁻¹, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure. Key: dot, International Critical Tables (adjusted values, see text); solid square, the melt (estimated in this work); star, Semmler et al. ³⁵ (above 273.15 K only); square, Hervello and Sanchez,¹²⁹ lines, the fitted model. Note that the dashed line is for a temperature of 15 °C. (b) Measured and fitted apparent molar volumes (V^{ϕ}) of $(NH_4)_2SO_4$ at fixed concentrations, plotted against temperature (°C). Key: cross, Fang et al;¹²⁸ triangle, Tammann¹²⁴ (referenced to V^{ϕ} at 25 °C calculated using the fitted equation determined in this work); inverted solid triangle, de Lannoy⁴⁴ (referenced as described for Tammann); solid lines, fitted model for the indicated wt % of $(NH_4)_2SO_4$; dashed lines, fitted model for $(NH_4)_2SO_4$ molalities of 0.2528 (shown as 0.25), 0.5131 (0.51), 1.0595 (1.06), and 2.2847 (2.28) mol kg⁻¹. (c) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated) as a function of $(NH_2SO_4$ concentration (\sqrt{wt}). Key: the symbols have the same meanings as in (a) and (b). (d) Densities (ρ) from 0 to 60 °C generated using the fitted model, as a function of $(NH_4)_2SO_4$ concentration (\sqrt{wt} %). (Densities for 20 and 40 °C are shows as dotted lines.)

temperatures. In order to use the International Critical Tables data in fits covering a range of temperatures, we corrected the listed densities as follows. First, for 4–30 wt % concentrations at all temperatures we calculated $V^{\phi}((NH_4)_2SO_4)$ from the densities in the International Critical Tables. Second, the difference between our best fit value at 25 °C and that obtained from the International Critical Tables (also at 25 °C) at each concentration was added to the corresponding $V^{\phi}((NH_4)_2SO_4)$ at the temperature of interest.

(Note that values for 1 and 2 wt % solutions at all temperatures were ignored as their accuracy was poor. They were not included in our fits.) Finally, the resulting corrected $V^{\phi}((NH_4)_2SO_4)$ were checked against values calculated directly from our best fit at 25 °C and the relative volumes of Tammann¹²⁴ and de Lannoy.⁴⁴ There was excellent agreement at all temperatures. It is these corrected $V^{\phi}((NH_4)_2SO_4)$ that have been used in the fits described in this section.



Figure 44. (a) Measured and fitted densities (ρ) of aqueous (NH₄)₂SO₄ at high concentrations, plotted against temperature (t). Key: dot (7.5677 mol kg⁻¹), de Lannoy;⁴⁴ square (8.1716 mol kg⁻¹), Hervello and Sanchez;¹²⁹ star (40.03 wt %), Semmler et al.³⁵ (b) The difference between measured and fitted densities ($\Delta\rho$, observed – calculated), as a function of the weight percent of (NH₄)₂SO₄ in solution. The symbols have the same meanings as in (a), with the addition of: plus, generated using the fitted model of V^{ϕ} developed in this work.



Figure 45. Calculated densities of 0 to 100 wt % $(NH_4)_2SO_4$ as a function of temperature (*t*). Dotted lines show densities at intermediate concentrations (10, 30, 50, 70, and 90 wt %).

Next, values of the apparent molar volume at infinite dilution, $V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4)$, were obtained. Two approaches were used: first, by determining the variation of $V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4)$ with temperature as a part of the fit and, second, estimating it independently as the quantity $(V^{\phi\infty}(\mathrm{Na}_2\mathrm{SO}_4) - 2V^{\phi\infty}(\mathrm{NaCl}) + 2V^{\phi\infty}(\mathrm{NH}_4\mathrm{Cl}))$. For this approach values of $V^{\phi\infty}(\mathrm{NaCl})$ were calculated using the equation of state of Archer⁶¹ which was adopted as the reference study for aqueous NaCl (section 6.2), and values of $V^{\phi\infty}(Na_2SO_4)$ were taken from our own results for this salt (section 6.5). Estimates of $V^{\phi\infty}(NH_4Cl)$ were obtained from our own fits to apparent molar volume data at individual temperatures, and values from the literature, as discussed in section 6.3.3. The resulting estimates of $V^{\phi\infty}((NH_4)_2SO_4)$ from the relationship above were then fitted to an equation, as a function of temperature, in which the value at 25 °C was fixed to the 50.25 cm³ mol⁻¹ determined above.

Densities of the hypothetical melt at different temperatures are also needed. We took a value of 85.623 cm³ mol⁻¹ for the melt at 25 °C, which was obtained from the extrapolations involving NH₄HSO₄ and (NH₄)₃H(SO₄)₂ described above, and assumed a linear relationship with temperature such that the value of ρ (melt) at 0 K is equal to that of the solid salt at 25 °C (1.77 g cm⁻³). This yields the equation

$$\rho(100\%) = 1.77 - (7.60427 \times 10^{-4})T \tag{38}$$

Next, apparent molar volumes obtained from the sources listed in Table 8, including the estimated values for the melt, were fitted for 0-100 wt % salt and from 0 to 60 °C. In the fitting equation the coefficients for 25 °C were fixed to the values listed in Table S3 (Supporting Information), and only terms in the square root and square of weight fraction (in addition to the Debye-Hückel term and $V^{\phi\infty}((NH_4)_2SO_4)$ were allowed to vary with temperature. The data included in the fit are those of Tammann,¹²⁴ de Lannoy,⁴⁴ Fang et al.,¹²⁸ Hervello and Sanchez,¹²⁹ and Semmler et al.³⁵ and adjusted values from the International Critical Tables (given a low weight). Other sources listed in Table 8 were not used. There are no measurements for solutions supersaturated with respect to the solid salt at temperatures other than 25 °C (the work of Tang and Munkelwitz²⁵). Consequently the fits, which predict monotonically varying V^{ϕ} with respect to temperature from the upper limit of the International Critical Tables data (50 wt %) to 100 wt % are only estimates in this region of composition.

Table 9. Sources of Data for Aqueous HNO₃

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
|-----------------|---------------------------|--------------|-----------------------|--|----------|------|---------------------------------|
| 1-100 | wt % | 0-100 | ρ | $g m L^{-1}$ (old) | yes | | 2 |
| 0.04025-0.15224 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 mol^{-1}$ | yes | | 137 |
| 0.987-11.92 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | $\rho(t, 4^{\circ})$ | | yes | | 130 |
| 1.835-100 | mol % | 25 | $\rho(t, 4^{\circ})$ | | yes | | 131 |
| 2.28-79.83 | wt % | 20 | $\rho(t, 4^{\circ})$ | | no | b, c | 44 (Hantzsch and Durigen, 1928) |
| 0.00574-5.806 | $mol \ L^{-1}$ | 20 | $\rho(t, 4^{\circ})$ | | no | Ь | 44 (Tollert, 1939) |
| 4.72-39.28 | wt % | 20 | $ ho(t, 4^\circ)$ | | no | Ь | 44 (Guillaume, 1946) |
| 1.06-99.81 | wt % | 15 | V^* | ${\rm cm}^3~{\rm mol}^{-1}~{\rm soln}$ | no | | 202 |
| 89.63-100 | wt % | 0-40 | ρ | $\rm g~cm^{-3}$ | yes | | 141 |
| 10-100 | wt % | -40 to 149 | ρ | $lb ft^{-3}$ | yes | | 132 |
| 0.0901-3.302 | $mol kg^{-1}$ | 20-30 | ρ | $\rm g~cm^{-3}$ | yes | | 139 |
| 0.116-1.1115 | $mol kg^{-1}$ | 10-55 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 40 |
| 0.01657-0.5498 | $mol kg^{-1}$ | 5 - 55 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | d | 136 |
| 7.82-99.5 | wt % | 0-30 | $ ho(t, 4^\circ)$ | no | | с | 44 (Chanukvadze, 1947) |
| 25-89.4 | wt % | -15 to 30 | ΔV | $\mathrm{cm}^3 \mathrm{g}^{-1}$ | see note | b, e | 44 (Kuster and Kremen, 1904) |
| | | | | | | | |

^{*a*} $\rho(t, u)$ is the density of the solution at $t \,^{\circ}$ C relative to that at $u \,^{\circ}$ C, V^* is the volume per mole of total solution, and ΔV is the difference in solution volume caused by a temperature change of 15 °C (see also note °). ^{*b*} Tabulated by Timmermans.^{44 c} Timmermans notes in his introduction that tabulated densities are $\rho(t, 4^{\circ})$ unless otherwise stated, but the pattern of residuals of the data of Hantzsch and Durigen, when compared to others, suggests either this is not the unit (or that there is a systematic error in the data). ^{*d*} Experiments were carried out at a pressure of 0.35 MPa. ^{*e*} Volume differences for changes in temperature of -15 to 0 °C, 0-15 °C, and 15-30 °C. Only a single value was used in this study (a density at -15 °C estimated for the reference concentration).



Figure 46. Apparent molar volumes (V^{ϕ}) of HNO₃ in aqueous solution at 25 °C, with the Debye–Hückel term in eq 8 (DH) subtracted, plotted against HNO₃ molality. Key: dot, International Critical Tables; solid triangle, Partanen et al.;¹³⁹ solid diamond, Enea et al.;¹³⁷ circle, Hovey et al.;¹³⁸ cross, Ingham;¹³⁰ square, Luhdemann;¹³¹ line, best fit equation (this work).

Two alternative fits using eq 10 were investigated: one in which $V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4)$ values were fixed to the estimates obtained from values of other salts, and described above, and a second one in which the variation of $V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4)$ with temperature was determined as a part of the fit. There was found to be very little difference between the two results, even for $V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4)$ itself. The second fit was accepted as the final result, and parameters are listed in Table S3 (Supporting

Information). The equation for the apparent molar volume of $(NH_4)_2SO_4$ at infinite dilution is given below

$$V^{\phi\infty}((\mathrm{NH}_4)_2\mathrm{SO}_4) = 50.25 - (6.4647047 \times 10^5)(1/T - 1/T_r) -(3.5742394 \times 10^3) \ln(T/T_r) + 4.8315121(T - T_r) (39)$$

where T_r is 298.15 K. Measured and calculated values of V^{ϕ} are displayed in Figure 43. The deviation plots suggest that errors and uncertainties for the subsaturated solutions are typically of the order of $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ (increasing to about double that at the lowest concentrations), corresponding to a difference of about 0.00005 g cm⁻³ in ρ at 0.5 mol kg⁻¹ and 0.0004 g cm⁻³ at 4 mol kg⁻¹. *6.6.4. Aqueous Solutions Below 0* °C. Except for Semmler et

6.6.4. Aqueous Solutions Below 0 °C. Except for Semmler et al.³⁵ who measured densities for two concentrations to -20 °C, there are no measured densities below 0 °C. For concentrations greater than or equal to the reference concentration (40 wt %), we use eq 14, which approximately reproduces values from the fit described above (0–60 °C), is constrained to the equations given previously for the densities of the reference concentration and melt, and extrapolates densities for all intermediate concentrations monotonically to very low temperature. The fitted coefficients are listed in Table S6 (Supporting Information), and the results of the fit shown in Figure 44. Equation 14 reproduces values in the 0–60 °C range calculated using eq 10 to within $\pm 1 \times 10^{-3}$ g cm⁻³.

Equation 14 above can be used to estimate densities of aqueous solutions for concentrations >40 wt % at all temperatures. For more dilute solutions we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to T in eq 16 are calculated using eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. The value of m^* is 5.04538 mol kg⁻¹, and the coefficients of eq 18 for Y(m) are given in Table S5 (Supporting Information).

6.6.5. All Concentrations and Temperatures. By combining the results described above, it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and for



Figure 47. Measured and fitted apparent molar volumes of HNO₃ at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of HNO₃ weight percent in solution ($\sqrt{\text{wt }\%}$). Key: dot, International Critical Tables; solid triangle, Partanen et al.;¹³⁹ solid diamond, Enea et al.;¹³⁷ circle, Hovey et al.;¹³⁸ cross, Ingham;¹³⁰ square, Luhdemar;¹³¹ line, the fitted equation. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against the square root of HNO₃ weight percent in solution ($\sqrt{\text{wt }\%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous HNO₃, plotted against the square root of HNO₃ weight percent in solution ($\sqrt{\text{wt }\%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous HNO₃, plotted against the square root of HNO₃ weight percent in solution ($\sqrt{\text{wt }\%}$). Key: the symbols have the same meanings as in (a); line, the fitted model.

subsaturated solutions and to estimate them for lower temperatures and for supersaturated solutions; see Figure 45.

6.7. HNO₃. Sources of data for aqueous HNO₃ are listed in Table 9 and are surprisingly few for such a common electrolyte. At 25 °C there are only two studies,^{130,131} apart from the evaluation in the International Critical Tables, that extend to highly concentrated solutions. A total of 51 sources of data were considered in the evaluation in the International Critical Tables, with results from 10 studies being given high weight. Pure nitric acid is a white fuming liquid at room temperature and contains

a small percentage of water as usually supplied. The acid freezes at -42 °C. The International Critical Tables lists densities for 1-100 wt % acid from 5 to 30 °C, and 1-63 wt % acid at other temperatures between 0 and 100 °C. Sibbitt et al.¹³² tabulate densities over the entire concentration range, including temperatures below 0 °C. However, their own measurements were only for solution compositions close to the pure acid and other values were obtained from the literature or extrapolated. Haase et al.¹³³ tabulate densities to -20 °C, but these appear to be extrapolations from the data in the International Critical Tables. Values



Figure 48. Densities (ρ) of 30 wt % HNO₃ (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: circle, International Critical Tables; dot, Kuster and Kremen;⁴⁴ square, Sibbitt et al.¹³² (not fitted); cross, Haase et al.,¹³³ (not fitted); plus, calculated using the best fit model of apparent molar volumes developed in this work; line, the fitted equation. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated). Key: the symbols have the same meanings as in (a).



Figure 49. Apparent molar volumes of HNO₃ at infinite dilution $(V^{\phi \infty})$, as a function of temperature (t). Key: circle, this work; dot, Zen;¹⁴⁰ solid triangle, Hovey and Hepler;⁴⁰ triangle, Hovey et al.;¹³⁸ diamond, Enea et al.;¹³⁷ star, Millero;¹⁰¹ plus, Partanen et al.¹³⁹ (obtained using a simplified extrapolation to infinite dilution); solid line, eq 40 in this study; dotted line, Patterson and Woolley.¹³⁶

given by Haase et al.¹³⁴ and by Davis and DeBruin¹³⁵ at 25 °C were similarly obtained. Patterson and Woolley¹³⁶ have determined apparent molar volumes of dilute aqueous HNO₃ from 5 to 95 °C at a pressure of 0.35 MPa. They suggest that the effect of the increase in pressure relative to 0.1 MPa is quite small, citing changes of between 0.04 and -0.02 cm³ mol⁻¹ for aqueous

 $MgCl_2$ below 1 mol kg⁻¹. Their data have therefore been considered in this study.

6.7.1. Aqueous Solutions at 25 °C. Apparent molar volumes of HNO₃ at infinite dilution, $V^{\phi\infty}$ (HNO₃), have been determined by Enea et al.¹³⁷ (29.3 cm³ mol⁻¹), Hovey et al.¹³⁸ (29.32 ± 0.02 cm³ mol⁻¹), and later by Hovey and Hepler⁴⁰ (29.41 ± 0.01 cm³ mol⁻¹) from the same data. Roux et al.,⁴¹ who tabulate single ion $V^{\phi\infty}$, recommend a value of 29.5 cm³ mol⁻¹. Millero,¹⁰¹ in a larger study covering a very wide range of electrolytes, gives 28.99 cm³ mol⁻¹. The equation of Patterson and Woolley¹³⁶ yields $V^{\phi\infty}$ (HNO₃) equal to 29.27 cm³ mol⁻¹ for a pressure of 0.35 MPa.

In Figure 46 we compare the data for low concentrations, plotted as $V^{\phi}(\text{HNO}_3)$ minus the Debye–Hückel limiting law expression from eq 8. Values of $V^{\phi^{\infty}}$ are commonly obtained by a linear extrapolation of this quantity to zero molality. Clearly there is quite a large uncertainty in $V^{\phi^{\infty}}$ due to the systematic differences between the results of the various studies. It is worth noting that there is some dependence of $V^{\phi^{\infty}}$ on the form of Debye–Hückel term used. Hovey et al.¹³⁸ employed $\omega A_V I^{1/2}$ (where ω is a valence factor of unity), whereas Hovey and Hepler⁴⁰ later used a more complex expression (from their eq 7) and obtained a value of $V^{\phi^{\infty}}(\text{HNO}_3)$ almost 0.1 cm³ mol⁻¹ higher than in their earlier study. In our model we have adopted a value of 29.35 cm³ mol⁻¹, which can be tested for consistency with the value of $(V^{\phi^{\infty}}(\text{HCI}) - V^{\phi^{\infty}}(\text{NaCI}) + V^{\phi^{\infty}}(\text{NaNO}_3))$. Taking Archer's value for NaCl,⁶¹ and $V^{\phi^{\infty}}$ for HCl and NaNO₃ obtained in this study yields 29.31 cm⁻³ mol⁻¹ which agrees very well.

Equation 10 was fitted to data from the sources listed in Table 9, yielding the parameters listed in Table S3 (Supporting Information). The data are compared with the fitted equation in Figure 47. This seems to confirm that the densities tabulated in the International Critical Tables for dilute solutions are too low by a small amount (because the plotted ΔV^{ϕ} are negative).



Figure 50. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of HNO₃ from 0 to 60 °C, plotted against the square root of HNO₃ weight percent in solution ($\sqrt{\text{wt }}\%$). All apparent molar volumes are offset by an amount ($t/t^{\circ} - 25$)/2.5 cm³ mol⁻¹, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure, with these exceptions: A, 4.4 °C; B, 15.5 °C; C, 26.7 °C; D, 37.8 °C; and E, 48.9 °C. Key: dot, International Critical Tables; diamond, Sibbitt et al.;¹³² circle, Partanen et al.;¹³⁹ star, Mason et al.;¹⁴¹ lines, the fitted equation. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in the measured density. (c) Densities (ρ) from 0 to 60 °C generated using the fitted model, as a function of HNO₃ concentration ($\sqrt{\text{wt }}\%$). (Densities for 20 and 40 °C are shown as dotted lines.)

6.7.2. The Reference Concentration. Thirty weight percent (6.8013 mol kg⁻¹) was chosen as the reference concentration and values of density from the International Critical Tables (0–100 °C), our fit to densities from all sources (0 to 60 °C), and an interpolated density at -15 °C (based on the results of Kuster and Kremen⁴⁴) were fitted to eq 13. The results are shown in Figure 48 together with densities at low temperature obtained from the work of Sibbitt et al.,¹³² and the extrapolation of Haase et al.,¹³³ which were not included in the fit. The coefficients of the fitted equation are listed in Table S2 (Supporting Information).

6.7.3. Aqueous Solutions Above 0 °C. The densities tabulated in the International Critical Tables, the data of Partanen et al.,¹³⁹ and a small number of other measurements were fitted as apparent molar volumes from 0 to 60 °C and from 0 to 100 wt % acid using eq 10. The other data sets that are available either are very scattered or are in poor agreement with the densities in the International Critical Tables. The apparent molar volumes of Patterson and Wolley¹³⁶ (for 0.35 MPa) were found to be consistently higher, by a small amount, above about 0.13 mol kg⁻¹ (but with very much larger deviations at lower molalities). The



Figure 51. (a) Measured and fitted densities (ρ) of aqueous HNO₃ at high concentrations, plotted against temperature (t). Key: dot, International Critical Tables; diamond, Sibbitt et al.;¹³² star, Mason et al.;¹⁴¹ lines, the fitted equation. For each set of data the wt % concentration of HNO₃ is noted on the plot. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated), as a function of the weight percent of HNO₃ in solution (wt %). Key: the symbols have the same meanings as in (a).



Figure 52. Calculated densities of 0 to 100 wt % HNO₃ as a function of temperature (t). Dotted lines show densities at intermediate concentrations (10, 30, 50, 70, and 90 wt %).

measured apparent molar volumes of Hovey and Hepler⁴⁰ were consistently higher than those from the fitted equation, by $0.2-0.3 \text{ cm}^3 \text{ mol}^{-1}$.

We determined the variation of $V^{\phi\infty}$ (HNO₃) with temperature as a part of the overall fit. The equation for $V^{\phi\infty}$ (HNO₃) was constrained to yield the previously determined 29.35 cm³ mol⁻¹ at 25 °C, and 25.51 cm³ mol⁻¹ at 0 °C. The latter value was taken from Table 1 of Millero, ¹⁰¹ and agrees very well with the value of 25.53 cm³ mol⁻¹ recommended earlier by Zen.¹⁴⁰ (The equation of Patterson and Woolley¹³⁶ for $V^{\phi\infty}$ (HNO₃) at 0.35 MPa yields a value at 25 °C that is 0.08 cm³ mol⁻¹ smaller than our adopted value and is not further considered.)

The fitted model parameters for eq 10 are listed in Table S3 (Supporting Information), and the fitted equation for $V^{\phi\infty}(\text{HNO}_3)$ is

$$V^{\phi\infty}(\text{HNO}_3) = 29.35 - (0.40949695 \times 10^5)(1/T - 1/T_r) - 0.013776168(T^{1.5} - T_r^{1.5})$$
(40)

where T(K) is temperature and T_r is equal to 298.15 K. Values of $V^{\phi\infty}(\text{HNO}_3)$ are plotted in Figure 49 together with predictions from the equation of Hovey and Hepler,⁴⁰ values from Millero,¹⁰¹ and estimates that we obtained by fitting eq 10 to data at individual temperatures. There is reasonable agreement.

The results of the overall fit are shown in Figure 50 and are broadly satisfactory although it is clear from Figure 50b that deviations between the data (mostly from the International Critical Tables) and the fitted equation range from about -0.2 and $0.1 \text{ cm}^3 \text{ mol}^{-1}$ and show some systematic variations with concentration.

6.7.4. Aqueous Solutions Below 0 °C. For concentrations greater than or equal to 30 wt % (the reference concentration), we have fitted the available density data using eq 14, which can be extrapolated to very low temperature. At 30 and 100 wt % the expression is equivalent to those for the reference and pure liquid concentrations established above. The fit is based upon the densities tabulated in the International Critical Tables and those of Sibbitt et al.¹³² and Mason et al.¹⁴¹ The volume difference measurements of Kuster and Kremann,⁴⁴ when converted to densities at -15 °C, do not appear to be generally consistent with the other data (they were low by typically 0.004–0.01 g cm⁻³). The data of Kuster and Kremen were therefore excluded from the fit. The results are shown in Figure 51, and the fitted parameters are listed in Table S6 (Supporting Information).

Table 10. Sources of Data for Aqueous NaNO₃

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
|---------------|---------------------------|--------------|-----------------------|-----------------------|------|------|---------------------------|
| 1-45 | wt % | 0-100 | ρ | $g m L^{-1}$ (old) | yes | | 2 |
| 42.2-67.6 | wt % | 0-119 | $\rho(t, 4^\circ)$ | | yes | Ь | 2 |
| 100 | wt % | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 30 |
| 0.1-2.0 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | ρ | $g m L^{-1}$ (old) | no | с | 203 |
| (30, 40)-98 | wt % | 25 | ρ | see note | yes | d | 25 |
| 0.1-10.83 | $mol kg^{-1}$ | 25 | $\rho(t, 4^{\circ})$ | | yes | | 204 |
| 0.186-4.850 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 205 |
| 0.0717-7.79 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | ρ | $g mL^{-1}$ | yes | | 206 |
| 0.0518-1.00 | $mol kg^{-1}$ | 25 | Δho | $\rm g~cm^{-3}$ | yes | е | 69 |
| 0.5-5.0 | $mol kg^{-1}$ | 25 | ρ | $g mL^{-1}$ | no | | 207 |
| 0.0268-2.116 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | f | 41 |
| 0.05-7.20 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | g | 208 |
| 46 | wt % | 25 | ρ | $g mL^{-1}$ | yes | | 209 |
| 0.049-0.408 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 137 |
| 0.205-8.066 | ${\rm mol}~{\rm dm}^{-3}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 210 |
| 0.197-2.84 | ${\rm mol}~{\rm dm}^{-3}$ | 30 | ρ | $g mL^{-1}$ | yes | | 211 |
| 1.589-42.05 | wt % | 20.1 | ρ | $g mL^{-1}$ (old) | yes | h | 80 |
| 0.6180-10.35 | $mol kg^{-1}$ | 0-300 | ρ | $\rm g~cm^{-3}$ | no | | 142 |
| 0.05-8.0 | $mol kg^{-1}$ | 15-55 | ρ | $kg m^{-3}$ | no | | 179 |
| 0.10-0.892 | $mol kg^{-1}$ | 20-70 | ρ | $kg m^{-3}$ | yes | i | 10 |
| 0.665-6.271 | $mol kg^{-1}$ | 16-88 | ρ | $kg m^{-3}$ | no | i | 11 |
| 0.012-0.232 | ${\rm mol}~{\rm dm}^{-3}$ | 30-50 | ρ | $\rm g~cm^{-3}$ | no | | 212 |
| 1.0 | $ m mol~dm^{-3}$ | 4-60 | ρ | $\rm g~cm^{-3}$ | no | | 213 |
| 0.050-0.457 | $mol kg^{-1}$ | 35-50 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | | 178 |
| 73.0-161.6 | see note | 0.3-90.3 | ρ | $\rm g~cm^{-3}$ | yes | j | 121 |
| 1.95-10.7 | mol % | 20-78.5 | rel vol | | yes | k | 44 (Nicol, 1886 and 1887) |
| 1.0-40.0 | wt % | 0-90 | rel vol | | yes | 1 | 44 (de Lannoy, 1895) |
| 0.008-9.0 | $mol kg^{-1}$ | 15-19.5 | $\rho(t, 4^{\circ})$ | | yes | | 44 (Buchanan, 1912–1913) |
| 0.01509-0.501 | $ m mol~kg^{-1}$ | 5-95 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | no | т | 136 |

^{*a*} $\rho(t, u)$ is the density of the solution at *t* °C relative to that at *u* °C, and rel vol is the solution volume at the experimental temperature divided by the volume occupied by the same mass of solution at a fixed reference temperature. ^{*b*} Values for saturated solutions. ^{*c*} The density of water is given as 0.99707, from which it appears that the experimental temperature is 25 °C and the unit of density is g mL⁻¹ (old) despite Sugden's²⁰³ use of "c.c." as volume unit. ^{*d*} Tang and Munkelwitz²⁵ present only a fitted equation. The value of the density of pure water is given as 0.9971, suggesting units of g mL⁻¹ (old), although this seems unlikely given the date of publication. However, the equation is used here only to obtain densities of supersaturated solutions for which the molality is high enough that uncertainty regarding the exact unit used is not significant. ^{*c*} Values of 10³($\rho - \rho_w$) are tabulated. ^{*f*} From the supplementary data to the paper, held by the Depository of Unpublished Data, CISTI, National Research Council of Canada. ^{*g*} From the equation fitted by Janz et al.²⁰⁸ to his own data and values tabulated in the International Critical Tables. ^{*h*} Assumed unit on the basis of densities of water that are also listed. ^{*i*} Only the composition and temperature ranges for measurements at atmospheric pressure are listed here. The authors also tabulate other sources of data. ^{*j*} The unit of concentration is g per 100 g of water. ^{*k*} Solution volumes relative to those at 20 °C. ^{*l*} Solution volumes relative to that occupied at 0 °C. ^{*m*} Measured at 0.5 MPa.

For concentrations below the reference concentration, we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to *T* in eq 16 are calculated using eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. The value of m^* is 6.8013 mol kg⁻¹, and the coefficients of eq 18 for *Y*(*m*) are given in Table S5 (Supporting Information).

6.7.5. All Concentrations and Temperatures. By combining the results described above, it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 $^{\circ}$ C and for subsaturated solutions, and to estimate them for lower temperatures and for supersaturated solutions; see Figure S2.

6.8. NaNO₃. Sources of data are listed in Table 10, which includes a number of studies upon which the International Critical Tables evaluation was based or which predate it.

Abdulagatov and Aziziv¹¹ also tabulate sources of data for densities of aqueous NaNO₃. Of those that include experiments at 0.1 MPa, all are listed in Table 10 except the study of Mitzner (apparently given by Abdulagatov and Azizov in error), Maksimova (a handbook, and therefore likely to be an evaluation of existing data), and Traktuev (which it was not possible to obtain). Abdulagatov and Aziziv¹¹ reproduce a number of equations used in other studies to correlate densities and apparent molar volumes for NaNO₃ solutions.

The evaluated densities in the International Critical Tables cover the ranges 0-45 wt % and 0-100 °C. A total of 48 sources of data were considered, of which 10 were given "some weight" and five were given "greater weight". The study of de Lannoy,⁴⁴ listed in Table 10, falls into this second category and is therefore one of the primary sources of information upon which the densities in the International Critical Tables are based.



Figure 53. Measured and fitted apparent molar volumes of NaNO₃ at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of NaNO₃ weight percent in solution ($\sqrt{\text{wt} \%}$). Key: dot, International Critical Tables; plus, Tang and Munkelwitz;²⁵ solid square, melt (this work); star, Puchkov and Matashkin,¹⁴² square, Pearce and Hopson,²⁰⁴ triangle, Gellings,²⁰⁵ diamond, Kartzmark,²⁰⁶ solid triangle, Millero et al.;⁶⁹ plus, Nehma et al.;²⁰⁹ solid diamond, Abdulagatov and Azizov;^{10,11} circle, Enea et al.;¹³⁷ inverted triangle, Pena et al.;²¹⁰ line, the fitted equation. The solid vertical arrow indicates a solution saturated with respect to NaNO₃(s). (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against the square root of NaNO₃ weight percent in solution ($\sqrt{\text{wt \%}}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous NaNO₃, plotted against the square root of NaNO₃ weight percent in solution ($\sqrt{\text{wt \%}}$). Key: the same meanings as in (a); line, the fitted model. The inset shows the difference between densities calculated using the fitted model and the equation of Tang²⁵ (model – Tang values).

Tang and Munkelwitz²⁵ have determined densities of supersaturated aqueous NaNO₃ to 98 wt % at 25 °C, and Zelenyuk et al.³⁰ have measured the density of the melt at the same temperature.

6.8.1. Aqueous Solutions at 25 °C. Abdulagatov and Azizov¹¹ obtained $V^{\phi\infty}$ (NaNO₃) equal to 28.15 cm³ mol⁻¹ at 25 °C and 0.1 MPa, and list a total of 22 estimates from other studies at the same temperature and pressure. The standard deviation asso-

ciated with all the values is $\pm 0.25 \text{ cm}^3 \text{ mol}^{-1}$. We have assigned $V^{\phi\infty}(\text{NaNO}_3)$ equal to 28.137 cm³ mol⁻¹, determined as $(V^{\phi\infty}(\text{NaCl}) - V^{\phi\infty}(\text{HCl}) + V^{\phi\infty}(\text{HNO}_3))$ from values obtained elsewhere in this study, which agrees closely with that of Abdulagatov and Azizov.¹¹

We have also adopted the melt density of 2.10 g cm⁻³ determined by Zelenyuk et al.,³⁰ which is consistent with the densities of Tang²⁵ for supersaturated solutions. The refitted



Figure 54. Densities (ρ) of 35 wt % NaNO₃ (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: circle, International Critical Tables; solid triangle, Puchkov and Matashkin;¹⁴² square, Barnes and Scott;⁸⁰ dot, Buchanan;⁴⁴ plus, calculated using the best fit model of apparent molar volumes developed in this work; line, the fitted equation. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated). Key: the symbols have the same meanings as in (a).



Figure 55. Apparent molar volumes of NaNO₃ at infinite dilution $(V^{\phi^{oo}})$, as a function of temperature (*t*). Key: circle, best fit value at 25 °C (this work); dot, Zen;¹⁴⁰ solid triangle, Abdulagatov and Azizov;¹¹ triangle, Roux et al.;⁴¹ diamond, Enea et al.;¹³⁷ star, Millero;¹⁰¹ solid line, eq 42; dotted line, equation of Patterson and Woolley.¹³⁶

densities of the NaNO₃ melt between 583 and 643 K⁵⁸ in Table 1 have a slope of -6.1805×10^{-4} g cm⁻³ K⁻¹. We have adopted this slope, and the measured melt density at 25 °C, to calculate values at all temperatures of interest in this study using the following equation

$$\rho(100\%) = 2.283697 - (6.1805 \times 10^{-4})T$$
(41)

where T (K) is temperature. We note that the equation for the refitted densities in Table 1, from which the above slope was obtained, predicts a melt density of 2.08 g cm⁻³ at 25 °C, very close to the measured value.

Of the studies listed in Table 10 a total of 17 (including the International Critical Tables) provide densities at 25 °C. Data from 12 of these were given nonzero weights, and fitted using eq 10. The parameters of the equation are listed in Table S3 (Supporting Information), and the data and fitted model are shown in Figure 53. There is good agreement between the measurements and the fitted equation over the entire concentration range.

6.8.2. The Reference Concentration. A value of 35 wt % (6.3352 mol kg⁻¹) was chosen, a little greater than that for NaCl (6.0 mol kg⁻¹), and also significantly above the molality for which an anomalous component of the heat capacity of the solution is observed. This gives confidence that solution densities for 35 wt % salt can be extrapolated in a near-linear way to very low temperature.

The data that were fitted to eq 13 include values from the International Critical Tables from 0 to 100 °C, from our own best-fit to data from 0 to 60 °C, and also interpolated values from the studies of Puchkov and Matashkin¹⁴² (0–150 °C), Barnes and Scott,⁸⁰ (293.25 K), and Buchanan⁴⁴ (292.65 K). The results are shown in Figure 54, and fitted coefficients are listed in Table S2 (Supporting Information).

6.8.3. Aqueous Solutions above 0 °C. The density data, especially those for high temperatures, are not sufficiently precise nor are the data from different sources consistent enough to determine $V^{\phi\infty}(\text{NaNO}_3)$ accurately. We have therefore set it equal to $(V^{\phi\infty}(\text{NaCl}) - V^{\phi\infty}(\text{HCl}) + V^{\phi\infty}(\text{HNO}_3))$ at all temperatures (as was done above for 25 °C). Values of $V^{\phi\infty}(\text{NaNO}_3)$ from 0 to 60 °C are given by the following equation

$$V^{\phi \infty}(\text{NaNO}_3) = 28.137 - (1.790506 \times 10^5)(1/T - 1/T_r) - 746.718587 \ln(T/T_r) + 0.658975(T - T_r)$$
(42)



Figure 56. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of NaNO₃ from 0 to 60 °C, plotted against the square root of NaNO₃ weight percent in solution ($\sqrt{wt \%}$). All apparent molar volumes are offset by an amount ($t/t^{\circ} - 25$)/2.5 cm³ mol⁻¹, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure. Key: dot, International Critical Tables; inverted triangle, International Critical Tables (saturated solutions); cross, Berkeley¹²¹ (saturated solutions); circle, Puchkov and Matashkin;¹⁴² plus, Berchiesi et al.;²¹¹ solid square, the melt (estimated in this work); square, Barnes and Scott;⁸⁰ star, Buchanan;⁴⁴ triangle, de Lannoy;⁴⁴ diamond, Nicol;⁴⁴ lines, the fitted model. The dashed line marked "Sat." is for saturated solutions at various temperatures. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated). Key: the symbols have the same meanings as in (a). (c) Densities (ρ) from 0 to 60 °C generated using the fitted model, as a function of NaNO₃ concentration ($\sqrt{wt \%}$). (Densities for 20 and 40 °C are shown as dotted lines.)

where T (K) is temperature and T_r is 298.15 K. Figure 55 displays $V^{\phi\infty}$ (NaNO₃) calculated using eq 42, together with several estimates from other studies.

Next, apparent molar volumes from 0 to 60 $^{\circ}$ C, and for concentrations up to the melt, were fitted using eq 10. Data from a total of 10 of the sources in Table 10 were given nonzero weights, and densities for the melt (eq 41) were included. The fitted parameters are listed in Table S3 (Supporting Information), and the results of the fit are shown in Figure 56.

Apparent molar volumes at the different temperatures have a quite a simple dependence upon concentration, and the fitted equation reproduces the measured V^{ϕ} to within (+0.2, -0.3) cm³ mol⁻¹. The variation of density with temperature is quite small.

6.8.4. Aqueous Solutions Below 0 °C. For molalities greater than or equal to the reference concentration, we have fitted eq 14 to the available data plus densities obtained from the 0 to 100 wt % fit above. This equation, which can be extrapolated to



Figure 57. (a) Measured and fitted densities (ρ) of aqueous NaNO₃ at high concentrations, plotted against temperature (t). For each set of data the concentration (in wt %) is noted on the plot. Only a subset of the measurements is shown, and does not include values generated from the fitted model of V^{ϕ} developed in this study. Key: dot, International Critical Tables; inverted triangle, International Critical Tables (saturated solutions); cross, Berkeley¹²¹ (saturated solutions); solid square, the melt (estimated in this work); lines, the fitted model. The dashed line marked "Sat." is for saturated solutions at various concentrations. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated), as a function of the weight percent of NaNO₃ in solution. Values of $\Delta \rho$ for all fitted points are shown. The symbols have the same meanings as in (a), with the following additions: plus, Berchiesi et al.;²¹¹ square, Barnes and Scott;⁸⁰ star, Buchanar;⁴⁴ triangle, de Lannoy;⁴⁴ diamond, Nicol;⁴⁴ plus, values generated from the fitted model of V^{ϕ} developed in this study (note use of same symbol as for results of Berchiesi et al.).



Figure 58. Calculated densities from 0 to 100 wt % NaNO₃ as a function of temperature (t). Dotted lines show densities at intermediate concentrations (10, 30, 50, 70, and 90 wt %).

low temperature, is constrained so that it gives the same values for the reference concentration and melt as eqs 13 and 41 above. The fitted parameters are listed in Table S6 (Supporting Information), and the results are shown in Figure 57. Most of the densities fitted (and all of them above 55 wt %) are generated values from eq 10. This direct representation of densities over the more limited concentration range agrees with those from eq 10 to within $\pm 0.4 \times 10^{-3}$ g cm⁻³ from 0 to 60 °C (Figure 57b).

For concentrations below the reference concentration, we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to *T* in eq 16 are calculated using eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. The value of m^* is 6.3352 mol kg⁻¹, and the coefficients of eq 18 for Y(m) are given in Table S5 (Supporting Information).

6.8.5. All Concentrations and Temperatures. By combining the results described above, it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 °C and for subsaturated solutions and to estimate them for lower temperatures and for supersaturated solutions; see Figure 58.

6.9. NH_4NO_3 . Sources of data are listed in Table 11, including several studies prior to the evaluation in the International Critical Tables, which covers the ranges 1-50 wt % NH_4NO_3 and 0-80 °C. A total of 31 sources of data were considered for the evaluation, of which one was given "some weight" and two were given "greater weight". The work of de Lannoy,⁴⁴ listed in Table 11, is one of those given greater weight. Bartovska et al.¹⁴³ have fitted their own measurements and

Bartovska et al.¹⁴³ have fitted their own measurements and data from 16 other sources (including the International Critical Tables) to produce a fitted equation for density from 0 to 100 °C and for concentrations up to saturation. Tang²⁶ presents an equation for densities of aqueous NH₄NO₃ at 25 °C, apparently including supersaturated solutions, but it is likely to have only been fitted to data up to saturation (67.8 wt % at 25 °C). Zelenyuk et al.³⁰ have determined a melt density of 1.60 \pm 0.025 g cm⁻³ at 25 °C in an electrodynamic balance. However,

| Table 11. S | Sources | of Data | for Aa | ueous N | NH4NO3 |
|-------------|---------|---------|--------|---------|--------|
|-------------|---------|---------|--------|---------|--------|

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
|----------------|-------------------|--------------|-----------------------|-----------------------|------|------|--------------------------------|
| 1-50 | wt % | 0-80 | ρ | $g mL^{-1}$ (old) | yes | | 2 |
| 100 | wt % | 170-200 | spec vol | $ml g^{-1}$ | yes | Ь | 103 |
| 100 | wt % | 25 | ρ | $g \text{ cm}^{-3}$ | yes | | 30 |
| 0.800-68.44 | wt % | 25 | ρ | $g mL^{-1}$ (old) | yes | | 214 |
| 0.800-68.49 | wt % | 25 | $\rho(t, 4^{\circ})$ | | yes | | 215 |
| 0.054-10.803 | $mol L^{-1}$ | 25 | ρ | $g mL^{-1}$ (old) | yes | | 216 |
| 50.37-68.47 | wt % | 25 | ρ | $g \text{ cm}^{-3}$ | yes | С | 143 |
| 0.0377-0.2152 | $mol kg^{-1}$ | 25 | V^{ϕ} | $cm^3 mol^{-1}$ | no | d | 41 |
| 0.0502-22.43 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | е | 41 |
| 0.256-4.664 | $mol L^{-1}$ | 25 | $\rho(t, 4^\circ)$ | | no | | 44 (Getman, 1908) |
| 1.481-24.76 | wt % | 25 | $\rho(t, 4^{\circ})$ | | yes | | 216 |
| 1.1555-7.4567 | $mol L^{-1}$ | 25 | $\rho(t, 4^{\circ})$ | | yes | | 131 |
| 0.9995-67.76 | wt % | 25 | spec vol | mL (old) g^{-1} | yes | | 217 |
| 0.798-100 | wt % | 180 | ρ | $g mL^{-1}$ (old) | no | | 146 |
| 1.00-86.8 | wt % | 100 | $\rho(t, 4^\circ)$ | yes | | f | 44 (Rabinowitsch, 1921) |
| 6.168-55.51 | wt % | 60 | ρ | $g \text{ cm}^{-3}$ | no | | 218 |
| 0.0538-10.749 | $mol L^{-1}$ | 35 | ρ | $g mL^{-1}$ (old) | yes | | 216 |
| 0.0776-0.0230 | $mol \ L^{-1}$ | 35 | ρ | $g mL^{-1}$ (old) | no | | 174 |
| 1.0-64.0 | wt % | 17.5 | $\rho(t, 4^\circ)$ | | no | | 44 (Gerlach, 1886 and 1889) |
| 24.51-70.68 | wt % | 32 | ρ | $g m L^{-1}$ (old) | yes | | 219 |
| 10.01-70.65 | wt % | 32.3 | $\rho(t, 4^\circ)$ | | yes | | 44 (Cohen et al., 1924) |
| 25.0-70.65 | wt% | 32.3 | $\rho(t, 4^\circ)$ | | yes | | 44 (Cohen and Breda, 1925) |
| 67.3, 71.5 | wt % | 25, 35 | ρ | $g m L^{-1}$ (old) | yes | g | 216 |
| 1.2-3.0 | nH_2O/nNH_4NO_3 | 30, 35 | ρ | $\rm g~cm^{-3}$ | no | h | 220 |
| 0.00989-0.999 | $mol L^{-1}$ | 25, 35 | ρ | $g mL^{-1}$ (old) | yes | | 221 |
| 20-99 | wt % | 20-180 | spec wt | $\rm g~cm^{-3}$ | yes | i | 145 |
| 14.17-92.05 | wt % | 25-120 | ρ | $\rm g~cm^{-3}$ | yes | | 144 |
| 8.005-73.96 | wt % | 30, 40 | ρ | $\rm g~cm^{-3}$ | yes | | 143 |
| 10-100 | wt % | 0-60 | ρ | $\rm g~cm^{-3}$ | yes | j | 143 |
| 0.01235-0.2358 | $mol \ dm^{-3}$ | 29.85-49.85 | ρ | $\rm g~cm^{-3}$ | no | | 212 |
| 9.06 | wt % | 10-69.9 | rel vol | yes | | k | 44 (De Heen, 1881) |
| 4-44 | wt % | 0-80 | rel vol | yes | | k | 44 (de Lannoy, 1895) |
| 25.65-40.05 | wt % | 12.2-40.0 | $\rho(t, 4^\circ)$ | no | | | 44 (Muller and Kaufmann, 1903) |
| 0.1599-20.42 | $mol kg^{-1}$ | 0-50 | ρ | $\rm g~cm^{-3}$ | no | 1 | 222 |

^{*a*} $\rho(t,u)$ is the density of the solution at *t* °C relative to that at *u* °C, spec vol is the specific volume, and rel vol is the solution volume at the experimental temperature divided by the volume occupied by the same mass of solution at a fixed reference temperature. ^{*b*} Densities from the work of Shirai and Ishibashi¹⁰³ were extrapolated to the temperatures of interest in this study, and included in the fits (see text). ^{*c*} Listed by Bartovska et al., ¹⁴³ from sources 9, 28, and 29 cited in their paper. ^{*d*} "Lethbridge" results, from the deposited supplementary data of Roux et al.⁴¹ *f* See text regarding the use of these high temperature data. ^{*g*} Units of g mL⁻¹ (old) assumed. Saturated solutions. ^{*h*} Moles of water per mole of NH₄NO₃. ^{*i*} The "specific weight" listed by Hoeg is assumed to be absolute density in g cm⁻³ (for the concentrations measured a unit of g mL⁻¹ (old) would not significantly affect calculated values of apparent molar volume). ^{*j*} The equation of Bartovska et al.,¹⁴³ to which this entry refers, was fitted to data over the temperature range 0–100 °C. We corrected one of the printed coefficients as described in the note accompanying the reference. ^{*k*} See text for a description of how the data were used. ^{*l*} Results are presented as fitted equations (as functions of temperature) at each molality.

comparisons with data for aqueous solutions at the same temperature suggest that it may be too high by an amount greater than the stated uncertainty.

Solubilities of NH_4NO_3 in water increase steeply with temperature so that, at 100 °C, a saturated solution contains about 90 wt % of salt. Densities of concentrated aqueous NH_4NO_3 at high temperatures have been measured, and this allows the values at lower temperatures (and including the density of the melt) to be estimated. This is done below.

6.9.1. Concentrated Solutions Including the Pure Liquid. Densities of the NH_4NO_3 melt are given as an equation (for 180 to 190 °C) by Janz,⁵⁸ and have also been measured by Shirai

and Ishibashi¹⁰³ from 170 to 200 °C (their densities can be represented by the equation $\rho = 1.69721 - (5.99 \times 10^{-4})T$). There are a number of studies listed in Table 11 in which densities have been measured to very high concentrations, and here we use the results to estimate densities for solutions approaching melt composition, starting at high temperature.

Rabinowitsch⁴⁴ has measured densities at 100 °C for a wide range of concentrations up to 86.8 wt % NH₄NO₃, and Klochko and Gubskaya¹⁴⁴ tabulate values for 75 and 125 °C at up to 92 wt %. Hoeg¹⁴⁵ has measured densities of aqueous solutions from 20 to 97 wt %, for temperatures up to 180 °C (for concentrations greater than or equal to 90 wt % all measurements are at 100 °C



Figure 59. (a) Densities (ρ) of aqueous NH₄NO₃ at concentrations approaching the pure liquid, as a function of NH₄NO₃ weight percent in solution (wt %). Temperatures (°C) of each set of densities are indicated on the plot. Key: circle and dot, Hoeg;¹⁴⁵ plus, Klochko and Gubskaya;¹⁴⁴ triangle, Campbell et al.;¹⁴⁶ solid diamond, equation of Janz;⁵⁸ diamond, equation of Shirai and Ishibashi.¹⁰³ Note that the data at 180 °C, with values joined by a dotted line, were obtained at high pressure (of the order of 25 atm). (b) Densities (ρ) of aqueous NH₄NO₃ at 100 °C, as a function of concentration (wt %). Key: dot, International Critical Tables; star, Rabinowitsch;⁴⁴ square, Hoeg,¹⁴⁵ diamond, Shirai and Ishibashi;¹⁰³ solid diamond, equation of Janz.⁵⁸ (c) The rate of change of density (ρ) of aqueous NH₄NO₃ with respect to temperature ($\partial \rho / \partial T$) at 100 °C, as a function of concentration (wt %). Key: dot, International Critical Tables; square, Hoeg;¹⁴⁵ diamond, Shirai and Ishibashi;¹⁰³ solid diamond, equation of Janz.⁵⁸

or above). We note that Hoeg lists extrapolated densities of 99 and 100 wt % mixtures at 160 to 220 °C which are lower than those of Shirai and Ishibashi¹⁰³ by only 0.04-0.06 g cm⁻³. These results are shown in Figure 59a together with results of Campbell et al.¹⁴⁶ obtained at high pressure. The measurements appear to be generally consistent and suggest overall a roughly linear relationship between density and wt % as the melt is approached.

At each concentration measured by Hoeg,¹⁴⁵ we fitted densities as functions of temperature and did the same for the densities tabulated in the International Critical Tables. Figure 59b shows predicted densities of liquid NH₄NO₃, from both sets of data, and also the results of Rabinowitsch⁴⁴ and predictions for the melt from the equation of Janz⁵⁸ and the work of Shirai and Ishibashi.¹⁰³ Overall, the results in the figure are remarkably consistent—only the equation of Janz⁵⁸ appears to yield a melt density that may be too high. The same results, when transformed to apparent molar volumes, also show a roughly linear relationship between V^{ϕ} and wt % at high concentration. A comparison of the slopes $\partial \rho / \partial T$ of the fitted equations, see Figure 59c, suggests that above 40 wt % the values are roughly



Figure 60. Measured and predicted densities (ρ) of pure liquid NH₄NO₃ (the melt), as function of temperature (t). Key: dot, measurement of Zelenyuk et al.;³⁰ circle, extrapolated equation of Tang;²⁶ square, predicted from the densities shown in part (b) of the previous figure; solid line, equation of Bartovska et al.;¹⁴³ dashed line, equation fitted to the data of Shirai and Ishibashi¹⁰³ (extrapolated); dash-dot line, equation of Janz⁵⁸ (extrapolated).

constant and lie in the range 6.5×10^{-4} to 7.0×10^{-4} g cm⁻³ K⁻¹. The equation given by Janz for the melt composition, $\rho = 1.759 - (6.675 \times 10^{-4})T$, is consistent with this.

In Figure 60 we show melt densities predicted by the equation of Bartovska et al.¹⁴³ which was fitted to data for subsaturated solutions and so is extrapolated, and also predictions obtained from the equation fitted to the results of Shirai and Ishibashi.¹⁰³ We have already shown in Figure 59b that the density obtained at 100 °C from this equation is consistent with other data and predictions. The equation of Bartovska et al.¹⁴³ agrees almost exactly with this value, and there is reasonable agreement at other temperatures also.

The available density data at 25 °C, when fitted using eq 10, extrapolate to a melt density of 1.5275 g cm⁻³. This agrees well with the predictions in Figure 60 and is also consistent with the predicted melt density at 100 °C and the values of $\partial \rho / \partial T$ noted above: taking the density of the melt at 100 °C from Figure 60, and $\partial \rho / \partial T$ equal to 6.675 × 10⁻⁴ from Janz,⁵⁸ yields a predicted density at 25 °C of 1.5238 g cm⁻³. This differs negligibly from the value of 1.5275 g cm⁻³ obtained above, which we adopt here. This density is 0.0425 g cm⁻³ lower than that measured by Zelenyuk et al.³⁰ which does not appear to be fully consistent with the higher temperature data.

In order to obtain the variation of the density of the supercooled melt with temperature, we fitted the densities listed by Shirai and Ishibashi,¹⁰³ constraining the fit to give 1.5275 g cm⁻³ at 25 °C, yielding

$$\rho(100 \text{ wt }\%) = 1.7227 - (6.54541 \times 10^{-4})T$$
 (43)

where T (K) is temperature. The intercept at 0 K differs by only 0.0027 g cm⁻³ from the density of the solid at 25 °C, and so this

result is consistent with the approach we have adopted for the other solutes for estimating the variation of the supercooled melt density at low temperature.

Finally, we note that it is possible to model densities close to the melt composition using equations based upon the Brunauer–Emmett–Teller isotherm.^{92,147,148} It is necessary, first of all, for water activities of the mixture to follow the isotherm over the concentration range of interest. We have found that this is true for aqueous NH_4NO_3 at 25 °C above about 90 wt %. However, Abraham's⁹² eq 16 for excess molar volume requires values of the infinite dilution apparent molar volume of the water in the molten salt and a (fitted) proportionality constant. There are insufficient data to make use of this equation.

¹6.9.2. Aqueous Solutions at 25 °C. Apparent molar volumes at infinite dilution ($V^{\phi\infty}(NH_4NO_3)$) of 47.5 and 47.2 cm³ mol⁻¹ have been determined by Roux et al.⁴¹ from two series of their own measurements. They recommend a value of 47.4 cm³ mol⁻¹, which is rather higher than the 46.86 cm³ mol⁻¹ that can be obtained from Table 1 of Millero.¹⁰¹ Combining literature values of $V^{\phi\infty}(HNO_3)$ (29.41 cm³ mol⁻¹),⁴⁰ $V^{\phi\infty}(HCl)$ (17.886 cm³ mol⁻¹),⁶⁵ and $V^{\phi\infty}(NH_4Cl)$ (35.83 cm³ mol⁻¹)⁹⁹ yields 47.35 cm³ mol⁻¹.

The solubility of NH_4NO_3 in water at 25 °C is 26.8 mol kg⁻¹ (68.2 wt %). Data from sources listed in Table 11 for this temperature were supplemented by a single point for 91.0 wt % ($\rho = 1.465 \text{ g cm}^{-3}$), based on a measurement by Hoeg¹⁴⁵ at 100 °C and then adjusted to 25 °C using $\partial \rho / \partial T$ obtained from other high temperature data. Data from a total of 11 sources were given nonzero weights. Test fits of the data, using eq 10, in which $V^{\phi\infty}(\rm NH_4NO_3)$ was fixed to the 47.35 cm³ mol⁻¹ noted above were unsatisfactory. The value of $V^{\phi\infty}(NH_4NO_3)$ was therefore determined as a part of the overall fit, yielding a slightly lower $47.24 \text{ cm}^3 \text{ mol}^{-1}$. The data and fitted equation are compared in Figure 61, and the parameters are listed in Table S3 (Supporting Information). It is clear from the figure that the data at low concentrations are quite scattered, leading to some uncertainty in $V^{\phi\infty}(NH_4NO_3)$ even at this temperature. The value of the melt density obtained from this fit, 1.5275 g cm⁻³, was adopted as described in the previous section.

6.9.3. The Reference Concentration. A value of 40 wt % (8.32886 mol kg⁻¹) was chosen, and data from 11 sources were fitted over the temperature range 0-100 °C. Data were interpolated to exactly 40.0 wt % concentration where necessary. The result is shown in Figure 62, and the fitted coefficients for eq 13 are listed in Table S2 (Supporting Information).

6.9.4. Aqueous Solutions above 0 °C. Measured densities, especially at high temperatures, are not accurate or extensive enough for $V^{\phi\infty}(\text{NH}_4\text{NO}_3)$ to be determined directly by fits at individual temperatures. Values of $V^{\phi\infty}(\text{NH}_4\text{NO}_3)$ from Bartovska et al.¹⁴³ (their Figure 2) show a continuous increase from 0 to 100 °C, though with an inflection at about 60 °C which is unlikely to be correct. We have therefore based $V^{\phi\infty}(\text{NH}_4\text{NO}_3)$ on values of $(V^{\phi\infty}(\text{NH}_4\text{Cl}) - V^{\phi\infty}(\text{HCl}) + V^{\phi\infty}(\text{HNO}_3))$ determined elsewhere in this work, and on $V^{\phi\infty}(\text{NH}_4\text{NO}_3, 25 \text{ °C})$ obtained above. Initial tests suggested that the best fit of the apparent molar volume data from 0 to 60 °C could be achieved by lowering the calculated $V^{\phi\infty}(\text{NH}_4\text{NO}_3)$ in the 40–60 °C range by about –0.05 to –0.15 cm³ mol⁻¹. This adjustment was made, and the resulting values were represented



Figure 61. Measured and fitted apparent molar volumes of NH₄NO₃ at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of NH₄NO₃ weight percent in solution ($\sqrt{}$ wt %). Key: dot, International Critical Tables; plus, Adams and Gibson;²¹⁷ cross, Luhdemann;¹³¹ star, Campbell and Kartzmark;²¹⁴ square, Campbell and Kartzmark;²¹⁵ triangle, Campbell et al.;²¹⁶ diamond, Campbell et al.²¹⁶ (sat. soln); circle, Hoeg¹⁴⁵ (extrapolated); inverted triangle, Campbell and Friesen;²²¹ solid diamond, Bartovska et al.;¹⁴³ inverted solid triangle, Roux et al.;⁴¹ line, the fitted equation. The solid vertical arrow indicates a solution saturated with respect to NH₄NO₃(s). (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against the square root of NH₄NO₃ weight percent in solution ($\sqrt{}$ wt %). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous NH₄NO₃, plotted against the square root of NH₄NO₃ weight percent in solution ($\sqrt{}$ wt %). Key: the symbols and vertical arrow have the same meanings as in (a); line, the fitted model. The inset shows the difference between densities calculated using the fitted model and the equation of Tang²⁶ (model – Tang values).

by the following equation

$$V^{\phi\infty}(\mathrm{NH_4NO_3}) = 47.2397 + 339.813074 \ln(T/T_r) - 1.023258(T-T_r)$$
(44)

where T (K) is temperature and T_r is the reference temperature of 298.15 K. The calculated $V^{\phi\infty}(\text{NH}_4\text{NO}_3)$ are shown in Figure 63, together with the values of $(V^{\phi\infty}(\text{NH}_4\text{Cl}) -$ $V^{\phi\infty}(\text{HCl}) + V^{\phi\infty}(\text{HNO}_3))$ the equation was fitted to and the adjustment noted above. Some values from other sources are also shown.

The measurements of de Heen⁴⁴ and de Lannoy⁴⁴ are volumes relative to those (for the same mass of solution) at 10 and 0 °C, respectively. These data were included in the fit by changing the reference to 25 °C and to our best fit densities at this temperature. Densities of the melt were obtained from eq 43. Data from a



Figure 62. Densities (ρ) of 40 wt % NH₄NO₃ (the reference concentration) as a function of temperature (*T*). (a) Measured and fitted densities. Key: circle, International Critical Tables; plus, Hoeg;¹⁴⁵ square, Campbell et al.;²¹⁶ solid square, Kodejs and Sacchetto;²¹⁸ triangle, Cohen and co-workers (three sources);⁴⁴ cross, Rabinowitsch;⁴⁴ solid triangle, Bartovska et al.;¹⁴³ dot, best fit model at 25 °C (this work); star, Gerlach;⁴⁴ line, fitted equation. Densities for 40 wt % NH₄NO₃ were interpolated where necessary. (b) The difference between measured and fitted densities ($\Delta \rho$, observed – calculated). Key: the symbols have the same meanings as in (a).



Figure 63. Apparent molar volumes of NH₄NO₃ at infinite dilution $(V^{\phi\infty})$, as a function of temperature (t). Key: diamond, calculated as $(V^{\phi\infty}(\text{NaNO}_3) - V^{\phi\infty}(\text{NaCl}) + V^{\phi\infty}(\text{NH}_4\text{Cl}))$; plus, calculated as $(V^{\phi\infty}(\text{NH}_4\text{Cl}) - V^{\phi\infty}(\text{HCl}) + V^{\phi\infty}(\text{HNO}_3))$; dot, as for "plus" but adjusted as described in the text; star, Roux et al.;⁴¹ circle, Millero;¹⁰¹ solid line, fitted equation; dashed line, equation of Bartovska et al.¹⁴³

total of 19 sources were given nonzero weights in the fit of eq 10 from 0 to 60 $^{\circ}$ C and 0 to 100 wt % NH₄NO₃. The results are shown in Figure 64, and the fitted parameters are listed in Table S3 (Supporting Information). It is clear from

Figure 64c that the apparent molar volumes from different sources are quite consistent with one another and are represented by the fitted equation to within about ± 0.1 cm³ mol⁻¹. The data show the most scatter at high temperatures, for which there remains some uncertainty in $V^{\phi\infty}$ -(NH₄NO₃) and in V^{ϕ} at low concentrations.

6.9.5. Aqueous Solutions Below 0 °C. For concentrations above 40 wt % (the reference concentration) we have fitted eq 14 to the available data from 0 to 60 °C together with densities generated using the fit described in the previous section. The equation is constrained to yield densities of the melt and of the reference concentration given by eq 43 and eq 13, respectively. Parameters for eq 14 were chosen so that a satisfactory extrapolation to very low temperatures could be obtained and are listed in Table S6 (Supporting Information). The data and fitted equation are compared in Figure 65. Most measurements are fitted to within $\pm 0.5 \times 10^{-3}$ g cm⁻³.

For concentrations below the reference concentration, we use the approach described in section 4.5. Values of $V^{\phi}(m, T_r)$ and its differentials with respect to *T* in eq 16 are calculated using eq 10, and eq 13 is used to calculate densities and apparent molar volumes for the reference concentration. The value of m^* is 8.32886 mol kg⁻¹, and the coefficients of eq 18 for Y(m) are given in Table S5 (Supporting Information).

6.9.6. All Concentrations and Temperatures. By combining the results described above, it is possible to calculate densities and apparent molar volumes for aqueous solutions above 0 $^{\circ}$ C and for subsaturated solutions and to estimate them for lower temperatures and for supersaturated solutions; see Figure 66.

6.10. NaOH. Sources of available data are listed in Table 12 of this work and also by Corti and Simonson¹⁴⁹ (including measurements at high pressures). We have restricted our treatment of apparent molar volumes of this solute and of NH₃ to 25 °C because atmospheric aerosols are, at most, weakly alkaline and



Figure 64. (a) Measured and fitted apparent molar volumes (V^{ϕ}) of NH₄NO₃ from 0 to 60 °C, plotted against the square root of NH₄NO₃ weight percent in solution ($\sqrt{wt \%}$). All apparent molar volumes are offset by an amount ($t/t^{\circ} - 25$)/2.5 cm³ mol⁻¹, where t (°C) is temperature and t° is equal to 1 °C. The experimental temperatures (°C) are noted on the figure. Key: dot, International Critical Tables; diamond, Campbell et al.;²¹⁶ star, Campbell and Frieser;²²¹ circle, Hoeg;¹⁴⁵ solid square, equation fitted to the data of Shirai and Ishibashi;¹⁰³ square, Cohen and Kooy;⁴⁴ plus, Cohen et al.;⁴⁴ plus, Cohen and Breda;⁴⁴ triangle, Bartovska et al.;¹⁴³ lines, the fitted equation. (b) Measured and fitted apparent molar volumes (V^{ϕ}) of NH₄NO₃ for various fixed concentrations (in wt %, noted on the plot), as a function of temperature (t). Key: inverted triangle, calculated from relative volumes measured by de Heen,⁴⁴ referenced to the best fit equation. (c) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated). Key: the symbols have the same meanings as in (a). (d) Densities (ρ) from 0 to 60 °C generated using the fitted model, as a function of NH₄NO₃ concentration ($\sqrt{wt \%}$). (Densities for 20 and 40 °C are shown as dotted lines.)

therefore NaOH and NH₃ will be only very minor components. The determination of the relationship between apparent molar volume and concentration at a single temperature (25 °C) is therefore sufficient for most applications.

Millero et al.⁶⁸ list apparent molar volumes at infinite dilution determined by a number of different groups and themselves obtain -5.19 cm³ mol⁻¹. More recently Roux et al.⁴¹ determined

a value of -5.259 ± 0.02 cm³ mol⁻¹, which is in reasonable agreement. Janz⁵⁸ lists an equation for the density of the melt from 623 to 723 K. Refitting values generated from his equation so that the intercept at 0 K is equal to the density of solid NaOH at 25 °C yields

$$\rho(100) = 2.13 - (5.70342 \times 10^{-4})T \tag{45}$$



Figure 65. (a) Measured and fitted densities (ρ) of aqueous NH₄NO₃ for various fixed concentrations (in wt %, noted on the plot), as a function of temperature (t). Key: dot, International Critical Tables; circle, Hoeg;¹⁴⁵ solid square, equation fitted to the data of Shirai and Ishibashi;¹⁰³ inverted solid triangle, calculated from relative volumes measured by de Lannoy,⁴⁴ referenced to the best fit equation for apparent molar volume developed in this study; plus, generated from the equation of Bartovska et al.;¹⁴³ square, generated using the best fit model for apparent molar volume developed in this work; lines, the fitted equation. (b) Measured and fitted densities (ρ) of aqueous NH₄NO₃ for various temperatures (in °C, noted on the plot), as a function of the square root of NH₄NO₃ weight percent in solution ($\sqrt{wt \%}$). All densities are offset by an amount ($t/t^{\circ} - 30$)/100 g cm⁻³, where t (°C) is temperature and t° is equal to 1 °C. Key: diamond, Campbell et al.;²¹⁶ star, Cohen and Kooy;⁴⁴ solid triangle, Cohen et al.;⁴⁴ solid diamond, Cohen and Breda;⁴⁴ triangle, Bartovska et al.;¹⁴³ lines, the fitted equation. (c) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated) plotted against concentration ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a) and (b).

where T (K) is temperature. This equation predicts a hypothetical melt density at 25 °C of 1.960 g cm⁻³, or V° (NaOH) equal to 20.407 cm³ mol⁻¹. We have adopted this value, as it is consistent with the measured apparent molar volumes of the aqueous solutions.

Data from 10 of the sources in Table 12 were given nonzero weights and fitted using eq 10. (Note that values from the International Critical Tables and from Akerlof and Kegeles¹⁵⁰ were obtained by interpolation, as their tables give values at

10 °C intervals not including 25 °C.) The results are shown in Figure 67, and the model parameters are listed in Table S3 (Supporting Information). The fitted value of $V^{\phi\infty}$ (NaOH) is -5.18 cm³ mol⁻¹. Akerlof and Kegeles have stated that densities from the International Critical Tables are only in fair agreement with their own, and the comparisons in the figure with more modern data suggest that their apparent molar volumes are too high below about 30 wt % NaOH. **6.11.** NaHSO₄. Sources of available data are listed in Table 13. There are few data at temperatures other than 25 °C, and there appear to be none for other acid sodium sulfate solutions (i.e., with $H^+:Na^+$ molar ratios other than 1:1). Because of this we have not attempted to create a Pitzer model of this system, and restrict our treatment to a representation of $V^{\phi}(NaHSO_4)$ from infinite dilution to the pure melt.

Zelenyuk et al.³⁰ have determined a melt density of 2.19 g cm^{-3} (a molar volume of 54.82 $\text{cm}^3 \text{ mol}^{-1}$) at 25 °C. Tang and



Figure 66. Calculated densities of 0 to 100 wt % NH₄NO₃ as a function of temperature (*t*). Dotted lines show calculated densities at intermediate concentrations (10, 30, 50, 70, and 90 wt %).

Munkelwitz²⁵ have measured the density of supersaturated aqueous solutions of the salt to 95 wt %, and an extrapolation of their equation yields a predicted melt density of 2.22 g cm⁻³ which is quite close to the experimental value. The equation in Table 1 which is based upon high temperature melt densities predicts a value of 2.35 g cm⁻³ or $V^{\circ}(\text{NaHSO}_4)$ equal to 51.2 cm³ mol⁻¹. In our fits we have adopted the measured density of 2.19 g cm⁻³.

Lindstrom and Wirth¹⁰⁶ determined a value of the apparent molar volume at infinite dilution of 12.86 cm³ mol⁻¹. In this work we determined $V^{\phi \infty}(2H^+, SO_4^{-2})$ equal to 14.213 cm³ mol⁻¹ (see section 4 of part 2), Roux et al.⁴¹ obtained $V^{\phi \infty}(Na^+)$ equal to -1.2 cm³ mol⁻¹, and Millero¹⁰¹ recommends -1.21 cm³ mol⁻¹. Combining these two values for the single ion with $V^{\phi \infty}(2H^+, SO_4^{-2})$ yields $V^{\phi \infty}(NaHSO_4)$ on a fully dissociated basis equal to about 13.0 cm³ mol⁻¹. It is also possible to calculate $V^{\phi \infty}(NaHSO_4)$ by other routes, for example $(V^{\phi \infty}(Na_2SO_4) - V^{\phi \infty}(NaCI) + V^{\phi \infty}(HCI))$ also yields 13.0 cm³ mol⁻¹ when using apparent molar volumes at infinite dilution that have been determined or adopted in this study. Accordingly, we have set $V^{\phi \infty}(NaHSO_4)$ equal to 13.0 cm³ mol⁻¹.

Comparisons of apparent molar volumes calculated from the densities of Tang²⁵ with those of Lindstrom and Wirth¹⁰⁶ showed that the former were consistently lower by about 0.73 cm³ mol⁻¹. Values from the International Critical Tables and from Wendt¹⁵¹ also agree much better with the results of Lindstrom and Wirth (while those of Zafarani-Moattar and Mehrdad¹⁵² appear to be in error and were rejected). It is likely that Tang and Munkelwitz²⁵ fitted their equation for aqueous NaHSO₄ densities to the International Critical Tables values in addition to their own measurements, so that the deviation we have noted is probably due to an inaccurate fit. We have added 0.73 cm³ mol⁻¹ to all values of $V^{\phi \infty}$ (NaHSO₄) from the equation of Tang and Munkelwitz in order to try and compensate for this.

Finally, data from five sources in Table 13 were given nonzero weights and the apparent molar volumes fitted by the following

| Table 12. Sources | s of Data for Aque | eous NaOH | | | | | |
|-------------------|--------------------|--------------|-----------------------|----------------------|------|------|----------------------|
| concn range | unit | t range (°C) | quantity ^a | unit | used | note | reference |
| 1-50 | wt % | 0-100 | ρ | $g mL^{-1}$ (old) | yes | ь | 2 (interpolated) |
| 0.0009-0.04721 | $mol kg^{-1}$ | 25 | $\rho(t, 4^\circ)$ | | no | | 223 |
| 0.5542-2.219 | $mol kg^{-1}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 166 |
| 0.00004-0.0871 | $mol dm^{-3}$ | 25 | ρ | $\rm g~cm^{-3}$ | no | с | 224 |
| 0.975-23.995 | $mol kg^{-1}$ | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 225 |
| 0.1002-0.9002 | $mol kg^{-1}$ | 25 | Δho | $\rm g~cm^{-3}$ | yes | | 68 |
| 1.009-25.74 | $mol kg^{-1}$ | 0-70 | V^{ϕ} | $\rm cm^3 mol^{-1}$ | yes | d | 150 (interpolated) |
| 0.0100-1.004 | $mol kg^{-1}$ | 5-45 | Δho | $\rm g~cm^{-3}$ | yes | | 65 |
| 0.0204-10.89 | $mol kg^{-1}$ | 4-55 | Δho | $\rm g~cm^{-3}$ | yes | е | 226 |
| 0.0008-0.1428 | $mol L^{-1}$ | 12.5-42.5 | rel dens | | no | d | 168 |
| 0.9751-8.309 | $mol L^{-1}$ | 20-40 | $\rho(t, 4^\circ)$ | | no | d | 44 (Hitchcock, 1935) |
| 0.0197-0.9453 | $mol kg^{-1} soln$ | 25-75 | ρ | $g mL^{-1} (old)$ | no | | 227 |
| 0.504-3.009 | $mol kg^{-1}$ | 25-75 | ρ | $g \text{ cm}^{-3}$ | yes | | 228 |
| 0.0-1.00 | $mol \ dm^{-3}$ | 25-40 | ρ | $kg m^{-3}$ | yes | | 229 |
| 0.13-23.983 | $mol kg^{-1}$ | 20-300 | ρ | $\rm g~cm^{-3}$ | no | d | 230 |

 ${}^{a} \rho(t, u)$ is the density of the solution at $t \,{}^{\circ}C$ relative to that at $u \,{}^{\circ}C$, spec vol is the specific volume, and rel dens is the solution density divided by the density of pure water at the same temperature. b Values for 25 °C were interpolated. c Densities are only listed to four decimal places and, for these very low concentrations, are insufficiently precise to be used. d A tabulation of evaluated densities at round values of wt %, from 0 to 70 °C, is also given. e Apparent molar volumes are also listed.



Figure 67. Measured and fitted apparent molar volumes of NaOH in aqueous solution at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of NaOH weight percent in solution ($\sqrt{wt \%}$). Key: dot, International Critical Tables; plus, Hershey et al.;^{65,84} cross, Roux et al.;²²⁶ circle, Lanman and Mair;¹⁶⁶ triangle, Tamas;²²⁵ square, Millero et al.;⁶⁸ inverted solid triangle, Herrington;²²⁸ star, Vazquez et al.;²²⁹ diamond, Aklerlof and Kegeles;¹⁵⁰ solid square, melt (estimated in this work); line, the fitted equation. The solid vertical arrow indicates a solution saturated with respect to NaOH. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against concentration ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous NaOH, plotted against the square root of NaOH weight percent in solution ($\sqrt{wt \%}$). Key: the symbols and vertical arrow have the same meanings as in (a); line, the fitted equation.

equation

$$\begin{split} V^{\phi}(\mathrm{NaHSO}_{4}) = & 13.0 - 37.4619 \mathrm{wf}^{0.25} + (0.655685 \times 10^{3}) \mathrm{wf}^{0.5} \\ &- (0.189519 \times 10^{4}) \mathrm{wf}^{0.75} + (0.200788 \times 10^{4}) \mathrm{wf} \\ &- 0.107208 \times 10^{4}) \mathrm{wf}^{1.5} + (0.426898 \times 10^{3}) \mathrm{wf}^{2} \\ &- (0.439164 \times 10^{2}) \mathrm{wf}^{3} \end{split}$$

where wf is NaHSO₄ weight fraction. Note the absence of a Debye–Hückel term, because a calculation of ionic strength is

required for this, including the $HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$ equilibrium. The results of the fit are plotted in Figure 68, which shows that $V^{\phi}(NaHSO_4)$ varies almost linearly with the square root of *wf* over most of the concentration range, but falls steeply below about 0.02 reflecting the influence of the changing degree of HSO_4^- dissociation in this region of concentration.

6.12. NH₃. The ammonium ion is frequently a significant or major component of atmospheric aerosols, but such aerosols are more often acid than alkaline, and we have restricted our

| concn range | unit | t range (°C) | quantity ^b | unit | used | note | ref |
|---------------|---------------|--------------|-----------------------|-----------------------|------|------------|-----|
| 1-22 | wt % | 25 | ρ | $g m L^{-1}$ (old) | yes | | 2 |
| 100 | wt % | 25 | ρ | $\rm g~cm^{-3}$ | yes | | 30 |
| 45-95 | wt % | 25 | ρ | $\rm g~cm^{-3}$ | yes | С | 25 |
| 0.98-29.82 | wt % | 25 | ρ | $\rm g~cm^{-3}$ | no | | 152 |
| 0.001-4.00 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 \ mol^{-1}$ | yes | | 106 |
| 1.038-2.166 | $mol kg^{-1}$ | 25 | ρ | g cm ⁻³ | yes | | 151 |
| 0.0497-0.9636 | $mol dm^{-3}$ | 30 | spec grav | | no | d | 231 |
| 4 C1 1 1 D | 1 235 | 1 (* C 1 * | | N HGO | 1. 6 | <u>C</u> (| b |

^{*a*} Chernenkaya and Revenko²³⁵ present fitted equations for density of 5-55 wt % aqueous NaHSO₄ as linear functions of temperature. ^{*b*} "spec grav" is the specific gravity of the solution, defined as the density of the solution divided by that of water at the same temperature. ^{*c*} Tang and Munkelwitz²⁵ present only a fitted equation. The value of the density of pure water is given as 0.9971, suggesting units of g mL⁻¹ (old), although this seems unlikely given the date of publication. However, the equation is used here only to obtain densities of supersaturated solutions for which the molality is high enough that uncertainty regarding the exact unit used is not significant. ^{*d*} Not used, because the only data for 25 °C were fitted.

treatment of the apparent molar volume of $\rm NH_3$ in aqueous solution to 25 $^{\circ}\rm C$ only.

Sources of data are listed in Table 14, including references to measurements at 15 and 20 °C. Measurements at or close to 100 wt % NH₃ are available at 20 °C¹⁵³ and at 15 °C.² We fitted V^{ϕ} (NH₃) at these temperatures as a function of wt %, and similarly the lower concentration values from the International Critical Tables at 15 °C, and the data of Rashkovskaya and Chernen'kaya.¹⁰⁴ The fitted equations were used to estimate values of ΔV^{ϕ} (NH₃) for 5 and 10 °C temperature differences, and so adjust the measurements of King et al.¹⁵³ and the lower concentration International Critical Tables data (<40 wt %) to 25 °C. Figure 69 shows the adjusted apparent molar volumes, together with other data. For this uncharged solute the apparent molar volume varies relatively little, and between 0 and about 50 wt % NH₃ V^{ϕ} (NH₃) remains between 24 and 25 cm³ mol⁻¹.

Allred and Wooley⁹⁹ have determined an apparent molar volume at infinite dilution ($V^{\phi\infty}(NH_3)$) equal to 24.43 cm³ mol⁻¹, which we have adopted here. The apparent molar volumes shown in the figure were fitted by the following equation

$$V^{\phi}(\mathrm{NH}_{3}) = 24.43 + 1.8684629 w f^{0.5} + 15.613800 w f$$

- 98.483801 w f^{1.5} + 145.16897 w f^{2} - 60.445534 w f^{2.5} (47)

where *wf* is weight fraction. Note the absence of a Debye– Hückel term, because the ionic strength of the solution is zero. (The effect of the reaction $NH_{3(aq)} + H^{+}_{(aq)} \Leftrightarrow NH_{4}^{+}_{(aq)}$ is significant in dilute solutions, and for this reason the apparent molar volumes of Allred and Woolley⁹⁹ in the fit were taken from their eq 3 which yields values corrected for the influence of dissociation.)

7. APPARENT MOLAR VOLUMES AT INFINITE DILUTION

The sulfates, nitrates, and chlorides studied here, H₂SO₄, HNO₃, HCl, Na₂SO₄, NaNO₃, NaCl, (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl, consist of only six ions (excluding HSO₄⁻). How closely their values can be represented at each temperature by a set of six individual ionic apparent molar volumes is a test of the consistency of the equations for $V^{\phi\infty}$ that we have obtained for each of these electrolytes. We have therefore calculated best fit $V^{\phi\infty}(i)$ ($i = Na^+, NH_4^+, SO_4^{-2-}, NO_3^-$, and Cl⁻) at temperatures from 0 to 50 °C from values for the nine electrolytes given by the equations determined earlier in this work. Estimates of $V^{\phi^{\infty}}$ were then recalculated for each electrolyte from the individual ionic values and compared with those predicted by our fitted equations; see Figure 70.

Of the nine electrolytes, $V^{\phi\infty}$ for NaNO₃ and NH₄Cl were determined entirely from values for other electrolytes, and $V^{\phi\infty}$ for NH₄NO₃ was mainly determined in this way but with an adjustment in order to fit the available apparent molar volume data better. If our equations for the apparent molar volumes of the electrolytes were completely consistent, then the $\Delta V^{\phi\infty}$ plotted in the figure would all be zero. In fact, the results in Figure 70 show mutual consistency to within about (-0.04, +0.02) cm³ mol⁻¹ for all electrolytes except NH₄NO₃ for which deviations approach 0.07 cm³ mol⁻¹. It is probably the presence of NH₄NO₃ that leads to some of the negative deviations for the other NO₃⁻ and NH₄⁺ containing electrolytes. The apparent molar volumes at infinite dilution of NH₄NO₃, given by eq 44, are therefore likely to have the largest errors of those studied and may be too low at high temperatures.

8. TEMPERATURES OF MAXIMUM DENSITY

Temperatures of maximum densities of aqueous solutions have been examined by Kaulgud and Pokale⁴⁷ who tabulate values of the Despretz constant $K_{\rm m}$ (°C kg mol⁻¹) for the equation

$$\Delta\theta + 1.074m^{1.5} = K_{\rm m}m\tag{48}$$

where $\Delta \theta$ is the depression of the temperature of maximum density relative to that of pure water (at 3.98 °C) and *m* is solute molality. Figure 71 shows values of $K_{\rm m}$ calculated from two sets of limiting ionic values in Table 2 of Kaulgud and Pokale, and calculated using the model developed in this work. It can be seen that in most cases our $K_{\rm m}$ are close to those given by Kaulgud. This, and the excellent agreement between the model predictions and measured densities of NaCl below 0 °C gives confidence in the model predictions at low temperatures and below the reference concentration.

9. SUMMARY

The aims of this study are, first, to represent densities and apparent molar volumes to within experimental error from 0 to approximately 60 °C and from infinite dilution to saturation with



Figure 68. Measured and fitted apparent molar volumes of NaHSO₄ in aqueous solution at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of NaHSO₄ weight percent in solution ($\sqrt{wt \%}$). Key: dot, International Critical Tables; square, Zelenyuk et al.³⁰ (melt); plus, Tang and Munkelwitz (adjusted);²⁵ triangle, Lindstrom and Wirth;¹⁰⁶ circle, Wendt;¹⁵¹ line, the fitted equation. The solid vertical arrow indicates a solution saturated with respect to NaHSO₄. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against the square root of NaHSO₄ weight percent in solution ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous NaHSO₄, plotted against concentration ($\sqrt{wt \%}$). Key: the symbols and vertical arrow have the same meanings as in (a), except that the densities of Tang and Munkelwitz²⁵ have not been adjusted; line, the fitted equation. The inset shows the difference between densities calculated using the fitted model and the equation of Tang²⁵ (model – Tang values).

respect to solid salts; second, to provide reasonable extrapolations to the extreme (supersaturated) concentrations that can occur in liquid aerosols; and third, to represent the available data for temperatures below 0 $^{\circ}$ C and provide extrapolations to very low temperature for solutions over the entire concentration range.

The work described in section 6 shows that the fitted equations presented here meet the first of the aims stated above. The use of two fitted equations—one for apparent molar volumes at relatively low concentrations and another for density at higher concentrations up to the pure liquid or hypothetical melt—enables volume properties to be extrapolated to very low temperature in a way that is consistent with the limited data that are available. There is good agreement between the fitted and/or extrapolated equations and the measurements for temperatures below 0 °C (mainly aqueous solutions of HCl, NaCl, and H_2SO_4).

Densities tabulated in the International Critical Tables are still widely used. Our comparisons of these densities (and the original

| Та | bl | e | 14. | Source | s of | Ē |)ata | for | Aqueous | NH_3 |
|----|----|---|-----|--------|------|---|------|-----|---------|--------|
|----|----|---|-----|--------|------|---|------|-----|---------|--------|

| concn range | unit | t range (°C) | quantity ^a | unit | used | note | ref |
|---------------|---------------|--------------|-----------------------|----------------------|-----------------------|------|-----|
| 1.0-10.0 | wt % | 25 | ρ | $g m L^{-1}$ (old) | yes | | 2 |
| 1.0-40.0 | wt % | 15 | ρ | $g mL^{-1}$ (old) | yes | Ь | 2 |
| 45-100 | wt % | 15 | $\rho(t, 4^{\circ})$ | | see note ^d | Ь | 2 |
| 1.198-11.184 | $mol kg^{-1}$ | 25 | ρ | g cm ⁻³ | yes | | 104 |
| 2.0-8.0 | $mol L^{-1}$ | 25 | $\rho(t, 25^\circ)$ | | no | | 232 |
| 0.0665-0.3437 | $mol kg^{-1}$ | 25 | V^{ϕ} | $\rm cm^3 mol^{-1}$ | yes | с | 99 |
| 47.45-97.18 | $mol kg^{-1}$ | 20 | ρ | g cm ⁻³ | yes | d | 153 |
| | | | ag ha | | 1.6 1.40 | | 0.0 |

^{*a*} $\rho(t, u)$ is the density of the solution at *t* °C relative to that at *u* °C. ^{*b*} Data at 15 °C for wt % between 16 and 48 were included in the fit, after adjusting the data by adding a fixed 0.46 cm³ mol⁻¹ to each of the points. ^{*c*} Values were taken from eq 3 of the authors, which gives apparent molar volumes adjusted for the effects of association to form NH₄⁺. ^{*d*} The data of King et al. ¹⁵³ were adjusted to 25 °C on the assumption that the difference in molar volume (at fixed concentration) between 15 and 20 °C is the same as that between 20 and 25 °C. Values of ΔV^{ϕ} for each concentration were obtained from smooth fits through the 15 °C data from the International Critical Tables, and the measurements of King et al. at 20 °C.

studies on which they are based) with modern data showed that adjustments were needed for two solutes, and these have been incorporated into our fits. The first of these solutes is HCl. Densities in the International Critical Tables for this solute are based mainly on relative volume measurements (at a series of different temperatures), which require referencing to known densities at a fixed temperature. Comparisons with modern measurements at 25 °C suggested an error-almost certainly in the densities used as the reference—and values of apparent molar volume determined from the densities in the International Critical Tables were adjusted by a ΔV^{ϕ} at all Tbased on the assumption that the relative volume measurements were accurate. This gave good agreement with other data at all temperatures, including the comprehensive measurements of Akerlof and Teare (after a similar adjustment was carried out to their results). The second solute for which some adjustment was required was $(NH_4)_2SO_4$. Densities of aqueous solutions of this salt in the International Critical Tables were similarly based upon measurements of relative volume at different temperatures, and calculated apparent molar volumes at all temperatures were adjusted based upon comparisons made with modern data at 25 °C.

The lowest concentrations for which densities are tabulated in the International Critical Tables are generally 1, 2, and 4 wt %. We note that data for these concentrations were mostly omitted from the fits because they were found to agree poorly with other data when compared as apparent molar volumes. It is likely that the results of this study yield more accurate densities than the International Critical Tables at the lowest concentrations. The apparent molar volumes at infinite dilution that we have determined are mutually consistent to better than 0.1 cm³ mol⁻¹, a good result, and agree well with existing literature values. We also note that we have not considered the data in the International Critical Tables for aqueous NaCl, but have instead adopted apparent molar volumes and densities calculated from the equation of state of Archer.⁶¹

For aqueous H_2SO_4 the only significant additions to the available data since the compilation of the International Critical Tables are for dilute solutions, and also the results of Myhre et al.¹⁴ for low temperatures. Our fitted equation represents the tabulated densities (for concentrations >6 wt %) essentially exactly, and extrapolations of the equations to low temperatures agree well with the measurements of Myrhe et al.

In part 2 of this work we apply an ion-interaction model to the data from 0 to 3 mol kg⁻¹ to obtain accurate apparent molar volumes and densities in the dilute range, including values at infinite dilution. The volume properties of aqueous H_2SO_4 tabulated in the Supporting Information to this study combine the two sets of results and extend from infinite dilution to the pure liquid acid.

Measurements of densities of supersaturated (highly concentrated) solutions at 25 °C are available for the following salts: NaCl, Na₂SO₄, NaNO₃, NH₄NO₃ (melt only), $(NH_4)_2SO_4$, and NaHSO₄ (including the melt). However, calculated densities of highly supersaturated solutions of the salts at temperatures far from 25 °C must be regarded as estimates, as they are based upon a number of assumptions, notably the value of $\partial \rho / \partial T$ for the melt, which is obtained from data for very high temperatures as discussed in section 3.3. The volume properties of concentrated NH₄NO₃ solutions are somewhat more certain, because its very high solubility means that data for concentrated solutions over a range of temperatures can be extrapolated to yield estimates for the melt (see section 6.9.1). Densities and apparent molar volumes of highly concentrated and liquid HCl are given a simplified treatment in this study (see Figure 4 and sections 6.1.1 and 6.1.5) and are mainly useful for calculations involving mixtures in which HCl is a minor component.

The solutes NaOH and NH₃ have been included in this study (for a temperature of 25 $^{\circ}$ C only), so that calculations can be carried out for slightly alkaline aerosol solutions. Where the two solutes are only minor components the use of apparent molar volumes and densities for a single temperature should not significantly affect the accuracy of the result.

Densities of dilute solutions at low temperatures are estimated using extrapolated apparent molar volumes (based upon values for temperatures greater than or equal to 25 °C), and the density of pure water. Below about 243 K, the densities of supercooled pure water given by our fitted equation are based upon measurements of Mallamace et al.⁵³ These have a claimed uncertainty of about <0.01 g cm⁻³. If more accurate data become available, then they can be straightforwardly substituted without affecting other elements of the model or fitted equations.

The equations for all solutes treated in this study, and in part 2, have been implemented in the Extended Aerosol Inorganics



Figure 69. Measured and fitted apparent molar volumes of NH₃ in aqueous solution at 25 °C. (a) Apparent molar volumes (V^{ϕ}) over the entire concentration range, plotted against the square root of NH₃ weight percent in solution ($\sqrt{wt \%}$). Key: dot, International Critical Tables (adjusted); plus, Rashovskaya and Chernen'kaya;¹⁰⁴ circle, Allred and Woolley⁹⁹ (fitted equation); triangle, King et al.¹⁵³ (adjusted from 20 °C); line, the fitted equation. (b) The difference between measured and fitted apparent molar volumes (ΔV^{ϕ} , observed – calculated), plotted against the square root of NH₃ weight percent in solution ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured density. (c) Measured and calculated densities (ρ) of aqueous NH₃, plotted against the square root of NH₃ weight percent in solution ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured densities have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured densities (ρ) of aqueous NH₃, plotted against the square root of NH₃ weight percent in solution ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); dotted lines, the effect of a ±0.00005 g cm⁻³ error in measured densities (ρ) of aqueous NH₃, plotted against the square root of NH₃ weight percent in solution ($\sqrt{wt \%}$). Key: the symbols have the same meanings as in (a); line, the fitted equation.

Model (*E-AIM*, http://www.aim.env.uea.ac.uk/aim/aim.php). Apparent and partial molar volumes of the solutes, and densities of the solutions, can be calculated using the model. We have not evaluated methods of estimating the densities of mixtures, but have included in *E-AIM* those referred to in the Appendix. Tables of densities and apparent molar volumes of the solutes HCl, NaCl, NH₄Cl, H₂SO₄, Na₂SO₄, (NH₄)₂SO₄, HNO₃, NaNO₃, and NH₄NO₃ from 0 to 100 wt % concentration and from -80 °C or -20 °C to +50 °C are given in the Supporting Information to this study.

APPENDIX

In Table 15 we have summarized the statistics of the fits of the temperature-dependent apparent molar volume equation (eq 10) for the principal solutes and also aqueous NaOH which was fitted at 25 °C only. Densities of aqueous H_2SO_4 (from the International Critical Tables) were fitted by a cubic spline to a very high precision, as described in section 6.4.3, and this solute is not included in the table.

The spline curves fitted to some of the data were obtained using routine E02BEF from the Fortran library of the Numerical



Figure 70. The difference $(\Delta V^{\phi \circ \circ})$ between infinite dilution apparent molar volumes given as functions of temperature (t) by equations presented in this work and values calculated using best-fit individual ionic values of $V^{\phi \circ \circ}$ at each temperature. Key: triangle, NH₄NO₃; solid square, Na₂SO₄; plus, H₂SO₄; star, HCl; dot, NaCl; circle, NH₄Cl; cross, HNO₃; square, (NH₄)₂SO₄; solid triangle, NaNO₃.



Figure 71. Comparison of Despretz constants (K_m) for nine electrolytes. Key: dot, values of Kaulgud⁴⁷ (his Table 2); open circle, Wakabayashi and Takaizumi²³⁴ (from Table 2 of Kaulgud); star, the model developed in this work. Note that sulfates were not studied by Wakabayashi and Takaizumi.²³⁴

Algorithms Group (NAG, http://www.nag.co.uk). This routine computes a normalized cubic b-spline approximation to an arbitrary set of points, with automatic location of the knots. The NAG Fortran library contains routines to evaluate the spline from the fitted knots and coefficients, as do other

Table 15. Statistics of the Fits of Apparent Molar Volumes asFunctions of Temperature

| quantity ^a | HCl | NaCl | NH ₄ Cl | Na_2SO_4 | $(\mathrm{NH}_4)_2\mathrm{SO}_4$ |
|--|---|------|--|---|---|
| $\begin{array}{l} N \\ \mathrm{mean} \ \Delta V^{\phi} \\ \mathrm{std} \ \mathrm{dev} \ (\Delta V^{\phi}) \\ \mathrm{mean} \ \Delta \rho \\ \mathrm{std} \ \mathrm{dev} \ (\Delta \rho) \end{array}$ | $\begin{array}{c} 337 \\ -0.0030 \\ 0.049 \\ 7.4 \times 10^{-6} \\ 0.00025 \end{array}$ | Ь | 248 -0.027 0.069 -0.00037 0.0012 | $383 \\ -0.0022 \\ 0.064 \\ 1.8 \times 10^{-7} \\ 4.2 \times 10^{-5}$ | $105 \\ -3.0 \times 10^{-5} \\ 0.06 \\ 2.6 \times 10^{-6} \\ 0.00035$ |
| | HNO_3 | | $NaNO_3$ | $\rm NH_4NO_3$ | NaOH |
| N mean ΔV^{ϕ} std dev (ΔV^{ϕ}) mean $\Delta \rho$ | $806 \\ -0.0058 \\ 0.054 \\ -1.3 \times 10^{-6}$ | 6 | 205 -0.018 0.091 0.00013 | $236 \\ 0.010 \\ 0.048 \\ -9.2 \times 10^{-5} \\ 0.0000 $ | $105 -3.0 \times 10^{-5} 0.061 \\ 2.59 \times 10^{-6} 0.0025$ |
| std dev $(\Lambda \rho)$ | 0.00073 | | 0.00058 | 0.00031 | 0.00035 |

^{*a*} *N* is the number of points given non-zero weights in each fit, ΔV^{ϕ} is the measured minus the fitted apparent molar volume (unweighted); $\Delta \rho$ is the unweighted difference in density (calculated from the measured and fitted apparent molar volumes); std dev is the standard deviation of the unweighted quantity in parentheses. ^{*b*} No values are given for NaCl, because apparent molar volumes from the equation of state of Archer⁶¹ are used in this study.

mathematical software packages. Public domain software is also available, and in our calculations we use subroutines from the module DBSPEV which can be found by searching for this name (and then class E3a1) on the Guide to Mathematical Software web site of the National Institute of Standards and Technology (NIST, http://gams.nist.gov). We adapted the required routines in DBSPEV by simplifying the interfaces and converting the code to modern loop and conditional structures, and then encapsulating the routines in a Fortran module. We have made this code available in the Supporting Information.

Densities and apparent and partial molar volumes of all solutes (including those treated in part 2 of this work) can be calculated online at the Extended Aerosol Inorganics Model (E-AIM) Web site, http://www.aim.env.uea.ac.uk/aim/aim.php. Volume properties of mixtures can also be estimated there using a choice of four methods: first, one in which the specific volume of the mixture is estimated from the specific volumes of the individual component electrolytes at the same wt % concentration as the total solutes in the mixture. This approach is due to Tang³⁴ and later Semmler et al.³⁵ (see their eq 12). The second method is similar, but instead densities of pure aqueous solutions of the individual electrolytes are summed to estimate that of the mixture (eq 10 of Semmler et al.³⁵). In the two remaining methods the apparent molar volume of the total solutes in the mixture is equal to the sum of the apparent molar volumes of the individual electrolyte components, each at the total ionic strength of the mixture. The contribution of each electrolyte is weighted according to its equivalent fraction in the solution. This "Young's rule" approach is one of several examined by Miller.⁸⁶ The two methods differ in that either mole fraction or molality-based ionic strength can be selected. All four methods require that the composition of a multicomponent solution be specified in terms of individual electrolyte solutes. This composition is calculated using the equation given by Clegg and Simonson.^{154,155}

Densities of the inorganic solids that can be formed in solutions containing the solutes treated in this study have been included in the *E-AIM* model and are listed together with molar volumes in Table 16. They are assumed to be invariant with temperature,

Table 16. Densities and Molar Volumes of Solids

| solid | $\rho~({\rm g~cm^{-3}})$ | $V^{\circ} (\mathrm{cm}^3 \mathrm{mol}^{-1})$ | source ^a |
|--|--------------------------|---|---------------------|
| $H_2SO_4 \cdot H_2O$ | 1.99 | 58.28 | 2 |
| $H_2SO_4 \cdot 2H_2O$ | 1.75 | 76.66 | 2 |
| $H_2SO_4 \cdot 3H_2O$ | 1.65 | 92.40 | |
| $H_2SO_4 \cdot 4H_2O$ | 1.57 | 108.10 | 2 |
| $H_2SO_4 \cdot 6.5H_2O$ | 1.43 | 150.37 | 2 |
| $HNO_3 \cdot H_2O$ | 1.80 | 44.91 | 3 |
| $HNO_3 \cdot 2H_2O$ | 1.71 | 57.89 | |
| $HNO_3 \cdot 3H_2O$ | 1.65 | 70.87 | 4 |
| HCl·3H ₂ O | 1.16 | 77.85 | 5 |
| $(NH_4)_2SO_4$ | 1.77 | 74.66 | 1 |
| $(NH_4)_3H(SO_4)_2$ | 1.77 | 139.32 | |
| NH ₄ HSO ₄ | 1.78 | 64.67 | 1 |
| NH ₄ NO ₃ | 1.72 | 46.54 | 1 |
| $2NH_4NO_3 \cdot (NH_4)_2SO_4$ | 1.74 | 167.73 | |
| $3NH_4NO_3 \cdot (NH_4)_2SO_4$ | 1.74 | 214.27 | |
| $\rm NH_4NO_3 \cdot \rm NH_4HSO_4$ | 1.75 | 111.20 | |
| NH ₄ Cl | 1.52 | 35.22 | 1 |
| Na_2SO_4 | 2.70 | 52.61 | 1 |
| $Na_2SO_4 \!\cdot\! 10H_2O$ | 1.46 | 220.68 | 1 |
| $Na_3H(SO_4)_2$ | 2.57 | 102.01 | |
| $NaHSO_4 \cdot H_2O$ | 2.10 | 65.75 | 1 |
| NaHSO ₄ | 2.43 | 49.41 | 1 |
| $NaH_3(SO_4)_2 \cdot H_2O$ | 2.11 | 111.95 | |
| $Na_2SO_4\boldsymbol{\cdot}(NH_4)_2SO_4\boldsymbol{\cdot} 4H_2O$ | 2.23 | 155.57 | |
| NaNO ₃ | 2.26 | 37.59 | 1 |
| $NaNO_3\!\cdot\!Na_2SO_4\!\cdot\!H_2O$ | 2.30 | 106.54 | |
| NaCl | 2.17 | 26.93 | 1 |
| | | | . 167 |

^{*a*} 1, CRC Handbook;¹⁰² 2, Hulsmann;⁶⁰ 3, Luzzati;¹⁵⁶ 4, Luzzati.¹⁵⁷ See text for a description of how the other molar volumes and densities were obtained.

although $\partial \rho / \partial T$ of (NH₄)₂SO_{4(s)} is known to be about -1.59×10^{-4} g cm⁻³ K⁻¹, for example.⁵⁹ Values for 10 of the solids in the table were obtained from the CRC Handbook.¹⁰² Densities of H₂SO₄ hydrates (for -78 °C) were taken from Table 8 of Hulsmann.⁶⁰ The value for H₂SO₄ · 6H₂O_(s) was adjusted to take into account the fact that the correct stoichiometry is H₂SO₄ · 6.5H₂O_(s), and that for H₂SO₄ · 3H₂O_(s) was estimated from the other data by determining the increment in molar volume due to the addition of a water molecule to the solid. The molar volume of HNO₃ · 2H₂O_(s) was estimated similarly, from data for the mono- and trihydrates.^{156,157}

Molar volumes of the simple nonhydrated double salts $2NH_4$ - $NO_3 \cdot (NH_4)_2SO_{4(s)}$, $3NH_4NO_3 \cdot (NH_4)_2SO_{4(s)}$, and $NH_4NO_3 \cdot NH_4HSO_{4(s)}$ were assumed to be equal to the sums of the molar volumes of the constituent single salts. Values for the two hydrates $NaNO_3 \cdot Na_2SO_4 \cdot H_2O_{(s)}$ and $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O_{(s)}$ were estimated in the same way, with the molar volume of the added water molecules determined from the difference between the molar volumes of NaHSO_4(s) and NaHSO_4 \cdot H_2O_{(s)}. The molar volume of letovicite $(NH_4)_3H(SO_4)_{2(s)}$ is assumed to be equal to the sum of those for $(NH_4)_2SO_{4(s)}$ and $NH_4HSO_{4(s)}$. The molar volume of $Na_3H(SO_4)_{2(s)}$ was estimated analogously.

The molar volume of NaH₃(SO₄)₂·H₂O_(s) was estimated in two stages. First the ΔV° caused by the substitution of H⁺ for Na⁺ in Na₂SO_{4(s)} (to produce NaHSO_{4(s)}) was added to twice the molar volume of NaHSO_{4(s)}, followed by the further addition of the molar volume of the water molecule in the same way as for the hydrated double salts.

Tabulated densities of ice were taken from the most recent edition of the CRC Handbook¹⁵⁸ (based upon values from Feistel and Wagner,¹⁵⁹ and the IAWPS¹⁶⁰), converted to molar volumes, and fitted to the following equation

$$V^{\circ}(\text{ice}) = 19.2720 + (3.694479 \times 10^{-7})T^{2.5} - (3.67795 \times 10^{-9})T^{3}$$
(49)

where V° is in cm³ mol⁻¹.

ASSOCIATED CONTENT

Supporting Information. Parameters for the fitted equations (Tables S1–S9), calculated densities and apparent molar volumes of the pure aqueous solutions of each solute (Tables S10–S21), and Fortran code for the evaluation of cubic B-splines. This information is available free of charge via the Internet at http://pubs.acs.org.

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