



HAL
open science

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

Mohamed Azaroual, Bruno Romand, Philippe Freyssinet, Jean-Robert Disnar

► **To cite this version:**

Mohamed Azaroual, Bruno Romand, Philippe Freyssinet, Jean-Robert Disnar. 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. *Geochimica et Cosmochimica Acta*, 2003, 67, pp.13, 2511-2513(3). 10.1016/S0016-7037(02)01415-1 . hal-00090184

HAL Id: hal-00090184

<https://insu.hal.science/hal-00090184>

Submitted on 13 Sep 2006

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Mohamed Azaroual¹, Bruno Romand^{1, 2}, Philippe Freyssinet¹ and Jean-Robert Disnar²

¹ BRGM, 3, av. C. Guillemin, BP 6009, 45060, Orléans cedex 02, France

² UMR 6531, Université d’Orléans, BP 6759, 45067, Orléans cedex 02, France – remplacé par l’UMR6113 – ISTO

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⁺ (OHβ₁) 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 ($\Delta G_f^\circ[\text{PtOH}^+] = -13,188 \pm 682$ 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	$\Delta G_f^\circ(\text{Pt}^{2+})$ (cal/mol)	$\Delta G_f^\circ(\text{PtOH}^+)$ (cal/mol)	log OHβ ₁ (25°C)	Source
Pt ²⁺ + OH ⁻ ⇌ PtOH ⁺	61,600 ^a	1560	16.45	a
	58,400 ^d	-13,188	24.91 ± 0.50	b
	—	—	23.89	c
Pt(s) ⇌ Pt ²⁺ + 2e ⁻	61,600 ^a	—	log K (25°C)	a
	60,900 ^e	—	-45.15	a
	58,400 ^d	—	-44.63	e
	57,000 ^f	—	<u>-42.80</u>	b
	56,913 ^g	—	-41.77	f
	54,800 ^h	—	-41.71	d
	51,800 ⁱ	—	-40.16	h
	46,200 ^j	—	-37.96	i
	44,410 ^k	—	-33.86	j
		-32.55	k	

^a Sassani and Shock (1998); ^b Azaroual et al. (2001); ^{c,d} Goldberg and Hepler (1968); ^e Glushko et al. (1972); ^f 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 Pt²⁺ 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 ($y = -31.76$

$[\pm 0.55] + 1.01 [\pm 0.07]x$) 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 $\Delta G^\circ_f(\text{Pt}^{2+})$ 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 $\Delta G^\circ_f(\text{Pt}^{2+})$, 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 $\text{Pt}(\text{OH})_2(\text{aq})$ 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 $\Delta G^\circ_f(\text{Pt}^{2+})$. 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 $\Delta G^\circ_f(\text{Pt}^{2+})$ 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 $[\text{Pt}^{2+}]/[\text{PtOH}^+]$ 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 $[\text{Pt}^{2+}]/[\text{PtOH}^+]$ 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 $_{OH}\beta_1(\text{Pt})$ and $\beta_1^*(\text{Pt})$ results (Eqn. 1 and 2) of Azaroual et al. (2001) require that formation of PtOH^+ is taken into account in the assessments of $_{Cl}\beta_1(\text{Pt})$. In the absence of such considerations it is apparent that the $_{OH}\beta_1(\text{Pt})$ and $_{Cl}\beta_1(\text{Pt})$ 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 $\Delta G^\circ_f(\text{Pt}^{2+})$ value. Here, we must point out that the reassessment of the stability constants has to be made according to the chosen $\Delta G^\circ_f(\text{Pt}^{2+})$ 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 $_{Cl}\beta_1(\text{Pt})$ 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.

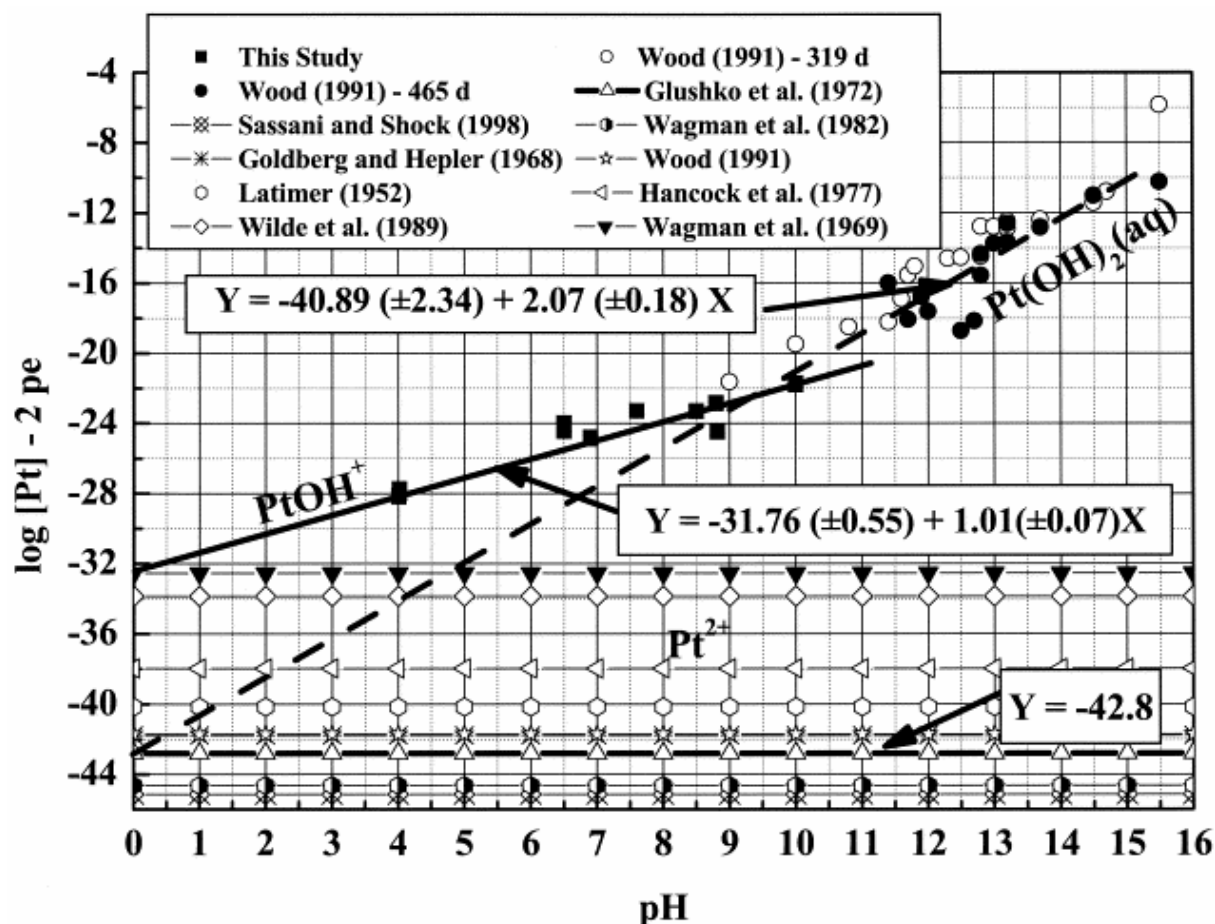


Fig. 1. Aqueous speciation of platinum in the Pt(II)-O-H system in equilibrium with platinum metal at 25°C. Literature data (Glushko et al 1972 and Wood 1991) are included to examine the relative importance of platinum hydroxide complexes (as given in Azaroual et al., 2001). For comparison, we have integrated 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 $\text{Pt}(\text{s}) \rightleftharpoons \text{Pt}^{2+} + 2 \text{e}^-$.

Acknowledgements

This work forms part of BRGM project PRR401 (contribution 02348). The authors would like to thank D. J. Wesolowski and S. A. Wood for their helpful reviews to improve the manuscript.

References

Azaroual, M., Romand, B., Freyssinet, P. and Disnar, J.-R., 2001. Solubility of platinum in aqueous solutions at 25°C and pHs 4 to 10 under oxidizing conditions. *Geochim. Cosmochim. Acta* **65**, pp. 4453–4466.

Baes, C.F. and Mesmer, R.E., 1976. *The Hydrolysis of Cations*, John Wiley, New York.

Glushko, V.P., Medvedev, V.A., Bergman, G.A., Gurvish, L.V., Yungman, V.S., Vorob'ev, A.F., Kolesov, V.P., Reznitskii, L.A., Mikailov, V.V., Gal'chenko, G.L. and Kharapet'yants, M.K.h., 1972. *Thermodynamic Constants of Matter*, Academy of Sciences of the USSR, Moscow.

Goldberg, R.N. and Hepler, L.G., 1968. Thermochemistry and oxidation potentials of the platinum group metals and their compounds. *Chem. Rev.* **68**, pp. 229–257.

Hancock, R.D., Finkelstein, N.P. and Evers, A., 1977. A linear free-energy relation involving the formation constants of palladium(II) and platinum(II). *J. Inorg. Nucl. Chem.* **39**, pp. 1031–1034.

Latimer, W.M., 1952. *Oxidation Potentials*, 2nd ed, Prentice Hall, Englewood Cliffs, NJ.

Sassani, D.C. and Shock, E.L., 1998. Solubility and transport of platinum-group elements in supercritical fluids: Summary and estimates of thermodynamic properties of ruthenium, rhodium, palladium, and platinum solids, aqueous ions, and complexes to 1000°C and 5 kbar. *Geochim. Cosmochim. Acta* **62**, pp. 2643–2671.

Wagman D. D., Evans W. H., Parker V. B., Halow I., Bailey S. M., Schumm R. H. (1969) *Selected Values of Chemical Thermodynamic Properties*. Technical note 270-4. U. S. National Bureau of Standards

Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., Nutall R. L. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in S1 units. *J. Phys. Chem. Ref. Data* **11**. (Suppl. 2)

Wilde A. R., Bloom M. S., Wall V. J. (1989) Transport and deposition of gold, uranium, and platinum-group elements in unconformity-related uranium deposits. In *The Geology of Gold Deposits: The Perspective in 1988* (eds. R. R. Keays et al.), *Econ. Geol. Monogr.* **6**, 637–650

Wood, S.A., 1991. Experimental determination of the hydrolysis constants of Pt²⁺ and Pd²⁺ at 25°C from the solubility of Pt and Pd in aqueous hydroxide solutions. *Geochim. Cosmochim. Acta* **55**, pp. 1759–1767.