

# Supplementary Materials: Stability of $\text{AuCl}_2^-$ from 25 to 1000 °C at Pressures to 5000 Bar, and Consequences for Hydrothermal Gold Mobilization

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## 1. Supplementary Values of Dissociation and Henry Constants

**Table S1.** The  $\log K^\circ$  values of the reaction  $\text{Na}^+ + \text{Cl}^- = \text{NaCl}^\circ_{(\text{aq})}$ .

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	-1.18	-1.20	-1.21	-1.22	-1.23	-1.29
100	-0.68	-0.72	-0.74	-0.77	-0.79	-0.90
200	-0.07	-0.14	-0.21	-0.26	-0.30	-0.49
250	0.29	0.16	0.07	-0.01	-0.07	-0.31
300	0.73	0.51	0.36	0.26	0.17	-0.12
350	1.46	0.95	0.69	0.54	0.43	0.05
400		1.59	1.08	0.85	0.69	0.23
450		2.80	1.54	1.19	0.98	0.41
500		4.32	2.11	1.57	1.29	0.58
550			2.76	1.99	1.62	0.76
600			3.43	2.44	1.96	0.94
650			4.04	2.90	2.32	1.12
700			4.59	3.34	2.67	1.30
750				3.75	3.02	1.47
800				4.14	3.35	1.65
850				4.50	3.66	1.83
900				4.82	3.96	2.00
950				5.13	4.24	2.17
1000				5.41	4.50	2.34

Calculated by the equation:  $\log K^\circ_{\text{NaCl}} = 0.997 - 650.07 \cdot T(\text{K})^{-1} - (10.420 - 2600.5 \cdot T(\text{K})^{-1}) \cdot \log d(w)$ , where  $d(w)$  is the pure water density (Ho et al. [1]).

**Table S2.** The  $\log K^\circ$  values of the reaction  $\text{HCl}^\circ_{(\text{aq})} = \text{H}^+ + \text{Cl}^-$  (Tagirov et al. [2]).

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	0.71	0.71	0.75	0.80	0.87	1.45
100	0.81	0.94	1.09	1.25	1.42	2.59
200	0.10	0.29	0.49	0.68	0.88	2.10
250	-0.49	-0.24	-0.01	0.21	0.41	1.63
300	-1.25	-0.88	-0.59	-0.34	-0.12	1.11
350	-2.41	-1.67	-1.23	-0.94	-0.70	0.56
400		-2.59	-1.95	-1.59	-1.31	0.00
450		-4.42	-2.78	-2.29	-1.95	-0.57
500		-7.95	-3.76	-3.04	-2.62	-1.13
550			-4.92	-3.86	-3.33	-1.70
600			-6.21	-4.75	-4.07	-2.26
650			-7.47	-5.67	-4.85	-2.81
700			-8.59	-6.61	-5.65	-3.37
750				-7.52	-6.45	-3.92
800				-8.39	-7.26	-4.46

850	-9.22	-8.05	-5.00
900	-10.00	-8.82	-5.54
950	-10.74	-9.57	-6.06
1000	-11.43	-10.29	-6.58

**Table S3.** The log  $K^\circ$  values of the reaction  $\text{H}_{2(\text{g})} = \text{H}_{2(\text{aq})}$  (Akinfiev and Diamond [3]).

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	-3.11	-3.33	-3.54	-3.73	-3.91	-4.90
100	-3.11	-3.29	-3.46	-3.62	-3.77	-4.58
200	-2.80	-2.98	-3.15	-3.30	-3.43	-4.13
250	-2.59	-2.79	-2.96	-3.11	-3.25	-3.92
300	-2.34	-2.58	-2.77	-2.93	-3.07	-3.73
350	-1.99	-2.34	-2.58	-2.75	-2.90	-3.55
400		-2.04	-2.38	-2.58	-2.73	-3.38
450		-1.65	-2.18	-2.41	-2.58	-3.22
500		-1.33	-1.99	-2.26	-2.43	-3.08
550			-1.82	-2.11	-2.30	-2.96
600			-1.68	-1.99	-2.19	-2.84
650			-1.58	-1.88	-2.08	-2.73
700			-1.51	-1.80	-2.00	-2.64
750				-1.73	-1.92	-2.55
800				-1.68	-1.86	-2.48
850				-1.63	-1.81	-2.41
900				-1.60	-1.77	-2.34
950				-1.57	-1.73	-2.29
1000				-1.55	-1.70	-2.24

**Table S4.** The log  $K^\circ$  values of the reaction  $\text{O}_{2(\text{g})} = \text{O}_{2(\text{aq})}$  (Akinfiev and Diamond [3]).

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	-2.92	-3.20	-3.47	-3.72	-3.96	-5.26
100	-3.10	-3.33	-3.55	-3.76	-3.96	-5.03
200	-2.87	-3.10	-3.31	-3.51	-3.69	-4.61
250	-2.66	-2.91	-3.13	-3.33	-3.51	-4.39
300	-2.39	-2.69	-2.94	-3.14	-3.32	-4.18
350	-2.00	-2.42	-2.73	-2.95	-3.13	-3.98
400		-2.10	-2.51	-2.76	-2.95	-3.79
450		-1.66	-2.29	-2.57	-2.78	-3.61
500		-1.33	-2.07	-2.39	-2.61	-3.45
550			-1.88	-2.23	-2.46	-3.30
600			-1.73	-2.08	-2.33	-3.16
650			-1.62	-1.97	-2.21	-3.04
700			-1.54	-1.87	-2.11	-2.92
750				-1.79	-2.02	-2.81
800				-1.73	-1.95	-2.72
850				-1.68	-1.88	-2.63
900				-1.64	-1.83	-2.55
950				-1.60	-1.79	-2.48
1000				-1.57	-1.75	-2.41

**Table S5.** The log  $K^\circ$  values of the reaction  $\text{SO}_{2(g)} = \text{SO}_{2(aq)}$  (Akinfiev and Diamond [3]).

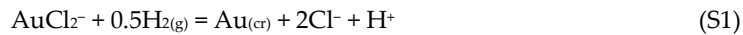
$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	0.13	-0.20	-0.51	-0.82	-1.11	-2.71
100	-0.62	-0.88	-1.14	-1.38	-1.62	-2.91
200	-0.89	-1.13	-1.35	-1.56	-1.76	-2.83
250	-0.89	-1.12	-1.35	-1.55	-1.74	-2.73
300	-0.84	-1.08	-1.31	-1.50	-1.69	-2.62
350	-0.74	-1.01	-1.25	-1.44	-1.62	-2.51
400		-0.91	-1.18	-1.38	-1.55	-2.39
450		-0.81	-1.12	-1.32	-1.49	-2.29
500		-0.78	-1.07	-1.27	-1.43	-2.19
550			-1.05	-1.23	-1.38	-2.10
600			-1.04	-1.20	-1.35	-2.01
650			-1.04	-1.19	-1.32	-1.94
700			-1.05	-1.18	-1.30	-1.88
750				-1.18	-1.29	-1.82
800				-1.18	-1.28	-1.77
850				-1.19	-1.27	-1.72
900				-1.19	-1.27	-1.68
950				-1.19	-1.27	-1.65
1000				-1.19	-1.27	-1.62

**Table S6.** The log  $K^\circ$  values of the reaction  $\text{H}_2\text{O}_{(l)} = \text{H}^+ + \text{OH}^-$  (Wagner and Pruss [4]; Bandura and Lvov [5]).

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	-13.99	-13.82	-13.67	-13.52	-13.39	-12.74
100	-12.25	-12.08	-11.93	-11.80	-11.67	-11.04
200	-11.31	-11.08	-10.88	-10.71	-10.56	-9.88
250	-11.20	-10.90	-10.65	-10.46	-10.29	-9.56
300	-11.34	-10.89	-10.57	-10.33	-10.13	-9.33
350	-11.92	-11.08	-10.60	-10.30	-10.06	-9.18
400		-11.56	-10.74	-10.34	-10.06	-9.09
450		-12.71	-11.00	-10.46	-10.12	-9.03
500		-14.20	-11.38	-10.64	-10.22	-9.01
550			-11.84	-10.87	-10.35	-9.01
600			-12.30	-11.12	-10.51	-9.02
650			-12.70	-11.37	-10.68	-9.05
700			-13.04	-11.61	-10.85	-9.09
750				-11.83	-11.02	-9.14
800				-12.03	-11.17	-9.19
850				-12.21	-11.31	-9.24
900				-12.36	-11.44	-9.30
950				-12.49	-11.56	-9.35
1000				-12.61	-11.66	-9.40

## 2. Treatment of Potentiometric Data of Nikolaeva et al. [6]

Nikolaeva et al. [6] reported results of potentiometric investigation of the reaction:



As a result, the values of the standard electrode potential of Reaction (S1) are reported for the standard state of 1M NaCl. In this case the electromotive force (e.m.f.) of the reaction is defined as:

$$E = E_{I=1} - \frac{2.3026RT}{nF} \cdot \log \frac{m_{\text{Cl}^-}^2 \cdot m_{\text{H}^+}}{m_{\text{AuCl}_2^-} \cdot P_{\text{H}_2}^{0.5}} \quad (\text{S2})$$

where  $E$  is the measured e.m.f for given solute concentrations and  $\text{H}_2$  fugacity,  $E_{I=1}$  stands for the standard electrode potential of Reaction (S1) (ionic strength  $I = 1\text{M}$ ),  $R$  is the universal gas constant,  $n$  represents the number of electrons participating in the reaction ( $n = 1$  for Reaction (S1)), and  $F$  is the Faraday constant. These values of  $E_{I=1}$  have to be recalculated taking account for the standard state conditions adopted in the present study: the hypothetical ideal solution with 1 m concentration of aqueous species. For this standard state the e.m.f. of the reaction can be formulated as:

$$\begin{aligned} E &= E_{I=1}^\circ - \frac{2.3026RT}{nF} \cdot \log \frac{m_{\text{Cl}^-}^2 \cdot m_{\text{H}^+}}{m_{\text{AuCl}_2^-} \cdot P_{\text{H}_2}^{0.5}} - \frac{2.3026RT}{nF} \cdot \log \frac{\gamma_{\text{Cl}^-}^2}{\gamma_{\text{AuCl}_2^-}} = \\ &= E_{I=0}^\circ - \frac{2.3026RT}{nF} \cdot \log \frac{m_{\text{Cl}^-}^2 \cdot m_{\text{H}^+}}{m_{\text{AuCl}_2^-} \cdot P_{\text{H}_2}^{0.5}} - \frac{2.3026RT}{nF} \cdot \left( -\frac{A\Delta Z^2\sqrt{I}}{1 + 4.5B\sqrt{I}} \right) \end{aligned} \quad (\text{S3})$$

where  $\Delta Z^2$  is the difference between the sum of squares of charges of the reaction products and initial substances,  $A$  and  $B$  are the Debye–Hückel activity coefficient parameters, and 4.5 stands for the ion size parameter. In the original work of Nikolaeva et al. [6] the activity coefficient of  $\text{H}^+$  has been taken into account during the calculation of  $E_{I=1}$ . Therefore,  $\Delta Z^2 = 1$  for Reaction (S1), and Equations (S2) and (S3) can be combined to give:

$$E_{I=0}^\circ = E_{I=1}^\circ + \frac{2.3026RT}{F} \cdot \left( -\frac{A}{1 + 4.5B} \right) \quad (\text{S4})$$

This equation was used to calculate  $E_{I=0}^\circ$  and Gibbs free energy of  $\text{AuCl}_2^-$  ( $\Delta_f G_{\text{AuCl}_2^-}$ ) (Table S7). Calculation of Au solubility constant is shown in Table S8.

**Table S7.** Calculation of Gibbs free energy of  $\text{AuCl}_2^-$  using data of Nikolaeva et al. [6].

$T, \text{K}$	$E_{I=1}^\circ$	$E_{I=0}^\circ$	$\Delta_f G^\circ(\text{S1})$	$\Delta G^\circ_{\text{Au}(\text{cr})}$	$\Delta G^\circ_{\text{H}_2(\text{g})}$	$\Delta G^\circ_{\text{Cl}^-}$	$\Delta G^\circ_{\text{AuCl}_2^-}$
	V			$\text{kJ}\cdot\text{mol}^{-1}$			
298.15	$1.152 \pm 0.001$	$1.140 \pm 0.005$	-109.995	0	0	-131.290	-152.584
323.15	$1.126 \pm 0.001$	$1.112 \pm 0.005$	-107.294	-1.211	-3.297	-132.591	-157.451
343.15	$1.106 \pm 0.001$	$1.091 \pm 0.005$	-105.268	-2.215	-5.975	-133.482	-160.924
353.15	$1.095 \pm 0.001$	$1.079 \pm 0.005$	-104.110	-2.728	-7.326	-133.880	-162.714

**Table S8.** Calculation of Gibbs free energy of  $\text{AuCl}_2^-$  using data of Nikolaeva et al. [6].

$T, \text{K}$	$\Delta G_{\text{AuCl}_2^-}$	$\Delta G_{\text{HCl}^\circ(\text{aq})}$	$\Delta G_{\text{Cl}^-}$	$\Delta G_{\text{Au}(\text{cr})}$	$\Delta G_{\text{H}_2^\circ(\text{aq})}$	$\log K_s^\circ$
	$\text{kJ}\cdot\text{mol}^{-1}$					
298.15	$-152.584 \pm 0.48$	-127.240	-131.290	0	17.777	$-20.12 \pm 0.08$
323.15	$-157.451 \pm 0.48$	-127.445	-132.594	-1.211	16.198	$-18.09 \pm 0.08$
343.15	$-160.924 \pm 0.48$	-127.846	-133.487	-2.215	14.708	$-16.74 \pm 0.07$
353.15	$-162.714 \pm 0.48$	-128.122	-133.887	-2.728	13.896	$-16.12 \pm 0.07$

### 3. Calculation of Equilibrium Au Solubility Constant, $\log K_s^\circ$ , for Reaction $\text{Au}_{(\text{Cr})} + \text{HCl}_{(\text{Aq})} + \text{Cl}^- = \text{AuCl}_2^- + 0.5\text{H}_2^\circ_{(\text{Aq})}$ from the Data Reported in the Literature

#### 3.1. Data of Ryabchikov and Orlova [7]

Here and below the calculations were performed using OptimA computer code (Shvarov [8]).

**Table S9.** Composition of experimental solutions and concentrations of Au determined in Ryabchikov and Orlova [7]; solute concentrations and Au solubility constant calculated in the present study. Concentrations are given in molality ( $\text{mol}\cdot(\text{kg}\cdot\text{H}_2\text{O})^{-1}$ ),  $T = 750\text{ }^\circ\text{C}$ ,  $P = 1500\text{ bar}$ . The value of  $f(\text{H}_2(\text{g}))$  was close to the Ni–NiO equilibrium.

Experimental, Ryabchikov and Orlova [7]		Calculated, this study, $\log m$				
$m\text{ NaCl}$	$\log m\text{ Au}$	$\text{AuCl}_2^-$	$\Delta\text{Au}$ calc. – exp.	$\text{Cl}^-$	$\text{HCl}^\circ_{(\text{aq})}$	$\text{H}_2^\circ_{(\text{aq})}$
1.02	–5.22	–5.50	–0.28	–1.28	–1.79	–0.96
4.38	–4.79	–4.51	0.28	–0.60	–1.47	–0.96

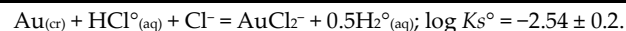
$$\text{Au}_{(\text{cr})} + \text{HCl}^\circ_{(\text{aq})} + \text{Cl}^- = \text{AuCl}_2^- + 0.5\text{H}_2^\circ_{(\text{aq})}, \log K_s^\circ = -2.91 \pm 0.30.$$

#### 3.2. Data of Guo et al. [9]

Only data of Guo et al. [9] obtained in experiments with redox buffers were used in the calculations. The value of  $\log K_s^\circ$  was calculated via the simultaneous regression of all selected experimental data. Thermodynamic properties of nickel–bunsenite (Ni–NiO) and hematite–magnetite ( $\text{Fe}_2\text{O}_3$ – $\text{Fe}_3\text{O}_4$ ) buffers were adopted from SUPCRT92 (Johnson et al. [10]), those of manganosite–hausmannite ( $\text{MnO}$ – $\text{Mn}_3\text{O}_4$ ) buffer from Robie and Hemingway (1995) [11]. Calculation results are given in Table S10.

**Table S10.** Composition of experimental solutions and concentrations of Au determined in Guo et al. [9]; solute concentrations and Au solubility constant calculated in the present study.  $T = 800\text{ }^{\circ}\text{C}$ ,  $P = 2000\text{ bar}$ .

Exper. No	Buffer	Experimental, Guo et al. [9]						Stat. weight	Calculated, this study				
		HCl		NaCl		Au	$\log m\text{ (mol}\cdot\text{(kg}\cdot\text{H}_2\text{O)}^{-1}\text{)}$						
		wt % in HCl-H <sub>2</sub> O mixture	mol (kg·H <sub>2</sub> O) <sup>-1</sup>	wt %	mol (kg·H <sub>2</sub> O) <sup>-1</sup>	mol (kg·H <sub>2</sub> O) <sup>-1</sup>	AuCl <sub>2</sub> <sup>-</sup>		$\Delta\text{ Au calc. - exp.}$	Cl <sup>-</sup>	HCl <sup>o</sup> <sub>(aq)</sub>	H <sub>2</sub> <sup>o</sup> <sub>(aq)</sub>	
#41	Ni-NiO	3.5	0.995	5	0.93	-3.12	1	-3.23	-0.11	-1.15	-0.00125	-0.93	
#45	Ni-NiO	3.5	0.995	10	1.97	-2.91	1	-2.94	-0.03	-0.86	-0.00120	-0.93	
#38	Ni-NiO	3.5	0.995	20	4.43	-2.55	1	-2.62	-0.07	-0.53	-0.00105	-0.93	
#30	Fe <sub>3</sub> O <sub>4</sub> -Fe <sub>2</sub> O <sub>3</sub>	3.5	0.995	20	4.43	-1.69	0.5	-1.60	0.09	-0.53	-0.0121	-3.01	
#15	MnO-Mn <sub>3</sub> O <sub>4</sub>	3.5	0.995	20	4.43	-2.02	0.5	-1.67	0.35	-0.53	-0.0103	-2.85	

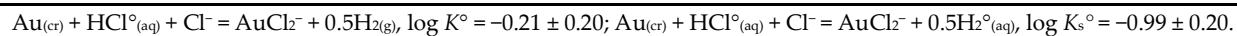


### 3.3. Data of Zajacz et al. [12]

Only data of Zajacz et al. [12] obtained in experiments without S added to the experimental system were used for thermodynamic calculations.

**Table S11.** Composition of experimental solutions and concentrations of Au determined in Zajacz et al. [12]; solute concentrations and Au solubility constant calculated in the present study. Concentrations are given in molality (mol·(kg·H<sub>2</sub>O)<sup>-1</sup>),  $T = 1000\text{ }^{\circ}\text{C}$ ,  $P = 1500\text{ bar}$ . The value  $f(\text{H}_2(\text{g})) = 19\text{ bar}$  was accepted for all the experiments.

Exper. No	Experimental, Zajacz al. [12]				Calculated, this study, $\log m$				
	$m\text{ NaCl}$	$m\text{ HCl}$	$\log m\text{ Au}$	Au	$\Delta\text{ Au calc. - exp.}$	AuCl <sub>2</sub> <sup>-</sup>	AuOH <sup>o</sup> <sub>(aq)</sub>	Cl <sup>-</sup>	HCl <sup>o</sup> <sub>(aq)</sub>
#52	0.75	0	-4.60	-4.70	-0.10	-5.39	-4.80	-2.67	-1.86
#53	0	0.75	-4.68	-4.79	-0.11	-6.79	-4.80	-5.81	-0.12
#56	0	1.5	-4.63	-4.78	-0.15	-6.35	-4.80	-5.66	0.18
#55	0	0.5	-4.85	-4.79	0.05	-7.06	-4.80	-5.90	-0.30
#54	0	0.25	-5.08	-4.79	0.28	-7.53	-4.80	-6.07	-0.60
#57	0.375	0.375	-3.93	-3.95	-0.02	-4.02	-4.80	-2.73	-0.43
#61	0.7	0.069	-4.36	-4.39	-0.03	-4.61	-4.80	-2.60	-1.14
#85	0.146	0.587	-4.07	-4.00	0.07	-4.08	-4.80	-2.98	-0.23



### 3.4. Data of Gammons and Williams-Jones [13]

**Table S12.** Recalculation of data of Gammons and Williams-Jones [13] (into the Au solubility constant).

Reactions	log $K^\circ$ (300 °C, $P_{\text{sat}}$ )
$\text{Au}_{(\text{cr})} + 2\text{Cl}^- + \text{H}^+ + 0.25\text{O}_{2(\text{g})} = \text{AuCl}_2^- + 0.5\text{H}_2\text{O}$	$3.86 \pm 0.39$
$\text{HCl}^\circ_{(\text{aq})} = \text{H}^+ + \text{Cl}^-$	-1.25
$0.5\text{H}_2\text{O} = 0.25\text{O}_{2(\text{g})} + 0.5\text{H}_{2(\text{g})}$	-8.90
$0.5\text{H}_{2(\text{g})} = 0.5\text{H}_{2^\circ(\text{aq})}$	-1.17
$\text{Au}_{(\text{cr})} + \text{HCl}^\circ_{(\text{aq})} + \text{Cl}^- = \text{AuCl}_2^- + 0.5\text{H}_{2^\circ(\text{aq})}$	log $K_s^\circ = -7.46 \pm 0.40$

### 3.5. Data of Zotov et al. [14] and Stefánsson and Seward [15]

Original Au solubility data reported in Stefánsson and Seward [15] (Table A1) and Zotov et al. [14] (Table 5.2) were recalculated using dissociation and Henry constants from Section 1 (Supplementary Values of Dissociation and Henry Constants Calculation) results are listed in Table S13.

**Table S13.** Original and recalculated values of Au solubility constant, log  $K_s^\circ$ , based on data of Zotov et al. [14] and Stefánsson and Seward [15]. All calculations were performed for 1000 bar pressure. The dissociation constant of KCl was adopted from Ho and Palmer [16].

$t$ , °C	Zotov et al. [14]		Stefánsson and Seward [15]	
	Original	Recalculated	Original	Recalculated
350	$-5.42 \pm 0.15$	-5.72		
400			$-6.61 \pm 0.05$	-6.62
450	$-4.50 \pm 0.15$	-4.59	$-6.30 \pm 0.09$	-6.12
500	$-4.00 \pm 0.09$	-4.12	$-6.04 \pm 0.13$	-5.86
550			$-5.75 \pm 0.06$	-5.21
600			$-5.53 \pm 0.11$	-4.69

## 4. Gibbs Free Energy of $\text{AuCl}_2^-$ and Aqueous Species for Which Equations of State Other Than HKF (Helgeson–Kirkham–Flowers) were Used

**Table S14.** Gibbs free energy of  $\text{AuCl}_2^-$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) calculated using Equation 5 for the Au solubility constant,  $K_s^\circ$ . The sources of thermodynamic data of the reaction components are listed in section 2.1.2.

$t$ , °C	Pressure, bar					
	$P_{\text{sat}}$	500	1000	1500	2000	5000
25	-152.5	-148.4	-144.3	-140.3	-136.4	-113.7
100	-167.3	-163.3	-159.1	-155.0	-150.9	-126.4
200	-187.6	-183.6	-179.8	-175.9	-172.0	-148.2
250	-196.3	-193.2	-189.8	-186.2	-182.6	-159.6
300	-203.7	-202.2	-199.5	-196.3	-193.0	-171.3
350	-206.7	-209.5	-208.6	-206.1	-203.3	-183.1
400		-215.4	-216.8	-215.5	-213.4	-195.1
450		-209.2	-223.4	-224.2	-223.2	-207.3
500		-175.3	-227.3	-231.8	-232.4	-219.7
550			-227.4	-238.1	-241.0	-232.3
600			-224.3	-242.9	-248.8	-245.0
650			-220.3	-246.5	-255.7	-257.9
700			-217.5	-249.2	-261.9	-270.8
750				-251.6	-267.5	-283.9
800				-254.3	-272.6	-296.9
850				-257.4	-277.6	-310.1

900	-261.1	-282.6	-323.4
950	-265.3	-287.7	-336.8
1000	-270.2	-293.1	-350.3

**Table S15.** Gibbs free energy of  $\text{NaCl}^{\circ}_{(\text{aq})}$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) calculated using data from Ho et al. [1] and thermodynamic properties of  $\text{Na}^+$  and  $\text{Cl}^-$  from SUPCRT92 (Johnson et al. [10]).

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	-386.4	-385.5	-384.4	-383.3	-382.2	-374.9
100	-396.4	-395.3	-394.1	-393.0	-391.8	-384.3
200	-409.5	-408.6	-407.6	-406.5	-405.3	-398.0
250	-415.9	-415.3	-414.4	-413.4	-412.3	-405.2
300	-421.6	-421.9	-421.4	-420.5	-419.5	-412.7
350	-425.8	-428.1	-428.5	-427.7	-426.9	-420.4
400		-436.1	-435.7	-435.1	-434.3	-428.3
450		-439.4	-442.7	-442.4	-441.9	-436.4
500		-418.2	-449.1	-449.6	-449.4	-444.7
550			-453.7	-456.4	-456.8	-453.1
600			-456.0	-462.3	-463.7	-461.7
650			-457.5	-467.5	-470.0	-470.2
700			-459.9	-471.9	-475.7	-478.8
750				-475.8	-480.6	-487.3
800				-479.5	-484.8	-495.8
850				-483.0	-488.3	-504.2
900				-486.5	-491.4	-512.4
950				-490.0	-494.0	-520.7
1000				-493.4	-496.4	-528.8

**Table S16.** Gibbs free energy of  $\text{SO}_2^{\circ}_{(\text{aq})}$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) calculated using data from Akinfiev and Diamond [3].

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	-300.9	-299.1	-297.3	-295.5	-293.9	-284.7
100	-314.8	-312.9	-311.0	-309.3	-307.6	-298.4
200	-337.4	-335.3	-333.2	-331.3	-329.5	-319.8
250	-350.1	-347.8	-345.5	-343.5	-341.6	-331.7
300	-363.5	-360.9	-358.5	-356.3	-354.3	-344.0
350	-377.9	-374.7	-371.9	-369.5	-367.4	-356.9
400		-389.2	-385.7	-383.1	-380.9	-370.1
450		-404.1	-399.8	-397.0	-394.7	-383.6
500		-418.3	-413.9	-411.0	-408.6	-397.4
550		-431.9	-428.0	-425.1	-422.7	-411.5
600		-445.7	-442.0	-439.2	-436.9	-425.7
650		-459.7	-455.9	-453.3	-451.1	-440.1
700		-473.8	-469.9	-467.5	-465.3	-454.6
750		-488.2	-484.0	-481.6	-479.6	-469.2
800		-502.6	-498.3	-495.9	-493.9	-483.9
850		-517.3	-512.7	-510.2	-508.3	-498.7
900		-532.0	-527.2	-524.7	-522.8	-513.6
950		-546.9	-541.9	-539.3	-537.4	-528.5
1000		-561.9	-556.6	-554.0	-552.1	-543.6

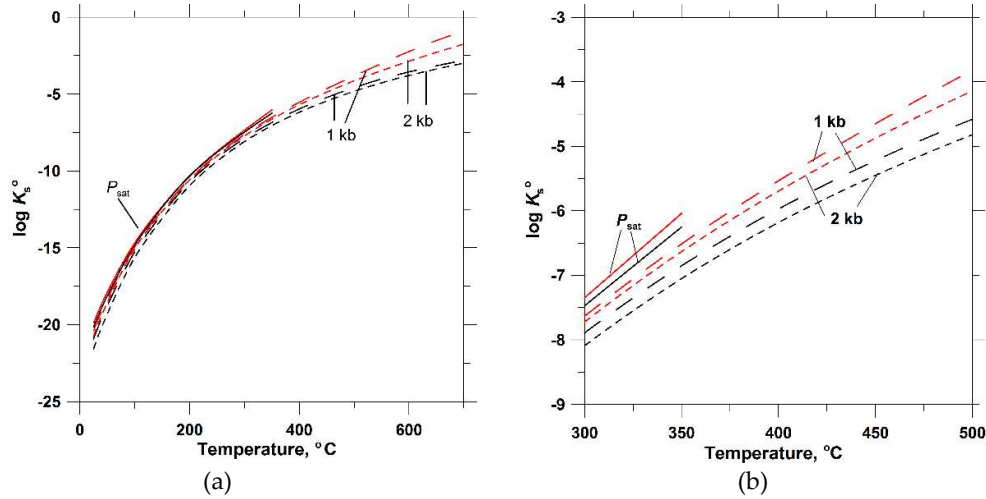


**Table S17.** Gibbs free energy of  $O_2^{\circ}(aq)$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) calculated using data from Akinfiev and Diamond [3].

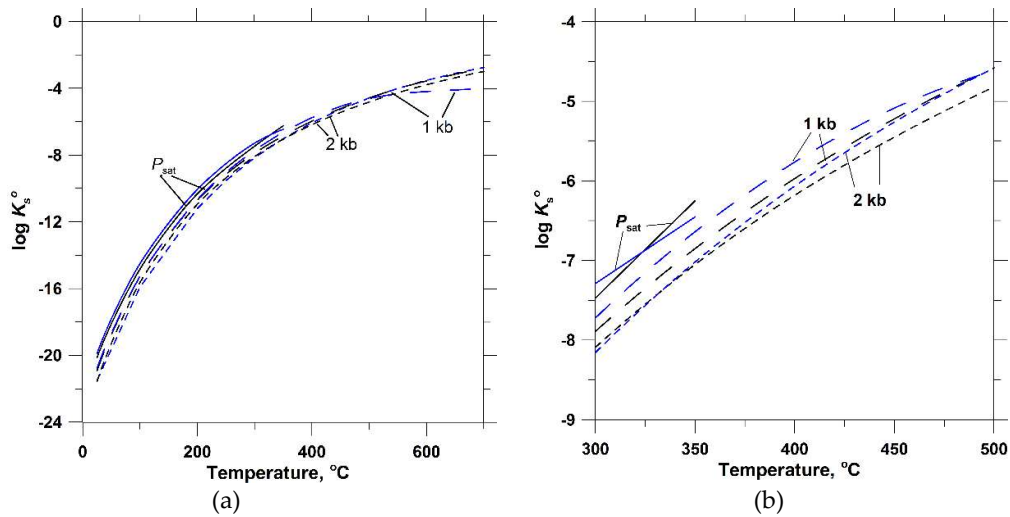
$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	16.6	18.3	19.8	21.2	22.6	30.0
100	6.5	8.2	9.7	11.2	12.7	20.3
200	-11.2	-9.1	-7.2	-5.4	-3.8	4.6
250	-21.6	-19.1	-16.9	-14.9	-13.1	-4.3
300	-33.2	-30.0	-27.2	-25.0	-23.0	-13.6
350	-46.8	-41.8	-38.2	-35.6	-33.4	-23.3
400		-55.2	-49.9	-46.7	-44.2	-33.4
450		-70.8	-62.1	-58.2	-55.3	-43.8
500		-85.8	-74.9	-70.1	-66.8	-54.4
550			-87.7	-82.2	-78.5	-65.3
600			-100.3	-94.3	-90.3	-76.3
650			-112.6	-106.4	-102.1	-87.5
700			-124.5	-118.4	-114.0	-98.8
750				-130.3	-125.9	-110.3
800				-142.1	-137.7	-121.8
850				-153.9	-149.5	-133.4
900				-165.7	-161.3	-145.1
950				-177.5	-173.1	-156.9
1000				-189.2	-184.9	-168.6

**Table S18.** Gibbs free energy of  $H_2^{\circ}(aq)$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) calculated using data from Akinfiev and Diamond [3].

$t, ^\circ\text{C}$	Pressure, bar					
	$P_{\text{sat.}}$	500	1000	1500	2000	5000
25	17.8	19.0	20.2	21.3	22.3	27.9
100	12.1	13.4	14.6	15.8	16.9	22.6
200	1.2	2.9	4.4	5.7	7.0	13.3
250	-5.5	-3.5	-1.7	-0.2	1.2	7.9
300	-13.2	-10.6	-8.4	-6.6	-5.1	2.1
350	-22.7	-18.5	-15.6	-13.5	-11.8	-4.1
400		-27.7	-23.3	-20.8	-18.8	-10.5
450		-39.0	-31.6	-28.4	-26.1	-17.2
500		-49.9	-40.2	-36.3	-33.6	-24.0
550			-49.0	-44.3	-41.3	-31.1
600			-57.6	-52.5	-49.2	-38.2
650			-65.9	-60.6	-57.0	-45.5
700			-73.9	-68.6	-64.9	-52.9
750				-76.5	-72.7	-60.4
800				-84.3	-80.5	-67.9
850				-92.1	-88.3	-75.5
900				-99.9	-96.1	-83.1
950				-107.7	-103.9	-90.8
1000				-115.4	-111.6	-98.5



**Figure S1.** The Au solubility constant of the reaction  $\text{Au}_{(\text{cr})} + \text{HCl}_{(\text{aq})} + \text{Cl}^- = \text{AuCl}_2^- + 0.5\text{H}_2_{(\text{aq})}$  as a function of temperature and pressure. Comparison of the results of our study (black lines) with data of Akinfiev and Zotov [17] (red lines): (a) temperature interval 25–700 °C; (b) temperature interval 300–500 °C.



**Figure S2.** The Au solubility constant of the reaction  $\text{Au}_{(\text{cr})} + \text{HCl}_{(\text{aq})} + \text{Cl}^- = \text{AuCl}_2^- + 0.5\text{H}_2_{(\text{aq})}$  as a function of temperature and pressure. Comparison of the results of our study (black lines) with data of Sverjensky et al. [18] (blue lines): (a) temperature interval 25–700 °C; (b) temperature interval 300–500 °C.

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