The solubility of oxygen in water and saline solutions

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Oxygen is one of the key reaction partners for many redox reactions also in the context of nuclear waste disposal. Its solubility influences radionuclides' behavior, corrosion processes and even microbial activity. Therefore, a reliable calculation of the solubility of molecular oxygen in aqueous solutions is relevant for any safety assessment. Available geochemical speciation and reactive transport programs handle these data very differently. In some codes, the hypothetical equilibrium between dissolved oxygen and water is used to balance redox reactions. Equilibrium constants are given in "temperature grids" for up to 573.15 K. In other cases, temperature functions for the solubility of gaseous oxygen in water are given, without any reference to a valid temperature range. These settings become even more complicated when used in the context of modeling equilibria in high-saline solutions applying the Pitzer formalism. This raised the question about the experimental foundation of equilibrium constants given in such data files and their validity for the solubility of molecular oxygen in saline solutions. For this article, a thorough literature review was conducted with respect to the solubility of molecular oxygen in pure water and saline solutions. From these primary experimental O_2 solubility data a temperature-dependent Henry's law function as well as temperature-dependent binary and ternary Pitzer ion-interaction coefficients were derived. An internally consistent set of thermodynamic data for dissolved oxygen is presented, along with statements about its validity in terms of temperature and, as far as Pitzer interaction coefficients are concerned, of solution composition. This self-consistent activity-fugacity model containing thermodynamic data, Henry's law temperature equation, and Pitzer interaction coefficients is capable of providing a more accurate description of redox transformations, allowing a reduction of conservatism in safety assessment calculations, not only in the context of a nuclear repository. The model reproduces well the reliable experimental data available, and is capable to predict the oxygen solubility in complex solution media. The temperature functions used to describe Henry's constant and the Pitzer interaction coefficients are consistent with the implementation in commonly used geochemical computational programs, allowing direct use without further modification.

1 Introduction

Redox reactions are important for the description of geochemical reactions in general (e.g., pyrite oxidation) and of solubility limitations of radioactive contaminants in particular. In a final deep geological repository (DGR) for radioactive waste, attainment of anoxic conditions is very likely in the post-closure phase of operation. In the event of any post-

closure access of an aqueous solution to the waste, and assuming anoxic conditions, many radionuclides are immobile to a large extent through the formation of poorly soluble (hydro-)oxides in their reduced tetravalent form [e.g., TcO_2(am), $U(OH)_4$(am), $Np(OH)_4$(am), PuO_2(am/cr), etc.] (Grenthe et al., 2020). However, under strongly reducing conditions even their trivalent forms e.g., $Pu(OH)_3$(am/cr) might exist, showing a higher solubility and thus mobility than the tetravalent actinides (Grenthe et al., 2020). This holds also for higher redox states (penta-, hexa- or heptavalent), which are more soluble in water. Concerning all of these redox-triggered transformations, exact knowledge of the redox potential (E_H/pe) is essential, which in turn depends on the correct description of dissolved oxygen. For an assessment of the maximum likely mobilization of radionuclides from the near field of a DGR under the prerequisite of intrusion of water, the mass of available dissolved oxygen (being present, e.g., by diffusional transport or freshwater intrusion) is one key factor for the retardation of radionuclides in aqueous solution.

In geochemical speciation codes such as PHREEQC (Parkhurst and Appelo, 2013), Geochemist's Workbench (Bethke, 2022), or EQ3/6 (Wolery, 1992), redox reactions of any kind are linked for computational reasons to the hypothetical half-cell reaction
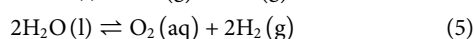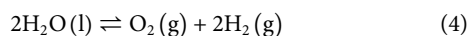
$$2\,H_2O\,(l) \rightleftharpoons O_2\,(g) + 4\,H^+ + 4\,e^- \qquad (1)$$
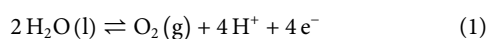
Or, alternatively, to another form involving dissolved oxygen:

$$2H_2O\,(l) \rightleftharpoons O_2\,(aq) + 4H^+ + 4e^- \qquad (2)$$

Adding the reaction

$$4H^+ + 4e^- \rightleftharpoons 2H_2\,(g) \qquad (3)$$
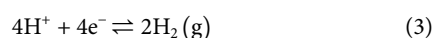
for which, by definition, $\log_{10} K\,(3) = 0$ the half-cell reactions become

$$2H_2O\,(l) \rightleftharpoons O_2\,(g) + 2H_2\,(g) \qquad (4)$$
$$2H_2O\,(l) \rightleftharpoons O_2\,(aq) + 2H_2\,(g) \qquad (5)$$

Reactions (Eq. 4) and (Eq. 5) are sometimes referred to as "$\log K$-E_H-reaction." In data files for the above-mentioned codes, equilibrium constants for these reactions are either given as functions of temperature or as "temperature grids," where pre-calculated values at defined temperatures (usually 0, 25, 60, 100, 150, 200, 250, and 300°C) are displayed. Unfortunately, this is usually done without any references to literature or a hint to the validity limits at all. The situation becomes even more obscure if the reaction (Eq. 5) containing O_2(aq) is used as half-cell reaction, because this reaction must in fact be considered as addition of reaction (Eq. 4) and

$$O_2\,(g) \rightleftharpoons O_2\,(aq). \qquad (6)$$

This poses the question about the experimental foundations for the calculation of the solubility of molecular oxygen in water at temperatures up to 573.15 K. If applied in calculations for high-saline solutions the question arises concerning the impact of ionic strength in general or the presence of specific electrolytes on the solubility of molecular oxygen in particular. In such cases, the Pitzer ion-interaction approach provides a tool for calculating the activity coefficient in concentrated salt solutions (Pitzer, 1991). For this purpose, coefficients for a virial equation are used for binary and ternary interactions between ions as well as uncharged species in aqueous

solution, reflecting the deviation from the behavior in pure water. In some data files, e.g., the "Yucca Mountain Pitzer file" (Mariner, 2004) delivered with the EQ3/6 code, Pitzer coefficients for O_2(aq) are included, some valid at 298.15 K only, others are given with a temperature function of unknown validity range. Compilations of data from different sources may cause inconsistencies, which, especially when using the interaction coefficients, may have a significant negative impact on the results of the models obtained.

Facing the task of extending a thermodynamic database based on traceable experimental data, simple adoption of precalculated equilibrium constants in temperature grids from parameter files in geochemical codes is not appropriate, particularly since they are provided in many databases without reference to the source of the primary data. Consequently, these data had to be comprehensibly and consistently recalculated from experimental data for the solubility of oxygen at various temperatures in both pure water and salt solutions and from standard formation data.

For this purpose, solubility data of O_2 in pure water as well as in a wide variety of electrolyte solutions were critically evaluated and combined with well-established thermodynamic data for liquid water H_2O(l), H_2(g), and O_2(g) to create an internally consistent set of equilibrium constants for reactions (Eqs 4–6). With respect to O_2(g) solubility data, the focus was on the system of oceanic salts (including carbonates), which are relevant as potential host rocks implying solutions of high ionic strengths. The alkali ((di-)hydrogen) phosphates were included for inorganic phosphate ions that can form in nuclear waste repositories when phosphate glasses or lanthanide phosphate monazites ($LnPO_4$), as waste forms of highly active waste streams, undergo dissolution processes in contact with water. The acids of the anions contained in the system were included in the data set to represent the case of acid-forming oxidation of minerals (acid mine drainage). Hydroxides were included to allow calculation for alkaline solutions from cement pore waters.

2 Theory and methods

Henry's law constant ($K_{O_2\text{(aq)}}$) using the partial pressure of O_2 in the gas phase describes the equilibrium condition for dissolution reaction of O_2 in water (Eq. 6) with $\gamma_{O_2\text{(aq)}}$ being the O_2 activity coefficient, $m_{O_2\text{(aq)}}$ the molal O_2 concentration in solution and $f_{O_2\text{(aq)}}$ the O_2 fugacity in the gas phase.

$$K_{O_2\,(aq)} = \frac{[O_2\,(aq)]}{[O_2\,(g)]} = \frac{\gamma_{O_2\,(aq)} \cdot m_{O_2\,(aq)}}{f_{O_2\,(g)}} \qquad (7)$$

Geochemical codes treat the temperature dependence of equilibrium constants as polynomial functions with several temperature-dependent terms (Eq. 8) or mathematically equivalent transformations thereof.

$$\log_{10} K\,(T) = A_1 + A_2 T + \frac{A_3}{T} + A_4 \ln T + \frac{A_5}{T^2} + A_6 T^2 \qquad (8)$$

The *Pitzer formalism* is widely used to account for the deviation from ideality of aqueous solutions of high ionic strength. It has proven capable of calculating solubilities in saturated solutions in the system of oceanic salts: Na^+, K^+, Mg^{2+}, Ca^{2+} – Cl^-, SO_4^{2-}, HCO_3^- – CO_2(g) – H_2O(l). The probably most cited paper in this

respect is the one by Harvie, Møller and Weare (Harvie et al., 1984), whose results are often referred to as "HMW-database." The usability of their database was demonstrated for a huge amount of application cases. One example especially relevant for nuclear waste disposal is by Herbert, who successfully modeled dissolution and precipitation processes in complex, saturated salt solutions in German rock salt formations (Herbert et al., 2000). Later, the HMW-database was extended to higher temperatures (Christov and Møller, 2004). Its popularity, as well as that of the Pitzer formalism in general, was promoted by the fact that it got implemented in various geochemical codes, such as PHREEQC, EQ3/6, Geochemist's Workbench, but also in CHEMAPP (Eriksson and Spencer, 1995; Eriksson et al., 1997), GEMS (Wagner et al., 2012; Kulik et al., 2013), or recently TOUGHREACT (Zhang et al., 2006). In parallel, the HMW-database was further developed and extended in response to the necessities of national programs for the disposal of radioactive waste in salt rock formations with the potential to contain high-saline solutions, e.g., the Yucca Mountain project (United States) (Mariner, 2004), the Waste Isolation Pilot Plant project (United States) (Domski and Nielsen, 2019), or the Oceanic Salt System from Voigt (2020) (Voigt, 2020a; Voigt, 2020b) with the alkali phosphate data from Scharge et al. (2013), Scharge et al. (2015) and the carbonate data from Harvie et al. (1984) as compiled in the THEREDA project in Germany (Moog et al., 2015; THEREDA, 2023). The Pitzer formalism was also applied to marine chemistry. Millero and co-workers over many years worked on a database specifically suited for seawater, e.g., (Pierrot and Millero, 2017). Recently, the Scientific Committee on Ocean Research of the International Council for Science (SCOR) created working group 145 to establish a reference seawater chemical speciation model, which is based on the Pitzer model (Turner et al., 2016).

The Pitzer formalism extends the Debye-Hückel equation with a virial expansion to account for binary and ternary ionic-strength-dependent specific interactions between ions of likewise and opposite charge (Pitzer, 1991). Explicit formulations for binary and ternary solutions of cations and anions are given by Scharge et al. (2012). In the present work, non-ideal interactions between a neutral component $O_2(aq)$ and cations or anions are investigated. More specifically, the focus is set on binary λ-interactions (between a neutral and a charged solute) and ternary ζ-interactions (one uncharged and two oppositely charged solutes), η-interactions (one uncharged and two similar charged solutes) and μ-interactions (two different uncharged and one charged solutes). The activity coefficient for a neutral species according to Pitzer (Pitzer, 1991) is:

$$\ln \gamma_N = 2 \left(\sum_c m_c \lambda_{Nc} + \sum_a m_a \lambda_{Na} + \sum_n m_n \lambda_{Nn} \right) + \sum_c \sum_a m_c m_a \zeta_{Nca}$$
$$+ \sum_c \sum_{c'} m_c m_{c'} \eta_{Ncc'} + \sum_a \sum_{a'} m_a m_{a'} \eta_{Naa'} + \sum_c \sum_n m_c m_n \mu_{Nnc}$$
$$+ \sum_a \sum_n m_a m_n \mu_{Nna}$$

$$(9)$$

Note, that in Eq. 9 $\eta_{Ncc'}$, $\eta_{Naa'}$, $\mu_{Nn'c}$ and $\mu_{Nn'a}$ refer to interactions between a neutral solute and to two different non-neutral solutes with likewise charge. These interactions are mathematically identical to a ternary ζ-interaction. It is perhaps for this reason, that sometimes they are not properly distinguished in data files and instead referred to as ζ- or even ψ-interactions altogether.

A few publications are available in the literature providing Pitzer interaction coefficients for molecular oxygen in electrolyte solutions. Namely, the works of Clegg and Brimblecombe (1990), Millero et al. (2002a), Millero et al. (2002b), Millero et al. (2003), Millero and Huang (2003), Geng and Duan (2010), and Zheng and Mao (2019) are worth mentioning here. However, combining these data sets with the only existing Pitzer data set valid for higher temperatures and including the whole Oceanic Salt System (THEREDA) leads to inconsistencies. Such inconsistent databases will produce incorrect modeling results. This is demonstrated in Figure 1 by recalculating experimental data of O_2 solubility in NaCl solution from literature (Millero et al., 2002a; Millero et al., 2002b; Millero et al., 2003). This does not mean that the various available Pitzer datasets for oxygen are of poor quality. However, it illustrates the importance of consistent data sets.

2.1 Data treatment

This work focusses on primary experimental results. Respective literature on the solubility of molecular oxygen in pure water as well as in electrolyte solutions was collected, critically assessed, and used to recalibrate the temperature-dependent Henry's law constant as well as the Pitzer interaction coefficients.

In many publications, the O_2 solubility data are given in figures only. In these cases, the data were re-digitized using the software package "Engauge Digitizer" from Mitchell et al. (2020). The uncertainty resulting from this digitization step depends on the quality of the graphics, but in most cases can be neglected compared to the experimental uncertainty.

Experimentally obtained O_2 solubility data are published using various different formats and units. Here, all datasets were recalculated to a micromolal scale (μmoles O_2 per kg of water) as a function of salt concentration in molal scale (moles salt per kg of water). If the concentration data were available in a volume-related concentration unit, e.g., molar (moles per liter solution), they were converted using the density functions according to Söhnel and Novotný (1985). All solubility data on molecular oxygen in both, pure water and electrolyte solutions are provided in the supporting information.

2.2 Parameter optimization

All parameters for temperature dependency equations—for Henry's law temperature equation as well as for the Pitzer interaction coefficients—were determined using the geochemical speciation software PHREEQC (batch version 3.7) (Parkhurst and Appelo, 2013) coupled with the parameter estimation software UCODE_2014 (Poeter et al., 2014) that uses a minimization of sum of squared residuals approach.

To determine the numerical values for the parameters of the temperature dependent Henry's law Eq. 8, data for the oxygen solubility in pure water were collected from the literature. These solubility datasets were used to fit the simplified temperature function

equation using parameters A_1, A_3, and A_4 only. The common geochemical codes (e.g., ChemApp, Geochemist's Workbench, PHREEQC, ToughReact) use six temperature parameters (Eq. 8 or mathematically equivalent transformations thereof) for the temperature-dependent description of reaction constants. Since a complete set of these temperature parameters must be specified in the code-specific parameter files, the other parameters (A_2, A_5 and A_6) are set to zero. Older codes like EQ3/6 use a temperature-dependend grif of up to eight $\log K$ values; these can be easily calculated from the parameterized equation.

Most geochemical programs treat the Pitzer coefficients and their temperature parameter in a different way. There, polythermal equations use terms where the temperature is given relative to a reference temperature (mostly T = 298.15 K, sometimes referred to as "25°-centered"), see Eq. 10 or mathematically equivalent transformations thereof.

$$P = X_0 + X_1\left(\frac{1}{T} - \frac{1}{T_r}\right) + X_2 \ln\left(\frac{T}{T_r}\right) + X_3\left(T - T_r\right) + X_4\left(T^2 - T_r^2\right)$$
$$+ X_5\left(\frac{1}{T^2} - \frac{1}{T_r^2}\right)$$

(10)

P is a Pitzer coefficient (here λ, ζ or η), T is the temperature in Kelvin, and T_r is the reference temperature (298.15 K) and ln the natural logarithm.

It was numerically impossible to fit all necessary temperature function parameters for all relevant Pitzer coefficients simultaneously. Therefore, a step-by-step approach was chosen: By definition, the coefficient $\lambda(O_2\text{-}Cl^-)$ and therefore all temperature parameters for (X_0–X_5) were set to 0. First, the Pitzer coefficients at T = 298.15 K were fitted using the experimental O_2 solubility data for the chemical subsystem H^+, Na^+, K^+ - Cl^-, OH^- - $H_2O(l)$ only. The resulting values of the coefficients were then used in the successive fitting of the chemical subsystems H^+, Na^+, K^+ - SO_4^{2-} - $H_2O(l)$, Na^+, K^+ - CO_3^{2-} - $H_2O(l)$ and H^+, Na^+, K^+ - PO_4^{3-} - $H_2O(l)$. All obtained interaction coefficients were then used as boundary conditions to fit interaction coefficients within the chemical subsystems of the Earth alkaline chlorides and Earth alkaline sulfates, respectively: Mg^{2+}, Ca^{2+} - Cl^-, OH^- - $H_2O(l)$ as well as Mg^{2+} - SO_4^{2-}, OH^- - $H_2O(l)$. Finally, the interaction coefficients $\eta(Cl^-\text{-}SO_4^{2-})$ and $\eta(Na^+\text{-}Mg^{2+})$ for ternary salt solutions ($NaCl + Na_2SO_4$, $NaCl + MgCl_2$) were fitted.

During the parameter determination, first all possible combinations of binary (λ) and ternary ($\zeta/\eta/\mu$) Pitzer coefficients should be determined. It became apparent that not all such coefficients were needed to describe the system, or that some combinations of binary and ternary coefficients were strongly cross-correlated. By reducing the number of adjustable coefficients, it was possible to create a data set that was sufficient to describe the system while using a minimum number of coefficients.

The coefficient for the ternary interaction $\zeta(O_2\text{-}Na^+\text{-}OH^-)$ is not needed for the description of the system at 298.15 K. However, for the polythermal description of the system, this interaction cannot be neglected. Therefore, the coefficient was set to zero at 298.15 K.

The values of the Pitzer coefficients at T = 298.15 K correspond to the X_0 parameters in Eq. 10. Thus, in the following steps, the Pitzer coefficients valid at T = 298.15 K were used as boundary parameters for the fits of the temperature dependency parameters X_1 to X_5. It was found that only the first two parameters (X_1 and X_2) had to be adjusted to fully describe the temperature dependency of the $O_2(aq)$ Pitzer coefficients. Thus, all other parameters (X_3, X_4 and X_5) are set to zero.

A simultaneous fit of the temperature equations parameters including all chemical systems was not possible. Therefore, temperature parameters for the systems of solutions of binary electrolytes were iteratively fitted individually and sequentially until none of the parameters changed. Figure 2 shows the fitting scheme for the generation of the Pitzer interaction coefficients temperature parameters. Thus, a consistent set of parameterized temperature equations of the Pitzer interaction coefficients could be deduced.

The coefficient for the ternary interaction $\zeta(O_2\text{-}K^+\text{-}HSO_4^-)$ could not be retrieved at 298.15 K as there are no experimental data for this temperature. The only O_2 solubility data available for the alkali hydrosulfate ($NaHSO_4$ and $KHSO_4$) system were acquired at 310.2 K (Lang and Zander, 1986). The experimental data of the chemical system O_2-Na_2SO_4-H_2O could be described without a ternary interaction coefficient. For the description of the experimental data of the chemical system O_2-K_2SO_4-H_2O, however, a ternary interaction coefficient $\zeta(O_2\text{-}K^+\text{-}HSO_4^-)$ had to be introduced. To do so, the value for the $\zeta(O_2\text{-}K^+\text{-}HSO_4^-)$ coefficient was determined only in the context of the fits of the temperature parameters but had to be used as temperature independent one, since only experimental measured values for a single temperature are available. Verifying calculations including this coefficient in the fits of the 298.15 K data (X_0 parameter) showed that this coefficient has no influence on the previously determined systems—namely, O_2-K_2SO_4-H_2O.

For the chemical systems for which no O_2 solubility data are available at temperatures different from T = 298.15 K (carbonate system, phosphate system, ternary salt mixtures) no temperature parameters of the Pitzer coefficients could be obtained. Consequently, these Pitzer coefficients are valid at T = 298.15 K only and not included in Figure 2.

3 Data assessment

3.1 Literature review and data selection

The aim of this work was to create a thermodynamic data set to calculate the oxygen solubility in pure water as well as in solutions containing ions ubiquitous in nature: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HSO_4^-/SO_4^{2-}, HCO_3^-/CO_3^{2-}, $H_2PO_4^-/HPO_4^{2-}/PO_4^{3-}$.

IUPAC published two reviews by Battino et al. (1981) and Clever et al. (2014) on available solubility data of molecular oxygen in pure water as part of the Solubility Data Series. This data collection was used here as a basis to create a temperature function for the solubility of O_2. From these reviews, only solubility data within the temperature range from 273.15 up to 373.15 K with an oxygen partial pressure of 101.325 kPa were used. Solubility data at temperatures above 373.15 K were omitted as they are not the focus of the intended future usage of this data set. Moreover, due to the large scattering of
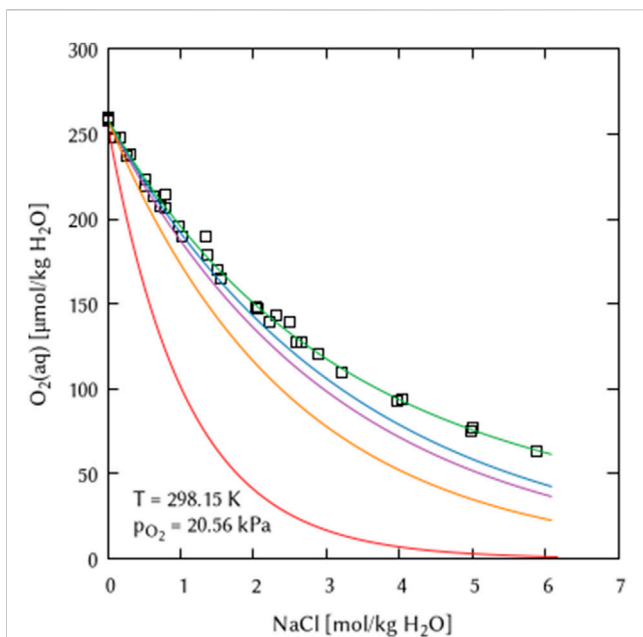
FIGURE 1
Effect of combining inconsistent Pitzer datasets on the example of O_2 solubility in NaCl solution. □ Experimental data from Millero et al. (2002a), Millero et al. (2002b), Millero et al. (2003), lines: Calculation using the THEREDA Pitzer dataset (Moog et al., 2015; Voigt, 2020a; Voigt, 2020b; THEREDA, 2023) in combination with: blue) Millero et al. (2003), purple) Clegg and Brimblecombe (1990), orange) Geng and Duan (2010), red) Zheng and Mao (2019), green) this work.

the experimental data, using them significantly impaired the quality of the fitting results of the Henry's law constant's temperature equation at lower temperatures—specifically below 298.15 K.

For the O_2 solubility in salt solutions, the number of publications containing experimental data is quite limited. A critical data evaluation was performed using the following criteria:

- Completeness of experimental conditions given,
- For datasets of electrolyte solutions: Agreement of the O_2 solubility in the peripheral system (pure water at the given temperature) with accepted experimental values of the review workers of IUPAC or the calculated values from the temperature function of this work,
- Consistency in the order of magnitude and progression of the O_2 solubility decrease with increasing salt concentration between datasets from different sources,
- Total gas pressure up to 101.325 kPa (1 atm): experimental datasets derived at higher pressures were discarded,
- Temperature range: References with experimental O_2 solubility were ranked higher when they 1) provide data at T = 298.15 K and 2) provide data over a broader temperature range. This was done in order to create a data set with the highest possible applicability while maintaining consistency with the interaction coefficients valid at T = 298.15 K that were created in the first fitting step.

The literature review and data assessment on O_2 solubility in salt solutions is given in Table 1.
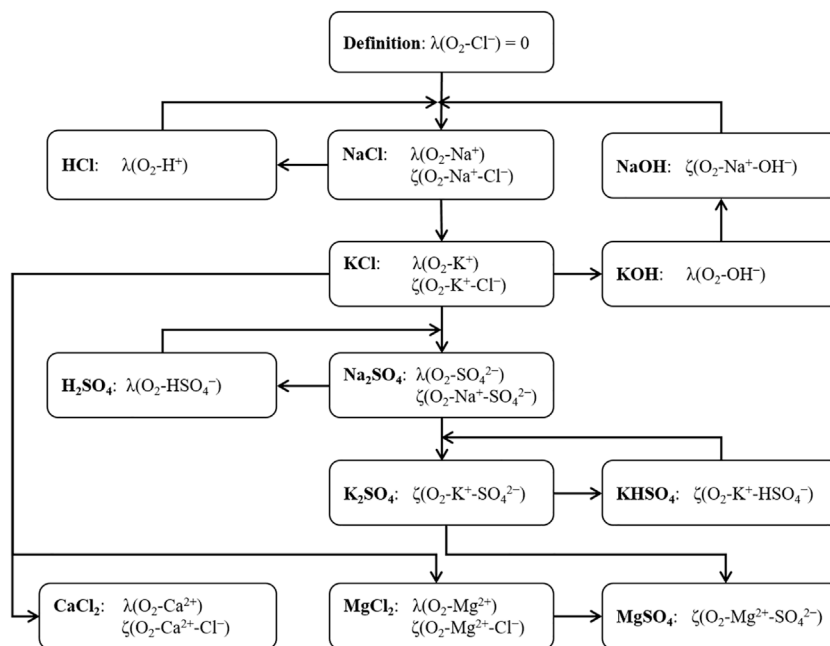

FIGURE 2
Fitting scheme for the generation of the Pitzer interaction coefficients temperature parameters.

TABLE 1 Literature review and data assessment on O$_2$ solubility in salt solutions.

References	Electrolyte	O$_2$ partial pressure	Temperature	Comments	Selected for fitting
		[kPa]	[K]		
Armenante and Karlsson (1982)	NaCl	20.9	293.15	Dataset shows a significantly stronger O$_2$ solubility decrease with increasing electrolyte concentration compared with other references dealing with NaCl.	No
Baykut and Aroguz (1989)	NaCl, MgCl$_2$, Na$_2$SO$_4$, Na$_3$PO$_4$,	102.26	293.15–308.15	A pressure of 767 mm Hg is given but no information on the O$_2$ partial pressure. The given O$_2$ concentrations suggest that air and not pure oxygen was used. The O$_2$ solubility value in pure water is significantly lower (−10%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014), the O$_2$ concentration calculated with the Henry's law function from this work. The O$_2$ solubility is only given for NaCl and Na$_2$SO$_4$ solutions as tabulated values. For other salt solutions only graphs are available, their quality is too poor to extract the solubility data.	No
Bikov (1937)	KCl	9,810	273.15–513.15	O$_2$ solubility in air and pure oxygen at p$_{tot}$ = 9.81 MPa is given. These O$_2$ partial pressures were considered to be outside the validity range of the Henry's law temperature function generated in this work.	No
Bohr (1910)	H$_2$SO$_4$	101.325	294.15	The O$_2$ solubility value in pure water is significantly lower (−24%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014), the O$_2$ concentration calculated with the Henry's law function from this work.	No
Broden and Simonson (1978)	NaHCO$_3$	1,000–5,000	333.15–433.15	The high-pressure datasets are out of the validity range of the Henry's law constant function obtained in this work. So, these datasets had to be rejected and no binary or ternary Pitzer interaction coefficients for O$_2$(aq) and HCO$_3^-$ could be obtained.	No
Broden and Simonson (1979)	NaHCO$_3$	1,000–5,000	333.15–433.15	The high-pressure datasets are out of the validity range of the Henry's law constant function obtained in this work. So, these datasets had to be rejected and no binary or ternary Pitzer interaction coefficients for O$_2$(aq) and HCO$_3^-$ could be obtained.	No
Bruhn et al. (1965)	NaOH, H$_2$SO$_4$	101.325	323.15–523.15	Only the experimental data at T = 323.15 K were used in this paper. H$_2$SO$_4$ dataset shows a much smaller decrease of the O$_2$ concentration with increasing acid concentration.	NaOH: Yes, H$_2$SO$_4$: No
Chatenet et al. (2000)	NaOH	98–99	298.15	No shortcoming	Yes
Cramer (1980)	NaCl	4,300–5,200	276.15–562.15	The O$_2$ partial pressures used were considered to be outside the validity range of the Henry's law temperature function generated in this work.	No

TABLE 1 (*Continued*) Literature review and data assessment on O$_2$ solubility in salt solutions.

References	Electrolyte	O$_2$ partial pressure [kPa]	Temperature [K]	Comments	Selected for fitting
Cramer (1984)	NaCl	21.21	273.15–298.15	The O$_2$ solubility in pure water does not match with values recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) nor the O$_2$ concentration calculated with the Henry's law function from this work.	No
Das (2005)	H$_2$SO$_4$	101.325	298.15	No shortcoming	Yes
Davis et al. (1967)	KOH	101.325	273.15–333.15	O$_2$ solubility deviates significantly (−1.5% to −6.8%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) and the O$_2$ concentration calculated with the Henry's law function from this work.	T = 298.15 K: Yes, other temperatures: No
Eucken and Hertzberg (1950)	NaCl, KCl, MgCl$_2$	101.325	273.15–298.15	O$_2$ solubility deviates significantly (up to +7.6%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) and the O$_2$ concentration calculated with the Henry's law function from this work.	No
Geffcken (1904)	NaCl, HCl, NaOH, KOH, K$_2$SO$_4$, H$_2$SO$_4$	101.325	288.15 and 298.15	In the alkaline chloride and alkaline sulfate datasets, the O$_2$ solubility decrease with electrolyte concentration strongly differs from the trend of the decrease in other references using these electrolytes. Furthermore, the available data exceed the solubility limit of K$_2$SO$_4$. The dataset was used in the systems where only few to no data are available.	HCl, NaOH, KOH, H$_2$SO$_4$: Yes, NaCl KCl, K$_2$SO$_4$: No
Glazunov et al. (1997)	NaOH	100	358.15	Observed O$_2$ solubility data are too low by a factor of ten.	No
Gubbins and Walker (1965)	KOH, H$_2$SO$_4$, H$_3$SO$_4$	101.325	298.15	Dataset shows a significantly lower O$_2$ solubility in the lower H$_2$SO$_4$ concentration range than the data from all other references dealing with H$_2$SO$_4$.	H$_2$SO$_4$: No, KOH, H$_3$PO$_4$: Yes
Hayduk (1991)	H$_2$SO$_4$	101.325–1013.2	298.15–458.15	Experimental data outside the validity range of the Henry's law temperature function used in this work.	No
Iwai et al. (1993)	NaCl, K$_2$HPO$_4$, KH$_2$PO$_4$	101.325	NaCl: 303.15 and 310.15, K$_2$HPO$_4$, KH$_2$PO$_4$: 298.15	As this is the only dataset available for the K$_2$HPO$_4$ and the KH$_2$PO$_4$ system, it is difficult to assess whether the data are reliable; the information in the reference does not contradict the use of this dataset. In the NaCl subsystem, the O$_2$ solubility decreases stronger with electrolyte concentration than in other datasets [e.g., (Millero et al., 2002a; Millero et al., 2002b; Millero et al., 2003)].	K$_2$HPO$_4$, KH$_2$PO$_4$: Yes, NaCl: No
Iwai et al. (1990)	NaCl	15	298.15	O$_2$ partial pressure of 15 kPa is given but does not match with the O$_2$ solubility in pure water which seems to be close to 101.325 kPa.	No
Kaskiala (2002)	H$_2$SO$_4$	100	298.15–328.15	In comparison with other experimental datasets, this one shows a much smaller decrease of the O$_2$ concentration with increasing acid concentration.	No

TABLE 1 (*Continued*) Literature review and data assessment on O$_2$ solubility in salt solutions.

References	Electrolyte	O$_2$ partial pressure	Temperature	Comments	Selected for fitting
		[kPa]	[K]		
Khomutov and Konnik (1974)	NaCl, KCl, NaOH, Na$_2$SO$_4$, K$_2$SO$_4$, Na$_2$CO$_3$, K$_2$CO$_3$, Na$_3$PO$_4$, K$_3$PO$_4$	21.278	298.15	Dataset shows a significantly stronger decrease of O$_2$ solubility with increasing electrolyte concentration than data from Millero et al. (2003) [28, 29]. However, since there are no other experimental O$_2$ solubility datasets for some chemical systems (Na$_2$CO$_3$, K$_2$CO$_3$, Na$_3$PO$_4$, K$_3$PO$_4$), these raw data are used in the fit.	Na$_2$CO$_3$, K$_2$CO$_3$, Na$_3$PO$_4$, K$_3$PO$_4$: Yes, NaCl, KCl, NaOH, Na$_2$SO$_4$, K$_2$SO$_4$: No
Knaster and Apelbaum (1964)	KOH	101.325	294.15–348.15	Datasets show a stronger decrease in O$_2$ solubility in the range of 2–5 m KOH than all datasets from other KOH references.	No
Lang and Zander (1986)	NaCl, KCl, MgCl$_2$, CaCl$_2$, NaOH, KOH, Na$_2$SO$_4$, NaHSO$_4$, K$_2$SO$_4$, KHSO$_4$, MgSO$_4$, H$_2$SO$_4$	101.325	310.2	Significantly stronger decrease in O$_2$ solubility with NaCl, KCl concentration than the Millero et al. (2003) data. As this is the only dataset available for the systems NaHSO$_4$ and KHSO$_4$, it is difficult to assess whether the data are reliable; the information in the reference does not contradict the use of this dataset.	KHSO$_4$: Yes, all others: No
Li (1994)	H$_2$SO$_4$	101.325	298.15–353.15	O$_2$ solubility deviates significantly (up to +5%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) and the O$_2$ concentration calculated with the Henry's law function from this work.	No
MacArthur (1916)	NaCl, KCl, MgCl$_2$, CaCl$_2$, Na$_2$SO$_4$, K$_2$SO$_4$	21.2	298.15	O$_2$ solubility deviates significantly (−3 to −5%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) and the O$_2$ concentration calculated with the Henry's law function from this work. Also, the K$_2$SO$_4$ dataset shows a significantly stronger decrease of O$_2$ solubility with increasing electrolyte concentration than data from Millero et al. (2003), Millero and Huang (2003). In NaCl system, the measured O$_2$ solubility at 6 mol/kg H$_2$O NaCl is too high (comparable values were reached at ~3 mol/kg H$_2$O in other papers).	No
Millero et al. (2002a)	NaCl, MgCl$_2$, Na$_2$SO$_4$, MgSO$_4$	20.56	298.15	No principle shortcoming. The dataset of the mixed electrolyte solution MgCl$_2$ + MgSO$_4$ was rejected because the authors mentioned the usage of two different stock solutions and inconsistent O$_2$ solubility in this subsystem.	NaCl + Na$_2$SO$_4$, Na$_2$SO$_4$+MgSO$_4$, NaCl + MgCl$_2$: Yes, MgCl$_2$+MgSO$_4$: No
Millero et al. (2002b)	NaCl, MgCl$_2$, Na$_2$SO$_4$, MgSO$_4$	20.56	273.15–318.15	No shortcoming	Yes
Millero et al. (2003)	NaCl, KCl, CaCl$_2$, K$_2$SO$_4$	20.56	298.15	No shortcoming	Yes
Millero and Huang (2003)	KCl, CaCl$_2$, K$_2$SO$_4$	20.56	278.15–318.15	No shortcoming	Yes
Narita et al. (1983)	H$_2$SO$_4$	101.325	298.15	No shortcoming	Yes
Ohkubo (2000)	NaCl	?	298.15–363.15	O$_2$ partial pressure unclear, O$_2$ solubility relative to solubility in pure water given	No

(Continued on following page)

TABLE 1 (*Continued*) Literature review and data assessment on O_2 solubility in salt solutions.

References	Electrolyte	O_2 partial pressure	Temperature	Comments	Selected for fitting
		[kPa]	[K]		
Pospíšol and Lužný (1960)	KOH	101.325	293.15	Dataset shows a much smaller decrease of the O_2 concentration with increasing KOH concentration (up to 2.5 times higher O_2 concentration than the other datasets).	No
Reynafarje et al. (1985)	KCl	20.2	278.15–313.15	No pure electrolyte solution: K-HEPES buffered KCl solutions	No
Shoor et al. (1968)	KOH	101.325	298.15–373.15	No shortcoming	Yes
Tan et al. (2001)	Na_2CO_3	1,000–10,000	308.15	Dataset was obtained using pressures above 101.325 kPa, which is out of scope of this work.	No
Yasunishi (1977)	Na_2SO_4	101.325	288.15–308.15	O_2 solubility deviates significantly (+4.8 to +10.0%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) and the O_2 concentration calculated with the Henry's law function from this work.	No
Yasunishi (1978)	KCl, $MgCl_2$, $CaCl_2$, NaOH, $MgSO_4$, Na_2CO_3	101.325	288.15–308.15	O_2 solubility deviates significantly (up to +11%) from data recommended by IUPAC (Battino et al., 1981; Clever et al., 2014) and the O_2 concentration calculated with the Henry's law function from this work.	No
Zhang et al. (2009)	NaOH	101.325	296	No shortcoming	Yes

TABLE 2 Temperature parameters of the logarithmic Henry's law constant ($\log K_{H,cp}$) for the O_2 solubility in pure water, Eq. 8.

Parameter	Value	Standard error
A_1	−71.95	0.35
A_3	3,625	34
A_4	9.984	0.056

4 Modelling results and discussion

4.1 Solubility of oxygen in pure water

The obtained temperature parameters for the $\log K_{H,cp}$ of the O_2 solubility in pure water are given in Table 2. The resulting temperature dependency equation describes the oxygen solubility in pure water very well (see Figure 3) while using only three of the six possible temperature terms.

Comparing the value at T = 298.15 K calculated with the obtained temperature function of Henry's constant with values found in other thermodynamic databases shows very good agreement, see Table 3.

4.2 Thermodynamic data for O_2(aq)

To create an internally consistent set of equilibrium constants for reactions (Eqs 4, 5) it is necessary to select thermodynamic data

for H_2O(l), O_2(g) and H_2(g). The temperature function for the standard molar Gibbs enthalpy of formation is calculated with

$$\Delta_f G_m^0(T) = \Delta_f G_{i,T=T_0}^0 - S_m^0(T - T_0) + \int_{T_0}^{T} C_{p,m}^0(T) dT$$

$$- T \int_{T_0}^{T} \frac{C_{p,m}^0(T)}{T} dT \qquad (11)$$

Within the frame of this chapter, we adopt the following general temperature function as extension of Eq. 8:

$$f(T) = A_1 + A_2 T + \frac{A_3}{T} + A_4 \ln T + \frac{A_5}{T^2} + A_6 T^2 + A_7 T^3 + A_8 T \ln T \qquad (12)$$

Application of this temperature function for $C_{p,m}^0(T)$, integration and rearrangement of Eq. 12 yields a general expression for the standard Gibbs energy of formation:

$$\Delta_f G_m^0(T) = B_1 + B_2 T + \frac{B_3}{T} + B_4 \ln T + \frac{B_5}{T^2} + B_6 T^2 + B_7 T^3 + B_8 T \ln T \qquad (13)$$

with

$$B_1 = \Delta_f G_{i,T=T_0}^0 + S_m^0 T_0 - A_1 T_0 - \frac{A_2}{2} T_0^2 - \frac{A_6}{3} T_0^3 - A_3 (\ln T_0 - 1) + \frac{A_5}{T_0} \qquad (14)$$
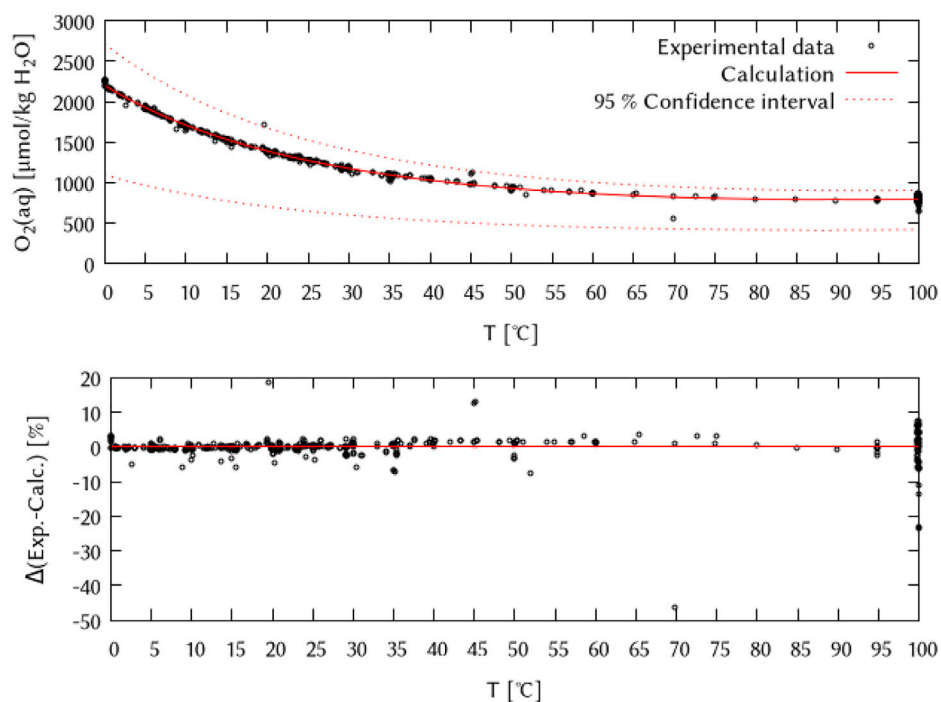
FIGURE 3
Temperature dependency of the logarithmic Henry's law constant of the O_2 solubility in pure water (expressed in µmol/kg $H_2O\cdot101.325$ kPa). Points: experimental data from literature references given by IUPAC (Battino et al., 1981; Clever et al., 2014), solid line: calculation (this work), dashed line: 95% confidence interval.

TABLE 3 Comparison of the logarithmic Henry's law constant ($\log K_{H,cp}$) for the O_2 solubility in pure water at T = 298.15 K used in different thermodynamic database projects and other sources.

Database	$\log K_{H,cp}$	Data references
OECD/NEA Thermochemical Database (TDB) Project Ragoussi and Costa (2019)	−2.90	Calculated from Cox et al. (1989)
ThermoChimie V11a Giffaut et al. (2014)	−2.90	Calculated from Cox et al. (1989)
PSI/Nagra Chemical Thermodynamic Database (12/07) Thoenen et al. (2014)	−2.8944	Calculated from Pearson and Berner (1991)
THERMODDEM Blanc et al. (2012)	−2.90	Calculated from Cox et al., (1989)
LLNL Delany and Lundeen (1991)	−2.8983	Calculated from Cox (1978)
JAEA Kitamura (2020)	−2.8983	Calculated from data in Kelley (1960) and Cox (1978)
JESS May and Muray (1991)	−2.96	Read and Broyd (1991)
JESS May and Muray (1991)	−2.90	Lumsdon and Evans (1995)
JESS May and Muray (1991)	−3.066	Carpenter (1966)
JESS May and Muray (1991)	−2.81	Phillips et al. (1985)
Mean of the above	−2.92	
This work	−2.904	

$$B_2 = -S^0_{i,T=T_0} + A_1 \left(1 + \ln T_0\right) + A_2 T_0 + \frac{A_6}{2} T_0^2 - \frac{A_3}{T_0} - \frac{A_5}{2T_0^2} \quad (15)$$

$$B_3 = -\frac{A_5}{2} \quad (16)$$

$$B_4 = A_3 \quad (17)$$

$$B_5 = 0 \quad (18)$$

$$B_6 = -\frac{A_2}{2} \quad (19)$$

$$B_7 = -\frac{A_6}{6} \quad (20)$$

$$B_8 = -A_1 \quad (21)$$

For the corresonding temperature function for $O_2(aq)$ the compiled solubility data for oxygen in pure water (Table 2) were used. The equilibrium constant for reaction (Eq. 6) can be expressed as [index numbers of coefficients refer to the general function (Eq. 12)]

$$\Delta_r G^0(T)(6) = -RT\ln(10)\log_{10} K(T)(6) = A_1 + A_2 T + A_8 T\ln T \quad (22)$$

Using the corresponding parameters for $O_2(g)$ the temperature function for the standard molar Gibbs enthalpy of formation is then calculated with

$$\Delta_f G^0_{O_2(aq)}(T) = \Delta_r G^0(T)(6) + \Delta_f G^0_{O_2(g)}(T) \quad (23)$$

For the next step, we use the following relations, where all temperature parameters A_i refer to the temperature function for $\Delta_r G^0(T)(6)$ in the form of the general function (Eq. 12). For this specific case only A_1, A_2, and A_8 are unlike zero.

$$\Delta_r H^0(T)(6) = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta_r G^0(T)(5)}{T}\right)_p$$
$$= A_1 + \frac{2A_3}{T} - A_4(1 - \ln T) + \frac{3A_5}{T^2} - A_6 T^2 \quad (24)$$
$$- 2A_7 T^3 - A_8 T$$

$$\Delta_r S(T)(6) = -\frac{\partial}{\partial T}\left(\Delta_r G^0(T)(6)\right)_p$$
$$= -A_2 + \frac{A_3}{T^2} - \frac{A_4}{T} + \frac{2A_5}{T^3} - 2A_6 T - 3A_7 T^2 - A_8(1 + \ln T) \quad (25)$$

$$\Delta_r C^0_p(T)(6) = \frac{\partial}{\partial T}\left(\Delta_r H^0(T)(6)\right)_p$$
$$= -\frac{2A_3}{T^2} + \frac{A_4}{T} - \frac{6A_5}{T^3} - 2A_6 T - 6A_7 T^2 - A_8 \quad (26)$$

One notes that the T^{-3}-term in Eq. 26 is not present in the standard T-function, Eq. 12. However, it is unequal to zero only if there is a T^{-2}-term in $\log K(T)$. This happens to be not the case in our proposal for $\log K(T)(6)$.

After evaluation for $T = T_0$ standard molar enthalpy of formation, standard entropy, and standard partial molal heat capacity of $O_2(aq)$ is calculated using the relations:

$$\Delta_f H^0_{O_2(aq),T=T_0} = \Delta_r H^0_{T=T_0}(6) \quad (27)$$

$$S^0_{O_2(aq),T=T_0} = \Delta_r S^0_{T=T_0}(6) + S^0_{O_2(g),T=T_0} \quad (28)$$

$$C^0_{p,O_2(aq)}(T) = \Delta_r C^0_p(T)(6) + C^0_{p,O_2(g)}(T) \quad (29)$$

with $\Delta_f H^0_{O_2(g),T=T_0} = 0$.

Selected and calculated thermodynamic data are summarized in Tables 4–6. Standard formation data were adopted from Cox et al. (1989); heat capacities between 280 and 500 K were adopted from Chase (1998). For liquid water $\Delta_f H^0_{H_2O(l),T=T_0}$ and $S^0_{H_2O(l),T=T_0}$ are identical in both sources. Applying the temperature function for $C^0_{p,H_2O(l)}(T)$ as indicated in Table 5, a value of $C^0_{p,H_2O(l),T=T_0} = 75.418$ J/mol·K could be obtained, which is in good agreement with $C^0_{p,H_2O(l),T=T_0} = 75.351 \pm 0.080$ J/mol·K from Cox et al. (1989) and Chase (1998). For gaseous oxygen Cox et al. (1989) lists $S^0_{O_2(g),T=T_0} = 205.152 \pm 0.005$ J/mol·K which covers $S^0_{O_2(g),T=T_0} = 205.147$ J/mol·K given by Chase (1998). For gaseous oxygen, a value of $C^0_{p,O_2(g),T=T_0} = 29.376$ J/K mol could be obtained, which exactly matches the value given by Chase (1998) and is in close agreement with $C^0_{p,O_2(g),T=T_0} = 29.378 \pm 0.003$ J/mol·K given in (Cox et al., 1989). For gaseous hydrogen Cox et al. (1989) and Chase (1998) list identical values for $S^0_{H_2(g),T=T_0}$ and $C^0_{p,H_2(g),T=T_0}$.

Uncertainties for standard formation data for $O_2(g)$, $H_2(g)$, and $H_2O(l)$ were adopted from Cox et al. (1989). Uncertainties for standard reaction and standard formation data for $O_2(aq)$ were calculated from the error of the temperature parameters for reaction (Eq. 6) in Table 2.

The obtained values are in good agreement with $\Delta_f H^0_{O_2(aq),T=T_0} = -12,134$ J/mol and $S^0_{O_2(aq),T=T_0} = 109$ J/mol·K as given by Shock et al. (1989). A significant difference remains for the standard partial molal heat capacity for $O_2(aq)$ at 298.15 K which is given in the same source as $C^0_{p,T=T_0} = 234$ J/mol·K. A reason for this is probably that Shock et al. in their work evaluated experimental data by Benson et al. (1979) and Stephan et al. (1956) only. Finally, with

$$\Delta_r G^0_m(T) = \sum_i \upsilon_i \Delta_f G^0_i(T) \quad (30)$$

$$\Delta_r G^0_m(T) = -RT\ln(10)\log_{10} K(T) \quad (31)$$

it was possible to calculate the temperature functions for $\log K(T)$ for reaction (Eqs 4, 5) by rearrangement of Eq. 31 and summation of corresponding temperature parameters for $\Delta_f G^0_i(T)$. Table 6 summarizes the results.

The valid range of temperature for reaction (Eq. 4) [formation of $O_2(g)$] is determined by the available heat capacity data for $H_2O(l)$. For reaction (Eq. 5) [formation of $O_2(aq)$] it is limited by the availability of solubility data. Note, that for the latter reaction the given validity range is valid for low saline solutions only. In saline solutions where Pitzer coefficients are applied and the geochemical code works with a half-cell reaction involving $O_2(aq)$, the valid temperature range can be lower and depends on the particular system, see Section 4.5.

TABLE 4 Standard reaction data for $O_2(aq)$.

Data type	Unit	Value
$\Delta_r H^0_{i,T=T_0}$	J/mol	$-12{,}411 \pm 971$
$\Delta_r S^0_{i,T=T_0}$	J/mol K	-97 ± 14
$\Delta_r G^0_{i,T=T_0}$	J/mol	$16{,}593 \pm 3{,}168$
$\Delta_r C^0_{p,T=T_0}$	J/mol K	191 ± 1

TABLE 5 Standard formation data for $H_2O(l)$, $O_2(g)$, $H_2(g)$, and $O_2(aq)$. Temperature parameters for $C_p^0(T)$ with regard to the general function (Eq. 12) were fitted to values from Chase (1998).

Species	$\Delta_f H^0_{i,T_0}$ (J/mol)	References	S^0_{i,T_0} (J/mol K)	References	$\Delta_f G^0_{i,T_0}$ (J/mol)	References	$C_p^0(T)$ (J/mol K)				T_{min}/T_{max} (K)	$C^0_{p,T=T_0}$ (1) (J/mol K)	References
							A_1	A_2	A_5	A_6			
$H_2O(l)$	−285,830 ± 40 (2)	Cox et al. (1989)/ Chase (1998)	69.95 ± 0.03 (2)	Cox et al. (1989)/ Chase (1998)	−237,140 ± 41	(1)	149 ± 11	−0.33 ± 0.04	−1,056,714 ± 250,728	0.00042 ± 0.00004	280/500	75.418	Chase (1998)
$O_2(g)$	0	(By definition)	205.152 ± 0.005 (2)	Cox et al. (1989)	0	(By definition)	24.64 ± 0.03	0.0121 ± 0.0001	100,230 ± 1,433	0	298.15/500	29.376	Chase (1998)
$O_2(aq)$	−12,411 ± 971	(This work)	108 ± 14	(This work)	16,593 ± 3,168	(This work)	(3)	(3)	(3)	(3)	(3)	249.90 ± 0.07	(This work)
$H_2(g)$	0	(By definition)	130.68 ± 0.003 (2)	Cox et al. (1989)	0	(By definition)	33.6 ± 0.2	−0.012 ± 0.001	−174,946 ± 3,652	$1.01 \pm 0.05 \times 10^{-5}$	298.15/500	28.836	Chase (1998)

(1) Internally calculated. (2) Data uncertainty adopted from Cox et al. (1989). (3) With our selection for the temperature dependence of Henry's law constant (Eq. 8 and Table 2) no temperature function for the standard molar heat capacity of reaction $\Delta_r C^0_{p,m}(T)$(6) can be derived. Hence, no temperature dependence for the standard molar heat capacity for $O_2(aq)$ can be given.

Using the temperature parameters in Table 6 the so-called "temperature grid" for "log$K$ for E_H-reaction" for codes like EQ3/6 was re-calculated. The results are given in Table 7. The range of temperature for which our parameters should be used is in fact narrower than is suggested in some data files for EQ3/6 or Geochemist's Workbench.

Not surprisingly, equilibrium constants given in Table 7 are similar to those currently available in data files for geochemical codes. The values given in this work, however, can be traced back to published standard formation and solubility data.

4.3 Solubility of oxygen in electrolyte solutions at T = 298.15 K

4.3.1 The system Na⁺, K⁺, H⁺/Cl⁻, OH⁻ - H₂O(l)

All binary mixtures of the chemical systems Na⁺, K⁺, H⁺/Cl⁻, OH⁻ - H₂O(l) were fitted simultaneously to obtain the Pitzer coefficients. As an initial coefficient λ(O_2(aq)-Cl⁻) was set to zero. Binary interaction coefficients (λ) for all cations and anions in the system could be obtained. During parameter reduction, it was found that only the ternary interaction coefficients ζ(O_2(aq)-Na⁺-Cl⁻) and ζ(O_2(aq)-K⁺-Cl⁻) are necessary to describe the system (Figure 4). Later fits of the temperature dependence parameters showed that a ternary ζ(O_2(aq)-Na⁺-OH⁻) coefficient becomes necessary at higher temperatures. At T = 298.15 K this coefficient was set to 0.

4.3.2 The system Na⁺, K⁺, H⁺/HSO₄⁻, SO₄²⁻ - H₂O(l)

The obtained binary interaction coefficients (λ) were used as initial values for the simultaneous fitting of the binary mixtures of the system Na⁺, K⁺, H⁺/HSO₄⁻, SO₄²⁻ - H₂O(l). The full set of binary [λ(O_2(aq)-HSO₄⁻) and λ(O_2(aq)-SO₄²⁻)] and ternary interaction coefficients [ζ(O_2(aq)-Na⁺- SO₄²⁻) and ζ(O_2(aq)-K⁺-SO₄²⁻)] was found do be necessary for a full description of the system (Figure 5).

For the solubility of oxygen in NaHSO₄ or KHSO₄ solutions, there are no data at T = 298.15 K available in literature. Thus, the ζ(O_2(aq)-K⁺-HSO₄⁻) value was not fitted from data at 298.15 K but from the only available data at 310.2 K from Lang and Zander (1986). The value was derived from a fitting using the polythermal data set (see Section 4.4). Since no temperature dependency could be retrieved, the ζ(O_2(aq)-K⁺-HSO₄⁻) value was set temperature independent. Therefore, the obtained value must be set to the 298.15 K term (A_0) in Eq. 10. The implementation of the ζ(O_2(aq)-K⁺-HSO₄⁻) coefficient had no influence of the fitting of the ζ(O_2(aq)-K⁺-SO₄⁻) coefficient, which was counterchecked. No value had to be fitted for ζ(O_2(aq)-Na⁺-HSO₄⁻) in NaHSO₄ solutions because the dataset derived in this work was already sufficient to describe the oxygen solubility in this solution without another ternary interaction coefficient (see Section 4.4.2).

4.3.3 The system Na⁺, K⁺/CO₃²⁻ - H₂O(l)

The previously obtained binary interaction coefficients (λ) were used as boundary conditions for the simultaneously fitting of the binary mixtures of the system Na⁺,K⁺/CO₃²⁻ - H₂O(l). A binary [λ(O_2-CO₃²⁻)] as well as two ternary interaction coefficients [ζ(O_2(aq)-Na⁺-CO₃²⁻) and ζ(O_2(aq)-K⁺-CO₃²⁻)] are required to describe the two systems (Figure 6).

TABLE 6 Temperature parameters for log$K$(T) for E_H reaction (Eqs 4, 5) according to Eq. 8.

Reaction	A_1	A_2	A_3	A_4	A_5	A_6	T_{min}/T_{max}
$2\,H_2O\,(l) \rightleftharpoons O_2\,(aq) + 2H_2\,(g)$	9.54885	0.01699	−28,638.33637	−0.78510	48,675.35491	−0.00001	273.15/373.15
$2\,H_2O\,(l) \rightleftharpoons O_2\,(g) + 2H_2\,(g)$	81.49885	0.01699	−32,263.33637	−10.76910	48,675.35491	−0.00001	298.15/473.15

TABLE 7 Calculated equilibrium constants for E_H reactions (Eqs 4, 5) as a function of temperature. Values in brackets are beyond the recommended range of validity.

T	$2\,H_2O(l) \rightarrow O_2(aq) + 2H_2(g)$	$2\,H_2O(l) \rightarrow O_2(g) + 2H_2(g)$
273.15	−94.9376	−92.2692
298.15	−85.9967	−83.0898
333.15	−75.6640	−72.5880
373.15	−66.1484	−63.0380
433.15	(−55.0488)	−52.0814
473.15	(−49.1486)	−46.3556
533.15	(−41.8864)	(−39.4232)
573.15	(−37.8522)	(−35.6368)

TABLE 8 Binary and ternary ion-neutral species interaction coefficients (λ, ζ, η) for the solubility of O_2 in salt solutions at T = 298.15 K. The uncertainty information refers to one standard deviation.

λ (species 1-2)	Value	ζ/η (species 1-2-3)	Value
$O_2(aq)$-Cl^-	0 (by definition)	$O_2(aq)$-H^+-HSO_4^-	−0.002472 ± 0.000302
$O_2(aq)$-H^+	0.02598 ± 0.00171	$O_2(aq)$-Na^+-Cl^-	−0.003767 ± 0.00579
$O_2(aq)$-Na^+	0.1315 ± 0.0093	$O_2(aq)$-Na^+-CO_3^{2-}	0.007437 ± 0.0224
$O_2(aq)$-K^+	0.135 ± 0.010	$O_2(aq)$-Na^+-SO_4^{2-}	−0.0381 ± 0.0073
$O_2(aq)$-Mg^{2+}	0.2293 ± 0.0032	$O_2(aq)$-Na^+-PO_4^{3-}	−0.0594 ± 0.0564
$O_2(aq)$-Ca^{2+}	0.2519 ± 0.0063	$O_2(aq)$-K^+-Cl^-	−0.01711 ± 0.00647
$O_2(aq)$-OH^-	0.06785 ± 0.00965	$O_2(aq)$-K^+-CO_3^{2-}	−0.09697 ± 0.017
$O_2(aq)$-SO_4^{2-}	0.1334 ± 0.0082	$O_2(aq)$-K^+-HPO_4^{2-}	−0.09593 ± 0.0286
$O_2(aq)$-HSO_4^-	0.03842 ± 0.00201	$O_2(aq)$-K^+-$H_2PO_4^-$	−0.1678 ± 0.0547
$O_2(aq)$-CO_3^{2-}	0.3234 ± 0.015	$O_2(aq)$-K^+-HSO_4^-	0.07411 ± 0.00741
$O_2(aq)$-PO_4^{3-}	0.2946 ± 0.0496	$O_2(aq)$-K^+-SO_4^{2-}	−0.1618 ± 0.078
$O_2(aq)$-HPO_4^{2-}	0.2512 ± 0.0241	$O_2(aq)$-Mg^{2+}-Cl^-	−0.006612 ± 0.00101
$O_2(aq)$-$H_2PO_4^-$	0.3718 ± 0.0233	$O_2(aq)$-Mg^{2+}-SO_4^{2-}	−0.05115 ± 0.00586
$O_2(aq)$-$H_3PO_4(aq)$	0.04841 ± 0.00241	$O_2(aq)$-Ca^{2+}-Cl^-	−0.01269 ± 0.00291
		$O_2(aq)$-Na^+-Mg^{2+}	−0.01753 ± 0.00601
		$O_2(aq)$-Cl-SO_4^{2-}	−0.01445 ± 0.00811

4.3.4 The system Na^+, K^+, H^+/H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} - $H_2O(l)$

The O_2 solubility in solutions of Na_3PO_4, K_3PO_4, K_2HPO_4, KH_2PO_4, and H_3PO_4 were fitted simultaneously to obtain the

interaction coefficients. For the System O_2-K_3PO_4 it was found that no ternary interaction coefficient ζ($O_2(aq)$-K^+-PO_4^{3-}) is necessary to describe the experimental data while a ζ($O_2(aq)$-Na^+-PO_4^{3-}) was required for the System O_2-Na_3PO_4. Also for
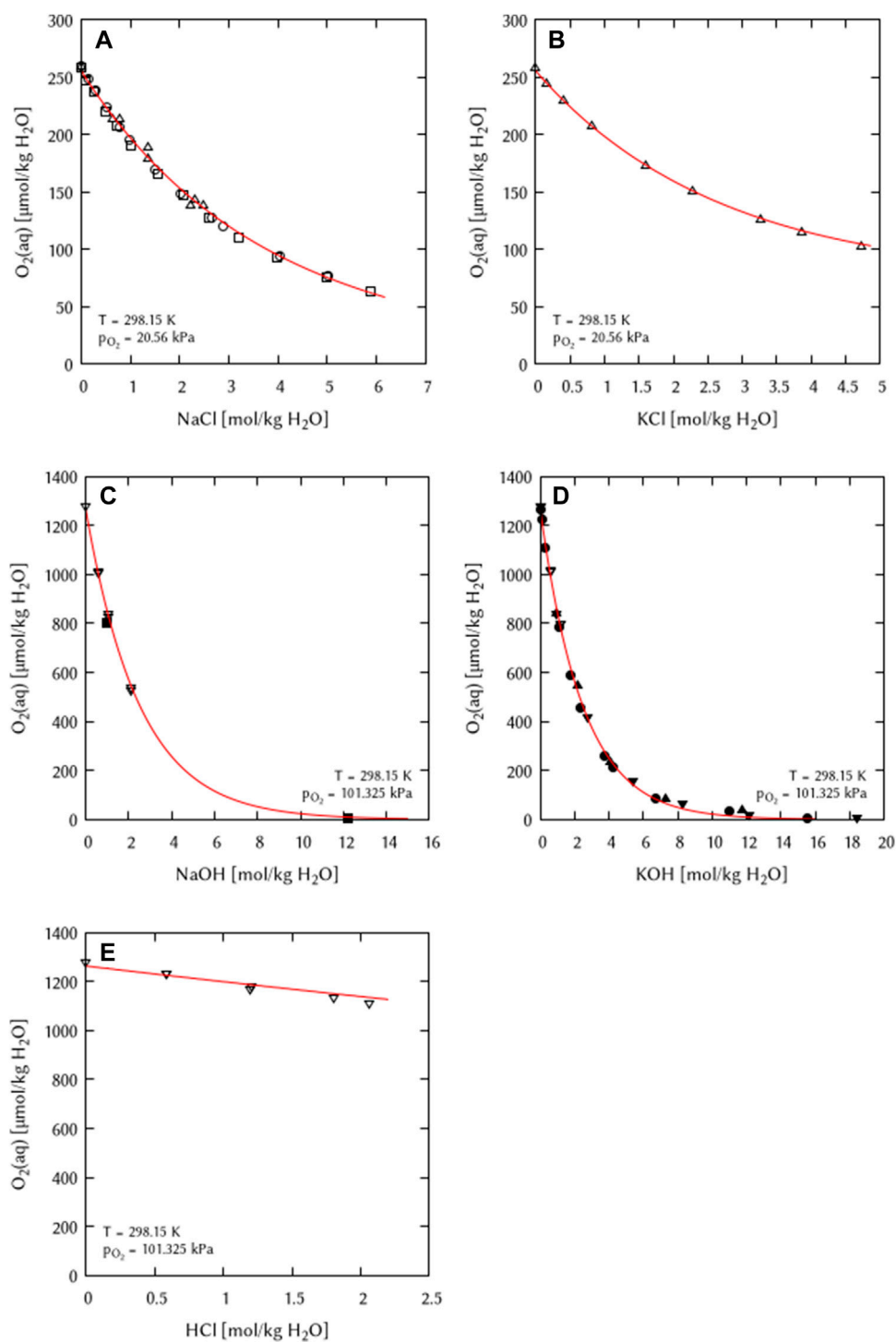
FIGURE 4
Modelling of the O_2 solubility in binary solutions of **(A)** NaCl, **(B)** KCl, **(C)** NaOH, **(D)** KOH, and **(E)** HCl as a function of the electrolyte concentration at T = 298.15 K (Points: Experimental data from: □ Millero et al. (2002a), ○ Millero et al. (2002b), △ Millero et al. (2003), ▽ Geffcken (1904), ■ Chatenet et al. (2000), ● Davis et al. (1967), ▲ Gubbins and Walker (1965), ▼ Shoor et al. (1968), Lines: this work).

the acidic potassium phosphate solutions (KH_2PO_4 and K_2HPO_4) as well as for phosphoric acid solutions, ternary interaction coefficients were found to be indispensable to fully describe these systems (Figure 7). No experimental O_2 solubility data were available for the acidic sodium phosphate solutions (NaH_2PO_4 and Na_2HPO_4). Therefore, it cannot be specified whether or not ternary interaction coefficients are necessary in these subsystems.
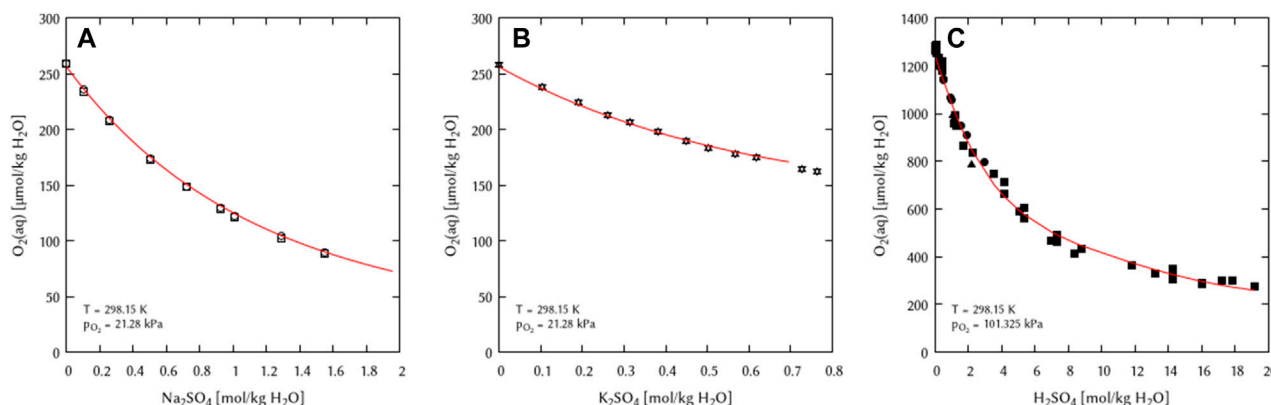
FIGURE 5
Modelling of the O_2 solubility in binary solutions of **(A)** Na_2SO_4, **(B)** K_2SO_4, and **(C)** H_2SO_4 as a function of the electrolyte concentration at T = 298.15 K (Points: Experimental data from: □ Millero et al. (2002a), ○ Millero et al. (2002b), △ Millero et al. (2003), ▽ Millero and Huang (2003), ■ Das (2005), ● Geffcken (1904), ▲ Narita et al. (1983), Lines: this work).
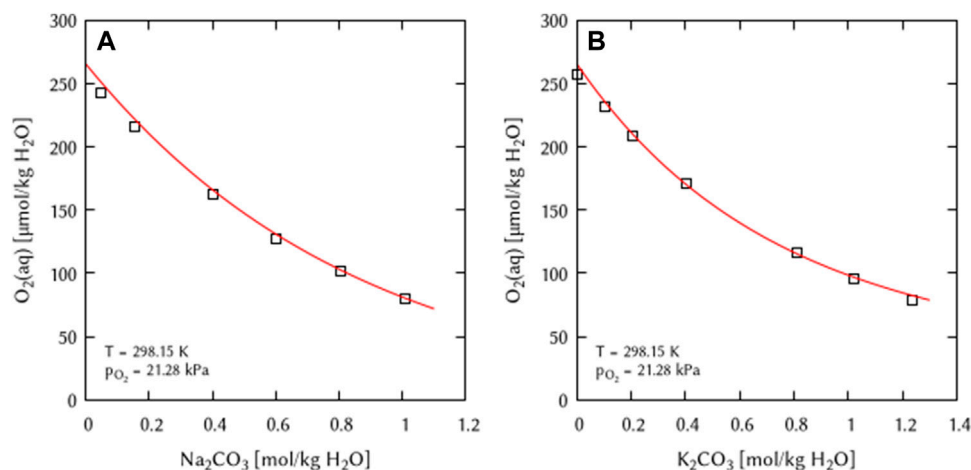

FIGURE 6
Modelling of the O_2 solubility in binary solutions of **(A)** Na_2CO_3, and **(B)** K_2CO_3 as a function of the electrolyte concentration at T = 298.15 K (Points: Experimental data from □ Khomutov and Konnik (1974), Lines: this work).

4.3.5 Earth alkaline salt solutions (CaCl$_2$, MgCl$_2$, MgSO$_4$)

Using the previously determined Pitzer coefficients as boundary conditions, the interaction coefficients for Earth alkaline salts and mixtures of salt solutions were deduced. For all three systems, a binary as well as a ternary interaction coefficient was necessary for a complete description (Figure 8).

4.3.6 Interaction coefficients for ternary salt solutions

The O_2 solubility data in ternary solutions of NaCl + MgCl$_2$ and NaCl + Na$_2$SO$_4$ was used to deduce the coefficients $\eta(O_2(aq)$-Na$^+$-Mg^{2+}) and $\eta(O_2(aq)$-Cl$^-$-SO$_4^{2-}$). The O_2 solubility data in the ternary solution of Na$_2$SO$_4$ + MgSO$_4$ was not used in the fitting procedure but to verify the obtained η coefficient (Figure 9). The obtained calculation results are in good agreement with the experimental data. The O_2 solubility data in the

ternary solution of MgCl$_2$ + MgSO$_4$ was also not used in the fitting, the authors claimed the usage of two different stock solutions within the experiment (Millero et al., 2002a). Only one data point matches with the calculation suggesting that—in agreement with the primary source—this point belonged to one charge of stock solutions while the other points belong to the experiments with other stock solutions.

Millero et al. (2002a) also experimentally studied O_2 solubility in the quaternary-reciprocal systems Na$^+$, Mg^{2+}/Cl$^-$, SO$_4^{2-}$ - H$_2$O were given. Interaction coefficients for these kind of systems could not be deduced because the Pitzer ion-interaction approach is limited to coefficients for ternary interactions while in this case a coefficient would be necessary for an interaction between four different species (O$_2$-c-a-a'/O$_2$-c-c'-a) in solution.

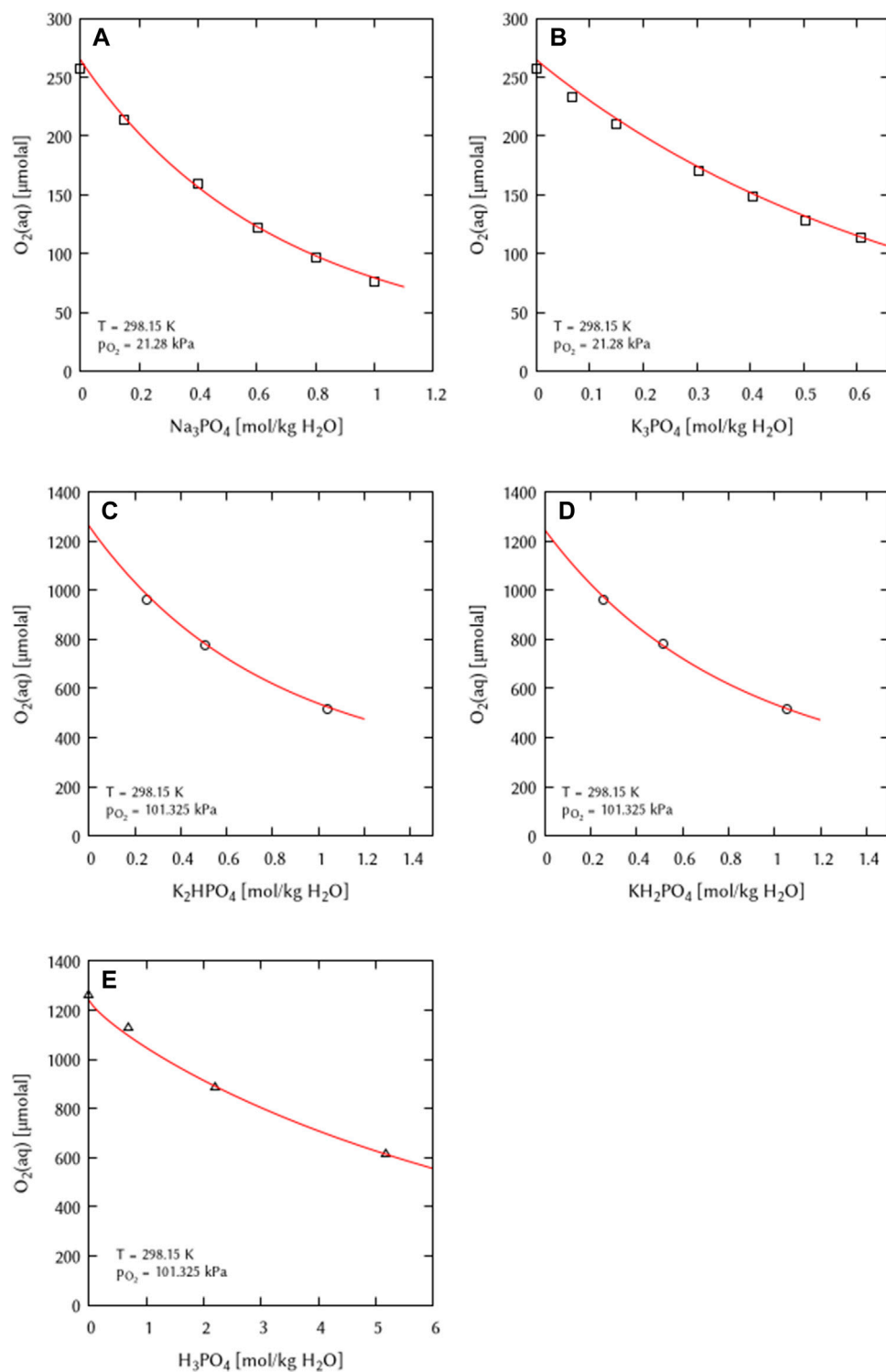The obtained Pitzer interaction coefficients—ion-neutral species pairs, λ and ion-neutral species triplets, ζ and η—are given in Table 8.

FIGURE 7
Modelling of the O_2 solubility in binary solutions of **(A)** Na_3PO_4, **(B)** K_3PO_4, **(C)** K_2HPO_4, **(D)** KH_2PO_4, and **(E)** H_3PO_4 as a function of electrolyte concentration at T = 298.15 K (Points: Experimental data from □ Khomutov and Konnik (1974), ○ Iwai et al. (1993), △ Gubbins and Walker (1965), Lines: this work).

FIGURE 8
Modelling of the O_2 solubility in binary solutions of **(A)** $CaCl_2$, **(B)** $MgCl_2$, and **(C)** $MgSO_4$ as a function of electrolyte concentration at T = 298.15 K (Points: Experimental data from □ Millero et al. (2003), ○ Millero et al. (2002a), △ Millero et al. (2002b) Lines: this work).

FIGURE 9
Modelling of the O_2 solubility in equimolal solutions of **(A)** $NaCl + MgCl_2$, **(B)** $NaCl + Na_2SO_4$, **(C)** $Na_2SO_4+MgSO_4$, and **(D)** $MgCl_2 + MgSO_4$ as a function of electrolyte concentration at T = 298.15 K (Points: Experimental data from □ Millero et al. (2002a), Lines: this work).
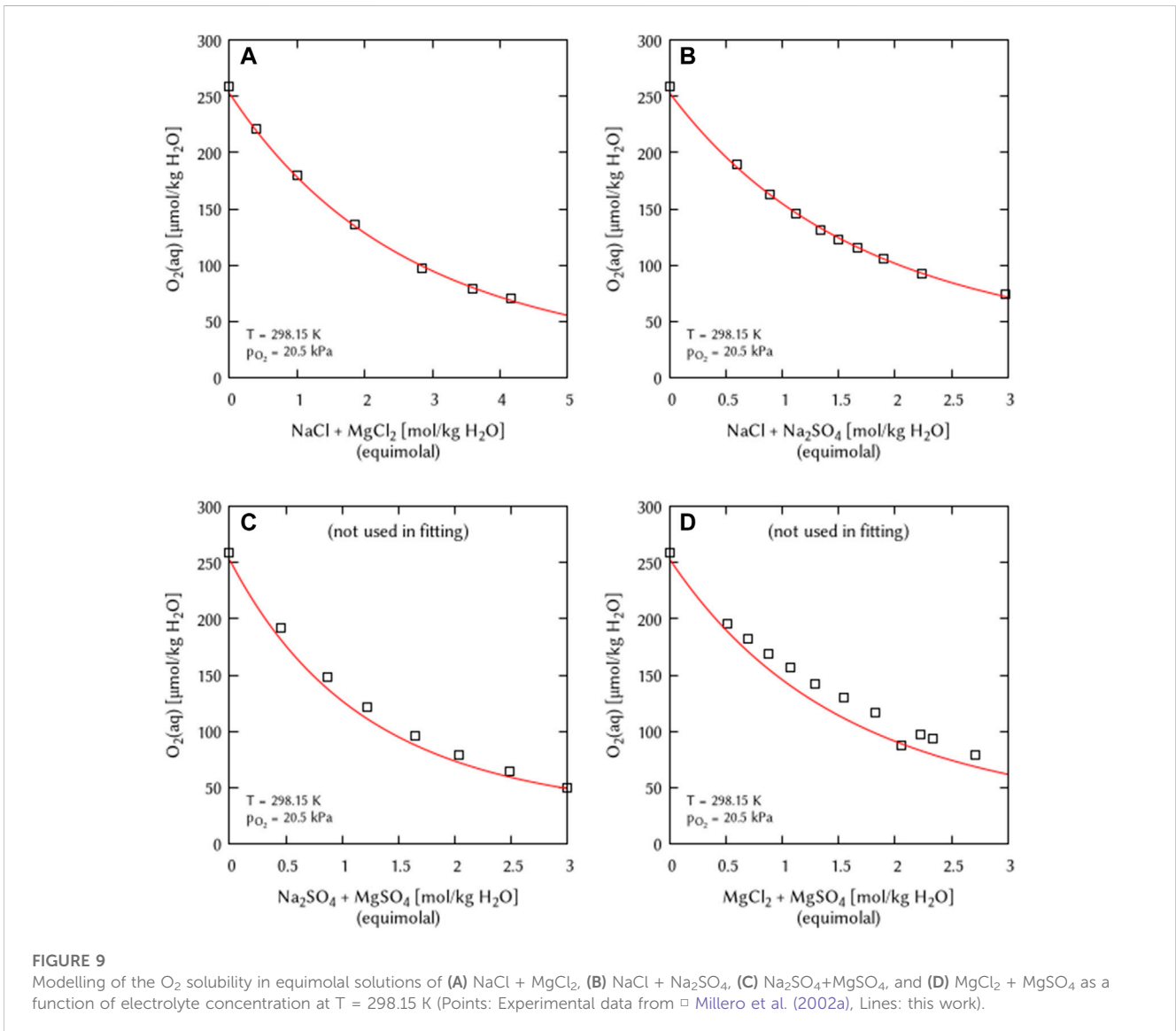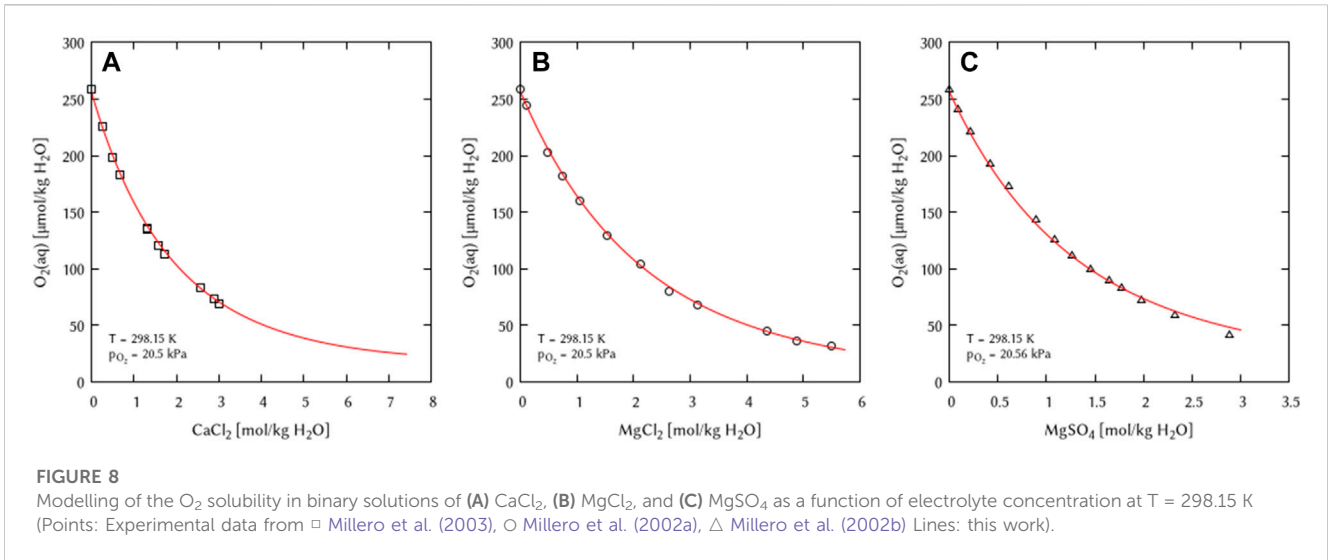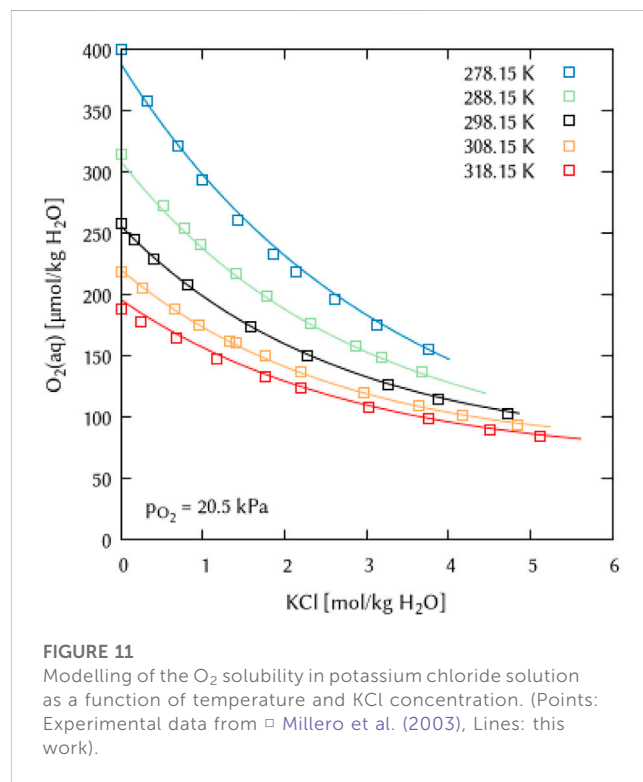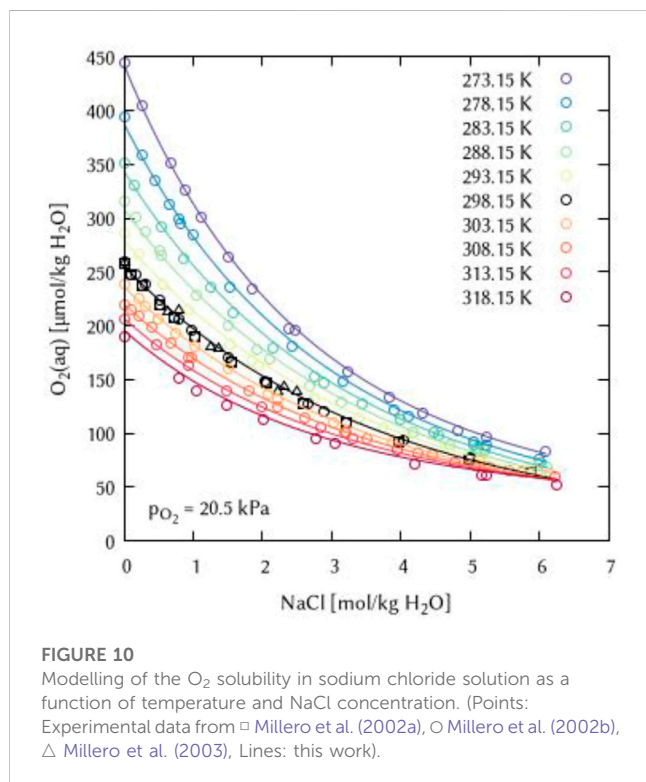
TABLE 9 Parameters for the temperature dependency function of the binary and ternary interaction coefficients (λ, ζ). The uncertainty information refers to one standard deviation.

λ/ζ (Species: 1-2-3)	X_0	X_1	X_2
$O_2(aq)$-Cl^-	0 (by definition)	0 (by definition)	0 (by definition)
$O_2(aq)$-H^+	0.02598 ± 0.00171	$4{,}941 \pm 533$	16.4 ± 1.8
$O_2(aq)$-Na^+	0.1315 ± 0.0093	$2{,}897 \pm 274$	9.614 ± 0.947
$O_2(aq)$-K^+	0.135 ± 0.010	$-1{,}004 \pm 527$	-3.513 ± 1.79
$O_2(aq)$-Mg^{2+}	0.2293 ± 0.0032	$2{,}981 \pm 860$	9.9 ± 2.9
$O_2(aq)$-Ca^{2+}	0.2519 ± 0.0063	$2{,}821 \pm 651$	9.449 ± 2.26
$O_2(aq)$-OH^-	0.06785 ± 0.00965	$1{,}230 \pm 280$	3.934 ± 0.882
$O_2(aq)$-SO_4^{2-}	0.1334 ± 0.0082	$-6{,}654 \pm 1{,}150$	-22.01 ± 3.38
$O_2(aq)$-HSO_4^-	0.03842 ± 0.00201	-45.38 ± 27.7	0 (fixed)
$O_2(aq)$-H^+-HSO_4^-	-0.002472 ± 0.000302	0 (fixed)	0 (fixed)
$O_2(aq)$-Na^+-Cl^-	-0.003767 ± 0.00579	$-1{,}075 \pm 128$	-3.663 ± 0.442
$O_2(aq)$-Na^+-OH^-	0 (fixed)	-40.7 ± 17.9	0 (fixed)
$O_2(aq)$-Na^+-SO_4^{2-}	-0.0381 ± 0.0073	$4{,}216 \pm 1{,}820$	13.49 ± 5.92
$O_2(aq)$-K^+-Cl^-	-0.01711 ± 0.00647	747.7 ± 319	2.464 ± 1.07
$O_2(aq)$-K^+-SO_4^{2-}	-0.1618 ± 0.078	164.7 ± 102	0 (fixed)
$O_2(aq)$-Mg^{2+}-Cl^-	-0.006612 ± 0.00101	-875.5 ± 351	-2.974 ± 1.18
$O_2(aq)$-Mg^{2+}-SO_4^{2-}	-0.05115 ± 0.00586	$5{,}181 \pm 550$	16.86 ± 1.86
$O_2(aq)$-Ca^{2+}-Cl^-	-0.01269 ± 0.00291	24.49 ± 1.81	0 (fixed)

FIGURE 10
Modelling of the O_2 solubility in sodium chloride solution as a function of temperature and NaCl concentration. (Points: Experimental data from □ Millero et al. (2002a), ○ Millero et al. (2002b), △ Millero et al. (2003), Lines: this work).

FIGURE 11
Modelling of the O_2 solubility in potassium chloride solution as a function of temperature and KCl concentration. (Points: Experimental data from □ Millero et al. (2003), Lines: this work).
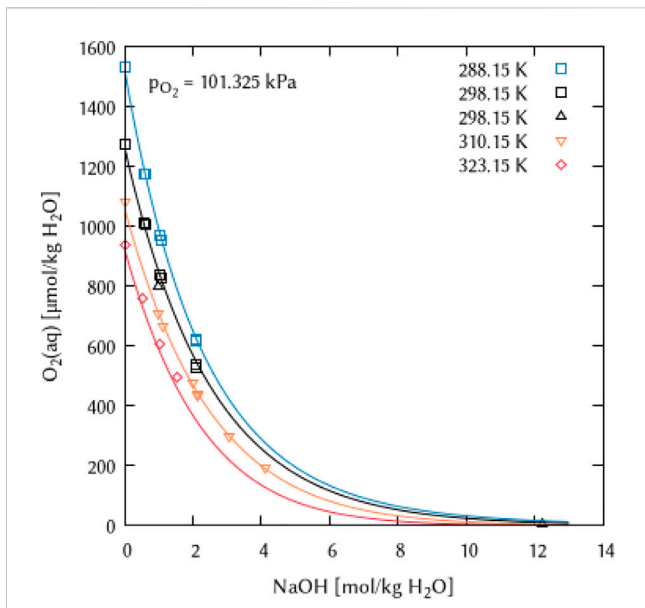
FIGURE 12
Modelling of the O_2 solubility in sodium hydroxide solution as a function of temperature and NaOH concentration. (Points: Experimental data from □ Geffcken (1904), △ Chatenet et al. (2000), ▽ Lang and Zander (1986) and ☐ Bruhn et al. (1965), Lines: this work).
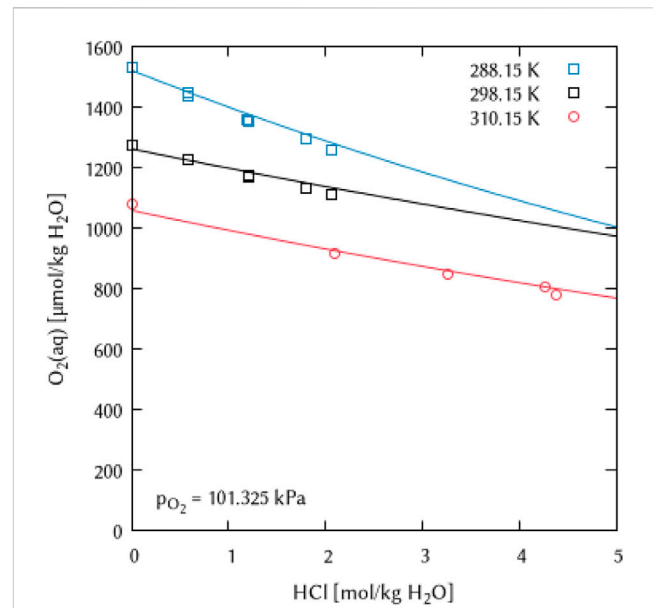

FIGURE 14
Modelling of the O_2 solubility in hydrochloric acid solution as a function of temperature and HCl concentration. (Points: Experimental data from □ Geffcken (1904) and ○ Lang and Zander (1986), Lines: this work).
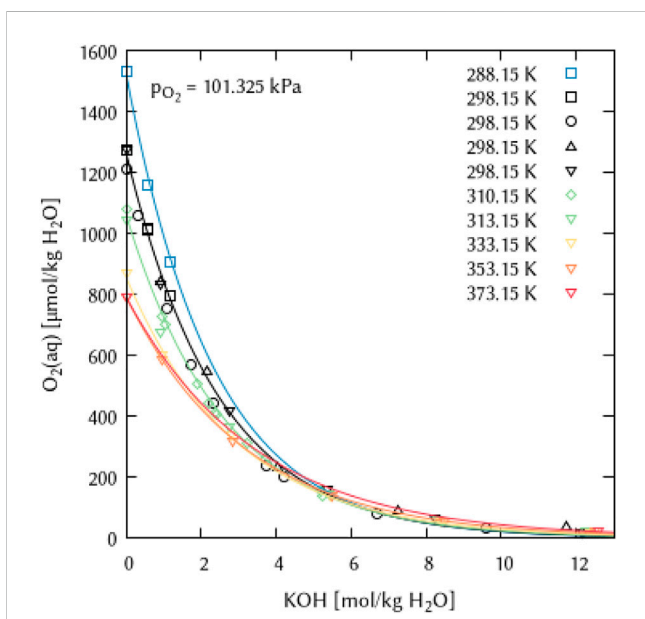

FIGURE 13
Modelling of the O_2 solubility in potassium hydroxide solution as a function of temperature and KOH concentration. (Points: Experimental data from □ Geffcken (1904), ○ Davis et al. (1967), △ Gubbins and Walker (1965), ▽ Shoor et al. (1968) and ☐ Lang and Zander (1986), Lines: this work).
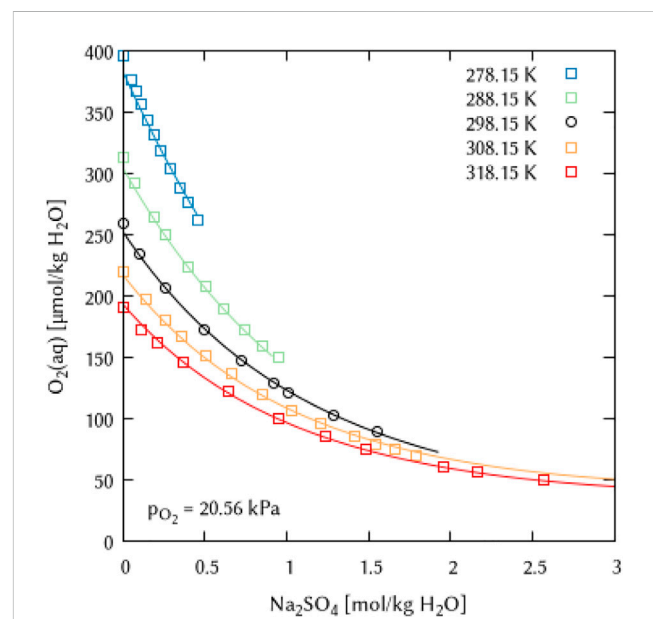

FIGURE 15
Modelling of the O_2 solubility in sodium sulfate solution as a function of temperature and Na_2SO_4 concentration. (Points: Experimental data from ○ Millero et al. (2002a) and □ Millero et al. (2002b), Lines: this work).

4.4 Temperature dependency of O_2 solubility in salt solutions

For the polythermal description of O_2 solubility in electrolyte solutions, the Pitzer interaction coefficients valid for 298.15 K were used as a boundary condition for fitting of the temperature parameters for Eq. 10 on top of them. These parameter fittings were run individually for each electrolyte and then iterated until no changes were observed anymore.

4.4.1 The system Na^+, K^+, H^+/Cl^-, OH^- - $H_2O(l)$

The binary systems of the alkali metal chlorides, alkali metal hydroxides and hydrochloric acid allowed to determine the temperature dependency for two binary interaction coefficients: $\lambda(O_2(aq)\text{-}Na^+)$, $\lambda(O_2(aq)\text{-}K^+)$, and $\lambda(O_2(aq)\text{-}H^+)$ as well as for two ternary coefficients $\zeta(O_2(aq)\text{-}Na^+\text{-}Cl^-)$ and $\zeta(O_2(aq)\text{-}K^+\text{-}Cl^-)$ (see Figures 10, 11). For each coefficient, the temperature dependency can be described using only two of the six parameters of Eq. 10, which are the $X_1(1/T - 1/T_r)$ and the $X_2\ln(T/T_r)$ terms.

For the ternary coefficient $\zeta(O_2(aq)\text{-}Na^+\text{-}OH^-)$ with a value of 0 at T = 298.15 K, only the first parameter of the temperature dependency equation was found to be necessary to adequately describe the experimental points available (Figure 12).

Even though the few available experimental points on O_2 solubility at higher KOH concentrations and raised temperatures (T = 353.15–373.15 K) are not well reproduced in terms of the expected trend of temperature dependence (Figure 13), the introduction of another ternary coefficient $\zeta(O_2(aq)\text{-}K^+\text{-}OH^-)$ or temperature dependence parameters thereof did not lead to any improvement. Furthermore, it can be assumed that the deviation of the calculation from the expected trend (lowering the O_2 solubility with increasing temperature) in this concentration and temperature range is lower than the experimental uncertainty to be expected.

For solutions of hydrochloric acid, even in the polythermal system, no ternary interaction coefficient and thus no temperature parameters were necessary to describe the very few points on O_2 solubility as a function of temperature and electrolyte concentration (Figure 14).

4.4.2 The system Na^+, K^+, H^+/HSO_4^-, SO_4^{2-} - $H_2O(l)$

In the systems of alkali metal sulfate and sulfuric acid solutions, it was possible to obtain parameters describing the temperature dependence of the Pitzer interaction coefficients. Again, the fitting of a maximum of two terms was sufficient to describe the available data points for the Na_2SO_4 and H_2SO_4 systems (Figures 15, 16).

In the K_2SO_4 solutions, O_2 solubility is poorly described at both very low (278.15 K) and very high (318.15 K) temperatures, yielding too high values with increasing electrolyte concentration (Figure 17) in both cases. Since the temperature dependence equation of the Pitzer interaction coefficients in the geochemical codes centers around the value of 298.15 K (see Eq. 10), these effects cannot be compensated, as a fit improvement in the temperature range above 298.15 K causes a corresponding deterioration below 298.15 K and *vice versa*.

The systems Na^+/HSO_4^- - $H_2O(l)$ and K^+/HSO_4^- - $H_2O(l)$ could not be used for the estimation of the ternary interaction coefficients $\zeta(O_2(aq)\text{-}Na^+\text{-}HSO_4^-)$ or $\zeta(O_2(aq)\text{-}K^+\text{-}HSO_4^-)$ because of the lack of O_2 solubility data at 298.15 K. The only
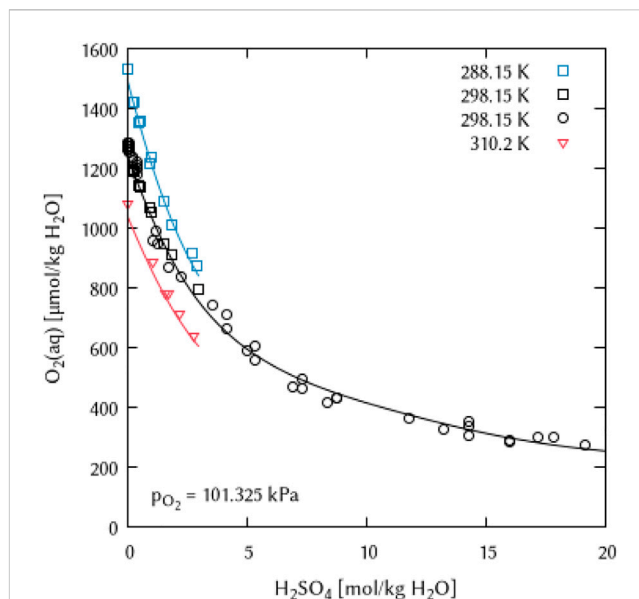

FIGURE 16
Modelling of the O_2 solubility in sulfuric acid solution as a function of temperature and H_2SO_4 concentration. (Points: Experimental data from □ Geffcken (1904), ○ Das (2005) and ▽ Lang and Zander (1986), Lines: this work).
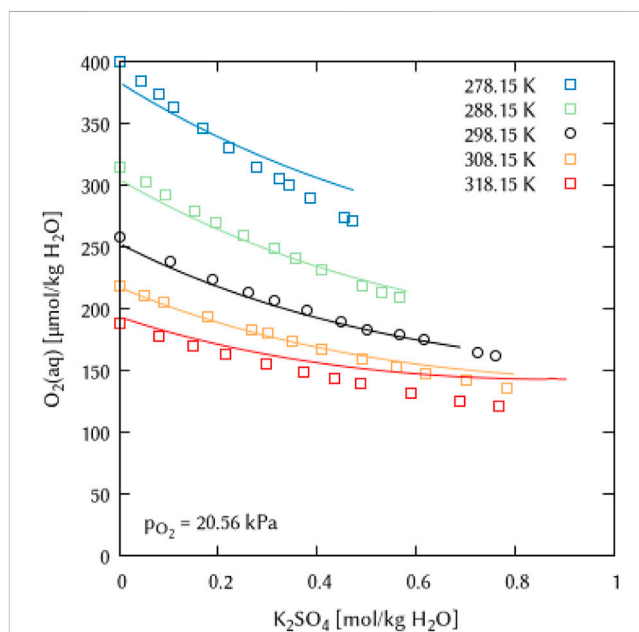

FIGURE 17
Modelling of the O_2 solubility in potassium sulfate solution as a function of temperature and K_2SO_4 concentration. (Points: Experimental data from ○ Millero et al. (2003) and □ Millero and Huang (2003), Lines: this work).

available experimental datasets are at 310.2 K generated by Lang and Zander (1986). Thus, it is not possible to obtain a ζ coefficient at 298.15 K that is necessary for the fitting with the temperature dependency equation used in this study. The systems Na^+/HSO_4^- - $H_2O(l)$ and K^+/HSO_4^- - $H_2O(l)$ were
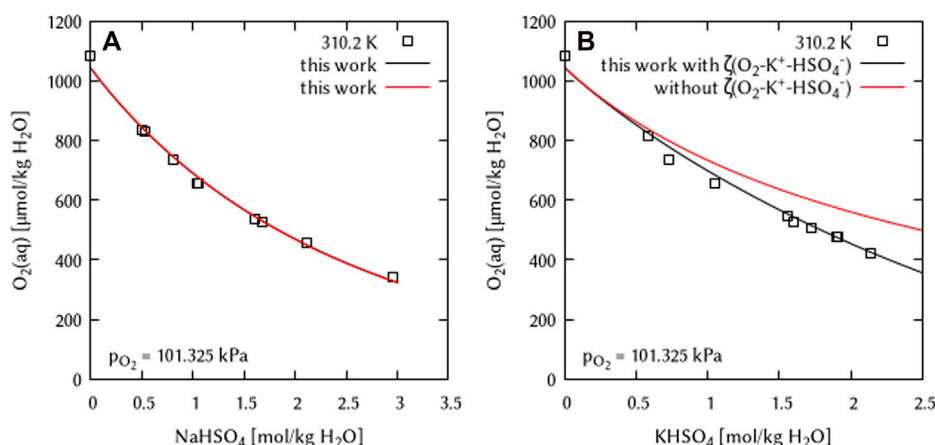
FIGURE 18
Modelling of the O_2 solubility in binary solutions of **(A)** NaHSO$_4$, and **(B)** KHSO$_4$ as a function of electrolyte concentration at 310.2 K using the Pitzer coefficient set of this work. [Points: Experimental data from □ Lang and Zander (1986), Lines: this work].
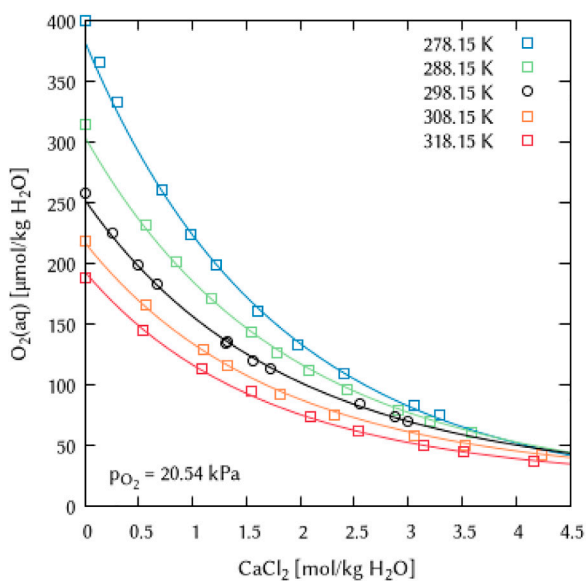

FIGURE 19
Modelling of the O_2 solubility in calcium chloride solution as a function of temperature and CaCl$_2$ concentration. [Points: Experimental data from ○ Millero et al. (2003) and □ Millero and Huang (2003), Lines: this work].
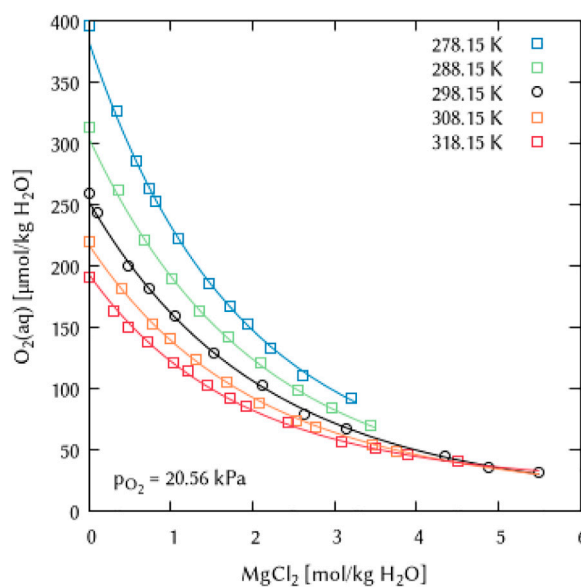

FIGURE 20
Modelling of the O_2 solubility in magnesium chloride solution as a function of temperature and MgCl$_2$ concentration. [Points: Experimental data from ○ Millero et al. (2002a) and □ Millero et al. (2002b), Lines: this work].

modelled using the obtained dataset. Results indicate that no ternary interaction coefficient $\zeta(O_2(aq)\text{-}Na^+\text{-}HSO_4^-)$ is necessary to describe the O_2 solubility data in the system Na^+/HSO_4^- - $H_2O(l)$ (see Figure 18).

Modelling results for the chemical system K^+/HSO_4^- - $H_2O(l)$ without an ternary interaction coefficient show a discrepancy between the experimental results from Lang and Zander (1986) and the modelling. Thus, a ternary interaction coefficient $\zeta(O_2(aq)\text{-}$

$K^+\text{-}HSO_4^-)$ was fitted at T = 310.2 K. Due to the lack of solubility data at other temperatures, no parameters for the temperature function could be derived. Therefore, this ternary coefficient was assumed to be temperature independent.

4.4.3 Earth alkaline salt solutions (CaCl$_2$, MgCl$_2$, MgSO$_4$)

The binary systems of the alkaline Earth metal salts CaCl$_2$, MgCl$_2$ and MgSO$_4$ were used to derive the temperature

FIGURE 21
Modelling of the O_2 solubility in magnesium sulfate solution as a function of temperature and $MgSO_4$ concentration. [Points: Experimental data from ○ Millero et al. (2002a) and □ Millero et al. (2002b), Lines: this work].
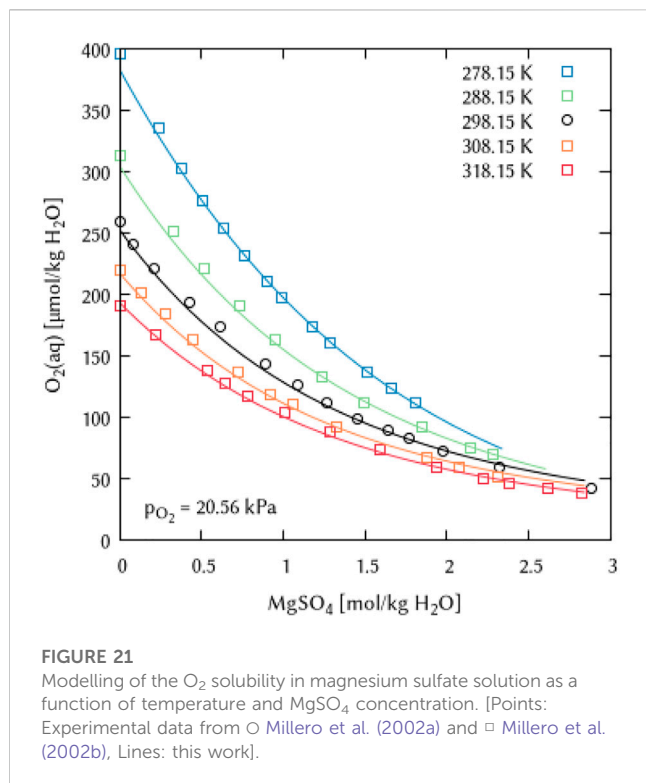
dependency parameters for the binary interaction coefficients $\lambda(O_2(aq)\text{-}Ca^{2+})$ and $\lambda(O_2(aq)\text{-}Mg^{2+})$ as well as for the ternary coefficients $\zeta(O_2(aq)\text{-}Ca^{2+}\text{-}Cl^-)$, $\zeta(O_2(aq)\text{-}Mg^{2+}\text{-}Cl^-)$ and $\zeta(O_2(aq)\text{-}Mg^{2+}\text{-}SO_4^{2-})$, see Figures 19–21. For the magnesium salt solutions, the temperature dependency of the interaction coefficients requires two parameters $[X_1(1/T - 1/T_r)$ and $X_2\ln(T/T_r)]$ while for the calcium chloride solution, the $X_1(1/T - 1/T_r)$ temperature parameter alone was sufficient for the complete description of the system.

The full list of obtained temperature parameters for the polythermal Pitzer interaction coefficients is given in Table 9.

For the carbonate, the phosphate, and ternary systems in the oceanic salt system, no temperature dependency parameters of the interaction coefficients could be deduced so far due to the very limited data available. Therefore, for polythermal datasets, the temperature function parameters X_1–X_5 for the Pitzer interaction coefficients are set to zero.

4.5 Validity ranges

The conservative validity range for this dataset is given as follows:

- Temperature: T = 273–318 K,

TABLE 10 Validity ranges (T, I, p) according to the experimental conditions used for the parameter fitting.

Electrolyte	Temperature [K]	Electrolyte concentration [mol/kg H_2O]	O_2 partial pressure [kPa]	Total pressure [kPa]
Pure water	273.15–373.15	0	101.325	101.325
NaCl	273.15–318.15	0–6.5	20.56	101.325
KCl	278.15–318.15	0–5.5	20.56	101.325
$MgCl_2$	278.15–318.15	0–5.5	20.56	101.325
$CaCl_2$	278.15–318.15	0–4.5	20.54	101.325
HCl	288.15–310.2	0–5	101.325	101.325
H_2SO_4	288.15–310.2	0–20	101.325	101.325
Na_2SO_4	278.15–318.15	0–2.7	20.56	101.325
K_2SO_4	278.15–318.15	0–0.8	20.56	101.325
$MgSO_4$	278.15–318.15	0–3	20.56	101.325
NaOH	288.15–323.15	0–13	101.325	101.325
KOH	288.15–373.15	0–19	101.325	101.325
Na_2CO_3	298.15	0–2.2	21.28	101.325
K_2CO_3	298.15	0–1.3	21.28	101.325
H_3PO_4	298.15	0–6	101.325	101.325
KH_2PO_4	298.15	0–1.2	101.325	101.325
K_2HPO_4	298.15	0–1.2	101.325	101.325
K_3PO_4	298.15	0–0.6	21.28	101.325
Na_3PO_4	298.15	0–1	21.28	101.325

- Ionic strength: I ≤ 5 mol/kg H$_2$O,
- O$_2$ partial pressure: p(O$_2$) ≤ 101.325 kPa.

This generalized specification is not valid for all chemical subsystems. The validity ranges of temperature and ionic strength of the individual background electrolyte are given in Table 10 according to the experimental data sets used for the parameter fitting.

4.6 Known deficiencies

4.6.1 Missing interactions coefficient for binary solutions

For the O$_2$ solubility in binary solutions of bicarbonates only one experimental dataset (O$_2$ in NaHCO$_3$ solutions with T = 323–423 K and p = 1–5 MPa) is available in literature (Broden and Simonson, 1978) and (Broden and Simonson, 1979). It was not possible to extrapolate to 298.15 K and 101.325 kPa using the temperature and pressure dependency functions given in the articles or other extrapolation methods. Therefore, neither this binary interaction coefficient λ(O$_2$(aq)-HCO$_3$$^-$) nor its temperature function parameters could be deduced so far.

4.6.2 Missing interaction coefficients for ternary solutions

There are no O$_2$ solubility data for other ternary mixtures of salt solutions published in literature beside the work of Millero et al. (2002a) (system Na$^+$, Mg^{2+}/Cl$^-$, SO$_4$$^{2-}$ - H$_2$O(l) at 298.15 K). Therefore only the interaction coefficients ζ(O$_2$(aq)-Na$^+$-Mg^{2+}) and ζ(O$_2$(aq)-Cl$^-$-SO$_4$$^{2-}$) for these ternary systems could be deduced. Here, especially the ternary interaction coefficients with hydroxide [ζ(O$_2$(aq)-OH$^-$-Cl$^-$) and ζ(O$_2$(aq)-OH$^-$-SO$_4$$^{2-}$)] would be of interest, since the O$_2$ solubility decreases significantly more in alkaline solutions than in neutral or acidic electrolyte solutions. For all other ternary (or higher) mixtures, no interaction coefficients could be obtained. The same applies to the temperature dependence of the O$_2$ interaction parameters in ternary electrolyte solutions.

Ternary interactions coefficients for systems with alkaline Earth ions (Mg^{2+}, Ca^{2+}) and bivalent or trivalent anions (CO$_3$$^{2-}$, SO$_4$$^{2-}$, PO$_4$$^{3-}$)— except ζ(O$_2$(aq)-Mg^{2+}-SO$_4$$^{2-}$)—are assumed to be unnecessary because of the low solubility of the formed solid phases, e.g., calcite, dolomite, gypsum or apatite. The contributions of these ions in such solutions are sufficiently covered by the binary interaction coefficients.

5 Conclusion

In this paper, a set of thermodynamic formation data for dissolved oxygen O$_2$(aq) consistent with standard formation data for O$_2$(g), H$_2$(g), H$_2$O(l), and a temperature-dependent Henry's law constant is presented. In combination with binary and ternary Pitzer coefficients they allow the calculation of oxygen solubility in concentrated salt solutions of the system Na$^+$, K$^+$, H$^+$, Ca^{2+}, Mg^{2+}/Cl$^-$, SO$_4$$^{2-}$, CO$_3$$^{2-}$, PO$_4$$^{3-}$, OH$^-$ - H$_2$O(l), including also the associated acids and bases. By combining a very large number of experimental papers, which have been subjected to critical evaluation, the data set is based on a wide range of data, which in turn ensures robustness.

Contrary to values for the so-called log$K$-E$_H$-grid circulating among geochemical modelers, values given herein can be traced back to experimental solubility data and standard formation data. Moreover, their validity in terms of temperature and solution composition is clearly stated.

The use of the dataset allows a more accurate description of the redox state of saline solutions. This does not only improve the description of the solubility of redox-sensitive radionuclides, but is also applicable to a variety of other processes—from material corrosion to microbial activity. The presented dataset allows modeling with a broader application range than the data compilations previously available in the literature, both in terms of the number of chemical subsystems and the temperature range. With a more precise description of redox conditions, it is possible to further reduce conservatism in safety assessment calculations, not only in the context of a nuclear repository.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

FB: conceptualization, methodology, data analysis, software, fitting (Henry's law constant and Pitzer ion-interaction coefficients), writing; HM: methodology and data review (thermodynamics), writing; VB: review and editing, supervision, funding acquisition.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fnuen.2023.1158109/full#supplementary-material

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