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# Response to the comment by R. H. Byrne on "Solubility of platinum in aqueous solutions at 25°c and pHs 4 to 10 under oxidizing conditions" (2001) *Geochim. Cosmochim. Acta* 65, 4453–4466

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In Byrne's comment (this issue) on the solubility of platinum in aqueous solutions (Azaroual et al., 2001), he claims that our recommended values for the formation constant of $PtOH^+$ ($_{OH}\beta_1$) are unreasonably high. We would like to thank him for his interest in our work and for the opportunity to clarify certain points that were not fully explicit in our initial paper.

We would like to point out that our paper comprised two parts. First, we presented the experimental measurements of platinum metal solubility (Pt[s]) in solutions of weak ionic strength at 25°C under oxidizing conditions at pHs 4 to 10. These measurements are very precise and enabled, for the first time, an evaluation of the Gibbs free energy of $PtOH^+$ aqueous species ($\Delta G°_f[PtOH^+] = -13{,}188 \pm 682$ cal/mol) at 25°C. Note that this value is very close to that proposed by Sassani and Shock (1998) for $PdOH^+$ (−13,130 cal/mol) but very different from that proposed by the same authors for $PtOH^+$ (1560 cal/mol; see Table 1).

Table 1. Thermodynamic constants of platinum hydroxide complexes and platinum solubility reactions at 25°C.

| Reaction | $\Delta G_f^0$ ($Pt^{2+}$) (cal/mol) | $\Delta G_f^0$ ($PtOH^+$) (cal/mol) | log OHβ1 (25°C) | Source |
|---|---|---|---|---|
| | 61,600[a] | 1560 | 16.45 | a |
| $Pt^{2+} + OH^- \Leftrightarrow PtOH^+$ | 58,400[d] | −13,188 | 24.91 ± 0.50 | b |
| | — | — | 23.89 | c |
| | | | log $K$ (25°C) | |
| | 61,600[a] | — | −45.15 | a |
| | 60,900[e] | — | −44.63 | e |
| | 58,400[d] | — | −42.80 | b |
| $Pt(s) \Leftrightarrow Pt^{2+} + 2e-$ | 57,000[f] | — | −41.77 | f |
| | 56,913[g] | — | −41.71 | d |
| | 54,800[h] | — | −40.16 | h |
| | 51,800[i] | — | −37.96 | i |
| | 46,200[j] | — | −33.86 | j |
| | 44,410[k] | — | −32.55 | k |

[a] Sassani and Shock (1998); [b] Azaroual et al. (2001); [c,f] Goldberg and Hepler (1968); [d] Glushko et al. (1972); [e] Wagman et al. (1982); [g] adopted by Wood (1991); [h] Latimer (1952); [i] Hancock et al. (1977); [j] Wilde et al. (1989); [k] Wagman et al. (1969). Underlined values are those recommended in Azaroual et al. (2001).

Second, we discussed the selection of the Gibbs free-energy value for $Pt^{2+}$ aqueous species. The retained value was selected so that platinum speciation in the experimental aqueous solution is consistent with the solubility measurements. The fact that we did not explain this step in greater detail may well have led to some confusion. The value suggested by Glushko et al. (1972) (see Table 1) was retained because this not only gives the "best speciation" of the experimental aqueous solutions but also respects the slope of 1 of the equation ($y = -31.76$

[±0.55] + 1.01 [±0.07]$x$ ) obtained by adjusting our measurements to the line representing the $PtOH^+$ species (Fig. 1). In other words, by using the data of Glushko et al. (1972), the slope of the line established from the solubility measurements remains unchanged. Obviously, any $\Delta G°_f(Pt^{2+})$ value greater than that of Glushko et al. (1972) fulfills this constraint. Conversely, lower values can influence this line and lead to an overestimation of the concentrations of dissolved Pt in the experimental solutions ( Fig. 1). We thus recommended using the value given in Glushko et al. (1972) for $\Delta G°_f(Pt^{2+})$, i.e., 58,400 cal/mol. In addition, Wood (1991) adopted a value similar to that of Glushko et al. (1972), namely, 56,913 cal/mol, to evaluate the stability constant of the $Pt(OH)_2(aq)$ species from his platinum solubility measurements under a pH range of 9 to 15.5. We then reevaluated the stability constants of the chloride and sulfate complexes of $Pt^{II}$ (Table 5 in Azaroual et al., 2001), assuming that the $Pt^{2+}$ free species is unstable (not observable) under our experimental conditions and in particular under those for which the free-energy formation of these complexes was determined. In other words, the free-energy formation of these complexes (Sassani and Shock, 1998) was determined independently of $\Delta G°_f(Pt^{2+})$. Sassani and Shock (1998) provided an excellent literature review of the Gibbs free-energy values of $Pt^{2+}$. Moreover, they adopted an even higher value (61,600 cal/mol) than that of Glushko et al. (1972). Our choice may well be debatable, but our measurements of platinum solubility in buffered pH solutions do not indicate lower $\Delta G°_f(Pt^{2+})$ values. Because this is precisely on what Byrne's comment focuses, we here reply in the following four steps:

1. Byrne argues, "Previous work on the hydrolysis of $Pd^{II}$, whose equilibrium behavior is generally quite similar to that of $Pt^{II}$… ." This is true, but the difference of "approximately 13 orders of magnitude" will vary according to the source used (see Table 1). Moreover, recent measurements show that the first evaluations of stability constants of several aqueous hydroxides, even for the best characterized elements (i.e., Pb, Zn, etc.), were highly approximate. Moreover, all data in the compilation of Baes and Mesmer (1976) may not necessarily be correct.
2. In another statement, Byrne contends that "there are compelling reasons to conclude that the $PtOH^+$ stability results shown in Eqn. 1 and 2 are greatly in error." He seems surprised that our data assume that the free $Pt^{2+}$ species is unstable in aqueous solutions under surface conditions. However, Table 1 shows that out of the nine Gibbs free-energy values for $Pt^{2+}$ published in the literature, only the lowest values (44,410 cal/mol, Wagman et al., 1969; 46,200 cal/mol, Wilde et al., 1989) give $[Pt^{2+}]/[PtOH^+]$ molar ratios with respective values of 0.2 and 0.01 in a $HClO_4$ solution with an ionic strength of 1. Wagman et al. (1982) later abandoned their initial value and proposed a new value of 60,900 cal/mol for the Gibbs free energy of the $Pt^{2+}$ aqueous species. Note that this last value gives a $[Pt^{2+}]/[PtOH^+]$ molar ratio of $10^{-12.7}$, which is even lower than that obtained (i.e., $10^{-10.9}$) with the data of Glushko et al. (1972) recommended in our paper (Azaroual et al., 2001). Consequently, we still maintain that the free $Pt^{2+}$ aqueous species is not observable in aqueous solutions under surface conditions. Table 1 and Figure 1 clearly support this statement.
3. Byrne claims that our stability constant brings into question all previously published data. Following our selection, we merely reused the value given by Glushko et al. (1972) to evaluate the thermodynamic constants of the $Pt^{2+}$ chloride and sulfate complexes, which Byrne himself admits are not very different from the known values. The hypothesis, which we did not enumerate in our paper (Azaroual et al., 2001) when we reassessed the stability constants of the platinum aqueous complexes (see Table 5 in Azaroual et al., 2001), is the fact that the $Pt^{2+}$ species is unstable in aqueous solutions at ambient conditions. Moreover, we believe that the instability of this species partly explains the multitude of Gibbs free-energy values found in the literature.

4. Byrne adds, "The extraordinarily large ${}_{OH}\beta_1$(Pt) and $\beta_1^*$(Pt) results (Eqn. 1 and 2) of Azaroual et al. (2001) require that formation of $PtOH^+$ is taken into account in the assessments of ${}_{Cl}\beta_1$(Pt). In the absence of such considerations it is apparent that the ${}_{OH}\beta_1$(Pt) and ${}_{Cl}\beta_1$(Pt) results of Azaroual et al. (2001) are not internally consistent." We did reassess the chloride stability constants to ensure consistency with our choice of a $\Delta G°_f(Pt^{2+})$ value. Here, we must point out that the reassessment of the stability constants has to be made according to the chosen $\Delta G°_f(Pt^{2+})$ value because, as we firmly believe, the free $Pt^{2+}$ species is unstable under any experimental conditions (including our own). Calculations of the speciation of platinum in seawater (Fig. 5 in Azaroual et al., 2001) showed that the data of Sassani and Shock (1998) did not at all suppose an observability of the $Pt^{2+}$ species in sea water.

We admit that Byrne's comment on the inconsistency of our $Pt^{II}$ database in the absence of consideration of $PtOH^+$ in the assessment of ${}_{Cl}\beta_1$(Pt) is probably true. Faced with this situation, it would be necessary to reexamine all the data previously published, particularly those of Sassani and Shock (1998). This global review would be highly complicated, and it did not enter into the scope of our initial paper. Finally, the serious uncertainty on the stability of $Pt^{2+}$ (its free energy of formation) necessitates further experimental studies to be resolved.

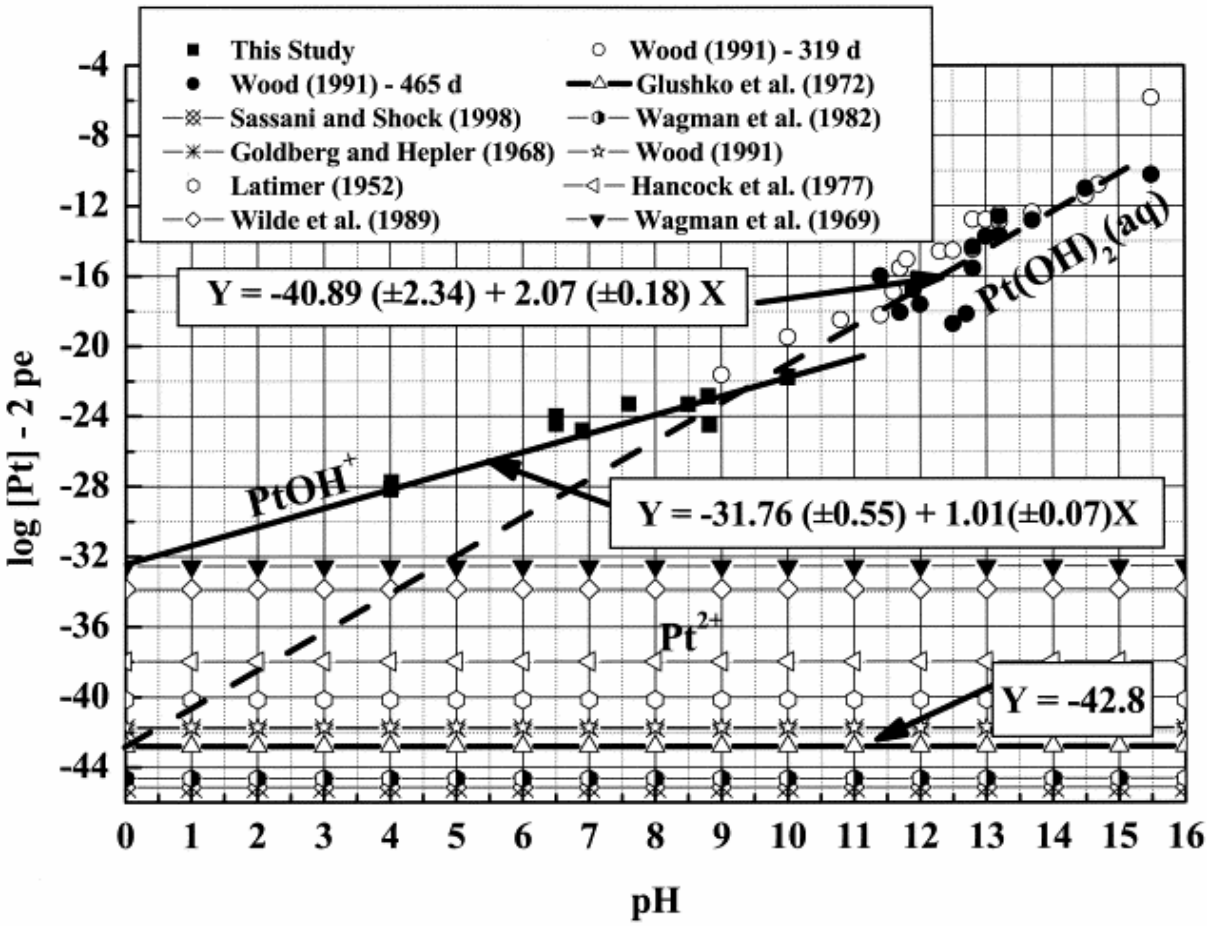


Fig. 1. Aqueous speciation of platinum in the Pt(II)-O-H system in equilibrium with platinum metal at 25°C. Literature data (Glushko et al 1972 and Wood 1991) are included to examine the relative importance of platinum hydroxide complexes (as given in Azaroual et al., 2001). For comparison, we have integrated the effect of various literature data on the Gibbs free energy of the $Pt^{2+}$ aqueous species (Latimer 1952; Goldberg and Hepler 1968; Wagman et al 1969; Wagman et al 1982; Hancock et al 1977; Wilde et al 1989 and Sassani and Shock 1998) on the equilibrium constant (log $K$) of the reaction Pt(s) $\Leftrightarrow Pt^{2+} + 2\,e^-$.

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