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Goodbye to S^{2-} in Aqueous Solution

Peter M May*, David Batka, Glenn Hefter, Erich Königsberger and Darren Rowland

Chemistry, School of Engineering and Information Technology, Murdoch University,
Murdoch, WA 6150, Australia

Email: P.May@murdoch.edu.au

Materials and Methods

Raman spectra were recorded using an instrument (Renishaw) with a spectral resolution of 0.5 cm^{-1} and a high-speed motorised stage with three selectable monochromatic laser sources. Measurements were made confocally in 180° backscattering mode with the 532 nm laser on full power.

Spectra of NaHS(aq) (0.01 M) in highly concentrated NaOH(aq) and CsOH(aq) were recorded using ClO_4^-(aq) or SO_4^{2-}(aq) as internal standards respectively. Carbonate contamination was minimised and hydroxide solutions standardised following our usual procedures [1]. The stock solution was always freshly prepared from Na_2S(s), stored under high purity nitrogen (using Schlenk techniques) and protected from light. Other solutions of Na_2S(s) in either NaOH(aq) or CsOH(aq) were prepared freshly and the spectrum taken immediately as a single scan in < 2 s after 2-3 drops were placed on the microscope plate.

Scoping experiments (Figure S1) revealed small shifts in the peaks due to both HS^- (at ~2570 cm^{-1}) and ClO_4^- (at ~933 cm^{-1}) with increasing [OH^-]. Miller and Macklin [2] attributed this change for ClO_4^- to the formation of contact ion pairs. However, no other peaks developed even at the highest NaOH(aq) concentration. Absorption of atmospheric CO_2(g) was shown (by deliberately varied exposure times) to have no significant effect on the Raman features of interest.

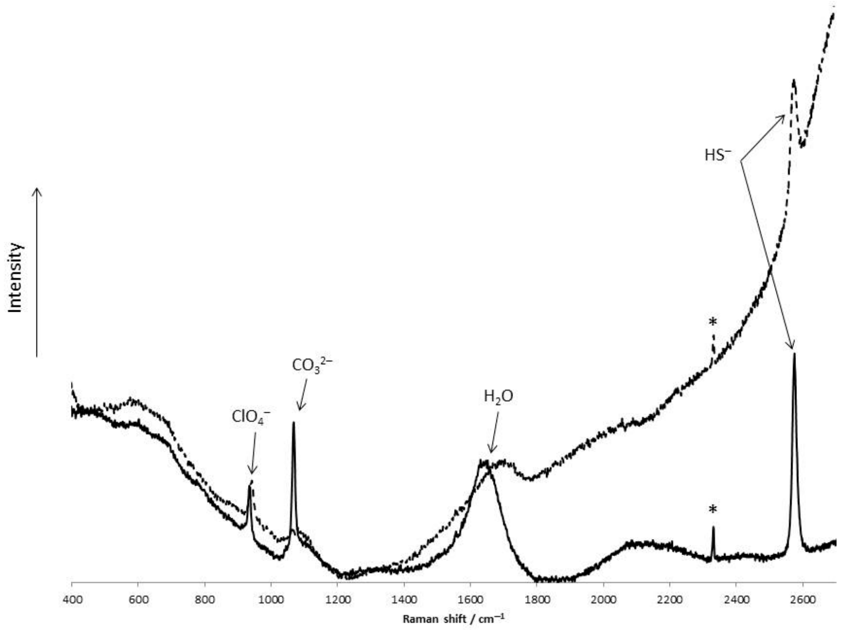

Figure S1. Representative Raman spectra for HS^- in NaOH(aq) at 0.1 $mol.dm^{-3}$ (lower) and 21 $mol.kg^{-1}$ (upper) with ClO_4^- internal standard and CO_3^{2-} contaminant. Peaks marked by an asterisk (*) are attributable to a laser-induced artefact.

ESTA calculations

Our ESTA (Equilibrium Simulation and Titration Analysis) software [3; 4] was used to fit the Raman data. ESTA, without Debye-Hückel corrections activated, assumes all activity coefficients are fixed (i.e., it uses conditional equilibrium constants) which would be strictly applicable at any given high concentration of NaOH(aq), and would remain reasonably appropriate under other, closely-surrounding concentrations.

The results are shown in Figure 1 for three separate calculations, each invoking a 'model' with $HS^{-}(aq)$ as a basis species and just one relevant (conditional) equilibrium constant, as follows:

Case 1: $HS^{-} - H^{+} = S^{2-}$ [pK′a2 = 15.7]
Case 2: $HS^{-} + Na^{+} - H^{+} = NaS^{-}$ [pK′(NaS) = 16.8]
Case 3: $HS^{-} + Na^{+} = NaHS^{0}$ [pK′(NaHS) = 1.7]

If the equations were expressed more realistically in terms of OH^{-} rather than H^{+} (which is the basis species used by ESTA) they would be:

Case 1: $HS^{-} + OH^{-} = S^{2-} + H_2O$ [$pK'_b = 1.7$]
Case 2: $HS^{-} + Na^{+} + OH^{-} = NaS^{-} + H_2O$ [$pK'(NaS) = 2.8$]

Each conditional equilibrium constant was obtained from the ESTA1 program by a rough adjustment to match the observed Raman data (Figure 1) as satisfactorily as possible when determined proportionately in terms of the calculated percentage of 'free' HS^{-} (task ERR%). Only the total component concentrations and conditional equilibrium constants are needed for this task. The total concentration of HS^{-} was held constant (0.01 M) throughout.

Simulated results for Case 1 (S^{2-}) and Case 3 ($NaHS^{0}$) were essentially identical and reflect a domination of the formation equilibria by the concentrations of OH^{-} and Na^{+} at equal concentrations in large excess.

Our 'null hypothesis'

In statistics, the 'null hypothesis' is simply a statement that sample observations result purely from chance. It can be assumed as axiomatic unless and until convincing, tangible evidence indicates otherwise. Null hypotheses are an important tool in modern science for dealing objectively with un-testable notions that arise from time-to-time out of co-incidence, incorrect inference, prevailing prejudices, and such like. Here we take the term 'null hypothesis' to mean there is no physical relationship between particular experimental phenomena so supposed effects occur as if they were random. This assertion is useful because it can be tested, unlike the idea itself. This is why 'fairies at the bottom of the garden' are dismissed by scientists: it is not because they can be disproved (which is impossible), but because no demonstrable *relationship* between independent and dependent observations has ever been found. Here, we postulate that there is no sound analytical or thermodynamic way to study and, hence, no way to support an experimental relationship involving S^{2-}(aq) under any conditions. S^{2-}(aq) should therefore no longer be taken to exist. For any who may not agree, the challenge is to invalidate this null hypothesis, *i.e.* prove beyond reasonable doubt with experimental evidence that S^{2-}(aq) does exist.

Once Upon a Time …

Since metal sulfide ores (of immense commercial value) occur naturally and in abundance, sulfide species are of great interest. Such species occur in spring and sub-surface waters, seawater, wetlands, hydrothermal vents, acid mine drainage, mineral oils and their fractionation cuts, industrial process liquors, *etc*. [5, p. 211]. Their chemistry pervades chemical analysis, hydrometallurgy and environmental science and is often cast in terms of S^{2-}(aq). For instance, a leading environmental text [6, p. 187] tabulates micromolar concentrations of 'sulfide' in natural waters and gives estimated molar concentrations for $[S^{2-}] = 2.3\times10^{-10}$. 'Hydrated' S^{2-} is also listed in Marcus's monograph on 'Ion Properties' [7, p. 126]. Various popular authors [8, p. 484; 9, p. 1006; 10, p. 743; 11, p. 1012; 12, p. 60; 13, p. 5-83] provide a standard redox potential for $S + 2e^{-} \rightarrow S^{2-}$ in aqueous solution (sometimes to 5 significant digits [13, p. 5-83]). Stumm and Morgan [14, p. 127] plot the pH dependence of S^{2-}(aq) formation amongst other species. Fawcett [15] tabulates its solvation parameters. No wonder that formation of S^{2-}(aq) is widely assumed [16; 17; 18; 19; 20].

Much of this ready acceptance has evolved from two seminal studies of the presumed second acid dissociation constant, K_{a2}, for H_2S(aq). The pioneering work of Ellis and Golding [21] reported K'_{a2} (Table S1) for different concentrated alkali metal hydroxide solutions using UV-Vis absorption spectrometry [21]. Their results seemed to be confirmed by Widmer and Schwarzenbach [22] who estimated pK'_{a2} = 14.15±0.05 by potentiometry in 1 M KCl(aq) at the same temperature. Unfortunately, the agreement is deceptive since both studies overlooked the systematic effects of oxidation.

Table S1. Concentration quotients, K'_{a2} , reported by Ellis and Golding [21] at 20 °C.

[MOH]/mol.kg^{-1}	**5.00**	**2.46**	**2.00**	**1.00**	**0.50**	**0.25**
KOH(aq)	14.8		14.01	13.83	13.81	13.91
NaOH(aq)		14.00		13.96	13.97	13.96
LiOH(aq)				13.89		

Values for pK_{a2} given in books are shown in Table S2 and those from various other sources in Table S3. Note that the overall variation, which spans ~7 orders of magnitude, is vastly greater than the reported experimental uncertainties.

Table S2. Values for pK_{a2} from books.

Text	**Ref. and page**	$\boldsymbol{pK_{a2}}$
The Oxidation States of the Elements	23, p. 71	14
Handbook of Biochemistry	24, p. J-189	12.92
Critical Stability Constants, Vol. 4	25, p. 76	13.9
Handbook of Thermodynamic Data	26, p.258	12.91
Chemical Oceanography	27, p. 220	14.15
Critical Stability Constants, Vol. 5	28, p. 410	13.9
Standard Potentials in Aqueous Solution	29, p. 94	11.9
CRC Handbook of Chemistry and Physics, 67th Edn.	30, p. D-163	12.0
Aquatic Chemistry Concepts	31, p. 58	14-15
OECD Chemical Thermodynamics Series, Vol. 1	32, p. 81	19.0
Principles and Applications of Aquatic Chemistry	6, p. 161	13.9
OECD Chemical Thermodynamics Series, Vol. 2	33, p. 64	19.0
CRC Handbook of Chemistry and Physics, 76th Edn.	34, p. 8-43	19
Aquatic Chemistry, 3rd Edn.	14, p. 400	13.9
Aqueous Environmental Geochemistry	35, p. 448	18.5
Fundamentals of Analytical Chemistry, 7th Edn.	36, p. A-8	13.9
Ionic Equilibrium	37, p. 528	12.9
Advanced Inorganic Chemistry, 6th Edn	38, p. 506	~13 [a]
Inorganic Chemistry, First Engl. Edn. Revised	39, p. 520	12.9
Perry's Standard Tables and Formulas for Chemical Engineers	40, p. 5	15.0
CRC Handbook of Chemistry and Physics, 86th Edn.	41, p. 8-40	19
Quantitative Chemical Analysis, 7th Edn.	42, p. AP14	14.0
Inorganic Chemistry	43, p. 527	14.9
Inorganic Chemistry, 6th Edn.	44, p. 444	19.00
Water Chemistry	45, p. 371	17.3
OECD Chemical Thermodynamics Series, Vol. 13a	46, p. 72	19.0
CRC Handbook of Chemistry and Physics, 95th Edn.	13, p. 5-92	19.0

[a] $S^{2-} + H_2O = SH^- + OH^-$, K = –1 (sic)

Table S3. Values of pK_{a2} from various literature sources.

Author(s)	**Reference**	pK_{a2}
Kury JW; Zielen AJ; Latimer WM	47	12.9
Dickson FW; Tunell G	48	16.32[a]
Dickson FW	49	15.3
Ellis AJ; Milestone NB	50	13.8
Goldhaber MB; Kaplan IR	51	13.0-13.8
Giggenbach W	52	17.1±0.2
Tsonopoulos C; Coulson DM; Inman LB	53	15.7
Brewer	See footnote[b]	17±2
Myers RJ	54	19±2
Licht S; Manassen J	55	17.6±0.3
Schoonen MAA; Barnes HL	56	18.51±0.56
Dyrssen D; Kremling K	57	16.52±0.94
Licht S; Forouzan F; Longo K	58	17.0±0.3
Pourbaix M; Pourbaix A	59	14.006
Sato M	60	14.00
Posey ML; Rochelle GT	61	17.0
Eckert W	62	13.86
Phillips DJ; Phillips SL	63	12.9±0.1
Migdisov AA et al.	64	17.6±0.3
Rickard D; Luther GW III	65	18
Okocha C; Sorbie K	66	17.0
Haghtalab A; Izadi A	67	17.0[c]

[a] as calculated in [49, p. 619]

[b] In ‘Flue Gas Desulfurization’; Hudson J.L, and Rochelle G.T. (Eds.) Am. Chem. Soc., Washington DC, USA, Symp. Ser. 188 (ref. 8 cited in [54]).

[c] taken from Aspen Physical Property System, Version 7.2, Aspen Technology Inc., Cambridge, 2010.

The equilibrium expressed in Equation (1) appears in many geochemical and hydrometallurgical calculations which, in a sense, provide the main ‘evidence’ for the formation of S^{2-}(aq). However, given that the dissociation of water, expressed as $pK_W = -\log_{10}(\{H^+\}.\{OH^-\}) < pK_{a2}$, HS^-(aq) will be the predominant sulfide species in most, if not all, aqueous alkaline solutions. Exceedingly low levels of S^{2-}(aq) are implied at pH < 14 by every K_{a2} reported since the problem of oxidation was understood [57; 68], negating the earlier work [21; 22]. Such minute traces pose a currently-insurmountable analytical challenge – spectroscopies are largely uninformative and, in general, other methods (such as solubility or radioisotope tracers) are confounded by the dynamic interconversion which can take place between the various sulfur species present. Consequently, most of the discussion supporting S^{2-}(aq) comes only from chemical speciation modelling using a pK_{a2} presumed by the modeller and despite the reported values being wildly divergent (Tables S2 and S3). The understanding and interpretation of many sulfide-containing systems is profoundly affected by this dichotomy. For example, it has been noted that "the calculations of solubility products K_{s0} for the equilibrium $M_aS_b(s) = aM^{n+} + bS^{2-}$ in general are too low" [57]. Similar problems also seem likely to arise with K_{a2} for $H_2Se(aq)$ and $H_2Te(aq)$ but these systems are much less important than $H_2S(aq)$ and are infrequently described.

On the other hand, over the past three or four decades, there has been a growing awareness amongst solution chemists that the $S^{2-}(aq)$ emperor may have no clothes. As early as 1986, Myers [54] drew attention to the uncertainty associated with pK_{a2} and the need to treat $S^{2-}(aq)$ as unimportant. There have, accordingly, been numerous studies [69; 70, p. 233; 71; 72; 73; 74; 75, p. 552; 76; 77; 78; 79; 80; 41, p. 8-118; 81; 65; 82; 83; 84] which just avoid the issue of $S^{2-}(aq)$ by casting sulfide equilibria more realistically in terms of $HS^-(aq)$, using Equations such as (4) or (5) (written for a divalent cation):

$$H_2S^0 \rightleftharpoons HS^- + H^+ \qquad K_{a1} = \{HS^-\}.\{H^+\} / \{H_2S^0\} \tag{4}$$

$$MS(s) + H_2O \rightleftharpoons M^{2+} + HS^- + OH^- \qquad K_{sp1} = \{M^{2+}\}.\{HS^-\}.\{OH^-\} \tag{5}$$

This assumes $\{H_2O\}$ is constant and recognises that HS^-, like OH^-, has no discernible acidic property in water or moderately alkaline solutions but it seems much better than the approach adopted by Myers [54] and followers (Table S2) who have conjured a number for $pK_{a2} = 19$ based solely on trends in the Periodic Table.

In acidic solutions, which are more relevant in practical applications involving metal sulfides, Equations (6) and (7) apply:

$$MS(s) + 2H^+ \rightleftharpoons M^{2+} + H_2S^0 \qquad K_{sp2} = \{M^{2+}\}.\{H_2S^0\} / \{H^+\}^2 \tag{6}$$

$$MS(s) + H^+ \rightleftharpoons M^{2+} + HS^- \qquad K_{sp3} = \{M^{2+}\}.\{HS^-\} / \{H^+\} \tag{7}$$

and the question of $S^{2-}(aq)$ does not arise.

The activities (concentrations) of the aqueous sulfide species in Equations (6) and (7) cannot be measured directly in acidic solutions since there is always some $H_2S(g)$ formed. This has far-reaching adverse implications for many solubility studies reported in the literature. The most direct and probably the most exact measurement of solubility constants for sulfides is by equilibration with $H_2S(g)$ whose partial pressure can be controlled accurately [71 and references therein].

$$MS(s) + 2H^+ \rightleftharpoons M^{2+} + H_2S(g) \qquad K_{sp0} = \{M^{2+}\}.p(H_2S) / \{H^+\}^2 \tag{8}$$

Nevertheless, the more realistic practice embodied in the use of Equations (4) to (8) is obviously still being widely overlooked (see above). This constitutes a notable failure in scientific practice, which is pervasive, pedagogically worrying, and thermodynamically problematic.

An Unhappy Ending

Solubility products are frequently tabulated in the form of pK_{sp} values, Equation (9), rather than using the pKs from Equations (4) to (8) [85; 30, p. B-207; 36, p. A-6; 86; 87, p. A-6; 88, p. 539; 89, p. 174; 65]). Even Myers reproduces a list of pK_{sp} commenting that Equation (9) is less “clumsy” [54].

$$\mathrm{MS(s)} \rightleftharpoons \mathrm{M^{2+}} + \mathrm{S^{2-}} \qquad K_{sp} = \{\mathrm{M^{2+}}\}.\{\mathrm{S^{2-}}\} \qquad pK_{sp} = -\log_{10}(K_{sp}) \tag{9}$$

The two constants K_{sp} and K_{sp1} give equivalent results in dilute solutions **provided K_{a2} is well established**: Equation (10).

$$K_{sp1} = \{\mathrm{M^{2+}}\}.\{\mathrm{S^{-}}\}\,.\,K_W\,/\,K_{a2} = K_{sp}\,.\,K_W\,/\,K_{a2} \tag{10}$$

As a trivial illustration, consider the solubility of MnS(s) where pK_{sp} = 12, pK_{a2} = 17 and K_W = 14 are given. Ignoring activity coefficients and other equilibria, at pH = 9 in the presence of $[\mathrm{HS^-}]$ = 0.001 M, $[\mathrm{Mn^{2+}}]$ = 0.1 M whichever approach is taken: (a) using $[\mathrm{S^{2-}}] = 10^{-11}$ M ($10^{-3} \times 10^{-17} / 10^{-9}$) so $[\mathrm{Mn^{2+}}] = 10^{-12} / 10^{-11}$ or (b) using $K_{sp1} = 10^{-9}$ ($10^{-12} \times 10^{-14} / 10^{-17}$) whereupon $[\mathrm{Mn^{2+}}] = 10^{-9} / (10^{-3} \times 10^{-5})$.

However, the validity of Equations (9) and (10) requires that value of K_{a2} used in the calculation of K_{sp} **must** be the same in each case. In other words, to calculate metal ion concentrations from experimentally-characterised sulfide equilibria the identical (artefactual) value of pK_{a2} must be subtracted from pK_{sp} as was added to it at the time of the analysis. This addition and subtraction is at best redundant but, more importantly, it will be erroneous (possibly by orders-of-magnitude) if the two operations do not correspond exactly. Typically what happens is that the latest value of pK_{a2} is applied to a pK_{sp} published previously on a different basis. Even though this problem is well known to specialists in aquatic chemistry – Brezonik and Arnold [45, pp. 369-372] discuss it at length – the trap is inescapable as long as $\mathrm{S^{2-}}$(aq) is involved and the concurrent value K_{a2} is unavailable or forgotten; indeed, an inconsistent pK_{a2} = 17.3 was used by Brezonik and Arnold themselves [45] on the remarkable grounds that it was found in the MINEQL+ ver. 4.6 database and was “consistent with recent measurements” (albeit involving an unusual and extremely tenuous extrapolation [64]).

Such pK_{a2} mismatches commonly arise in aquatic chemistry because modelling programs depend on databases of thermodynamic parameters, such as equilibrium constants or Gibbs energies of formation, which are almost impossible to keep properly synchronised. Thus S^{2-} (aq) has appeared in the authoritative NBS [90, p. 2-56] and NEA [46, p. 58] tables, in Speight's widely-used handbooks [40; 91], as well as in the USGS translation of the Russian 'Handbook of Thermodynamic Data' [91, p. 252 & p. 268] and other such compilations such as PHREEQC [92, p. 281; 37, p. 528]. Creation of these thermodynamic databases is an enormous task made all the more challenging by the need to maintain consistency between diverse literature sources [93, 94, 95]. Matters have been made worse by the knock-on consequences of a sign error for the enthalpy of formation of HS^{-}(aq) in an early NBS compilation – see Wolery and Colón [94, p. 654]. Such problems become acute when S^{2-}(aq) is adopted as a 'Master' or 'Basis' species in the thermodynamic harmonisation process, which has tended to happen by default. The resulting differences between databases (Table S4) are a recipe for thermodynamic chaos. For instance, "calculations of the temperature effect on metal sulphide solubilities have been confused by unnecessary estimates of temperature trends for the parameter [of the second dissociation constant,] K_2" [96]. And again, "As the traditional solubility products for metal sulphides at all temperatures are based on improbable values for the free energy of the S^{2-} ion in solution, it would be preferable to recalculate all sulphide solubility data in terms of the constant K_{hS}, for the hydrolysis equilibria" [96].

Table S4. Standard Gibbs energy of formation $\Delta_f \boldsymbol{G}^{\mathbf{0}}$ for S^{2-}(aq) from some thermodynamic databases.

$\Delta_f \boldsymbol{G}^{\mathbf{0}}$ / kJ.mol^{-1}	**Reference**
85.8	26, p. 190
85.8	91, p. 289
111±2	97
86.31	98, p. 95
85.8	99, p. 851
85.8[a]	14, p. 1001
85.8	41, p. 5-67
86	100, p. A-11
120.695±11.610(!)	46, p. 58
85.8	13, p. 5-67
91.872	101

[a] noted by the authors as being too low

In essence, the problem is that these standard sources, and the many others, give a misleading impression that S^{2-}(aq) occurs in alkaline solution much like any other chemical species (albeit at very low concentrations). For example, Cotton *et al.* state that "Although S^{2-} is present in concentrated alkali solutions, it cannot be detected below ~ 8M NaOH” [38, p. 506]; Rickard and Luther, in *Chem. Rev.*, write: “Free sulfide, S(-II), exists in aqueous solutions mainly in the form of H_2S and HS^{-} with minor S^{2-}” [102]. Titova et al. [103] determine “sub-micromolar amounts of sulfide” based on the reaction $2Ag^{+} + S^{2-} \rightleftharpoons Ag_2S(s)$. Predictions that K_{a2} changes with temperature [104; 105, p. 836, 64] reinforce the idea that calculations involving S^{2-}(aq) are meaningful. If, on the contrary, there is as we contend no plausible evidence that S^{2-}(aq) ever actually exists, it would be highly beneficial to expunge it from the literature and avoid all such misleading inferences. It is well understood that spurious chemical species plague thermodynamic modelling calculations [106; 107]. Positive action is now required to ensure that this deleterious S^{2-}(aq) artefact is eliminated.

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