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Filella, Montserrat; May, Peter M.

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The aqueous solution chemistry of germanium under conditions of environmental and biological interest: Inorganic ligands

Montserrat Filella [a,*], Peter M. May [b]

[a] Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205, Geneva, Switzerland
[b] Chemistry, College of Science, Health, Engineering and Education, Murdoch University, Murdoch, WA 6150, Australia

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ABSTRACT

Available equilibrium constant data for reactions of germanium with inorganic ligands in aqueous solution have been critically evaluated. Even though the relevant literature is sparse and mostly rather old, we have established a working thermodynamic description of germanium in aqueous, multicomponent media for its most important interactions with inorganic ligands. These thermodynamic parameters will be useful in environmental and (eco) toxicology studies. However, within the limitations of the presently available literature, significant uncertainties are inescapable. The implications for thermodynamic modelling in general are far-reaching.

1. Introduction

Germanium behaves as a chemical analogue of Si (when Mendeleev predicted its existence, he called it eka-silicon). For this reason, Ge/Si ratios have been used as a tracer of silica behaviour and sources in surface environments (Murnane and Stallard, 1990; Froelich et al., 1992; Kurtz et al., 2002). Similarly, in ocean waters, it is incorporated in diatoms making the concentration profiles of germanium mimic those of Si, which has been useful in paleoclimate studies (Mortlock et al., 1991).

Germanium and some derived substances (GeO_2 and $GeCl_4$) are key materials for a wide variety of applications. Germanium, considered a ‘technology-critical element’ (Melcher and Buchholz, 2014), was the first semiconductor of industrial importance and it is now used extensively in semiconductors, catalysis, and optical apparatus.

We seek here to establish a working thermodynamic description of germanium in aqueous, multicomponent media for its most important interactions with inorganic ligands. Our aim is to support future investigations in environmental chemistry and (eco)toxicology that require a coherent thermodynamic database for this element.

2. Methodology

The first step in this review has been the collection of a comprehensive set of equilibrium constant data from the chemical literature. The IUPAC (International Union of Pure and Applied Chemistry) Stability Constants Database has been used as the starting point of a systematic ‘up-tree’ citation search strategy. All original sources have been acquired. Germanium has been the subject of one critical compilation (Wood and Samson, 2006). This and other germanium data in secondary sources have been checked.

Our procedure for establishing a set of ‘best’ constants differs from conventional approaches (e.g, NBS (National Bureau of Standards), NIST (National Institute of Standards and Technology), NEA (Nuclear Energy Agency), etc.), as described in previous work (Filella and May, 2019a, 2019b, 2020). It is based on the computer-aided harmonisation of thermodynamic parameters of chemical reactions to achieve global thermodynamic consistency (May and Rowland, 2018). Reliable sets of standard reaction Gibbs energies and their corresponding equilibrium constants are determined from all the reaction data reported in the literature. The procedure involves an ordered Gaussian elimination to determine the so-called ‘basis species’ as well as the linear combinations of reactions that are used to describe the whole chemical system. The basis species correspond to the ‘master variables’ in speciation and other thermodynamic modelling calculations (Stumm and Morgan, 1996, p. 118). The order of the reactions depends on ‘weights’ assigned during compilation to each data item for the conditional equilibrium constants and reaction enthalpies. Estimates of the relevant standard thermodynamic quantities (*i.e.*, at 1 bar and infinite dilution), at 25 °C, are determined by least squares regression using a well-established function (May, 2000) based on the IUPAC-recommended SIT (specific ion

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* Corresponding author.
E-mail addresses: montserrat.filella@unige.ch (M. Filella), p.may@murdoch.edu.au (P.M. May).

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interaction) equation to express, where possible, the effects of activity coefficient change.

3. Results

All relevant species for which equilibrium constants have been located are included in the database. The relevant equilibrium constant values reported in the literature are given in Tables 1–5, in the form expressed by their authors. Results from this work are shown in Tables 6 and 7 for infinite dilution (0 mol L^{-1} ionic strength). Constant values are not accompanied by confidence intervals, which can only be based on the propagation of random errors, under circumstances in which systematic errors are overwhelmingly dominant. Users of the data need to assess for themselves the impact of these systematic errors on their model calculations. The use of rounding to express uncertainty has been discouraged by other thermodynamic database builders (Robie and Waldbaum, 1968; Coufal et al., 2005; Wolery and Jové Colón, 2017).

When needed, auxiliary data for a number of reactions have been taken from JESS database (http://jess.murdoch.edu.au and https://zenodo.org/record/7700023).

In the literature, various notations have used for germanium species. This is confusing because, although equilibrium data are not characterised by molecular-level structures, order or degree of solvation, it is necessary to regularise the formulae in order to ensure that there is no species duplication. Extended X-ray absorption fine structure (EXAFS) data in solution (Bernstein and Waychunas, 1987; Pokrovski et al., 2000) are consistent with the existence of $Ge(OH)_4$ (coordination number 4 ± 0.2, Ge–O distance 1.75 ± 0.02 Å) at neutral pH, and of $GeO(OH)_3^-$ (coordination number 3.8 and Ge–O average distance 1.74 Å) in basic solutions. Thus, our preferred formulae for germanium species, here used throughout, are: $Ge(OH)_4$ (not H_2GeO_3, $H_2GeH_2O_4$, H_4GeO_4); $GeO(OH)_3^-$ (not $HGeO_3^-$ or $HGeH_2O_4^-$); and, $GeO_2(OH)_2^{2-}$ (not $GeH_2O_4^{2-}$, GeO_3^{2-}, $Ge(OH)_6^{2-}$).

3.1. Germanium(II)

Compounds containing Ge(II) have been synthesized but not observed in nature. Synthesis of Ge(II) compounds always requires strong reducing agents (the most commonly used is hypophosphorous acid (phosphinic acid) (Everest, 1953)) and an inert atmosphere (Everest 1953; Lee and Weng 2008). Some books and reviews (Fleischer and Mandarino 1995; Anthony et al., 1997; Höll et al., 2007) mention brunogeierite as the only mineral where germanium has a formal charge 2+. However, Cempirek and Groat (2013) showed that the correct ideal end-member formula of brunogeierite is $(Fe^{2+})_2Ge^{4+}O_4$.

The solution chemistry of Ge(II) has been rarely explored; existing data are limited and old (Table 1). According to Jolly and Latimer (1952a): "Freshly prepared hydrous germanous oxide (precipitated with alkali in the cold) is yellow, and it stays this colour if stored under water at room temperature. But, if an aqueous suspension of the yellow oxide is boiled, or if it is treated with aqueous hydrochloric acid, the colour changes to dark brown." These authors are the source of what seems to be the only experimental data on the redox potential of the couple between brown GeO and GeO_2 ($E = -0.118 \pm 0{\cdot}010$ V, for reaction GeO (brown) + $H_2O = GeO_2 + 2\,H^+ + 2\,e^-$), and the corresponding solubility of the brown form. Jolly and Latimer (1952a) also state that the "free enthalpy" (old term for Gibbs energy) of yellow GeO is 7200 cal greater than that of the brown GeO (values reported in calories can be standardised throughout by taking 1 cal = 4.184 J). In their experiments, the crystalline form of GeO_2 was not investigated but assumed to be the hexagonal. Reid (1965) reported the redox potential of the couples $Ge^0 = Ge^{2+} + 2\,e^-$ and $Ge^{2+} = Ge^{4+} + 2\,e^-$ in 1 mol L^{-1} H_2SO_4. The meaning of these values is unclear because Ge^{4+} as such might exist in solution (see discussion in next section), but it does not exist under these experimental conditions. It seems likely that these two studies are the origin of equilibrium values for many redox reactions in secondary sources such as Charlot et al. (1971), de Zoubov et al. (1974), Barin and Platzki (1995), Lide and Frederikse (1995), Inzelt (2006).

The solution chemistry of Ge(II) remains largely unexplored. Initial claims regarding the acid nature of GeO (Hantzsch, 1902) proved unfounded; Everest and Terrey (1950) showed that changes observed in conductivity in alkaline media were due to formation of germanium dioxide and not to Ge(II) hydroxide deprotonation, as thought earlier. Baes and Mesmer (1976), assuming that Ge(II) behaves like Zn(II), suggested the reaction GeO(c) + $H_2O = Ge(OH)_2$ and estimated the logarithm of the solubility product of GeO from the solubility value of Jolly and Latimer (1952a) at −3.7.

Given the limited and doubtful data existing for Ge^{2+}, all thermochemical and equilibrium data for Ge(IV) in secondary sources based on Ge^{2+} data should be rejected. The value given for the reaction $Ge(OH)_4 + 2\,e^- + 4\,H^+ = Ge^{2+} + 4\,H_2O$ in Table 7, based on the combination of reactions $Ge^{2+} + 2\,e^- = Ge(s)$ and $Ge(OH)_4 + 4\,e^- + 4\,H^+ = Ge(s) + 4\,H_2O$ needs to be considered as tentative at best (see section 3.6).

3.2. Germanium(IV) oxides solubility

The two predominant polymorphs of crystalline GeO_2 are tetragonal and hexagonal. The tetragonal form (mineral argutite) has the rutile structure. In this motif, germanium has the coordination number 6. It is stable up to 1065 °C and 1 atm (Kosova et al., 1987). The hexagonal form, which has the same structure as β-quartz, with coordination number 4, is much more soluble. In the presence of water, the hexagonal form is converted into the stable tetragonal GeO_2 at 180 °C (Laubengayer and Morton, 1932). The formation of an amorphous GeO_2 having a higher solubility in water than GeO_2(hexag): 5.1×10^{-2} mol L^{-1} at 100 °C is mentioned by Müller (1926).

We could locate only three experimental determinations of tetragonal GeO_2 solubility (Müller, 1926; Kosova et al., 1987; Pokrovski and Schott, 1998). The logarithm of the solubility products are −4.37, −5.34, −5.02, respectively (Table 2). Considering publication dates, the values embedded in several secondary references are probably based on Müller's value. This is the case, for instance, with "Pourbaix" (Zoutov et al., 1974) who explicitly cites Müller (1926) and Charlot et al. (1971) through Lovreček and Bockris (1959).

The solubility of hexagonal GeO_2 has been the target of many more studies (Table 2). All published values for logarithm of the solubility product lie in the curiously narrow range, from −1.32 to −1.4, including the first determination from Winkler (1886) (−1.4)! This coincidence is particularly remarkable considering differences in methods used for its preparation and its solubility measurements.

3.3. Germanium(IV) acid-base equilibria

The forms of germanium in dilute aqueous solution, where only mononuclear complexes are formed, are $Ge(OH)_4$ (sometimes called germanic acid) and its deprotonation products $GeO(OH)_3^-$ and $GeO_2(OH)_2^{2-}$. These dilute conditions are the ones applicable in natural aquatic systems (germanium concentrations in seawater: 0.7 pmol L^{-1} (Ellwood and Maher, 2003), 19 pmol L^{-1} in lake waters (Filella and Matoušek, 2022) and, probably, in biological fluids, for which data are badly lacking (<0.1 mg L^{-1} in blood plasma according to Rodushkin et al. (2000)). Note that 'dissolved' germanium concentrations are mostly present as methyl- and dimethylgermanium in seawater, not as $Ge(OH)_4$ (Lewis et al., 1988; Ellwood and Maher, 2003), i.e., not as 'inorganic' germanium.

The formation of polynuclear Ge(IV) species has been investigated by Carpéni (1948), Lourijsen- Teyssèdre (1955), Antikainen (1960), Ingri (1963), Ingri and Schorsch (1963), Haas et al. (1964a,b,c), and De la Cuadra (1990). Their existence requires germanium concentrations higher than 5 mmol L^{-1} (Ingri, 1963). The studies of $Ge(OH)_4$ dissociation and polynuclear germanium species prior to 1963 are discussed in detail in Ingri (1963) and, all values prior to 1976, were included by

Table 1

Published values of equilibrium constants and redox potentials for equilibria involving Ge(II).

Reaction[a]	Data	T/°C	pH range	Technique	Reference
$Ge^{2+} + 2\ e^- = Ge^0$	$E^0 = 0.247$ V			Reproduced from published values (references not given)	Inzelt (2006)
GeO_2(hexag) $+ 4\ H^+ + 4\ e^- = Ge^0 + 2\ H_2O$	$E^0 = -0.019$ V				
GeO_2(tetrag) $+ 4\ H^+ + 4\ e^- = Ge^0 + 2\ H_2O$	$E^0 = -0.058$ V				
$H_2GeO_3 + 4\ H^+ + 4\ e^- = Ge^0 + 3\ H_2O$	$E^0 = 0.012$ V				
$H_2GeO_3 + 4\ H^+ + 2\ e^- = Ge^{2+} + 3\ H_2O$	$E^0 = -0.223$ V				
GeO_2(hexag) $+ 2\ H^+ + 2\ e^- =$ GeO(brown) $+ H_2O$	$E^0 = -0.132$ V				
$Ge^{2+} + 2\ e^- = Ge^0$	$E^0 = 0.23$ V	25		Calculated from published values[a]	Charlot et al. (1971)
GeO(s) $+ 2\ H^+ + 2\ e^- = Ge^0 + H_2O$	$E^0 = \sim -0.2$ V				
$H_2GeO_3 + 4\ H^+ + 4\ e^- = Ge^0 + 3\ H_2O$	$E^0 = 0.01$ V				
GeO_2(hexag) $+ 4\ H^+ + 2\ e^- = Ge^{2+} + 2\ H_2O$	$E^0 = -0.25$ V				
GeO_2(tetrag) $+ 4\ H^+ + 2\ e^- = Ge^{2+} + 2\ H_2O$	$E^0 = -0.34$ V				
GeO_2(hexag) $+ 4\ H^+ + 4\ e^- = Ge^0 + 2\ H_2O$	$E^0 = -0.01$ V				
GeO_2(tetrag) $+ 4\ H^+ + 4\ e^- = Ge^0 + 2\ H_2O$	$E^0 = -0.05$ V				
$Ge^0 + 4\ H^+ + 4\ e^- = GeH_4$(g)	$E^0 = < -0.3$ V				
$Ge^0 = Ge^{2+} + 2\ e^-$	$E^0 = -0.24$ V	25?	1 mol L^{-1} H_2SO_4		Reid (1965)[a,b]
$Ge^{2+} = Ge^{4+} + 2\ e^-$	$E^0 = 0.00$ V				
$Ge^0 = Ge^{4+} + 4\ e^-$	$E^0 = -0.12$ V				
GeO(yellow) solubility	0.02 mol L^{-1}	25	0–8.4		Gayer and Zajicek (1964)
$Ge^0 = Ge^{2+} + 2\ e^-$	$E^0 = -0.231$ V	25		Calculated from thermochemical data and equilibrium data[b]	Lovreček and Bockris (1959)
$Ge^0 + 3\ H_2O = H_2GeO_3 + 4\ H^+ + 4\ e^-$	$E^0 = -0.011$ V				
$Ge^0 + H_2O =$ GeO(brown) $+ 2\ H^+ + 2\ e^-$	$E^0 = -0.100$ V				
$Ge^0 + H_2O =$ GeO(yellow) $+ 2\ H^+ + 2\ e^-$	$E^0 = -0.256$ V				
$Ge^0 + H_2O = GeO_2$(hexag) $+ 4\ H^+ + 4\ e^-$	$E^0 = 0.009$ V				
$Ge^0 + H_2O = GeO_2$(tetrag) $+ 4\ H^+ + 4\ e^-$	$E^0 = 0.053$ V				
GeO(brown) solubility	(2 ± 1) x10^{-4} mol L^{-1}	25		Solubility (filtration and titration $KMnO_4$)	Jolly and Latimer (1952a)
GeO(brown) $+ H_2O = GeO_2 + 2\ H^+ + 2\ e^-$	$E^0 = 0.118 \pm 0.010$ V				
GeO(yellow) = GeO(brown)	$E^0 =$ *ca* 0.155			Electromotive cell	
	$\Delta G = -7.2$ kcal mol^{-1}				
GeO(yellow) solubility	5.0×10^{-3} mol L^{-1}				Everest and Terrey (1950)

[a] Reid (1965), Lovreček and Bockris (1959), Latimer (1952).

[b] Müller (1926), Pugh (1929a,b), Jolly and Latimer (1952a,b), Latimer (1952).

Table 2
Published values of solubility product of germanium dioxides.

Reaction[a]	lg$K$[a]	T/°C	I electrolyte	pH range	Technique	Reference
Tetragonal						
GeO_2(tetrag) + 2 H_2O = $Ge(OH)_4$	−5.02 ± 0.13	25	0 Self-medium	1.6–10.0	Solubility	Pokrovski and Schott (1998)
	−4.57 ± 0.20	50			pH 1.5–10	
	−3.96 ± 0.15	90			Filtration	
	−3.26 ± 0.12	150			FAAS, ICP-MS, colorimetry	
	−2.76 ± 0.10	200				
	−2.16 ± 0.10	250				
	−1.78 ± 0.07	300				
	−1.68 ± 0.05	350				
GeO_2(tetrag) + 2 H_2O = $Ge(OH)_4$	−4.23	25	0 Self-medium		Thermodynamic data	Kosova and Dem'yanets (1988)
	−3.35	100				
	−2.69	150				
	−2.43	200				
	−1.99	250				
	−1.69	300				
GeO_2(tetrag) + 2 H_2O = $Ge(OH)_4$	−5.34	25	0 Self-medium		Solubility	Kosova et al. (1987)
	−4.54	50			Equilibration: 6-45 d, 100 and 300 C; 1 year 50 and 100 C	
	−3.42	100				
	−2.60	160				
	−2.35	190				
	−1.96	250				
	−1.77	300				
GeO_2(tetrag) + 2 H_2O = $Ge(OH)_4$	−4.37	25	0		Critical evaluation	Baes and Mesmer (1976)
GeO_2 alpha (insoluble) form solubility	−4.37	25	0 Self-medium		Equilibration 2 weeks Weighting after dryness of remaining oxide	Müller (1926)
Hexagonal						
GeO_2(hexag) + 2 H_2O = $Ge(OH)_4$	−1.631	0			Treatment of published data (Vehov et al., 1964)	Kosova et al. (1987)
	−1.370	25				
	−1.168	50				
	−0.994	75				
	−0.848	100				
GeO_2(s) = GeO_2(aq)	−1.38	25			Precipitation of GeO_2(s) by neutralisation of a basic solution; solid not characterised. Equilibration 2 weeks Centrifugation (conditions not given), Ge analysis Spectrophotometry	Gayer and Zajicek (1964)
GeO_2 + 2 H_2O = H_4GeO_4	−1.59	0				Vehov et al. (1964); values as given in Wood and Samsen (2006)
	−1.32	25				
	−1.14	50				
	−1.03	75				
	−0.94	100				
GeO_2 + 2 H_2O = H_4GeO_4	−1.22	40				Evdokimov and Kogan (1963) values as given in Wood and Samsen (2006)
	−1.12	60				
	−1.01	80				
	−0.94	100				

(*continued on next page*)

Table 2 (*continued*)

Reaction[a]	lg$K$[a]	T/°C	I electrolyte	pH range	Technique	Reference
Water solubility at 25 °C = 4.53 g L^{-1}	−1.36	25			Precipitation, evaporation to dryness	Laubengayer and Morton (1932)
GeO_2 solubility	−1.42	11				Schwarz and Huf (1931)
	−1.39	20				
	−1.35	26				
	−1.28	35				
	−1.23	41				
Solubility GeO_2 *insoluble* form: 447 mg in 100 mL	−1.37	25			Solubility Equilibration: 6 days	Pugh (1929a)
Solubility GeO_2: 4:1000	−1.4	30			Calcination of precipitate	Dennis (1928)
Solubility GeO_2	−1.37	25			Precipitate with a hexagonal texture	Müller (1926)
Solubility: 209 mg GeO_2 in 100 mL (m/50)	−1.7	0			Calcination of precipitate	Roth and Schwartz (1926)
Solubility: 418 mg GeO_2 in 100 mL (m/25)	−1.4	18				
Solubility: 1 part GeO_2 in 274.1 parts of H_2O	−1.4	20			Calcination of precipitate	Winkler (1886)
Solubility: 1 part GeO_2 in 95.3 parts of H_2O	−1.0	100				

Baes and Mesmer. The formation of the complex $[(Ge(OH)_4))_8(OH)_3]^{3-}$ seems to describe the titration data adequately (Ingri, 1963; Haas et al., 1964c).

The measured first and second proton dissociation constants of $Ge(OH)_4$ are given in Table 3. The presence of polynuclear species is especially relevant in the interpretation of published protonation constants because the results from several of the earlier studies (Roth and Schwartz, 1926; Schwarz and Huf, 1931) could well be affected by their presence. Excluding these latter studies, the reported first dissociation constant values are all relatively close.

There are far fewer measurements of the second dissociation constant, the most recent being nearly 60 years old (Haas et al., 1964c). The 'best' value (Table 6), 12.76, suggests that the species $GeO_2(OH)_2^{2-}$ will be predominant only at very alkaline pH values (at 25 °C). Published constants need to be treated with care because of the less-than-perfect response of the glass electrode under such alkaline conditions. Moreover, these titrations can only have covered a limited range of formation of $GeO_2(OH)_2^{2-}$. For instance, $-lg[OH^-]$ reaches just 5.6 in one of the titrations and is even less in the others described by Ingri (1963). Fig. 1 shows the variation of the first and second hydrolysis constants as a function of ionic strength as calculated by JESS.

Nazarenko et al. (1962), Andrianov and Nazarenko (1966), Nazarenko and Flyantikova (1968), and Alekseeva and Nemzer (1971) reported the existence of cationic species of Ge(IV), e.g., Ge^{4+}, $Ge(OH)^{3+}$, $Ge(OH)_2^{2+}$, and $Ge(OH)_3^{+}$. Baes and Mesmer (1976) questioned the evidence presented in these studies and believed that no accurate estimates of the stabilities of cationic Ge(IV) species existed. From solubility and Raman spectra, Pokrovski and Schott (1998) ruled out the presence of any germanium species in solution other than $Ge(OH)_4$ at pH > 0.3. Unfortunately, studies persist in reporting the existence of cationic Ge (IV) species in solution uncritically (e.g., Marchon et al., 1979; Haghighi and Irannajad, 2022). A series of cationic species have also been proposed by USSR authors for other strongly hydrolysed elements (e.g., tantalum, niobium, antimony) (Babko et al., 1963; Antonovich et al., 1977) which have been rejected (Filella and May 2019b, 2020).

3.4. *Germanium(IV) halide equilibria*

Several experimental studies on fluoride complexes of Ge(IV) have been conducted at room temperature in acid media, the most recent being that of Ciavatta et al. (1990). Using solvent extraction, solubility, and potentiometric methods, Benoit and Place (1963) found evidence for the formation of species with the general form $GeF_4(OH)_i$ and $GeF_5(OH)_i$ in solutions with acidities >0.5 mol L^{-1}, but they do not specify the values of i. This reflects difficulties in measuring the effect of OH^- under acid conditions, a problem common to other readily hydrolysable elements (e.g., Nb, Ta). In a series of papers, Ryss and Kulish (1964a,b, 1965) investigated the hydrolysis of the hexafluoridogermanate(2−) ion, GeF_6^{2-}, and concluded that $GeF_5(H_2O)$ and $Ge(OH)F_4(H_2O)$ were formed in acid media (pH 0.03–2.9). Later, Parpiev and co-workers (Parpiev, and Maslennikov, 1968; Parpiev, 1972) reported a step-wise equilibrium constant for GeF_6^{2-} and Nazarenko and Varlamova (1979) identified successive complexes ML_n (n from 1 to 6). These complexes did not contain any hydroxyl group, with the reactions were written as $Ge^{4+} + n\ F^-$ even though Ge^{4+} does not exist in solution under their experimental conditions. From potentiometric measurements with a fluoride-selective electrode, Ciavatta et al. (1990) proposed the formation of the species $Ge(OH)F_2^{+}$, GeF_4, $Ge(OH)F_4^{-}$, GeF_6^{2-}, and $HGeF_6^{-}$. Differences in values of constants obtained in $NaClO_4$ and $LiClO_4$ solutions (both 3 mol L^{-1}) were attributed to the salting out effect on the activity of HF. Ciavatta and co-workers reinterpreted the data of Benoit and Place (1963) in terms of the formation of GeF_4, and $HGeF_6^{-}$ complexes.

The expected weak complexation of germanium by chloride (Ahrland et al., 1958) has been confirmed by Sohrin (1991) in a solvent extraction study; this shows that at 25 °C chloride complexes are not significant unless the concentration of HCl exceeds 4 mol L^{-1}. This is

Table 3
Published values of equilibrium constants for acid-base equilibria of germanium.

Reaction[a]	lg$K$[a]	T/°C	I electrolyte	Ge range, molar units	Technique	Reference
$Ge(OH)_4 = GeO(OH)_3^- + H^+$	−9.16	25	0.1 mol L^{-1} $NaClO_4$	0.00009–0.0039	Potentiometry (glass electrode)	Kanekiyo et al. (2000)
$Ge(OH)_4 = GeO(OH)_3^- + H^+$	−9.32 ± 0.05	25	0	0.0184, 0.008	Potentiometry (glass electrode)	Pokrovski and Schott (1998)
	−8.92	50				
	−8.70	75				
	−8.55	100				
	−8.48	125				
	−8.41	150				
	−8.35	175				
	−8.37	200				
$Ge(OH)_4 + OH^- = GeO(OH)_3^- + H_2O$	4.68	25	0		Calculated by using equation 10 in the paper	Kosova and Dem'yanets (1988)
	3.93	50				
	2.77	100				
	1.94	150				
	1.32	200				
	0.873	250				
	0.536	300				
First protonation constant	9.26 ± 0.03	25	0.1 mol L^{-1} KCl	0.002–0.005	Potentiometry (glass electrode)	Häkkinen et al., 1986
$Ge(OH)_4 = GeO(OH)_3^- + H^+$	−9.31	25	0		Critical evaluation	Baes and Mesmer, 1976
$Ge(OH)_4 = GeO_2(OH)_2^{2-} + 2\ H^+$	−21.9					
$Ge_8O_{16}(H_2O)_5(OH)_3^{3-}$	−14.24					
$GeO_2 + 4\ H_2O = Ge(OH)_5(OH_2)^- + H^+$	−9.27	20	0.1 mol L^{-1} KNO_3	0.0035–0.0222	Potentiometry (glass electrode)	Mikešová and Bartušek (1979)
$Ge^{4+} + 4\ OH^- = Ge(OH)_4$	55.6	25	0.1 mol L^{-1} KNO_3	1×10^{-5}	Spectrophotometry pH 1.05–1.85	Nazarenko and Flyantikova (1968)
$Ge^{4+} + 3\ OH^- = Ge(OH)_3^+$	42.2					
$Ge^{4+} + 2\ OH^- = Ge(OH)_2^{2+}$	28.5					
$Ge^{4+} + OH^- = Ge(OH)^{3+}$	14.45					
$Ge^{4+} + 4\ OH^- = Ge(OH)_4$	56	25	8 mol L^{-1} (Li,H)Cl	0.005	Solvent extraction	Andrianov and Nazarenko (1966)
$Ge^{4+} + 3\ OH^- = Ge(OH)_3^+$	43					
$Ge^{4+} + 2\ OH^- = Ge(OH)_2^{2+}$	29					
$Ge^{4+} + OH^- = Ge(OH)^{3+}$	14					
Acid dissociation constant of metagermanic acid	−11.56	25	Not controlled		Solubility Error: the authors think that pK2 is pK1	Gayer and Zajicek (1964)
$Ge(OH)_4 + OH^- = GeO(OH)_3^- + H_2O$	4.704 ± 0.002	25	0.5 mol kg^{-1} $NaClO_4$	0.0015–0.02	Potentiometry	Haas et al. (1964c)
	4.763 ± 0.004		1 mol kg^{-1} $NaClO_4$			
$Ge(OH)_4 + 2\ OH^- = GeO_2(OH)_2^{2-} + 2\ H_2O$	5.60 ± 0.48		0.5 mol kg^{-1} $NaClO_4$			
	6.80 ± 0.07		1 mol kg^{-1} $NaClO_4$			
$8\ Ge(OH)_4 + 3\ OH^- = [Ge(OH)_4]_8(OH)_3^{3-}$	29.55 ± 0.01		0.5 mol kg^{-1} $NaClO_4$			
	30.37 ± 0.02		1 mol kg^{-1} $NaClO_4$			
$Ge(OH)_4 + OH^- = GeO(OH)_3^- + H_2O$	4.678 ± 0.006	25	0.5 mol kg^{-1} Na(Cl)	0.005–0.040	Potentiometry (hydrogen electrode)	Ingri (1963)
$Ge(OH)_4 + 2\ OH^- = GeO_2(OH)_2^{2-} + 2\ H_2O$	6.14 ± 0.13					
$8\ Ge(OH)_4 + 3\ OH^- = [Ge(OH)_4]_8(OH)_3^{3-}$	29.14 ± 0.05					
$GeO(OH)_3^- + OH^- = GeO_2(OH)_2^{2-}$	−12.43 ± 0.03	25	3 mol L^{-1} Na(Cl)	0.005–0.025	Potentiometry (hydrogen electrode)	Ingri and Schorch, 1963
$GeO(OH)_3^- = GeO_2(OH)_2^{2-} + H^+$	1.64 ± 0.03					
Second dissociation constant	−12.31	32	Saturated Na_2SO_4		Potentiometry (quinhydrone electrode)	Krüger and Thilo (1958)
pK_1; no reaction given	9.045	10	Values are extrapolations at I 0; values measured at 0.0102–1.231 mol L^{-1} KCl	0.03–0.04	Potentiometry (quinhydrone electrode/glass electrode)	Antikainen (1957)
	8.980	15				
	8.920	20				

(*continued on next page*)

Table 3 (*continued*)

Reaction[a]	lg$K$[a]	T/°C	I electrolyte	Ge range, molar units	Technique	Reference
	8.730 8.615 8.450 8.175 7.900	25 30 35 40 45				
$H_2GeO_3 = H^+ + HGeO_3^-$	−9.08	25	0.5 mol kg^{-1} Na_2SO_4	<0.01	Potentiometry	Lourijsen-Teyssèdre, 1955
GeO_3H_2 ou GeO_4H_4, pK_1 and pK_2 $Ge_5O_{11}H_2 = Ge_5O_{11}^{2-} + 2\ H^+$	9.1, 12.7 7.0	12	2 mol L^{-1} KCl	0.025–0.4	Potentiometry	Carpéni (1948)
Dissociation constant of germanic acid	−8.8	25	?	~0.05	Average of conductimetry and colorimetry values	Gulezian and Müller (1932)
$H_2GeO_3 = H^+ + HGeO_3^-$	0.5 × 10^{-7} (−7.3)	20		0.0176, 0.0293	Conductimetry	Schwarz and Huf (1931)
$H_2GeO_3 = H^+ + HGeO_3^-$ $HGeO_3^- = H^+ + GeO_3^{2-}$	2.6 × 10^{-9} (−8.6) 1.9 × 10^{-13} (−12.7)	20	?		Potentiometry (hydrogen electrode)	Pugh (1929b)
Dissociation constant	1.2 × 10^{-7} (6.92)	18			Conductimetry	Roth and Schwartz (1926)

supported by the earlier solvent extraction results of Benoit and Clerc (1961) who found that $Ge(OH)_4$ was the main germanium species up to 5.6 *m* HCl. It is also in accord with a prior study by Everest and Harrison (1957) who, based on solubility measurements and anion-exchange studies, reported that anionic germanium chlorido-complexes of the type $[Ge(OH)_xCl_{5\text{-}x}]^-$ or $[Ge(OH)_xCl_{5\text{-}x}]^{2-}$, with x = 3, 4 are the main germanium species present in 6–9 mol L^{-1} HCl solutions. Below 6 mol L^{-1} HCl, however, these complexes hydrolyse to form germanium dioxide, and above 9 mol L^{-1} HCl they are converted into $GeCl_4$.

Given the scarcity of data and the apparent lack of germanium complexation by chloride in natural systems (e.g., blood plasma, seawater), no values for Ge–Cl complexes are proposed. They are not formed sufficiently strongly to justify any confidence in them.

Note that the formation of $GeCl_4$(l) in highly concentrated HCl solutions has direct implications for analytical procedures used to study environmental and biological systems (Biver and Filella, 2018) due to formation of $GeCl_4$(l), which is volatile at temperatures below 100 °C (boiling point 86.5 (Hildebrand, 1947).

3.5. *Organic ligands*

Equilibrium constants of germanium with 73 l.m.w. (low molecular weight) organic ligands have been identified and retrieved. All values have been entered into the JESS database. However, it has been decided not to include these equilibria in this work because of the considerable uncertainty about the ligand's state of deprotonation and the stoichiometry of the complexes formed.

3.6. *Thermochemical sources*

Many computer codes use databases containing standard Gibbs energies and associated thermochemical data instead of equilibrium constants for the specific chemical equilibria operating in solution. In general, it is difficult to trace the origin of these derived values. They are usually found in secondary references (e.g., Charlot et al., 1971; de Zoubov et al., 1974; Barin and Platzki, 1995; Lide and Frederikse, 1995; Inzelt, 2006) where authors often take data from two key sources of thermochemical data: the NBS (National Bureau of Standards) series and CODATA (Committee on Data of the International Science Council). The particular situation concerning germanium is typically unsatisfactory, as follows.

The NBS data series has been especially influential. An account of the different stages and publications can be found in Garvin et al. (1981). The most recent publication (Wagman et al., 1982) includes data for many germanium species that, according to the text, "exactly reproduced values in the 1965 edition". The NBS does not include references for the data but this implies that all primary sources were published before 1965 since, in the case of germanium, "prepared in 1965" is explicitly stated at the top of the table.

CODATA 89 (Cox et al., 1989) is a seminal work addressing many thermodynamic reference data. It includes the standard enthalpy of formation at 298.15 K, the entropy at 298.15 K, and the quantity H^0 (298.15 K)–H^0(0). Although it only covers 37 chemical elements, germanium is among them. It provides source references but offers no explicit discussion of the choices made. The process is described in various works (e.g. Abramowitz et al., 1984) and a revealing example of the complexity involved can be found (for thorium only) in Wagman et al. (1977). In the case of germanium, the only compounds considered are: Ge(cr) – defined as the reference state, Ge(g), GeO_2(tetrag), and GeF_4(g) (Table 8). Values come from studies published 1951-1982. Selected thermodynamic data for auxiliary compounds and complexes adopted by NEA (Nuclear Energy Agency) include the CODATA key values. NEA calculated the standard partial molar Gibbs energy of formation values from CODATA enthalpy and entropy values in the first book of their TDB (Thermochemical Database) series (Grenthe et al., 1992) and the same values have just been reproduced in subsequent

Table 4
Published values of equilibrium constants for fluorido complexes of germanium.

Reaction[a]	lg*K*[a]	*T*/°C	*I* electrolyte/mol L^{-1}	pH range	Technique	Reference
$Ge(OH)_4 + 2\ HF + H^+ = GeF_2(OH) + 3\ H_2O$	3.2 ± 0.2	25	3 $LiClO_4$	0.0317–2.90	MGL	Ciavatta et al. (1990)
	2.9 ± 0.1		3 $NaClO_4$			
$Ge(OH)_4 + 4\ HF = GeF_4 + 4\ H_2O$	7.73 ± 0.02		3 $LiClO_4$			
	7.18 ± 0.10		3 $NaClO_4$			
$Ge(OH)_4 + 4\ HF = GeF_4(OH) + 3\ H_2O + H^+$	6.65 ± 0.05		3 $NaClO_4$			
$Ge(OH)_4 + 6\ HF = GeHF_6^{2-} + 4\ H_2O + H^+$	10.8 ± 0.1		3 $LiClO_4$			
	9.94 ± 0.10		3 $NaClO_4$			
$Ge(OH)_4 + 6\ HF = GeF_6^{2-} + 4\ H_2O + 2\ H^+$	9.59 ± 0.05		3 $NaClO_4$			
$Ge(OH)_4 + 4\ HF = GeF_4 + 4\ H_2O$	7.5 ± 0.1	25	0.5 $LiClO_4$	0.5 mol L^{-1} $HClO_4$	Reinterpretation data Benoit and Place (1963)	Ciavatta et al. (1990)
$Ge(OH)_4 + 6\ HF = GeHF_6^- + H^+ + 4\ H_2O$	10.2 ± 0.1					
$Ge^{4+} + F^- = GeF^{3+}$	1.68	20	-	-	Solvent extraction	Nazarenko and Varlamova (1979)
$Ge^{4+} + 2\ F^- = GeF_2^{2+}$	3.03					
$Ge^{4+} + 3\ F^- = GeF_3^+$	4.18					
$Ge^{4+} + 4\ F^- = GeF_4$	5.17					
$Ge^{4+} + 5\ F^- = GeF_5^-$	6.07					
$Ge^{4+} + 6\ F^- = GeF_6$	7.24					
$GeF_5^- + F^- = GeF_6$	3.21	?	?		Ion-exchange	Parpiev (1972)
$GeF_5^- + F^- = GeF_6$	3.86	?	0.5 KCl		Ion-exchange	Parpiev, 1968
$GeF_5^- + HF = GeF_6^{2-} + H^+$	0.66	0	0.4 NaCl	0.050 equil L^{-1} HCl	Chemical analysis	Ryss and Kulish (1964b)
	0.52	10				
	0.58	20				
	0.50	30				
	0.42	40				
	0.34	50				
$GeF_6 + H_2O = GeF_4(OH)^- + HF + F^-$	−5.92	0	Self-medium		Chemical analysis	Ryss and Kulish (1964a)
	−5.28	25				
$GeO_2 + 4\ HF + (j–2)\ H_2O = GeF_4(OH)_j^{j-} + j\ H^+$	7.30	25	0.5 $LiClO_4$	0.5 mol L^{-1} $HClO_4$	Potentiometry (ferri method)	Benoit and Place (1963)
$GeO_2 + 5\ HF + (j–2)\ H_2O = GeF_5(OH)_j^{(j+1)-} + (j+1)\ H^+$	8.94					

Table 5
Published values of equilibrium constants for chlorido complexes of germanium.

Reaction[a]	lg$K$[a]	T/°C	I electrolyte	pH range	Technique	Reference
$Ge(OH)_4 + H^+ + Cl^- = GeCl(OH)_3 + H_2O$ $GeCl(OH)_3 + H^+ + Cl^- = GeCl_2(OH)_2 + H_2O$ $GeCl(OH)_2 + H^+ + Cl^- = GeCl_3(OH) + H_2O$ $GeCl(OH) + H^+ + Cl^- = GeCl_4 + H_2O$	−3.02 ± 0.29 −3.84 ± 0.31 −4.82 ± 0.51 −5.09 ± 0.56	25	3 mol L^{-1} Unknown	Unknown	Liquid-liquid extraction, solid-liquid extraction, ^{1}H NMR	Sohrin (1991)
$GeCl_4 = 2\ Cl^- = GeCl_6^{2-}$	0.87 × 10^{-5} *(−5.06)*	?	HCl	>6 equil L-*1* HCl	Spectrophotometry	Angerstein and Davidson (1961)

Table 6
Best stability constant values for germanium species with inorganic ligands, 25 °C and infinite dilution.[a]

Equilibria	lgK^0
$Ge(OH)_4 + 2\ e^- + 4\ H^+ = Ge^{2+} + 4\ H_2O$	−7.206
$GeO_2(OH)_2^{2-} + H^+ = GeO(OH)_3^-$	12.76
$GeO(OH)_3^- + H^+ = Ge(OH)_4$	9.099
$8\ Ge(OH)_4 + 3\ OH^- = Ge_8(OH)_{35}^{3-}$	28.33
$GeO_2(hexag,s) + 2\ H_2O = Ge(OH)_4$	−1.373
$GeO_2(tetrag,s) + 2\ H_2O = Ge(OH)_4$	−4.999
$Ge(OH)_4 + 4\ H^+ + 6\ F^- = GeF_6^{2-} + 4\ H_2O$	27.98
$Ge(OH)_4 + 5\ H^+ + 6\ F^- = GeHF_6^- + 4\ H_2O$	28.80
$Ge(OH)_4 + 4\ H^+ + 4\ F^- = GeF_4 + 4\ H_2O$	20.14
$Ge(OH)_4 + 3\ H^+ + 4\ F^- = GeF_4(OH)^- + 3\ H_2O$	19.08
$Ge(OH)_4 + 3\ H^+ + 2\ F^- = GeF_2(OH)^+ + 3\ H_2O$	9.345

[a] Four significant figures are retained to minimise propagation of round-off errors, typically caused by subtractions between two such large numbers; the number of significant figures should not be taken to indicate the relative uncertainty of the values, which is always at least an order of magnitude less than indicated (see text).

Table 7
Estimated Δ_fG^0 for germanium species.[a]

Species	Δ_fG^0 (kJ mol^{-1})
$Ge(OH)_4$	−944.67
$GeO(OH)_3^-$	−892.73
$GeO_2(OH)_2^{2-}$	−819.93
$Ge_8(OH)_{35}^{3-}$	−8190.9
$GeO_2(hexag,s)$	−478.14
$GeO_2(tetrag,s)$	−498.84
GeF_6^{2-}	−1839.2
$GeHF_6^-$	−1843.9
GeF_4	−1233.3
$GeF_4(OH)^-$	−1464.4
$GeF_2(OH)^+$	−847.65

[a] Five significant figures are retained to minimise propagation of round-off errors, typically caused by subtractions between two such large numbers; the number of significant figures should not be taken to indicate the relative uncertainty of the values, which is always at least an order of magnitude less than indicated (see text).

books of the series.

Values for the compounds covered in our study in NBS and NEA publications are given in Table 8. Significant differences with our suggested values in Table 7 are observed in the few cases where comparison is possible. It is instructive to consider in detail the thermodynamic data available for one particular substance - GeO_2(tetrag,s). This clearly reveals not only how unreliable are the literature published values for the Gibbs energy of formation but also how easy it is to gain the opposite impression from the frequent re-iteration of the same or similar values that derive so often from, sparse, highly tenuous and generally inconsistent experimental measurements. It is not just the uncertainty itself which is at issue but rather the common notion that because the published values appear in many (often authoritative) sources, some significance is assured.

The Gibbs energy of formation for GeO_2(tetrag,s) depends directly on the formation of $Ge(OH)_4$ in aqueous solution by reaction with water for which there are a fair and reasonable number of measured equilibrium constants. On the other hand, the necessary relationship between $Ge(OH)_4$ and Ge(s) is fraught with difficulty. The principal literature source appears to be that of Charlot et al. (1971) who attributes $E^0 = 0.010$ V for $Ge(OH)_4 + 4\ e^- + 4\ H^+ = Ge(s) + 4\ H_2O$ to values from Latimer (1952), Lovreček and Bockris (1959) and Reid (1965), but in a worryingly non-specific manner without supporting argument. This is particularly problematic because it involves characterisations of Ge^{2+} and Ge^{4+} redox reactions (Reid (1965), neither of which species ever

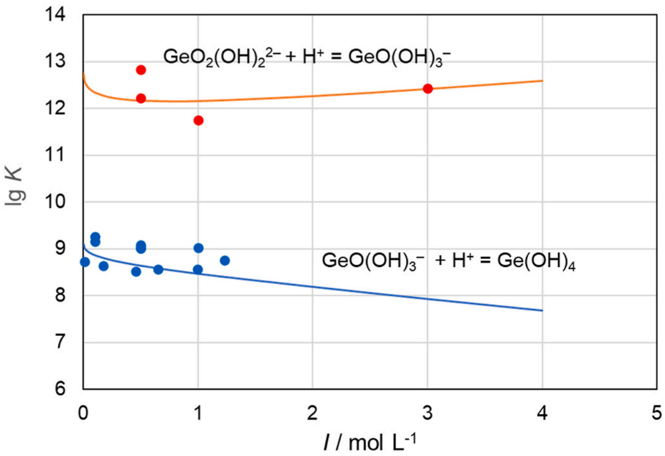

Fig. 1. Predicted dependence on ionic strength of the protonation constants of the different germanium hydrolytic species (solid lines).

exist in significant concentration, and because the value given by Lovreček and Bockris (1959) was not in fact measured but rather calculated “by conventional means”. To our knowledge, the only alternative approach is based on the heat of formation of $GeO_2(s)$, as quoted by Latimer (1952), leading to an $E^0 = -0.18$ V for the above reaction! However, this does not refer specifically to the tetragonal polymorph and, as well as making assumptions about entropy, it suffers from considerable measurement discrepancies (see references in Lovreček and Bockris, 1959). There can thus be little or no confidence in whichever result might be accepted, exposing the general fallacy behind a belief that critically-selected and tabulated thermodynamic constants are the “best” ones, i.e., at least to some extent dependable.

The above deliberation suggests that thermodynamic modellers should, as much as possible, eschew Gibbs energies of formation found in compilations and databases. They ought to use only equilibrium constants for relevant and measurable reactions. Even then, it remains critical for modellers always to probe the reliability of speciation calculations by assessing for themselves the available thermodynamic parameters that dominate their particular calculation. Gibbs energies of formation for reactions and species, as provided in Table 7 herein for example, are generally only useful as a convenient summary of the underlying set of data for universal comparative purposes.

4. Conclusions

As is generally the case with elements whose solution chemistry has not been extensively studied, existing data for germanium are old and scarce. In the context of this study (i.e., environmental and biological media), germanium(IV) reduction is not expected to be relevant but it needs nevertheless to be noted that the knowledge about its redox chemistry is very limited. Germanium(IV) acid-base chemistry is well-established, except in basic media where possible formation of polynuclear complexes in concentrated solutions is likely. The solubility of $GeO_2(s)$ polymorphs is reasonably well characterised. Germanium(IV) interactions with halogens have not been much investigated and tend to be limited by difficulties in identifying the stoichiometry of hydroxido-halogenido-complexes in acid media.

Some important implications for thermodynamic modelling in general are uncovered by this review. Three in particular are most significant. First, the use of Gibbs energies of formation (from the elements) is highly susceptible to error propagation because it often requires quantification of unrealistic (or poorly characterised) intermediate reactions. Wherever possible, it is much better to confine modelling calculations to equilibria that can be measured experimentally. For computational and interface convenience, many thermodynamic software packages disregard this self-evident proposition. Second, the choice of species whose concentrations are taken as the independent variables in the equations being solved (the so-called ‘basis/master species’) can have significant consequences. Remarkable increases in uncertainty (as well as numerical instability) occur unless an appropriate set of species with the highest possible concentrations is adopted. Third, thermodynamic modelling (particularly of ‘non-laboratory’ solutions such as occur in the environment) can only serve to reveal the main features of the system and should not be expected to yield quantitative answers (May and Rowland, 2017). Efforts to improve the reliability of the relevant thermodynamic parameter values are obviously desirable so that the main chemical features can be represented as best they can be; however, limitations inevitably arise because nature is always far more intricate than any

Table 8
Thermochemical data as published in key references. All values at 298.15 K.

	state	NBS 82 (Wagman et al., 1982)			CODATA (Cox et al., 1989)		NEA (Grenthe et al., 1992)
		$\Delta_f H^0$/kJ mol^{-1}	$\Delta_f G^0$/kJ mol^{-1}	S^0/J mol^{-1} K^{-1}	$\Delta_f H^0$/kJ mol^{-1}	S^0/J mol^{-1} K^{-1}	$\Delta_f G^0$/kJ mol^{-1}
Ge	cr	0	0	31.09	0	31.09 ± 0.15	0
	g	376.6	335.9	167.900	372 ± 3	167.904 ± 0.005	331.209
GeO brown	cr	−261.9	−237.2	50.			
GeO yellow	cr	-	−207.1	-			
	g	−46.19	−73.19	224.29			
GeO_2 hexagonal	cr	−551.0	−497.0	55.27			
	am	−537.2	-	-			
GeO_2 tetragonal	cr	-	-		−580.0 ± 1.0	39.71 ± 0.15	−521.404
GeH_4	g	90.8	113.4	217.13			
H_2GeO_3	aq	−818.93	-				
GeF_4	g	-	-	302.86	−1190.20 ± 0.50	301.9 ± 1.0	−1150.017
GeCl	g	155.18	124.2	247.			
$GeCl_4$	l	−531.8	−462.7	245.6			
	g	−495.8	−457.3	347.72			
GeS	cr	−69.0	−71.5	71.			
	g	92.	42.	234.			
GeS_2	cr	−189.5	-	-			

[a] “prepared 1965”.

[b] $\Delta_f G^0$ calculated from CODATA values using $\Delta_t G^o_m = \Delta_t H^o_m - T\sum S^o_m$.

model of it. Indeed, models should be kept simple to describe the essential features of complicated systems intelligibly, implying that they can never be exactly correct.

Of the three issues listed above, the high susceptibility to error propagation of Gibbs energies of formation (from the elements) is extraordinarily impactful. Such values are published for universal reference in numerous secondary and tertiary sources of thermodynamic information (e.g., Wagman et al., 1982; Barin and Platzki, 1995) as well as in popular textbooks (Atkins and de Paula, 2006). Despite an obvious lack of robustness and consequent need for frequent revisions, the motivations for this widespread practice appear to be irresistible; they include the great convenience in having an easily-defined universal set of chemical reactions and a database that is ready-made to illustrate thermochemical cycles. However, the sorry consequence is a profound tendency to corrupt the primary data. This corruption arises at one level through the uncertainties discussed above (i.e., regarding the dependence of overall uncertainty on the weakest link in the chemical reaction chain) but, at another level, even more so when attempts are made to incorporate newly-acquired data into existing datasets without redoing the whole evaluation process. There is no better illustration of this than the train wreck which has occurred through the unsurpassed acceptance and regurgitation of the thermodynamic data originated by the NBS (Wagman et al., 1982). This is not to criticise the remarkable NBS effort itself but rather to decry subsequent, deficient derivations from it. For example, we have found that vast amounts of the data generated by Barin and Platzki (1995) have had to be rejected as inconsistent with more reliable sources. The only sensible, long-term answer to this problem is to preserve and to assess as much thermodynamic information as possible in forms that are as close as possible to the original experimental observations. By explicitly recording chemical reactions and their equilibrium constants in tables of selected data, the OECD Chemical Thermodynamics Series go part way towards this goal but by no means far enough (because they limit their critically-evaluated parameters to constants extrapolated to infinite dilution). Recent IUPAC reviews (e.g., Powell et al., 2013) take a promising step further by including some effects of electrolyte medium/ionic strength. Ideally, however, every published datum should be compiled and assessed individually such that computer-assisted comprehensive evaluations of the thermochemical properties (as, say, described by Wagman et al. (1977)) can be easily repeated as often as necessary. More sophisticated, generalised and powerful computational facilities will be essential for this future task.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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