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Author(s) / Coauthor(s): George Dan Miron	Composed 24.09.2024, MG44
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Subject:

This project investigated the extension of the PSI/Nagra thermodynamic database for improved calculations at different temperatures and pressures. In particular the selection of molar volumes for mineral phases, partial molar heat capacities and molar volumes with temperature and pressure dependence for master aqueous species, and heat capacity temperature function coefficients for gaseous species.

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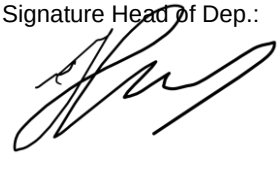
	TM-Dossier (Sekretariat)	1*				Signature Head of Dep.: 	

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v3	09.08.2025	Added properties of H2O(g)
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0 Terms, definitions, and standards

Selected thermodynamic data refer to the reference temperature $T_r°$ of 298.15 K (25 °C) and to the standard state, i.e., a reference pressure $P_r°$ of 0.1 MPa (1 bar), for aqueous species, infinite dilution (I = 0), for gases, ideal gas and pure solids and water solvent.

0.1 Terms and abbreviations

$\log_{10}K°$	logarithm (base-10) of the equilibrium constant of a reaction
$\Delta_r G_m°$	molar Gibbs free energy of reaction (kJ · mol^{-1})
$\Delta_r H_m°$	molar enthalpy of reaction (kJ · mol^{-1})
$\Delta_r S_m°$	molar entropy of reaction (J · K^{-1} · mol^{-1})
$\Delta_r C_{p,m}°$	molar heat capacity of reaction (J · K^{-1} · mol^{-1})
$\Delta_r V_m°$	molar volume of reaction (g · cm^{-3})
$\Delta_f G_m°$	standard partial molar Gibbs free energy of formation (kJ · mol^{-1})
$\Delta_f H_m°$	standard partial molar enthalpy of formation (kJ · mol^{-1})
$\Delta_f S_m°$	standard partial molar entropy of formation (J · K^{-1} · mol^{-1})
$\Delta_f C_{p,m}°$	standard partial molar heat capacity of formation (J · K^{-1} · mol^{-1})
$S_m°$	standard partial molar entropy (J · K^{-1} · mol^{-1})
$C_{p,m}°$	standard partial molar heat capacity (J · K^{-1} · mol^{-1})
$V_m°$	standard partial molar volume (cm^3 mol^{-1})
Ξ_m°	standard partial molar property
$T_r°$	reference temperature of 298.15 K (25 °C)
$P_r°$	reference pressure of 1·10^5 Pa (1 bar)
M	molarity (mol · L^{-1} solution)
m	molality (mol · kg^{-1} H_2O)

I	ionic strength (mol · kg^{-1} H_2O)
P_{sat}	water saturated vapor pressure
TDB 2020	update to the PSI/Nagra chemical thermodynamic database (Hummel and Thoenen, 2023)
SIT	specific ion interaction theory aqueous activity model
HKF	Helgeson-Kirkham-Flowers model

1 Introduction

The PSI/Nagra Thermodynamic database project supports the ongoing safety assessments for the planned repositories for low- and intermediate-level (L/ILW) and high-level (HLW) radioactive waste in Switzerland. The database was updated in version TDB 2020 (Hummel and Thoenen, 2023). The TDB 2020 includes thermodynamic data for 53 elements and their aqueous species, solids and gases.

Early versions of the PSI/Nagra chemical thermodynamic database (Hummel et al., 2002) focused on selecting thermodynamic properties for compounds and product species described in reactions from master species at reference temperature (T_r 298.15 K) and pressure (P_r $1 \cdot 10^5$ Pa or 1 bar). Such data is used for chemical thermodynamic calculations with the law of mass action algorithm based on the equilibrium constant ($\log_{10}K°$). Values of reaction constants for all involved aqueous product species, solids, and gases and represents are included. This represents the minimal dataset required for calculating chemical equilibria at 1 bar and 25˚C, whereas no thermodynamic data are required for the master species.

The TDB 2020 (Hummel and Thoenen, 2023) update of the PSI/Nagra chemical thermodynamic database considered the effect of temperature on the thermodynamic properties of aqueous species when selecting reference thermodynamic data. When sufficient experimental data at various temperatures were available, they were used in Hummel and Thoenen (2023) to determine values for the standard molar reaction enthalpy ($\Delta_r H_m°$) or entropy ($\Delta_r S_m°$) and heat capacity ($\Delta_r C_{p,m}°$). A complete set of $\Delta_r H_m°$ values and sometimes also $\Delta_r C_{p,m}°$ was retrieved for compounds and complexes involving Li, Na, K, Mg, Ca, Sr, Ba, Ra, Mn, Al, Fe, and Si elements and aqueous complexes with OH^-, F^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-}.

A comprehensive thermodynamic database contains not only reaction properties, but also thermodynamic properties of individual master and product species, and the parameters needed to make temperature and pressure corrections. Such an extensive database provides the means to maintain formal thermodynamic consistency between properties of substances and reactions and extends the ranges of validity for geochemical calculations.

To use a thermodynamic database in GEM (Gibbs energy minimisation) codes (e.g., GEM-Selektor (Kulik et al., 2013)) it must include the standard molar Gibbs energy ($\Delta_f G_m°$) of all substances. These are related to the reaction constant by:

$$\log_{10}K° = \Delta_r G_m° \cdot [R \cdot T° \cdot \ln(10)]^{-1} \qquad 1\text{-}1$$

For calculations at conditions different from T_r and P_r, the $\Delta_f G_m°$ values need to be corrected to the temperature and pressure of interest. For this, data on standard molar entropy ($S_m°$) or enthalpy ($\Delta_f H_m°$), heat capacity ($C_{p,m}°$), and volume ($V_m°$) at T_r and P_r, and data on their temperature and pressure dependencies, are required for each individual species in the chemical system.

Provided information on $S_m°$ or $\Delta_f H_m°$, and $C_{p,m}°$, at T_r and P_r of master species, the $S_m°$ or $\Delta_f H_m°$, and $C_{p,m}°$, of all dependent substances can be calculated, from their respective reaction partial molar properties ($\Delta_r \Xi^\circ_m$):

$$\Delta_r \Xi_m^\circ = \sum_{i=1}^{n} v_i \cdot \Xi_{m,i}^\circ \qquad 1\text{-}2$$

where Ξ_m° is a partial molar property of a species i, and v_i represents the stoichiometric coefficients, negative for reactants and positive for products.

In addition to values for $\Delta_f G_m°$, the TDB 2020 contains values for $S_m°$ or $\Delta_f H_m°$ for most master species, while most do not have $C_{p,m}°$ values. No $V_m°$ data were evaluated for any of the compounds selected in the TDB 2020 or in any previous PSI-Nagra database releases.

The missing $S_m°$ or $\Delta_f H_m°$, $C_{p,m}°$, and $V_m°$ values, and lack of data on their temperature and pressure dependency, prevents use of the database for calculations at conditions other than at T_r and P_r. Additionally, data on $V_m°$ of solids are necessary for using the database in reactive transport model calculations where changes in porosity due to mineral dissolution/precipitation are important. For improved modelling calculations applied to deep geological repositories, a consistent and complete set of thermodynamic properties of substances and reactions, including molar volumes as well as their temperature (pressure) dependence, is necessary.

In this report, the standard molar volumes at T_r and P_r of pure solid phases present in the PSI/Nagra database were collected based on literature for measured density, crystal structure data, or estimated based on analogue phases.

For aqueous ions and complexes, the revised Helgeson-Kirkham-Flowers (HKF) (Tanger and Helgeson, 1988) model was selected as the method for calculating the standard partial molar thermodynamic properties at different temperatures and pressures for this report .The missing values for $S_m°$ or $\Delta_f H_m°$, $C_{p,m}°$, and $V_m°$ and HKF model coefficients were selected or derived based on experimental data. If values for $S_m°$ or $\Delta_f H_m°$, $C_{p,m}°$ were already available in TDB 2020 these were taken as such unless a re-evaluation was necessary to make them consistent with the HKF model. The newly determined $C_{p,m}°$ and $V_m°$ (not available previously) are consistent with measured data of electrolyte solutions. Their values are calculated based on the selected HKF coefficients (Table 6-5) and Eq. 3-3 and Eq. 3-4.

The evaluation in this report was conducted for master species and selected dependent species containing H, O, P, C, S, Cl, F, Na, K, Mg, Ca, Al, Fe, and Si elements. These are relevant for calculations related to host rock and model porewaters, as well as for the use of the PSI/Nagra database as a complement to the cemdata database (Lothenbach et al., 2018) for cement phases.

Data for gases were supplemented with $C_{p,m}°$ temperature function coefficients that were not available in previous database releases.

The data will be made available in GEMS and in PHREEQC formats in the upcoming electronic releases. The validity of the selected data is at least within the range 0-150 °C and P_{sat}-300 bar. For gases, the ideal gas model is used, which does not produce significant deviations below 50 bars.

The aim of future work is the compilation of a complete set of thermodynamic properties for all compounds to complement the reaction properties in the PSI/Nagra database in order to optimise temperature and pressure extrapolations. Hence, further updates as well as continuous improvement based on new experimental data and improved understanding of these systems are critical.

Future updates should also include selections of data for other pore water elements (e.g., Li, Ba, Ra, Sr, Mn) and missing properties and HKF model parameters for all master species (including radionuclides) for these elements. Data on heat capacity as a function of temperature for solid phases based on calorimetric measurements should also be selected and their consistency with derived values at T_r and P_r, based on solubility data in TDB 2020 where available, should be assessed. For gas solubility, SIT (Specific ion Interaction Theory) (Guggenheim and Turgeon, 1955) aqueous activity model parameters need to be evaluated. The selected data in this report are consistent with the SIT model and parameters evaluated in TDB 2020

2 Molar volumes of minerals

The molar volumes of minerals are generally derived from both single crystal structure refinements and powder-diffraction data. Although individual lattice parameters can be measured with high accuracy, compositional variation in many minerals implies that provided values may require adjustments to accurately represent the volumetric properties of the phase.

In this report only values for end-member standard molar volumes ($V_m°$ at 1 bar and 25 °C) were evaluated. Molar volumes can be modelled as a function of activity/composition accounting for the volumes of mixing, but such an approach was beyond the scope of this report. In addition, using data on thermal expansion and compressibility, corrections for changes in *T* and *P* can be accounted for. For low pressure environments relevant for deep geological repositories up to a few thousand bars, the pressure effect on the molar volume of minerals is negligible.

Selected molar volumes based on measured data are provided in Table 6-1. The selected values in the present report used as basis the extensive review of Robie and Hemingway (1995) and Robie and Bethke (1962) who critically reviewed the molar volumes and densities of several well defined mineral phases based on available unit cell parameters and density measurements. An additional source of molar volumes was the Thermoddem database (Blanc et al., 2012) and the original references provided within that database.

The molar volumes for clay minerals were taken as reported from the work of Blanc et al. (2015a, 2015b) while for Na and Ca bearing zeolites, molar volumes were taken from Ma and Lothenbach (2020a, 2020b). These studies were also the original sources for their selected standard thermodynamic properties in TDB 2020 (Hummel and Thoenen, 2023).

For the remaining minerals that did not have molar volumes reported in the aforementioned sources, reference values were determined based on the reported densities and crystallographic unit cell volume values taken from the established online databases: mindat.org, materialsproject.org (Jain et al., 2013), materials.springer.com, chemicalbook.com, webmineral.com, and ruff.geo.arizona.edu.

For some minerals where no density data were available, the molar volume was estimated as being equal to analogous phases of similar elements assuming that they have the same crystal structure. In a few cases the stoichiometric composition differs from the formula in TDB 2020, mainly in the amount of water in the formula. In these cases, the densities were assumed to be equal, and the molar volumes were calculated from the reported densities and respective molar masses.

For several hydrous phosphate and arsenate phases, $AB_2(XO_4)_2 \cdot xH_2O$, specifically those of the autunite or meta-autunite mineral groups, molar volumes were estimated from the available density data of similar phases containing different cations. From the available measured densities, average values are 3.8 ±0.2 $g \cdot cm^{-3}$ and 3.5 ±0.2 $g \cdot cm^{-3}$ for arsenates and phosphates, respectively. Molar volumes based on estimates are provided in Table 6-2.

Molar volumes were calculated from given density values using the formula:

$$V_m° = \frac{M}{\rho}$$

where M is the formula molar mass in g·mol^{-1} and ρ is the density in g·cm^{-3}, or from the unit cell volume values using the formula:

$$V_m° = \frac{V_U\,(\text{unit cell cm}^3)\cdot 6.02322\cdot 10^{23}\,(\text{mol}^{-1})}{Z}$$

Where V_U is the unit cell volume (cm^3) and Z is the number of formula units per unit cell.

With the exception of major rock-forming minerals, the molar volumes of other solids are generally not relevant for changes in porosity. However, having a complete set of molar volume data can be useful for estimating other thermodynamic properties based on potential correlations with molar volume (e.g., Glasser and Jenkins, 2016). Of the 395 minerals in the PSI/Nagra chemical thermodynamic database, 309 minerals (Table 6-1) have molar volumes derived based on available measured data, 61 minerals (Table 6-2) have estimated molar volumes, while 25 minerals (Table 6-3) have no molar volumes and no volumes could not be estimated in this report.

3 Temperature and pressure dependence of aqueous species

The revised HKF model (Tanger and Helgeson, 1988) is used for calculating the change in the partial molal Gibbs energy of aqueous species as a function of temperature and pressure. The model is a set of equations of state that allow the calculation of the contributions to the thermodynamic properties of dissolved aqueous species for the solvation and non-solvation effects. The solvation contributions are related to the water dielectric constant while the non-solvation contributions are related to semiempirical relations with coefficients a_1, a_2, a_3, a_4, c_1, and c_2 that can be retrieved from experimental data or estimated from correlations (Shock and Helgeson, 1988).

For the evaluated species, a set of $\Delta_f G_m°$, $S_m°(\Delta_f H_m°)$, $C_{p,m}°$, and $V_m°$ is selected, together with the HKF model coefficients that describe the temperature dependence of $V_m°$, a_1, a_2, a_3, a_4 and the temperature dependence of $C_{p,m}°$, c_1 and c_2. Unless otherwise specified, if already selected in TDB 2020, values for $\Delta_f G_m°$, $S_m°(\Delta_f H_m°)$ are taken as such and were consistent with the $\log_{10}K°$, $\Delta_r S_m°(\Delta_f H_m°)$ values for dependent species in the database.

Values for $C_{p,m}°$,and $V_m°$ and their respective HKF model coefficients were selected from sources that used the HKF model to fit measured data for apparent molar heat capacity and molar volume of electrolyte solutions at different temperatures and pressures. When any two of the three thermodynamic properties ($\Delta_f G_m°$, $S_m°$, $\Delta_f H_m°$) are available, the third can be derived from:

$$\Delta_f G_m° = \Delta_f H_m° - T°\cdot(S_m° - \sum \nu \cdot S_{m,\text{elements}}°) \qquad 3\text{-}1$$

Having a complete set of thermodynamic properties and HKF model coefficients enables extrapolation at various temperatures and pressures, and combined with Eq. 1-1 and 1-2, allows for the calculation of the thermodynamic properties of reactions. This complete set of data allows formal thermodynamic consistency to be maintained between the thermodynamic properties of substances and reactions at a given temperature and pressure.

Conventional partial molar volumes and heat capacities of ions can be derived from measurements of apparent molar heat capacity and apparent molar volume of electrolyte solutions, setting the conventional partial molar property of the proton Ξ_m° (H^+) = 0. The relationship between the partial molar properties of the ions and the electrolytes that share common ions is additive, as follows (Tanger and Helgeson, 1988):

$$\Xi_k^\circ = \sum_j \nu_{j,k} \Xi_j^\circ, \qquad 3\text{-}2$$

where $\nu_{j,k}$ represents the stoichiometric number of moles of the j^{th} ion in one mole of the k^{th} electrolyte. In the conventional form, the values of $\Xi_m^\circ(H^+) = \Xi_m^\circ$ (HCl) and thus the values of cations (X) and anions (Y) may be estimated from $\Xi_m^\circ(X) = \Xi_m^\circ(XCl) - \Xi_m^\circ(HCl)$ and $\Xi_m^\circ(Y) = \Xi_m^\circ(NaY) - \Xi_m^\circ(NaCl)$, respectively (Millero, 2014).

Selected $C_{p,m}°$ and $V_m°$ are calculated at T_r and P_r using the HKF model coefficients:

$$C_{p,m}° = c_1 + c_2 \cdot (T_r - \theta)^{-2} + \omega° \cdot T_r \cdot X° \quad 3\text{-}3$$

$$V_m° = 41.84 \cdot (a_1 + a_2 \cdot (1 + \psi)^{-1} + a_3 \cdot (T_r - \theta)^{-1} + a_4 \cdot ((1 + \psi) \cdot (T_r - \theta))^{-1} - \omega° \cdot Q°) \quad 3\text{-}4$$

where θ = 228 (K) and ψ = 2600 (bars) are solvent parameters, ω° is the conventional Born coefficient of the ion (cal·mol^{-1}), and X° = -3.09e-07 (bar^{-1}) and $Q°$ = 5.903e-7 (K^{-2}) are Born functions.

When the values at T_r and P_r of $V_m°$, $C_{p,m}°$ are known and but no data for electrolyte solutions at different temperatures and pressures are available, the HKF parameters can be estimated using the following relationships (Shvarov, 2015; Walker et al., 2024):

$$a_1 = 0.013684 \cdot (V_m° + 41.84 \cdot \omega° \cdot Q°) + 0.1765 \quad 3\text{-}5$$

$$a_2 = 33.4115 \cdot (V_m° + 41.84 \cdot \omega° \cdot Q°) - 347.179 \quad 3\text{-}6$$

$$a_3 = -0.13132 \cdot (V_m° + 41.84 \cdot \omega° \cdot Q°) + 7.11465 \quad 3\text{-}7$$

$$a_4 = -4.134 \cdot a_2 - 27790 \text{ (empirical relation, } -4.134 \text{ unit of K)} \quad 3\text{-}8$$

$$c_1 = 0.58606 \cdot C_{p,m}° - \omega° \cdot T_r \cdot X° + 6.1666 \quad 3\text{-}9$$

$$c_2 = 2037 \cdot C_{p,m}° - 30346 \quad 3\text{-}10$$

$$\omega° = Z^2 \cdot \eta / r_e - \omega H^+_{abs}° \, Z \quad 3\text{-}11$$

where Z is the charge number of the ion (unitless), η = 166027 (Å·cal·mol^{-1}) is a dimensional constant, $\omega H^+_{abs}°$ = 53870 (cal·mol^{-1}) is the absolute Born coefficient of the hydrogen ion, $r_e = r_x$ + (0.0 Å for anions) or (0.94 Å for cations) at T_r is the effective electrostatic radius, and r_x is the crystallographic radius (Pauling) (deterrence given in tables in the appendix).

The selected partial molar heat capacities and volumes of ions are compared against measured data (not exhaustive). Studies of Marcus and Millero (Marcus, 1993; Millero, 1971) provide important compilations on molar volumes of ions. Values for ions were derived using the additivity relation (Eq. 3-2) from measured values for electrolyte solutions reported in the literature. To keep consistency with previous fits of the HKF model coefficients from the team of Helgeson are preferred and selected in this work. The $C_{p,m}°$ and $V_m°$ values are calculated based on the selected HKF coefficients (Table 6-5) and Eq. 3-3 and Eq. 3-4. Other values for $C_{p,m}°$ and $V_m°$ and HKF coefficients (Table 6-5) are estimated (Eqs. 3-5 to 3-11). This is done when previous values were based on estimates limited to data at 25 °C, or differ from new electrolyte data or selections in the NEA reviews (see details below).

Cl^-

Electrolyte data:

$V_m°$(HCl, 298.15 K) = 17.82 ± 0.02 cm^3 mol^{-1} (Millero et al., 1972)

$C_{p,m}°$(HCl, 298.15 K) = -(123.12 ± 0.6) $J·K^{-1}·mol^{-1}$ (Fortier et al., 1974a).

Tremaine (1986) report $C_{p,m}°$(HCl, 298.15 K) = -(126.6 ± 0.22) $J·K^{-1}·mol^{-1}$.

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Tanger and Helgeson (1988), based on fits to several datasets, calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(Cl^-, 298.15 K) = **17.79** cm^3 mol^{-1}

$C_{p,m}°$(Cl^-, 298.15 K) = **-123.12** $J·K^{-1}·mol^{-1}$

These values were used in the following part to derive the properties of ions from values of electrolytes for comparison with the selected values. By convention the properties of H^+ are equal to zero, therefore the properties of Cl^- are equal to that of HCl.

K^+

Electrolyte data:

$V_m°$(KCl, 298.15 K) = 26.97 ± 0.04 cm^3 mol^{-1} (Hnedkovsky and Hefter, 2021)

$C_{p,m}°$(KCl, 298.15 K) = -116.2 $J·K^{-1}·mol^{-1}$ (Archer, 1999)

using Eq. 3-2:

$V_m°$(K^+, 298.15 K) = 9.18 cm^3 mol^{-1}

$C_{p,m}°$(K^+, 298.15 K) = 6.92 $J·K^{-1}·mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(K^+, 298.15 K) = **9.07** cm^3 mol^{-1}

$C_{p,m}°$(K^+, 298.15 K) = **8.31** $J·K^{-1}·mol^{-1}$

These values for K^+ were used in the following to derive other values of ions from measurements.

Na^+

Electrolyte data:

$V_m°$(NaCl, 298.15 K) = 16.6 cm^3 mol^{-1} (Archer, 1992)

$C_{p,m}°$(NaCl, 298.15 K) = -85.3 $J·K^{-1}·mol^{-1}$ (Archer, 1992)

using Eq. 3-2:

$V_m°$(Na^+, 298.15 K) = -1.19 cm^3 mol^{-1}

$C_{p,m}°$(Na^+, 298.15 K) = 37.82 $J·K^{-1}·mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(Na^+, 298.15 K) = **-1.11** cm^3 mol^{-1}

$C_{p,m}°$(Na^+, 298.15 K) = **37.98** $J·K^{-1}·mol^{-1}$

These values for Na^+ were used to derive the values of ions from measurements, using Eq. 3-2, for comparison.

Ca^{2+}

Electrolyte data:

$V_m°$($CaCl_2$, 298.15 K) = 18.35 cm^3 mol^{-1} (Perron et al., 1981)

$C_{p,m}°$($CaCl_2$, 298.15 K) = -278.33 $J·K^{-1}·mol^{-1}$ (Perron et al., 1981)

using Eq. 3-2:

$V_m°$(Ca^{2+}, 298.15 K) = -17.23 cm^3 mol^{-1}

$C_{p,m}°$(Ca^{2+}, 298.15 K) = -32.09 $J·K^{-1}·mol^{-1}$

Selected data:

Selected $V_m°$ from and Shock and Helgeson (1988) and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(Ca^{2+}, 298.15 K) = **-18.06** cm^3 mol^{-1}

$C_{p,m}°$(Ca^{2+}, 298.15 K) = **-31.47** $J·K^{-1}·mol^{-1}$

Fe^{2+}

Thermodynamic properties of iron were updated in TDB 2020 based on measured data to derive a consistent set of values for Fe^{2+} and Fe^{3+}. Values for $\Delta_f H_m°$, $S_m°$, and $C_{p,m}°$ were selected in TDB 2020.

Electrolyte data:

$V_m°(FeCl_2, 298.15\ K) = 12.88 \pm 0.09\ cm^3\ mol^{-1}$ (Pogue and Atkinson, 1988)

$C_{p,m}°(FeCl_2, 298.15\ K) = -(256 \pm 30)\ J \cdot K^{-1} \cdot mol^{-1}$ (Pogue and Atkinson, 1988)

using Eq. 3-2:

$V_m°(Fe^{2+}, 298.15\ K) = -22.7\ cm^3\ mol^{-1}$

$C_{p,m}°(Fe^{2+}, 298.15\ K) = -9.76\ J \cdot K^{-1} \cdot mol^{-1}$

Selected data:

Selected $V_m°$ from Shock et al. (1997) and $C_{p,m}°$ from Lemire et al. (2020) (HKF coefficients estimated Table 6-5), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(Fe^{2+}, 298.15\ K) = -\mathbf{22.25}\ cm^3\ mol^{-1}$

$C_{p,m}°(Fe^{2+}, 298.15\ K) = \mathbf{-(23.0 \pm 10)}\ J \cdot K^{-1} \cdot mol^{-1}$

The selected $C_{p,m}°$ in this work, from Lemire et al. (2020), is more negative than the one obtained from $FeCl_2$ electrolyte measurements, but is within the uncertainty, and is consistent with the evaluation of solubility data for magnetite and Fe^{2+}/Fe^{3+} redox reaction data. The HKF parameters c_1 and c_2 were estimated from Eqs. 3-9 and 3-10, the coefficients in Shock et al. (1997) were also estimates.

Fe^{3+}

Electrolyte data:

$V_m°(Fe(ClO_4)_3, 298.15\ K) = 95.9 \pm 0.5\ cm^3\ mol^{-1}$ (Swaddle and Mak, 1983)

No measured data for $C_{p,m}°$ was found.

Using Eq. 3-2 and ClO_4^- data bellow:

$V_m°(Fe^{3+}, 298.15\ K) = -36.77\ cm^3\ mol^{-1}$

Selected data:

Selected $V_m°$ from Shock et al. (1997) and $C_{p,m}°$ from Lemire et al. (2020) (HKF coefficients estimated Table 6-5), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(Fe^{3+}, 298.15\ K) = \mathbf{-37.0}\ cm^3\ mol^{-1}$

$C_{p,m}°$(Fe^{3+}, 298.15 K) = **-108.0** $J·K^{-1}·mol^{-1}$

Mg^{2+}

Data for the Mg ion were re-evaluated in the NEA TDB review of thermodynamic data (Rand et al., 2024). This resulted in small changes to the $\Delta_f G_m°$ and $S_m°$ which were implemented in this report (Table 6-4).

Electrolyte data:

$V_m°$($MgCl_2$, 298.15 K) = 15 cm^3 mol^{-1} (Perron et al., 1981)

$C_{p,m}°$($MgCl_2$, 298.15 K) = -252.55 $J·K^{-1}·mol^{-1}$ (Perron et al., 1981)

using Eq. 3-2:

$V_m°$(Mg^{2+}, 298.15 K) = -20.58 cm^3 mol^{-1}

$C_{p,m}°$(Mg^{2+}, 298.15 K) = -6.31 $J·K^{-1}·mol^{-1}$

Selected data:

Selected $V_m°$ from and Shock and Helgeson (1988) and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(Mg^{2+}, 298.15 K) = **-21.54** cm^3 mol^{-1}

$C_{p,m}°$(Mg^{2+}, 298.15 K) = **-22.31** $J·K^{-1}·mol^{-1}$

The selected $C_{p,m}°$ value is more negative than the one derived from $MgCl_2$ above, but is selected as it was derived from fits to multiple temperature data and is consistent with the HKF coefficients (Tanger and Helgeson, 1988).

Al^{3+}

Thermodynamic properties of aluminum were updated in TDB 2020 based on available solubility data for aluminum hydroxide phases. These data were selected in TDB 2020 from the review of Brown and Ekberg (2016) based on boehmite solubility experiments. The resulted $C_{p,m}°$ of Al^{3+} was -(96 ±30) $J·K^{-1}·mol^{-1}$ is less negative than the $C_{p,m}°$ that could be retrieved from measurements of the apparent molar volume of $AlCl_3$ solutions, $C_{p,m}°(Al^{3+})$ = -129.94 $J·K^{-1}·mol^{-1}$. The value obtained from $AlCl_3$ solutions is closer to the selected value in this study, **-134.5** $J·K^{-1}·mol^{-1}$, which is from Shock and Helgeson (1988). This heat capacity value is in agreement with the temperature dependency of the gibbsite solubility data summarized in Brown and Ekberg (2016) that can be described by a 2-term $\log_{10}K°$ temperature extrapolation. The selected thermodynamic properties for Al^{3+} (Table 6-4, Table 6-5) are calculated from the properties of gibbsite (Robie and Hemingway, 1995) $\Delta_f G_m°$ −(1154.905 ±1.194) $kJ·mol^{-1}$, $\Delta_f H_m°$ −(1293.130 ±1.190) $kJ·mol^{-1}$, $S_m°$ 68.44 ±0.3 $J·K^{-1}·mol^{-}$

[1], $C_{p,m}°$ 91.7 ±0.3 J·K^{-1}·mol^{-1} and the gibbsite solubility reaction properties (Brown and Ekberg, 2016), $\log_{10}K°$ = 7.753 ±0.08, $\Delta_r H_m°$ −(104.301 ± 2.317) kJ·mol^{-1}, and $\Delta_r C_{p,m}°$ = 0.0 ±10 J·K^{-1}·mol^{-1}.

Electrolyte data:

$V_m°(AlCl_3, 298.15\ K)$ = 9.0 ± 1 cm^3 mol^{-1} (Hovey and Tremaine, 1986)

$C_{p,m}°(AlCl_3, 298.15\ K)$ = -(499.3 ± 10) J·K^{-1}·mol^{-1} (Hovey and Tremaine, 1986)

using Eq. 3-2:

$V_m°(Al^{3+}, 298.15\ K)$ = -44.37 cm^3 mol^{-1}

$C_{p,m}°(Al^{3+}, 298.15\ K)$ = -129.94 J·K^{-1}·mol^{-1}

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Shock and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(Al^{3+}, 298.15\ K)$ = **-44.40** cm^3 mol^{-1}

$C_{p,m}°(Al^{3+}, 298.15\ K)$ = **-134.5** J·K^{-1}·mol^{-1}

ClO_4^-

Electrolyte data:

$V_m°(NaClO_4, 298.15\ K)$ = 43.1 cm^3 mol^{-1} (Roux et al., 1978)

$C_{p,m}°(NaClO_4, 298.15\ K)$ = 3.6 J·K^{-1}·mol^{-1} (Roux et al., 1978)

$V_m°(Mg(ClO_4)_2, 298.15\ K)$ = 66.5 cm^3 mol^{-1} (Spitzer et al., 1978)

$C_{p,m}°(Mg(ClO_4)_2, 298.15\ K)$ = -65.7 J·K^{-1}·mol^{-1} (Spitzer et al., 1978)

using Eq. 3-2 and $NaClO_4$ data:

$V_m°(ClO_4^-, 298.15\ K)$ = 44.21 cm^3 mol^{-1}

$C_{p,m}°(ClO_4^-, 298.15\ K)$ = -34.38 J·K^{-1}·mol^{-1}

using Eq. 3-2 and $Mg(ClO_4)_2$ data:

$V_m°(ClO_4^-, 298.15\ K)$ = 44.02 cm^3 mol^{-1}

$C_{p,m}°(ClO_4^-, 298.15\ K)$ = -21.70 J·K^{-1}·mol^{-1}

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Shock et al. (1997), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(ClO_4^-, 298.15\ K)$ = **44.21** $cm^3\ mol^{-1}$

$C_{p,m}°(ClO_4^-, 298.15\ K)$ = **-24.42** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

F^-

Electrolyte data:

$V_m°(NaF, 298.15\ K)$ = -2.48 $cm^3\ mol^{-1}$ (Fortier et al., 1974b)

$C_{p,m}°(NaF, 298.15\ K)$ = -73.2 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Fortier et al., 1974b)

$V_m°(KF, 298.15\ K)$ = 7.78 $cm^3\ mol^{-1}$ (Fortier et al., 1974b)

$C_{p,m}°(KF, 298.15\ K)$ = -102.6 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Fortier et al., 1974b)

using Eq. 3-2 and NaF data:

$V_m°(F^-, 298.15\ K)$ = -1.37 $cm^3\ mol^{-1}$

$C_{p,m}°(F^-, 298.15\ K)$ = -111.18 $J{\cdot}K^{-1}{\cdot}mol^{-1}$

using Eq. 3-2 and KF data:

$V_m°(F^-, 298.15\ K)$ = -1.29 $cm^3\ mol^{-1}$

$C_{p,m}°(F^-, 298.15\ K)$ = -110.91 $J{\cdot}K^{-1}{\cdot}mol^{-1}$

Selected data:

Selected $V_m°$ from and Shock and Helgeson (1988) and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(F^-, 298.15\ K)$ = **-1.32** $cm^3\ mol^{-1}$

$C_{p,m}°(F^-, 298.15\ K)$ = **-113.89** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

HCO_3^-

Electrolyte data:

$V_m°(NaHCO_3, 298.15\ K)$ = 23.62 ± 0.02 $cm^3\ mol^{-1}$ (Barbero et al., 1983)

$C_{p,m}°$($NaHCO_3$, 298.15 K) = -(4.1 ± 0.4) $J·K^{-1}·mol^{-1}$ (Barbero et al., 1983)

$C_{p,m}°$($NaHCO_3$, 298.15 K) = -7.2 $J·K^{-1}·mol^{-1}$ (Desnoyers et al., 1976)

$C_{p,m}°$($NaHCO_3$, 298.15 K) = -11.6 $J·K^{-1}·mol^{-1}$ (Larson et al., 1982)

$C_{p,m}°$($NaHCO_3$, 298.15 K) = -5.1 $J·K^{-1}·mol^{-1}$ (Perron et al., 1975)

$V_m°$($KHCO_3$, 298.15 K) = 33.9 ± 0.1 $cm^3\ mol^{-1}$ (Barbero et al., 1983)

$C_{p,m}°$($KHCO_3$, 298.15 K) = -(40 ± 0.8) $J·K^{-1}·mol^{-1}$ (Barbero et al., 1983)

From $NaHCO_3$ using Eq. 3-2:

$V_m°$(HCO_3^-, 298.15 K) = 24.73 $cm^3\ mol^{-1}$

$C_{p,m}°$(HCO_3^-, 298.15 K) = -42.08 $J·K^{-1}·mol^{-1}$

$C_{p,m}°$(HCO_3^-, 298.15 K) = -45.18 $J·K^{-1}·mol^{-1}$

$C_{p,m}°$(HCO_3^-, 298.15 K) = -49.58 $J·K^{-1}·mol^{-1}$

$C_{p,m}°$(HCO_3^-, 298.15 K) = -43.08 $J·K^{-1}·mol^{-1}$

From $KHCO_3$ using Eq. 3-2:

$V_m°$(HCO_3^-, 298.15 K) = 24.83 $cm^3\ mol^{-1}$

$C_{p,m}°$(HCO_3^-, 298.15 K) = -48.31 $J·K^{-1}·mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Shock and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(HCO_3^-, 298.15 K) = **24.6** $cm^3\ mol^{-1}$

$C_{p,m}°$(HCO_3^-, 298.15 K) = -35.4 $J·K^{-1}·mol^{-1}$

The $C_{p,m}°$ value selected in Shock and Helgeson (1988) was based on experimental data at 25 °C and the HKF c_1 and c_2 coefficients were estimated by Shock and Helgeson (1988) from Eqs. 3-9, 3-10. In this study, a new $C_{p,m}°$ was selected as the average of data from Barbero et al. (1983), Larson et al. (1982), Perron et al. (1975), and Desnoyers et al. (1976) $C_{p,m}°$ = -(**45.6 ±6**) $J·K^{-1}·mol^{-1}$ and the HKF c_1, c_2 parameters were estimated from Eqs. 3-9 and 3-10.

HS^-

Electrolyte data:

$V_m°$(NaHS, 298.15 K) = 19.54 ±0.3 $cm^3\ mol^{-1}$ (Barbero et al., 1982)

$C_{p,m}°$(NaHS, 298.15 K) = -(50.9 ±0.7) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Barbero et al., 1982)

using Eq. 3-2:

$V_m°$(HS^-, 298.15 K) = 20.65 $cm^3\ mol^{-1}$

$C_{p,m}°$(HS^-, 298.15 K) = -88.88 $J{\cdot}K^{-1}{\cdot}mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(HS^-, 298.15 K) = **20.65** $cm^3\ mol^{-1}$

$C_{p,m}°$(HS^-, 298.15 K) = **-92.68** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

NO_3^-

Electrolyte data:

$V_m°$($Al(NO_3)_3$, 298.15 K) = 43.1 ±1 $cm^3\ mol^{-1}$ (Hovey and Tremaine, 1986)

$C_{p,m}°$($Al(NO_3)_3$, 298.15 K) = -(335.3 ±10) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Hovey and Tremaine, 1986)

using Eq. 3-2:

$V_m°$(NO_3^-, 298.15 K) = 29.16 $cm^3\ mol^{-1}$

$C_{p,m}°$(NO_3^-, 298.15 K) = -68.45 $J{\cdot}K^{-1}{\cdot}mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Shock and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(NO_3^-, 298.15 K) = **29.00** $cm^3\ mol^{-1}$

$C_{p,m}°$(NO_3^-, 298.15 K) = **-67.29** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

OH^-

Electrolyte data:

$V_m°$(NaOH, 298.15 K) = -5.6 cm^3 mol^{-1} (Simonson et al., 1989)

$C_{p,m}°$(NaOH, 298.15 K) = -100.9 $J·K^{-1}·mol^{-1}$ (Simonson et al., 1989)

$V_m°$(KOH, 298.15 K) = 4.92 cm^3 mol^{-1} (Hovey et al., 1988)

$C_{p,m}°$(KOH, 298.15 K) = -130.52$J·K^{-1}·mol^{-1}$ (Hovey et al., 1988)

using Eq. 3-2 and NaOH data:

$V_m°$(OH^-, 298.15 K) = -4.49 cm^3 mol^{-1}

$C_{p,m}°$(OH^-, 298.15 K) = -138.88 $J·K^{-1}·mol^{-1}$

using Eq. 3-2 and KOH data:

$V_m°$(OH^-, 298.15 K) = -4.15 cm^3 mol^{-1}

$C_{p,m}°$(OH^-, 298.15 K) = -138.83 $J·K^{-1}·mol^{-1}$

Selected data:

Selected $V_m°$ from and Shock and Helgeson (1988) and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°$(OH^-, 298.15 K) = **-4.18** cm^3 mol^{-1}

$C_{p,m}°$(OH^-, 298.15 K) = **-137.13** $J·K^{-1}·mol^{-1}$

Using the $C_{p,m}°$(H_2O(l), 298.15 K) of 75.351 $J·K^{-1}·mol^{-1}$ and $V_m°$(H_2O(l), 298.15 K) of 18.0684 cm^3 mol^{-1}, values of -212.481 $J·K^{-1}·mol^{-1}$ and 22.25 cm^3 mol^{-1} were obtained for the $\Delta_r C_{p,m}°$ and $\Delta_r V_m°$ of water ionisation, respectively. These are close to the values -(216 ± 3) $J·K^{-1}·mol^{-1}$ and -(22.2 ± 0.5) cm^3 mol^{-1} recommended by Plyasunov and Bugaev (2024) based on the assessment of several experimental datasets.

CO_3^{2-}

Electrolyte data:

$V_m°$(Na_2CO_3, 298.15 K) = -6.8 cm^3 mol^{-1} (Larson et al., 1982)

$C_{p,m}°$(Na_2CO_3, 298.15 K) = -215.5 $J·K^{-1}·mol^{-1}$ (Larson et al., 1982)

using Eq. 3-2:

$V_m°$(CO_3^{2-}, 298.15 K) = -4.58 cm^3 mol^{-1}

$C_{p,m}°(CO_3^{2-}, 298.15\ K) = -291.45\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Shock and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(CO_3^{2-}, 298.15\ K) =$ **-5.02** $cm^3\ mol^{-1}$

$C_{p,m}°(CO_3^{2-}, 298.15\ K) =$ **-290.78** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

HPO_4^{2-}

Electrolyte data:

$V_m°(Na_2HPO_4, 298.15\ K) = 2.8\ cm^3\ mol^{-1}$ (Larson et al., 1982)

$C_{p,m}°(Na_2HPO_4, 298.15\ K) = -168.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Larson et al., 1982)

using Eq. 3-2:

$V_m°(HPO_4^{2-}, 298.15\ K) = 5.02\ cm^3\ mol^{-1}$

$C_{p,m}°(HPO_4^{2-}, 298.15\ K) = -244.05\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

Selected data:

Selected $V_m°$ and $C_{p,m}°$ from Shock and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(HPO_4^{2-}, 298.15\ K) =$ **5.38** $cm^3\ mol^{-1}$

$C_{p,m}°(HPO_4^{2-}, 298.15\ K) =$ **-244.22** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

SO_4^{2-}

Electrolyte data:

$V_m°(Na_2SO_4, 298.15\ K) = 11.4\ cm^3\ mol^{-1}$ (Olofsson et al., 1978)

$C_{p,m}°(Na_2SO_4, 298.15\ K) = -190.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Olofsson et al., 1978)

$V_m°(K_2SO_4, 298.15\ K) = 32.8\ cm^3\ mol^{-1}$ (Olofsson et al., 1978)

$C_{p,m}°(K_2SO_4, 298.15\ K) = -251\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Olofsson et al., 1978)

From Na_2SO_4 using Eq. 3-2:

$V_m°(SO_4^{2-}, 298.15\ K) = 13.62\ cm^3\ mol^{-1}$

$C_{p,m}°(SO_4^{2-}, 298.15\ K) = -266.05\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

From K_2SO_4 using Eq. 3-2:

$V_m°(SO_4^{2-}, 298.15\ K) = 14.67\ cm^3\ mol^{-1}$

$C_{p,m}°(SO_4^{2-}, 298.15\ K) = -267.61\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

Selected data:

Selected $V_m°$ from and Shock and Helgeson (1988) and $C_{p,m}°$ from Tanger and Helgeson (1988), calculated from Eqs. 3-4 and 3-3 using the reported HKF coefficients:

$V_m°(SO_4^{2-}, 298.15\ K) =$ **13.88** $cm^3\ mol^{-1}$

$C_{p,m}°(SO_4^{2-}, 298.15\ K) =$ **-267.45** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

PO_4^{3-}

Electrolyte data:

$V_m°(Na_3PO_4, 298.15\ K) = -(28.6 \pm 1.3)\ cm^3\ mol^{-1}$ (Bianchi and Tremaine, 1995)

$C_{p,m}°(Na_3PO_4, 298.15\ K) = -(371 \pm 5)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ (Bianchi and Tremaine, 1995)

$V_m°(Na_3PO_4, 298.15\ K) = -34.12\ cm^3\ mol^{-1}$ (Surdo et al., 1979)

$V_m°(K_3PO_4, 298.15\ K) = -3.34\ cm^3\ mol^{-1}$ (Surdo et al., 1979)

From Na_3PO_4 using Eq. 3-2:

$V_m°(PO_4^{3-}, 298.15\ K) = -25.27\ cm^3\ mol^{-1}$

$C_{p,m}°(PO_4^{3-}, 298.15\ K) = -484.93\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$V_m°(PO_4^{3-}, 298.15\ K) = -30.79\ cm^3\ mol^{-1}$

From K_3PO_4 using Eq. 3-2:

$V_m°(PO_4^{3-}, 298.15\ K) = -30.54\ cm^3\ mol^{-1}$

Selected $V_m°$ and $C_{p,m}°$ from Shock and Helgeson (1988) , calculated from Eq. 3-4 using the reported HKF coefficients:

$V_m°(PO_4^{3-}, 298.15\ K) =$ **-30.6** $cm^3\ mol^{-1}$

$C_{p,m}°(PO_4^{3-}, 298.15\ K) =$ **-480.75** $J{\cdot}K^{-1}{\cdot}mol^{-1}$

Shock et al. (1997) estimated $C_{p,m}°$ from correlation with $S_m°$ (-222 J·K^{-1}·mol^{-1}) and calculated a value of -521.35 J·K^{-1}·mol^{-1}. The $C_{p,m}°$ and $V_m°$ of PO_4^{3-} may require additional scrutiny.

Si(OH)$_4$(aq)

Thermodynamic properties of Si(OH)$_4$(aq) were evaluated in TDB 2020 (Hummel and Thoenen, 2023) based on quartz and amorphous silica solubility data summarized in Gunnarsson and Arnórsson (2000). Values for $\Delta_f G_m°$ (-1309.183 ±1.12 kJ·mol^{-1}), $S_m°$ (178.851 ±2.2 J·K^{-1}·mol^{-1}), and $C_{p,m}°$ (237.37 ±2.0 J·K^{-1}·mol^{-1}) were derived based on the dependency of the solubility data on temperature. These are in close agreement with the NEA selection (Rand et al., 2024) of $\Delta_f G_m°$ (-1309.201 ±1.017 kJ·mol^{-1}), $S_m°$ (181.105 ±2.501 J·K^{-1}·mol^{-1}), and somewhat less positive for $C_{p,m}°$ (195.0 ±3.0 J·K^{-1}·mol^{-1}). Walker et al. (2024) revised the thermodynamic properties of Si(OH)$_4$(aq) based on solubility data within the HKF model framework and evaluated values for $\Delta_f G_m°$ (-1309.215 ±1.76 kJ·mol^{-1}), $S_m°$ (182.13 ±2.092 J·K^{-1}·mol^{-1}), and even less positive for $C_{p,m}°$ (-153 ±28 J·K^{-1}·mol^{-1}). In all cases the experimental data are reproduced to within experimental uncertainty and the different $C_{p,m}°$ values obtained depend on the constraints used during data fitting.

In this report the NEA $C_{p,m}°$ value (**195.0 ±20.0** J·K^{-1}·mol^{-1}) was selected, assigning it a higher uncertainty, based on the constraint that $\Delta_r C_{p,m}° = 0.0$ J·K^{-1}·mol^{-1} for the isocoulombic reaction (Gu et al., 1994; Miron et al., 2020) quartz + 2H$_2$O(l) = Si(OH)$_4$(aq) and properties of α-quartz: from Cox et al. (1989) $C_{p,m}°$ = 44.602 ±0.3 J·K^{-1}·mol^{-1}, and of H$_2$O(l): $C_{p,m}°$ = 75.351 ±0.08 J·K^{-1}·mol^{-1}. The HKF parameters were then fitted to the quartz solubility data at different temperatures and pressures summarized by Walker et al. (2024), together with simultaneously fitting $S_m°$ (**178.260 ±3** J·K^{-1}·mol^{-1}) and $V_m°$ (**55.87** cm^3 mol^{-1}). There are no data independent from solubility for $C_{p,m}°$ and $V_m°$ to compare them with the ones obtained in this work.

4 Temperature dependence of gaseous species

The thermodynamic properties of common gases are well known from measurements of enthalpy, entropy and heat capacity of gases and from highly accurate statistical mechanics calculations. Values for $\Delta_f G_m°$, $S_m°$, $\Delta_f H_m°$, $C_{p,m}°$ have already been selected in Table 6-6 of the TDB 2020 (Hummel and Thoenen, 2023). and are consistent with the NEA TDB (Grenthe et al., 1992). In this study, additional $C_{p,m}°$ coefficients for the temperature function polynomial, necessary for temperature corrections, were selected from the literature (Table 6-7), primarily from the NIST-JANAF Thermochemical Tables (Chase, 1998). The effect of pressure on gases is approximated using the ideal gas law and will not produce significant deviations up to a pressure of 50 bars. For higher pressures a real gas formulation and respective model parameters are required.

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6 Selected data

Table 6-1 Molar volumes of minerals (298 K, 0.1 MPa) based on measured densities or crystallographic data.

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
Ag(cr)	Ag	10.27	(Robie and Hemingway, 1995)
Ag2CO3(cr)	Ag2CO3	45.38	(Haynes, 2016)
Ag2O(am)	Ag2O	34.18	materialsproject.org
Ag2O(cr)	Ag2O	34.18	materialsproject.org
Ag2S(cr)	Ag2S	34.19	(Robie and Hemingway, 1995)
Ag2Se(alpha)	Ag2Se	36.34	(Wiegers, 1971)
Ag2SeO3(cr)	Ag2SeO3	57.12	materialsproject.org
Ag2SeO4(cr)	Ag2SeO4	62.17	(Weil, 2003).org
Ag2SO4(s)	Ag2SO4	57.42	materialsproject.org
Ag3PO4(s)	Ag3PO4	65.50	materialsproject.org
AgBr(cr)	AgBr	28.99	(Robie and Hemingway, 1995)
AgCl(cr)	AgCl	25.73	(Robie and Hemingway, 1995)
AgCN(s)	AgCN	43.19	materialsproject.org
AgI(cr)	AgI	41.30	(Robie and Hemingway, 1995)
AgSeCN(cr)	AgSeCN	56.82	(Huttner and Knappe, 1930)
Gibbsite	Al(OH)3	31.96	(Robie and Hemingway, 1995)
Kaolinite	Al2Si2O5(OH)4	99.34	(Robie and Hemingway, 1995)
Boehmite	AlOOH	19.54	(Robie and Hemingway, 1995)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
Am(OH)3(cr)	Am(OH)3	46.56	(Milligan et al., 1968)
As(cr)	As	12.96	(Robie and Hemingway, 1995)
B(cr)	B	4.39	(Robie and Hemingway, 1995)
B(OH)3(cr)	B(OH)3	43.09	(Robie and Hemingway, 1995)
B2O3(am)	B2O3	27.26	(Robie and Hemingway, 1995)
B2O3(cr)	B2O3	27.26	(Robie and Hemingway, 1995)
Ba[(UO2)(AsO4)]2:7H2O(cr)	Ba[(UO2)(AsO4)]2(H2O)7	270.33	(Locock et al., 2005)
Meta-uranocircite_II	Ba[(UO2)(PO4)]2(H2O)6	251.66	(Locock et al., 2005)
Ba3(PO4)2(s)	Ba3(PO4)2	116.43	materialsproject.org
Witherite	BaCO3	45.81	(Robie and Hemingway, 1995)
BaHPO4(cr)	BaHPO4	58.47	materialsproject.org
BaSeO3(cr)	BaSeO3	53.18	materialsproject.org
BaSeO4(cr)	BaSeO4	57.67	materialsproject.org
Barite	BaSO4	52.10	(Robie and Hemingway, 1995)
Graphite	C	5.30	(Robie and Hemingway, 1995)
Portlandite	Ca(OH)2	33.06	(Robie and Hemingway, 1995)
Whewellite	Ca(Oxa)(H2O)	65.82	mindat.org
Weddelite	Ca(Oxa)(H2O)2	83.65	mindat.org
Ca(Oxa):3H2O(cr)	Ca(Oxa)(H2O)3	97.93	materials.springer.org
Ca[(UO2)(AsO4)]2:10H2O(cr)	Ca[(UO2)(AsO4)]2(H2O)10	262.82	Metauranospinite, mindat.org
Meta-autunite	Ca[(UO2)(PO4)]2(H2O)6	247.37	mindat.org

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
Uranophane	Ca[(UO2)(SiO3OH)]2(H2O)5	278.05	(Plášil et al., 2013)
Beidellite(Ca)	Ca0.17Al2.34Si3.66O10(OH)2	134.10	(Blanc et al., 2015a)
Nontronite(Ca)	Ca0.17Fe1.67Al0.67Si3.66O10(OH)2	133.74	(Blanc et al., 2015a)
Montmorillonite(MgCa)	Ca0.17Mg0.34Al1.66Si4O10(OH)2	135.58	(Blanc et al., 2015a)
Saponite(FeCa)	Ca0.17Mg2FeAl0.34Si3.66O10(OH)2	145.15	(Blanc et al., 2015a)
Saponite(Ca)	Ca0.17Mg3Al0.34Si3.66O10(OH)2	142.57	(Blanc et al., 2015a)
Beidellite_SBld-1	Ca0.185K0.104(Si3.574Al0.426) (Al1.812Mg0.09Fe0.112)O10(OH)2	137.98	(Gailhanou et al., 2012)
Nontronite_Nau-1	Ca0.247K0.02(Si3.458Al0.542) (Fe1.688Al0.276Mg0.068)O10(OH)2	136.38	(Gailhanou et al., 2013)
Mordenite-Ca	Ca0.34Al0.68Si5.32O12(H2O)2.9	209.80	(Robie and Hemingway, 1995)
Montmorillonite(HcCa)	Ca0.3Mg0.6Al1.4Si4O10(OH)2	140.32	(Blanc et al., 2015a)
Vermiculite(Ca)	Ca0.43Mg3Al0.86Si3.14O10(OH)2	149.800	(Blanc et al., 2015a)
Vermiculite_SO	Ca0.445(Si2.778Al1.222) (Al0.192Mg2.468Fe0.254Ti0.018 Mn0.007)O10(OH)2	148.36	(Gailhanou et al., 2013)
Clinoptilolite	Ca0.52Al1.04Si4.96O12(H2O)3.1	200.02	webmineral.com
Heulandite_1	Ca1.07Al2.14Si6.86O18(H2O)4.4	317.60	(Robie and Hemingway, 1995)
Stilbite	Ca1.11Al2.22Si6.78O18(H2O)6.8	333.40	(Robie and Hemingway, 1995)
Ca3(Cit)2:4H2O(cr)	Ca3(Cit)2(H2O)4	285.25	(Herdtweck et al., 2011)
Tuite	Ca3(PO4)2	97.62	(Robie and Hemingway, 1995)
Ca3B2O6(s)	Ca3B2O6	76.24	Takedaite, (Kusachi et al., 1995)
Cl-apatite	Ca5(PO4)3Cl	163.88	(Naumov et al., 1974)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
F-apatite	Ca5(PO4)3F	157.56	(Robie and Hemingway, 1995)
OH-apatite	Ca5(PO4)3OH	159.60	(Robie and Hemingway, 1995)
Low-silica_P-Ca	CaAl2Si2O8(H2O)4.5	124.75	materialsproject.org
Scolecite	CaAl2Si3O10(H2O)3	172.30	(Robie and Hemingway, 1995)
Chabazite-Ca	CaAl2Si4O12(H2O)6	251.16	(Coombs et al., 1997)
CaB2O4(s)	CaB2O4	43.65	Calciborite, rruff.geo.arizona.edu
CaB4O7(s)	CaB4O7	71.55	materialsproject.org
Aragonite	CaCO3	34.15	(Robie and Hemingway, 1995)
Calcite	CaCO3	36.93	(Robie and Hemingway, 1995)
Vaterite	CaCO3	37.63	(Robie and Hemingway, 1995)
CaCrO4(s)	CaCrO4	49.70	(Roberts et al., 1990)
Fluorite	CaF2	24.54	(Robie and Hemingway, 1995)
CaHK3(PO4)2(cr)	CaHK3(PO4)2	130.95	materialsproject.org
Monetite	CaHPO4	46.45	(Nriagu, 1984)
Brushite	CaHPO4(H2O)2	73.92	(Nriagu, 1984)
CaMg(CO3)2(cr)	CaMg(CO3)2	64.34	(Robie and Hemingway, 1995)
Powellite	CaMoO4	47.00	(Robie and Hemingway, 1995)
CaSeO3:H2O(cr)	CaSeO3(H2O)	58.16	Burtite, (Valkonen et al., 1985)
CaSn(OH)6(pr)	CaSn(OH)6	81.00	mindat.org
Anhydrite	CaSO4	46.01	(Robie and Hemingway, 1995)
Gypsum	CaSO4(H2O)2	74.69	(Robie and Hemingway, 1995)

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
Becquerelite	CaU6O19(H2O)11	386.35	mindat.org
Cd(OH)2(s)	Cd(OH)2	29.67	(Mercury et al., 2001)
CdB2O4(s)	CdB2O4	38.16	materialsproject.org
Otavite	CdCO3	34.30	(Robie and Hemingway, 1995)
CdS(s)	CdS	29.93	(Robie and Hemingway, 1995)
Cr(cr)	Cr	7.23	(Robie and Hemingway, 1995)
Cr2(SO4)3(s)	Cr2(SO4)3	130.21	(Pankratz, 1994)
Cr2O3(cr)	Cr2O3	29.09	(Robie and Hemingway, 1995)
Cr2S3(s)	Cr2S3	53.24	materialsproject.org
CrCl2(cr)	CrCl2	42.70	(Pankratz, 1984)
CrCl3(cr)	CrCl3	57.37	(Pankratz, 1984)
CrO2(cr)	CrO2	16.95	(Wolery, 1992)
CrO3(cr)	CrO3	35.14	(Wolery, 1992)
CrPO4(green)	CrPO4	42.60	materialsproject.org
CrS(s)	CrS	52.04	materialsproject.org
Cu(cr)	Cu	7.11	(Robie and Hemingway, 1995)
Cu(OH)2(s)	Cu(OH)2	28.97	(Pankratz et al., 1984)
Metazeunerite	Cu[(UO2)(AsO4)]2(H2O)8	265.00	(Locock and Burns, 2003)
Cu[(UO2)(PO4)]2:8H2O(cr)	Cu[(UO2)(PO4)]2(H2O)8	254.11	(Locock and Burns, 2003)
malachite	Cu2CO3(OH)2	54.86	(Robie and Hemingway, 1995)
cuprite	Cu2O	23.44	(Robie and Hemingway, 1995)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
chalcotite	Cu2S	27.48	(Robie and Hemingway, 1995)
azurite	Cu3(CO3)2(OH)2	91.01	(Robie and Hemingway, 1995)
CuCl(s)	CuCl	23.92	(Robie and Hemingway, 1995)
tenorite	CuO	12.22	(Robie and Hemingway, 1995)
covellite	CuS	20.42	(Robie and Hemingway, 1995)
EuF3(cr)	EuF3	30.50	materialsproject.org
EuOHCO3(cr)	EuOHCO3	88.96	(Michiba et al., 2011)
Fe(alpha)	Fe	7.04	(Fabrichnaya et al., 2004)
"""white rust"""	Fe(OH)2	24.48	(Mercury et al., 2001)
2-line ferrihydrite	Fe(OH)3	34.36	(Wolery, 1992)
Metakahlerite	Fe[(UO2)(AsO4)]2(H2O)8	265.76	Metakahlerite, rruff.info
4C pyrrhotite	Fe0.875S	17.49	(Robie and Hemingway, 1995)
Fe0.875Se(cr)	Fe0.875Se	25.88	Tetragonal, materialsproject.org
5C pyrrhotite	Fe0.9S	16.88	(Robie and Hemingway, 1995)
Fe1.042Se(cr)	Fe1.042Se	27.76	Fe1.042Se(cr)
Berthierine(FeIII)	Fe2.67Al0.33(Si1.34Al0.66)O5(OH)4	103.27	(Blanc et al., 2015a)
Berthierine(FeII)	Fe2Al(SiAl)O5(OH)4	103.86	(Blanc et al., 2015a)
Fe-hibbingite	Fe2Cl(OH)3	65.19	mindat.org
hematite	Fe2O3	30.27	(Robie and Hemingway, 1995)
maghemite	Fe2O3	29.087	(Wyckoff, 1963)
vivianite	Fe3(PO4)2(H2O)8	185.10	(Wyckoff, 1963)

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
Cronstedtite	Fe3(SiFe)O5(OH)4	370.63	(Blanc et al., 2015a)
magnetite	Fe3O4	44.52	(Robie and Hemingway, 1995)
greigite	Fe3S4	72.52	mindat.org
Fe3Se4(gamma)	Fe3Se4	69.05	Monoclinic, materialsproject.org
siderite	FeCO3	29.38	(Robie and Hemingway, 1995)
Chromite	FeCr2O4	44.01	(Robie and Hemingway, 1995)
goethite	FeOOH	20.82	(Robie and Hemingway, 1995)
lepidocrocite	FeOOH	22.213	(Wyckoff, 1963)
rodolicoite	FePO4	64.500	(Robie and Hemingway, 1995)
FePO4:2H2O(s)	FePO4(H2O)	64.50	(Robie and Hemingway, 1995)
mackinawite	FeS	21.082	(Wyckoff, 1963)
troilite	FeS	18.20	(Robie and Hemingway, 1995)
marcasite	FeS2	24.58	(Robie and Hemingway, 1995)
pyrite	FeS2	23.94	(Robie and Hemingway, 1995)
ferroselite	FeSe2	29.94	mindat.org
Sabugalite	HAl(UO2)4(PO4)4(H2O)16	680.55	(Locock et al., 2005)
Hg2Cl2(cr)	Hg2Cl2	32.94	(Robie and Hemingway, 1995)
HgHPO4(s)	HgHPO4	48.94	(Dubler et al., 1981)
HgO(cr)	HgO	19.32	(Robie and Hemingway, 1995)
HgS(s)	HgS	28.42	(Robie and Hemingway, 1995)
Ho(OH)3(cr)	Ho(OH)3	34.19	Am(OH)3(cr)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
HoF3(cr)	HoF3	28.13	materialsproject.org
HoOHCO3(cr)	HoOHCO3	40.19	(Michiba et al., 2011)
HoPO4(s)	HoPO4	42.33	materialsproject.org
K(UO2)(AsO4):3H2O(cr)	K(UO2)(AsO4)(H2O)3	138.16	Abernathyite, (Locock et al., 2004)
K(UO2)(PO4):3H2O(cr)	K(UO2)(PO4)(H2O)3	129.42	Meta-ankoleite, (Fitch and Cole, 1991)
Boltwoodite	K(UO2)(SiO3OH)(H2O)	101.51	(Plášil, 1999)
Beidellite(K)	K0.34Al2.34Si3.66O10(OH)2	133.22	(Blanc et al., 2015a)
Nontronite(K)	K0.34Fe1.67Al0.67Si3.66O10(OH)	132.85	(Blanc et al., 2015a)
Montmorillonite(MgK)	K0.34Mg0.34Al1.66Si4O10(OH)2	134.69	(Blanc et al., 2015a)
Saponite(FeK)	K0.34Mg2FeAl0.34Si3.66O10(OH)	144.27	(Blanc et al., 2015a)
Saponite(K)	K0.34Mg3Al0.34Si3.66O10(OH)2	144.27	(Blanc et al., 2015a)
Montmorillonite(HcK)	K0.6Mg0.6Al1.4Si4O10(OH)2	138.75	(Blanc et al., 2015a)
Glauconite	K0.75(Mg0.25Fe1.5Al0.25) (Al0.25Si3.75)O10(OH)	139.76	(Blanc et al., 2015a)
Illite_IMt-2	K0.762Na0.044(Si3.387Al0.613) (Al1.427Fe0.376Mg0.241)O10(OH)2	139.18	(Gailhanou et al., 2012)
Illite(Al)	K0.85Al2.85Si3.15O10(OH)2	138.98	(Blanc et al., 2015a)
Illite(FeII)	K0.85Fe0.25Al2.35Si3.4O10(OH)2	140.67	(Blanc et al., 2015a)
Illite(FeIII)	K0.85Fe0.25Al2.6Si3.15O10(OH)2	138.92	(Blanc et al., 2015a)
Illite(Mg)	K0.85Mg0.25Al2.35Si3.4O10(OH)2	140.06	(Blanc et al., 2015a)
Vermiculite(K)	K0.86Mg3Al0.86Si3.14O10(OH)2	147.560	(Blanc et al., 2015a)

Name	**Formula**	$V_m°$ **(cm³ mol⁻¹)**	**Reference**
KFe(CrO4)2:2H2O(s)	KFe(CrO4)2(H2O)2	125.26	(Gravereau and Hardy, 1972)
Li(UO2)(BO3):1.5H2O(cr)	Li(UO2)(BO3)(H2O)1.5	92.55	(Hao et al., 2020)
Li(UO2)(PO4):4H2O(cr)	Li(UO2)(PO4)(H2O)4	133.13	(Locock et al., 2004)
Brucite	Mg(OH)2	24.63	(Robie and Hemingway, 1995)
Glushinskite	Mg(Oxa)(H2O)2	80.19	mindat.org
Mg[(UO2)(AsO4)]2:10H2O(cr)	Mg[(UO2)(AsO4)]2(H2O)10	276.31	Nováčekite, mindat.org
Meta-saleite	Mg[(UO2)(PO4)]2(H2O)8	279.88	Saleeite, (Miller and Taylor, 1986)
Beidellite(Mg)	Mg0.17Al2.34Si3.66O10(OH)2	130.11	(Blanc et al., 2015a)
Nontronite(Mg)	Mg0.17Fe1.67Al0.67Si3.66O10(OH)2	129.74	(Blanc et al., 2015a)
Montmorillonite(MgMg)	Mg0.17Mg0.34Al1.66Si4O10(OH)2	131.58	(Blanc et al., 2015a)
Saponite(Mg)	Mg0.17Mg3Al0.34Si3.66O10(OH)2	138.58	(Blanc et al., 2015a)
Montmorillonite(HcMg)	Mg0.3Mg0.6Al1.4Si4O10(OH)2	133.27	(Blanc et al., 2015a)
Vermiculite(Mg)	Mg0.43Mg3Al0.86Si3.14O10(OH)2	139.690	(Blanc et al., 2015a)
Saponite(FeMg)	Mg2.17FeAl0.34Si3.66O10(OH)2	141.16	(Blanc et al., 2015a)
Mg2KH(PO4)2:15H2O(cr)	Mg2KH(PO4)2(H2O)15	303.20	(Peng et al., 2022)
Farringtonite	Mg3(PO4)2	95.25	(Nriagu, 1984)
Cattite	Mg3(PO4)2(H2O)22	386.18	Bobierrite + 14*(V_{gypsum}-$V_{anhydrite}$)/2
Mg3(PO4)2:4H2O(cr)	Mg3(PO4)2(H2O)4	128.06	Bobierrite – 3*(V_{gypsum}-$V_{anhydrite}$)/2
Bobierrite	Mg3(PO4)2(H2O)8	185.42	(Nriagu, 1984)
Magnesite	MgCO3	28.02	(Robie and Hemingway, 1995)
MgCr2O4(s)	MgCr2O4	43.56	(Robie and Hemingway, 1995)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
Newberyite	MgHPO4(H2O)3	83.02	(Nriagu, 1984)
Phosphorröslerite	MgHPO4(H2O)7	160.50	(Peng et al., 2022)
MgKPO4:H2O(cr)	MgKPO4(H2O)	70.50	(Peng et al., 2022)
K-struvite	MgKPO4(H2O)6	142.50	(Peng et al., 2022)
MgSeO3:6H2O(cr)	MgSeO3(H2O)6	124.43	(Andersen et al., 1984)
Pyrochroite	Mn(OH)2	24.63	(Robie and Hemingway, 1995)
Mn2O3(cr)	Mn2O3	31.37	(Robie and Hemingway, 1995)
Mn3O4(cr)	Mn3O4	46.95	(Robie and Hemingway, 1995)
MnCO3(cr)	MnCO3	31.07	(Robie and Hemingway, 1995)
MnO(cr)	MnO	13.22	(Robie and Hemingway, 1995)
MnO2(cr)	MnO2	16.61	(Robie and Hemingway, 1995)
Manganite	MnOOH	20.08	mindat.org
MnSeO3:2H2O(cr)	MnSeO3(H2O)2	66.64	MnH2SeO5, materialsproject.org
MoO2(cr)	MoO2	20.64	materialsproject.org
MoO3(cr)	MoO3	30.56	(Robie and Hemingway, 1995)
Na(UO2)(AsO4):3H2O(cr)	Na(UO2)(AsO4)(H2O)3	133.37	(Locock et al., 2004)
Na(UO2)(PO4):3H2O(cr)	Na(UO2)(PO4)(H2O)3	124.60	(Locock et al., 2004)
Na-boltwoodite	Na(UO2)(SiO3OH)(H2O)	98.57	mindat.org
Beidellite(Na)	Na0.34Al2.34Si3.66O10(OH)2	132.49	(Blanc et al., 2015a)
Nontronite(Na)	Na0.34Fe1.67Al0.67Si3.66O10(OH)2	132.12	(Blanc et al., 2015a)
Montmorillonite(MgNa)	Na0.34Mg0.34Al1.66Si4O10(OH)2	133.96	(Blanc et al., 2015a)

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
Saponite(FeNa)	Na0.34Mg2FeAl0.34Si3.66O10(OH)2	143.54	(Blanc et al., 2015a)
Saponite(Na)	Na0.34Mg3Al0.34Si3.66O10(OH)2	143.54	(Blanc et al., 2015a)
Saponite_SapCa-2	Na0.394K0.021Ca0.038)(Si3.569 Al0.397)(Mg2.949Fe0.055)O10(OH)2	141.66	(Gailhanou et al., 2013)
Smectite_MX80	Na0.409K0.024Ca0.009(Si3.738Al0.262) (Al1.598Mg0.214Fe0.208)O10(OH)2	134.92	(Gailhanou et al., 2012)
Montmorillonite(HcNa)	Na0.6Mg0.6Al1.4Si4O10(OH)2	137.47	(Blanc et al., 2015a)
Mordenite-Na	Na0.72Al0.72Si5.28O12(H2O)2.71	209.80	(Robie and Hemingway, 1995)
Vermiculite(Na)	Na0.86Mg3Al0.86Si3.14O10(OH)2	303.00	(Robie and Hemingway, 1995)
Phillipsite-NaK	Na1.5KAl2.5Si5.5O16(H2O)5	138.98	(Blanc et al., 2015a)
Phillipsite-Na	Na2.5Al2.5Si5.5O16(H2O)5	138.98	(Blanc et al., 2015a)
Natrolite	Na2Al2Si3O10(H2O)2	169.20	(Robie and Hemingway, 1995)
Analcime	Na2Al2Si4O12(H2O)2	97.40	(Robie and Hemingway, 1995)
Chabazite-Na	Na2Al2Si4O12(H2O)6	241.68	webmineral.com
Faujasite-Y	Na2Al2Si4O12(H2O)8	294.84	webmineral.com
Na2B4O7(cr)	Na2B4O7	87.49	materialsproject.org
Na2B4O7:10H2O(s)	Na2B4O7(H2O)10	225.67	materialsproject.org
Na2U2O7:H2O(cr)	Na2U2O7(H2O)	101.88	β-Na2U2O7, (Ijdo et al., 2015)
Na6Th(CO3)5:12H2O(cr)	Na6Th(CO3)5(H2O)12	377.11	materials.springer.com
Cancrinite-NO3	Na8Al6Si6O24(NO3)2(H2O)4	439.51	mindat.org
Sodalite	Na8Al6Si6O24Cl2	417.76	mindat.org
Dawsonite	NaAlCO3(OH)2	59.30	(Robie and Hemingway, 1995)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
NaBO2(s)	NaBO2	25.60	materialsproject.org
Nb2O5(pr)	Nb2O5	61.82	materialsproject.org
NH4(UO2)(AsO4):3H2O(cr)	NH4(UO2)(AsO4)(H2O)3	149.39	Uramarsite, mindat.org
NH4(UO2)(PO4):3H2O(cr)	NH4(UO2)(PO4)(H2O)3	118.13	Urmaphite, mindat.org
Ni(BO2)2(s)	Ni(BO2)2	32.14	materialsproject.org
Ni(OH)2(cr_beta)	Ni(OH)2	23.59	materials.springer.com
Rauchite	*Ni[(UO2)(AsO4)]2(H2O)10*	*277.36*	Metarauchite, mindat.org
NiCO3(cr)	NiCO3	27.05	(Robie and Hemingway, 1995)
NiCO3:5.5H2O(s)	NiCO3(H2O)5.5	110.76	(Wallner et al., 2002)
NiO(cr)	NiO	10.97	(Robie and Hemingway, 1995)
NiSeO3:2H2O(cr)	NiSeO3(H2O)2	65.20	materialsproject.org
Np(Oxa)2:6H2O(cr)	Np(Oxa)2(H2O)6	191.61	(Grigo'ev et al., 1997)
NpO2(am_hyd)	NpO2	24.02	Crystalline, materialsproject.org
NpO2CO3(cr)	NpO2CO3	56.44	Na0.5[NpO2(OH)1.5]·0.5H2O, materials.springer.com
Pa2O5(act)	Pa2O5	50.10	materials.springer.com
Pb(cr)	Pb	18.27	(Robie and Hemingway, 1995)
Pb[(UO2)(PO4)]2:8H2O(cr)	Pb[(UO2)(PO4)]2(H2O)8	280.13	(Ross, 1956)
Pb2(CO3)Cl2(s)	Pb2(CO3)Cl2	87.40	(Roberts et al., 1990)
Parsonite	Pb2(UO2)(PO4)2(H2O)2	146.60	mindat.org
Pb3(PO4)2(s)	Pb3(PO4)2	109.05	(Keppler, 1970)
Pb5(PO4)3Cl(s)	Pb5(PO4)3Cl	191.03	(Wyckoff, 1963)

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
PbClOH(s)	PbClOH	42.00	(Roberts et al., 1990)
PbCO3(s)	PbCO3	40.59	(Robie and Hemingway, 1995)
Crocoite	PbCrO4	52.81	(Haynes, 2016)
PbHPO4(s)	PbHPO4	53.77	(Effenberger and Pertlik, 1986a).
PbO(s_red)	PbO	23.67	(Baldinozzi et al., 2003)
PbO(s_yellow)	PbO	23.15	(Hill, 1985)
PbS(s)	PbS	31.49	(Robie and Hemingway, 1995)
PbSO4(cr)	PbSO4	47.95	(Robie and Hemingway, 1995)
Pd(cr)	Pd	8.861	(Sassani and Shock, 1998)
PdO(cr)	PdO	14.68	(Sassani and Shock, 1998)
Po(cr)	Po	22.73	(Goode, 1953)
PoO2(s)	PoO2	27.08	(Haynes, 2016)
PuO2(am_hyd)	PuO2	24.01	(Haynes, 2016)
PuPO4(am_hyd)	PuPO4	89.00	(Popa et al., 2015)
S(rhomb)	S	15.51	(Robie and Hemingway, 1995)
Se(cr)	Se	16.42	(Robie and Hemingway, 1995)
Berthierine_ISGS	Si1.332Al0.668(Al0.976Fe1.622Mg0.157)O5(OH)4	101.16	(Blanc et al., 2014)
Silica(am)	SiO2	27.27	(Robie and Hemingway, 1995)
SiO2(cr)	SiO2	22.69	(Robie and Hemingway, 1995)
Sm(OH)3(cr)	Sm(OH)3	38.43	hexagonal materialsproject.org
SmF3(cr)	SmF3	30.76	Orthorhombic, materialsproject.org

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Reference
SmOHCO3(cr)	SmOHCO3	42.74	(Michiba et al., 2011)
Sm-rhabdophane	SmPO4(H2O)0.667	53.96	(Mesbah et al., 2017)
Sn(beta)	Sn	16.29	(Robie and Hemingway, 1995)
SnO(s)	SnO	21.13	mindat.org
cassiterite	SnO2	21.55	(Robie and Hemingway, 1995)
SnO2(am)	SnO2	28.90	(Robie and Hemingway, 1995
Sr[(UO2)(AsO4)]2:8H2O(cr)	Sr[(UO2)(AsO4)]2(H2O)8	309.45	(Locock et al., 2005)
Sr[(UO2)(PO4)]2:6H2O(cr)	Sr[(UO2)(PO4)]2(H2O)10	283.19	(Locock et al., 2005)
Sr3(PO4)2(s)	Sr3(PO4)2	99.98	materialsproject.org
Strontianite	SrCO3	39.01	(Robie and Hemingway, 1995)
SrCrO4(s)	SrCrO4	51.82	(Effenberger and Pertlik, 1986b)
SrHPO4(beta)	SrHPO4	53.23	materialsproject.org
SrSeO3(cr)	SrSeO3	46.15	materialsproject.org
Celestite	SrSO4	46.25	(Robie and Hemingway, 1995)
TcO2(am_hyd_ag)	TcO2	19.27	Crystalline, materialsproject.org
Th3(PO4)4(s)	Th3(PO4)4	285.41	(Shankar and Khubchandani, 1957)
ThF4(cr_hyd)	ThF4	50.01	materialsproject.org
ThO2(am_hyd_ag)	ThO2	26.40	(Robie and Hemingway, 1995)
ThO2(am_hyd_fr)	ThO2	26.40	(Robie and Hemingway, 1995)
Titanium	Ti	10.63	(Robie and Hemingway, 1995)
TiO2(am_hyd)	TiO2	20.52	(Robie and Hemingway, 1995)

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
U(OH)2SO4(cr)	U(OH)2SO4	71.90	materials.springer.com
U(Oxa)2:6H2O(cr)	U(Oxa)2(H2O)6	202.39	(Jenkins et al., 1965)
UF4:2.5H2O(cr)	UF4(H2O)2.5	75.53	(Christian et al., 2021)
UO2(am_hyd)	UO2	24.62	(Robie and Hemingway, 1995)
Rutherfordine	UO2CO3	58.08	mindat.org
Chernikovite	UO2HPO4(H2O)4	134.34	mindat.org
Soddyite	(UO2)2SiO4(H2O)2	131.27	mindat.org
Trögerite	(UO2)3(AsO4)2(H2O)12	271.69	mindat.org, materials.springer.com
(UO2)3(PO4)2:4H2O(cr)	(UO2)3(PO4)2(H2O)4	238.42	(Locock and Burns, 2002)
UO2Oxa:3H2O(cr)	UO2Oxa(H2O)3	98.42	Uroxite, (Kampf et al., 2020)
Metaschoepite	UO3(H2O)2	39.236	(Robie and Hemingway, 1995)
Coffinite	USiO4	64.73	mindat.org
Wülfingite	Zn(OH)2	32.48	mindat.org
Zn[(UO2)(AsO4)]2:8H2O(cr)	Zn(UO2)(AsO4)(H2O)8	256.21	Metalodèvite, mindat.org
Zn[(UO2)(PO4)]2:8H2O(cr)	Zn(UO2)(PO4)(H2O)8	267.68	(Plášil et al., 2010)
Hydrozincite	Zn5(OH)6(CO3)2	139.34	(Wyckoff, 1963)
ZnB2O4(s)	ZnB2O4	41.48	chemicalbook.com
Smithsonite	ZnCO3	28.28	(Robie and Hemingway, 1995)
Zincite	ZnO	14.34	(Robie and Hemingway, 1995)
Sphalerite	ZnS	23.83	(Robie and Hemingway, 1995)
Zr(HPO4)2:H2O(cr)	Zr(HPO4)2(H2O)	146.83	(Wyckoff, 1963)

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Reference**
Zr(OH)4(am_fr)	Zr(OH)4	49.00	chemicalbook.com
Baddeleyite	ZrO2	21.15	(Robie and Hemingway, 1995)

Table 6-2 Molar volumes of minerals based on estimations from analogue phases, *assumed equal molar volumes, † assumed equal density, and ‡ from average arsenate/phosphate density.

Name	**Formula**	**$V_m°$ ($cm^3\ mol^{-1}$)**	**Analogue**
Ac(OH)3(aged)*	Ac(OH)3	46.56	Am(OH)3(cr)
Ac(OH)3(fresh)*	Ac(OH)3	46.56	Am(OH)3(cr)
Ac2(Oxa)3(s)†	Ac2(Oxa)3	267.93	Ac2(C2O4)3·10H2O
Am(OH)3(am)†	Am(OH)3	46.56	rdc_Am(OH)3(cr)
Am2(CO3)3(am_hyd)*	Am2(CO3)3	168.07	La2(CO3)3 · 5H2O
AmOHCO3(am_hyd)*	AmOHCO3	88.96	EuOHCO3
AmOHCO3:0.5H2O(cr)†	AmOHCO3(H2O)0.5	91.47	AmOHCO3
Ca0.5NpO2(OH)2:1.3H2O(cr)†	Ca0.5NpO2(OH)2(H2O)1.3	242.66	Na0.5[NpO2(OH)1.5]·0.5H2, (Fellhauer et al., 2022)
Heulandite_2*	Ca1.07Al2.14Si6.86O18(H2O)4.5	317.60	Heulandite_1
Ca4Al2O6(CrO4):15H2O(s)†	Ca4Al2O6(CrO4)(H2O)15	393.47	(Moore and Taylor, 1970)
Ca4H(PO4)3:2.5H2O(s)†	Ca4H(PO4)3(H2O)2.5	182.63	(Xu et al., 2022)
Ca6(Al(OH)6)2(CrO4)3:26H2O(s)†	Ca6(Al(OH)6)2(CrO4)3(H2O)26	742.83	(Moore and Taylor, 1970)
CaNpO2(OH)2.6Cl0.4:2H2O(cr)†	CaNpO2(OH)2.6Cl0.4(H2O)2	282.60	Ca0.5NpO2(OH)2:1.3H2O(cr)
Cd[(UO2)(AsO4)]2:8H2O(cr)‡	Cd[(UO2)(AsO4)]2(H2O)8	282.74	Average density arsenates
Cd[(UO2)(PO4)]2:10H2O(cr)‡	Cd[(UO2)(PO4)]2(H2O)10	292.16	Average density phosphates
Cd3(PO4)2(s)*	Cd3(PO4)2	109.05	Pb3(PO4)2
Cd5H2(PO4)4:4H2O(s) †	Cd5H2(PO4)4(H2O)4	248.42	Cd5(PO5)4, materialsproject.org
Cr(OH)2(H2PO4)(s)	Cr(OH)2(H2PO4)	79.57	CrP(HO)5, materialsproject.org
CrPO4(purple) †	CrPO4	42.60	CrPO4(green)

Name	Formula	$V_m°$ ($cm^3\ mol^{-1}$)	Analogue
Cs(UO2)(AsO4):2.5H2O(cr)*	Cs(UO2)(AsO4)(H2O)2.5	134.86	Rb(UO2)(AsO4)(H2O)2.5, (Locock et al., 2004)
Cs(UO2)(BO3):H2O(cr)*	Cs(UO2)(BO3)(H2O)	90.25	Li[(UO2)(BO3)]·(H2O), (Hao et al., 2020)
Cs(UO2)(PO4):2.5H2O(cr)*	Cs(UO2)(PO4)(H2O)2.5	130.40	Rb(UO2)(PO4)(H2O)2.5, (Locock et al., 2004)
Eu(OH)3(am)*	Eu(OH)3	46.56	Am(OH)3(cr)
Eu(OH)3(cr)*	Eu(OH)3	46.56	Am(OH)3(cr)
Eu2(CO3)3(cr)*	Eu2(CO3)3	168.07	La2(CO3)3 · 5H2O, (Çiftçi et al., 2022)
Eu-rhabdophane*	EuPO4(H2O)0.667	53.96	SmPO4w0.667(cr)
Fe2(SeO3)3:3H2O(cr)	Fe2(SeO3)3(H2O)3	242.51	Fe2(SO4)3·7H2O, mindat.org
Fe4(OH)8Cl:nH2O(s) chloride green rust one†	Fe4(OH)8Cl	187.15	Iowaite Mg6Fe3+2(OH)16Cl2·4H2O, mindat.org
Fe6(OH)12CO3:nH2O(s) carbonate green rust one†	Fe6(OH)12CO3	281.30	Mg6Mn3(OH)16[CO3]·4H2O, Desautelsite, mindat.org
Fe6(OH)12SO4:nH2O(s) sulfate green rust two†	Fe6(OH)12SO4	286.14	Fe6(OH)12SO4(H2O)8, (Simon et al., 2003)
Ho2(CO3)3(cr)*	Ho2(CO3)3	168.07	La2(CO3)3 · 5H2O
K(UO2)(BO3):H2O(cr)	K(UO2)(BO3)(H2O)	133.79	average density of phosphate and arsenate phases
Compreignacite†	K2U6O19(H2O)11	391.53	K2(UO2)6O4(OH)6·7H2O, mindat.org

Name	**Formula**	**$V_m°$ (cm^3 mol^{-1})**	**Analogue**
KNpO2CO3(s) †	KNpO2CO3	87.82	LiNpO2CO3·2H2O, (Charushnikova et al., 2004)
Li(UO2)(AsO4):4H2O(cr) †	Li(UO2)(AsO4)(H2O)4	138.16	K(UO2)(AsO4)w3(cr)
Mn[(UO2)(AsO4)]2:8H2O(cr) ‡	Mn[(UO2)(AsO4)]2(H2O)8	269.04	average density arsenates
Mn[(UO2)(PO4)]2:10H2O(cr) ‡	Mn[(UO2)(PO4)]2(H2O)10	256.69	average density arsenates
Na(UO2)(BO3):H2O(cr)	Na(UO2)(BO3)(H2O)	128.98	average density of phosphate and arsenate phases
Faujasite-X*	Na2Al2Si2.5O9(H2O)6.2	228.95	Faujasite-Y
Low-silica_P-Na*	Na2Al2Si2O8(H2O)3.8	122.42	Low-silica_P-Ca
Na2Np2O7:0.1H2O(cr) †	Na2Np2O7(H2O)0.1	99.04	Na2U2O7w1(cr)
Hydrosodalite†	Na8Al6Si6O24(OH)2(H2O)2	388.90	Cancrinite-NO3
NaNpO2CO3:3.5H2O(cr) †	NaNpO2CO3(H2O)3.5	118.60	NaNpO2PO4(H2O)3, (Forbes and Burns, 2007)
Ni(Oxa):2H2O(cr)*	Ni(Oxa)(H2O)2	83.65	Ca(Oxa)w2(cr)
Ni[(UO2)(PO4)]2:8H2O(cr) †	Ni[(UO2)(PO4)]2(H2O)8	266.52	Average density phosphates
(NH4)4NpO2(CO3)3(s) †	NpO2(NH4)4(CO3)3	110.66	(NH4)[NpO2(CO3)], (Nevolin et al., 2022)
NpO2(OH)2:H2O(cr_hex) †	NpO2(OH)2(H2O)	231.08	(Fellhauer et al., 2022)
Pb[(UO2)(AsO4)]2:10H2O(cr) ‡	Pb[(UO2)(AsO4)]2(H2O)10	317.17	average density arsenates
Po(SO4)2:H2O(s)*	Po(SO4)2(H2O)	134.58	Pu(SO4)2(H2O)4, (Wilson, 2011)
Pu(OH)3(am)*	Pu(OH)3	46.56	Am(OH)3(cr)
Pu(Oxa)2:6H2O(cr)*	Pu(Oxa)2(H2O)6	202.39	U(Oxa)2w6(cr)

Name	**Formula**	$V_m°$ **(cm³ mol⁻¹)**	**Analogue**
Pu2(Oxa)3:10H2O(cr)*	Pu2(Oxa)3(H2O)10	267.93	Ac2(C2O4)3·10H2O, (Weigel and Hauske, 1977)
PuO2CO3(cr)*	PuO2CO3	56.44	NpO2CO3(cr)
(PuO2)3(PO4)2:4(H2O)(am)*	(PuO2)3(PO4)2(H2O)4	238.42	(UO2)3(PO4)2:4H2O(cr)
RaCO3(cr)*	RaCO3	46.32	BaCO3, mindat.org
RaSO4(cr) †	RaSO4	55.66	Ra0.76Ba0.24SO4, (Matyskin et al., 2017)
Ripidolite_Cca-2†	Si2.633Al1.367(Al1.116Fe1.927Mg2.952 Mn0.012)(Ca0.011)O10(OH)8	158.77	Chlinochlore, mindat.org
Sm2(CO3)3(cr)*	Sm2(CO3)3	168.07	La2(CO3)3 · 5H2O, (Çiftçi et al., 2022)
TcO2(am_hyd_fr) †	TcO2	19.27	TcO2(am_hyd_ag)
Hydrogen_uranospinite†	UO2HAsO4(H2O)4	135.78	Trögerite, mindat.org
Zn3(PO4)2:4H2O(s)*	Zn3(PO4)2(H2O)4	109.05	Pb3(PO4)2, (Keppler, 1970)

Table 6-3 List of minerals present in the PSI/Nagra database with no molar volumes.

Name	**Formula**
AmO2OH(am)	AmO2OH
Ca(H3Isa)2(cr)	Ca(H3Isa)2
Cr(OH)2(cr)	Cr(OH)2
Cr(OH)3(cr)	Cr(OH)3
H4Edta(cr)	H4Edta
(HgOH)3PO4(s)	Hg3(OH)3PO4
Hg3(PO4)2(s)	Hg3(PO4)2
HgCO3(HgO)2(s)	HgCO3(HgO)2
K3NpO2(CO3)2(s)	K3NpO2(CO3)2
K4NpO2(CO3)3(s)	K4NpO2(CO3)3
KFe3(CrO4)2(OH)6(cr)	KFe3(CrO4)2(OH)6
Linda_type_A	Na1.98Al1.98Si2.02O8(H2O)5.31
Molecular_sieve_4Å	Na2Al2Si2O8(H2O)4.5
Na3NpO2(CO3)2(cr)	Na3NpO2(CO3)2
Na7HNb6O19:15H2O(cr)	Na7HNb6O19(H2O)15
NaAm(CO3)2:5H2O(cr)	NaAm(CO3)2(H2O)5
NaAmO2CO3(s)	NaAmO2CO3
Ni3(AsO3)2:xH2O(s)	Ni3(AsO3)2
Ni3(AsO4)2:8H2O(s)	Ni3(AsO4)2(H2O)8
NpO2OH(am)	NpO2OH
PbB2O4(s)	PbB2O4

Name	**Formula**
PoSO4(s)	PoSO4
Pu(HPO4)2(am_hyd)	Pu(HPO4)2
PuO2(OH)2(am_hyd)	PuO2(OH)2
PuO2OH(am)	PuO2OH

Table 6-4 Selected thermodynamic properties of aqueous ions (298 K, 0.1 MPa). Values in regular typeface font left unchanged from TDB 2020, values in bold typeface font were changed in this report (details in text).

name	**formula**	**$\Delta_f G_m°$ kJ·mol^{-1}**	**±**	**$\Delta_f H_m°$ kJ·mol^{-1}**	**±**	**$S_m°$ J·K^{-1}·mol^{-1}**	**±**
H_2O(l)	H2O	-237.140 [a]	0.041	-285.830 [a]	0.040	69.950 [a]	0.030
Cl^-	Cl-	-131.217 [a]	0.117	-167.080 [a]	0.100	56.600 [a]	0.200
Na^+	Na+	-261.953 [a]	0.096	-240.340 [a]	0.060	58.450 [a]	0.150
K^+	K+	-282.510 [a]	0.116	-252.140 [a]	0.080	101.200 [a]	0.200
Ca^{2+}	Ca+2	-552.806 [a]	1.050	-543.00 [a]	1.000	-56.200 [a]	1.000
Mg^{2+}	Mg+2	**-455.703** [b]	**0.786**	-467.000 [a]	0.600	**-135.900** [b]	**1.700**
Fe^{2+}	Fe+2	-90.720 [c]	0.640	-90.295 [c]	0.600	-102.171 [c]	3.000
Fe^{3+}	Fe+3	-16.226 [c]	0.650	-50.056 [c]	0.973	-282.404 [c]	3.927
Al^{3+}	Al+3	**-487.738** [d]	1.300	**-539.941** [d]	**2.600**	-342.800 [e]	5.000
OH^-	OH-	-157.220 [a]	0.072	-230.015 [a]	0.040	-10.900 [a]	0.200
F^-	F-	-281.523 [a]	0.692	-335.350 [a]	0.650	-13.800 [a]	0.800
$ClO4^-$	ClO4-	-7.890 [a]	0.600	-128.100 [a]	0.400	184.000 [a]	1.500
$NO3^-$	NO3-	-110.794 [a]	0.417	-206.850 [a]	0.400	146.700 [a]	0.400
HS^-	HS-	12.252 [a]	2.115	-16.300 [a]	1.500	67.000 [a]	5.000
HCO_3^-	HCO3-	-586.845 [a]	0.251	-689.930 [a]	0.200	98.400 [a]	0.400
CO_3^{2-}	CO3-2	-527.900 [a]	0.390	-675.230 [a]	0.250	-50.000 [a]	1.000
SO_4^{2-}	SO4-2	-744.004 [a]	0.418	-909.340 [a]	0.400	18.500 [a]	0.400
HPO_4^{2-}	HPO4-2	-1095.985 [a]	1.567	-1299.0 [a]	1.500	-33.500 [a]	1.500
PO_4^{3-}	PO4-3	-1025.491 [a]	1.576	-1284.40 [a]	4.085	-220.970 [a]	12.846
$Si(OH)_4$(aq)	Si(OH)4	-1309.183 [e]	1.120	**-1461.90** [d]	**1.400**	**178.260** [d]	**3.000**

[a] CODATA (Cox et al., 1989) consistent with NEA TDB (Grenthe et al., 1992), [b] Rand et al. (2024), [c] Lemire et al. (2020), [d] this work see text, [e] evaluated in TDB 2020,

Table 6-5 Partial molar heat capacities, molar volumes and HKF model coefficients (298 K, 0.1 MPa) of aqueous ions selected in this work, not available in previous TDB releases. Values of $C_{p,m}°$ and $V_m°$ are calculated from Eq. 3-3 and 3-4.

name	formula	$C_{p,m}°$ J·K^{-1}·mol^{-1}	$V_m°$ cm^3 mol^{-1}	$a_1 \cdot 10$ cal·mol^{-1}·bar^{-1}	$a_2 \cdot 10^{-2}$ cal·mol^{-1}	a_3 cal·K·mol^{-1}·bar^{-1}	$a_4 \cdot 10^{-4}$ cal·K·mol^{-1}	c_1 cal·K^{-1}·mol^{-1}	$c_2 \cdot 10^{-4}$ cal·K·mol^{-1}	$\omega° \cdot 10^{-5}$ cal·mol^{-1}
H_2O(l)	H2O	75.351 [a]	18.0684 [a]	-	-	-	-	-	-	-
Cl^-	Cl-	-123.115 [b]	17.786 [b]	4.032 [b]	4.801 [b]	5.563 [b]	-2.847 [b]	-4.40 [b]	-5.714 [b]	1.456 [b]
Na^+	Na+	37.976 [b]	-1.107 [b]	1.839 [b]	-2.285 [b]	3.256 [b]	-2.726 [b]	18.18 [b]	-2.981 [b]	0.3306 [b]
K^+	K+	8.306 [b]	9.068 [b]	3.559 [b]	-1.473 [b]	5.435 [b]	-2.712 [b]	7.40 [b]	-1.791 [b]	0.1927 [b]
Ca^{2+}	Ca+2	-31.469 [b]	-18.061 [c]	-0.1947 [c]	-7.252 [c]	5.297 [c]	-2.479 [c]	9.00 [b]	-2.522 [b]	1.237 [b]
Mg^{2+}	Mg+2	-22.314 [b]	-21.544 [c]	-0.822 [c]	-8.599 [c]	8.39 [c]	-2.39 [c]	20.80 [b]	-5.892 [b]	1.537 [b]
Fe^{2+}	Fe+2	-23.000 [d]	-22.249 [e]	-0.8 [f]	-9.735 [f]	9.58 [f]	-2.377 [f]	16.018 [f]	-4.1544 [f]	1.419 [ff]
Fe^{3+}	Fe+3	-108.000 [d]	-37.000 [e]	-2.389 [f]	-13.614 [f]	11.109 [f]	-2.216 [f]	15.820 [f]	-8.293 [f]	2.69 [ff]
Al^{3+}	Al+3	-134.500 [c]	-44.399 [c]	-3.34 [c]	-17.11 [c]	14.99 [c]	-2.072 [c]	10.700 [c]	-8.06 [c]	2.871 [c]
OH^-	OH-	-137.128 [b]	-4.180 [c]	1.253 [c]	0.0738 [c]	1.842 [c]	-2.782 [c]	4.150 [b]	-10.35 [b]	1.725 [b]
F^-	F-	-113.887 [b]	-1.319 [c]	0.687 [c]	1.359 [c]	7.603 [c]	-2.835 [c]	4.460 [b]	-7.488 [b]	1.787 [b]
ClO_4^-	ClO4-	-24.423 [e]	44.206 [e]	8.141 [e]	15.57 [e]	-7.808 [e]	-3.423 [e]	16.450 [e]	-6.57 [e]	0.97 [e]
NO_3^-	NO3-	-67.285 [c]	29.000 [c]	7.316 [c]	6.782 [c]	-4.684 [c]	-3.059 [c]	7.700 [c]	-6.725 [c]	1.098 [c]
HS^-	HS-	-92.683 [b]	20.650 [b]	5.012 [b]	4.98 [b]	3.475 [b]	-2.985 [b]	3.410 [b]	-6.046 [b]	1.441 [b]
HCO_3^-	HCO3-	-45.6 [g]	24.601 [c]	7.562 [c]	1.151 [c]	1.235 [c]	-2.827 [c]	11.510 [gg]	-5.255 [gg]	1.273 [gg]
CO_3^{2-}	CO3-2	-290.778 [c]	-5.020 [c]	2.852 [c]	-3.984 [c]	6.414 [c]	-2.614 [c]	-3.321 [c]	-17.192 [c]	3.391 [c]
SO_4^{2-}	SO4-2	-267.447 [b]	13.879 [c]	8.301 [c]	-1.985 [c]	-6.212 [c]	-2.697 [c]	1.640 [b]	-18.0 [b]	3.146 [b]
HPO_4^{2-}	HPO4-2	-244.221 [c]	5.380 [c]	3.632 [c]	1.084 [c]	5.323 [c]	-2.824 [c]	2.736 [c]	-14.91 [c]	3.344 [c]
PO_4^{3-}	PO4-3	-480.750 [c]	-30.601 [c]	-0.526 [c]	-9.066 [c]	9.313 [c]	-2.404 [c]	-9.480 [c]	-26.44 [c]	5.611 [c]
$Si(OH)_4$(aq)	Si(OH)4	195.0 [h]	55.869 [h]	11.022 [h]	9.85 [h]	2.579 [h]	-3.186 [h]	54.440 [h]	-3.259 [h]	0.1312 [h]

[a] CODATA, [b] Tanger and Helgeson (1988), [c] Shock and Helgeson (1988), [d] Lemire et al. (2020), [e] Shock et al. (1997), [f] this work Eqs. 3-5 to 3-10, [ff] Eq.3-11 and ion radius of Fe^{2+} 0.78 (Å), Fe^{3+} 0.65 (Å) (Marcus, 1994), [g] this work from electrolyte data see text, [gg] this work Eqs. 3-9, 3-10, [h] this work from solubility data see text

Table 6-6 Standard thermodynamic properties of gas species (298 K, 0.1 MPa).

name	**formula**	$\Delta_f G_m°$ **kJ·mol^{-1}**	**±**	$\Delta_f H_m°$ **kJ·mol^{-1}**	**±**	$S_m°$ **J·K^{-1}·mol^{-1}**	**±**
CH_4(g)	CH4	-50.530 [b]	0.200	-74.600 [b]	0.200	186.371 [b]	0.100
CO_2(g)	CO2	394.373 [a]	0.133	-393.510 [a]	0.130	213.785 [a]	0.010
H_2(g)	H2	0.000 [a]	0.000	0.000 [a]	0.000	130.680 [a]	0.003
H_2S(g)	H2S	-33.443 [a]	0.500	-20.600 [a]	0.500	205.810 [a]	0.050
H_2Se(g)	H2Se	15.217 [c]	2.000	29.000 [c]	2.000	219.000 [c]	0.100
Hg(g)	Hg	31.842 [a]	0.054	61.380 [a]	0.040	174.971 [a]	0.005
N_2(g)	N2	0.000 [a]	0.000	0.000 [a]	0.000	191.609 [a]	0.004
O_2(g)	O2	0.000 [a]	0.000	0.000 [a]	0.000	205.152 [a]	0.005
H_2O(g)	H2O	-228.584 [a]	0.04	-241.826 [a]	0.04	188.835 [a]	0.01

[a] CODATA (Cox et al., 1989) consistent with NEA TDB (Grenthe et al., 1992), [b] Gurvich et al. (1989), [c] Olin et al. (2005)

Table 6-7 Selected temperature coefficients for heat capacities in this work according to the formula: $C_{p,m}° = a_0 + a_1 \cdot T + a_2 \cdot T^{-2} + a_4 \cdot T^2 + a_5 \cdot T^3 + a_6 \cdot T^4 + a_8 \cdot T^{-1}$, where T is the temperature (K), not available in previous TDB releases.

name	formula	$C_{p,m}°$ [a] $J \cdot K^{-1} \cdot mol^{-1}$	a_0	a_1	a_2	a_4	a_5	a_6	a_8	T min (K)	T max (K)
CH_4(g)	CH4	35.648 [b]	-7.03029E-01	1.08477E-01	6.78565E+05	-4.25216E-05	5.86279E-09			298	1300
CO_2(g)	CO2	37.130 [b]	2.49974E+01	5.51870E-02	-1.36638E+05	-3.36914E-05	7.94839E-09			298	1200
H_2(g)	H2	28.837 [b]	3.30662E+01	-1.13634E-02	-1.58558E+05	1.14328E-05	-2.77287E-09			298	1000
H_2S(g)	H2S	34.197 [b]	2.68841E+01	1.86781E-02	1.35882E+05	3.43420E-06	-3.37870E-09			298	1400
H_2Se(g)	H2Se	34.720 [c]	2.32030E+01	3.23156E-02	1.46472E+05	-8.89220E-06	0.00000E+00		3.05500E+02	298	1500
Hg(g)	Hg	20.798 [b]	2.06724E+01	1.79353E-04	7.01300E+03	-8.01200E-08	1.05470E-11		0.00000E+00	630	6000
N_2(g)	N2	29.124 [d]	5.05750E+01	-7.09304E-02	1.83782E+05	1.15127E-04	-8.00338E-08	2.095E-11	-3.17486E+03	200	1000
O_2(g)	O2	29.383 [b]	3.13223E+01	-2.02353E-02	-7.37400E+03	5.78664E-05	-3.65062E-08			100	700
H_2O(g)	H2O	33.591 [e]	2.70570E+01	1.75840E-02	2.76960E+05	-2.50970E-06	-2.76560E+01*			298	2500

[a] calculated with $C_{p,m}°$ temperature function for T = 298.15 K, [b] Chase (1998), [c] Olin et al. (2005), [d] Gurvich et al. (1989), [e] Robie and Hemingway (1995) * $a_3 \cdot T^{-0.5}$