

## Supplementary Material

# **The aqueous chemistry of tellurium: critically-selected equilibrium constants for the low-molecular-weight inorganic species**

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Table S1. Published tellurium redox potentials.

Reaction <sup>a</sup>	$E / V$	$T / ^\circ C$	Conditions	Technique	Reference	Comments
$2 \text{Te(s)} + 2 e^- = \text{Te}_2^{2-}$	-0.845	?	$I$ unknown pH = 13	Polarography (Te electrode)	Panson 1964	Value for $\text{Te}_2^{2-} = \text{Te(s)} + \text{Te}^{2-}$ in Lingane (1952) wrong; Panson (1963) right
$\text{H}_2\text{Te} = \text{Te(s)} + 2 \text{H}^+ + 2 e^-$ $\text{Te}^{2-} = \text{Te(s)} + 2 e^-$ $\text{Te}_2^{2-} = \text{Te(s)} + \text{Te}^{2-}$	0.51 0.95 $K = 2 \times 10^{-4}$	?	$I$ unknown	Polarography	Panson 1963	First reaction: value similar to Awad (1962) but differs from Lingane (1952)  Second reaction: differs from Awad (1962) and Latimer (1952)
$\text{Te(s)} + 2 \text{H}^+ + 2 e^- = \text{H}_2\text{Te}$ $2 \text{Te(s)} + 2 \text{H}^+ + 2 e^- = \text{H}_2\text{Te}_2$ $2 \text{Te(s)} + 2 e^- = \text{Te}_2^{2-}$ $2 \text{Te(s)} + 4 e^- = 2 \text{Te}^{2-}$	-0.50 -0.365 -0.74 -1.1	30	$I$ unknown 0.003–0.02 M HCl	Polarography (overpotential measurements)	Awad 1962	
$\text{TeO}_2(\text{s}) + 4\text{H}_2\text{O} = \text{H}_6\text{TeO}_6(\text{s}) + 2\text{H}^+ + 2 e^-$ $2 \text{OH}^- + \text{TeO}_3^{2-} = \text{TeO}_4^{2-} + \text{H}_2\text{O} + 2 e^-$ $\text{Te(s)} + 6 \text{OH}^- = \text{TeO}_3^{2-} + 3 \text{H}_2\text{O} + 4 e^-$ $\text{H}_2\text{Te} = \text{Te(s)} + 2 \text{H}^+ + 2 e^-$ $\text{Te}^{2-} = \text{Te(s)} + 2 e^-$ $\text{Te}_2^{2-} = \text{Te(s)} + \text{Te}^{2-}$	-1.02 -0.4 0.57 0.72 1.14 $K = 5.5 \times 10^{-12}$	25	none, 0	Estimation	Latimer 1953	Error in the sign of $\text{H}_2\text{Te} =$ $\text{Te(s)} + 2\text{H}^+ + 2e^-$ in the original publication

Reaction <sup>a</sup>	<i>E</i> / V	<i>T</i> / °C	Conditions	Technique	Reference	Comments
$\text{TeO}_2(\text{s}) + 4 \text{H}_2\text{O} = \text{H}_6\text{TeO}_6(\text{s}) + 2 \text{H}^+ + 2 \text{e}^-$ $2 \text{OH}^- + \text{TeO}_3^{2-} = \text{TeO}_4^{2-} + \text{H}_2\text{O} + 2 \text{e}^-$ $\text{Te}(\text{s}) + 6 \text{OH}^- = \text{TeO}_3^{2-} + 3 \text{H}_2\text{O} + 4 \text{e}^-$ $\text{H}_2\text{Te} = \text{Te}(\text{s}) + 2\text{H}^+ + 2 \text{e}^-$ $\text{Te}^{2-} = \text{Te}(\text{s}) + 2 \text{e}^-$	-1.02 -0.4 0.02 0.69 0.92	25		Estimation	Latimer 1938	
$2 \text{H}_2\text{O} + \text{Te}(\text{s}) = \text{TeO}_2(\text{s}) + 4 \text{H}^+ + 4 \text{e}^-$ $2 \text{H}_2\text{O} + \text{Te}(\text{s}) = \text{TeOOH}^+ + 3 \text{H}^+ + 4 \text{e}^-$	-0.5286 -0.5213 -0.5590	25 45	Variable HCl	Direct measurement	Schuhmann 1925	
$2 \text{Te}(\text{s}) + 2 \text{e}^- = \text{Te}_2^{2-}$ $\text{Te}(\text{s}) = \text{Te}^{4+} + 4 \text{e}^-$	-0.818 0.549	19-20	2.5 M HCl	Direct cell measurements	Kasarnowsky 1923	

Table S2. Published Te(-II) acid-base equilibrium constants.

Reaction <sup>a</sup>	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	I electrolyte	Te concentration <i>pH</i> range	Technique	Reference	Comments
Te <sup>2-</sup> + H <sup>+</sup> = HTe <sup>-</sup>	(1.28 ± 0.02)x10 <sup>-12</sup>	-11.9	25	extrapolated to <i>I</i> = 0 (DHC)	<i>dilute NaOH and buffers pH 12</i>	Spectrophotometry	Myers 2007	
Te <sup>2-</sup> + H <sup>+</sup> = HTe <sup>-</sup>	6.9x10 <sup>-13</sup> abstract 5x10 <sup>-13</sup> conclusions	-12.2 -12.3	25	1 M NaOH	0.1 mM range <i>above pH 14</i>	Polarography	Panson 1963	Includes also Lingane's data in the calculations  Different value given in the abstract and in the conclusions
Te <sup>2-</sup> + H <sup>+</sup> = HTe <sup>-</sup>		-11		Unknown	<i>0-14</i>	Polarography	Lingane and Niedrach 1948	Value needed to fit their polarographic curves; not a 'real' determination
H <sub>2</sub> Te = HTe <sup>-</sup> + H <sup>+</sup>	2.27x10 <sup>-3</sup>	-2.64	18	Unknown		Conductimetry	de Hlasko 1922	No details about H <sub>2</sub> Te preparation
H <sub>2</sub> Te <sup>-</sup> = HTe <sup>-</sup> + H <sup>+</sup>		-2		Unknown		Solubility	Bruner-Krakau 1913	

<sup>a</sup>Value in italics calculated from original *K* value. If not in italics, log*K* value is as published.

<sup>b</sup>Values of pH in italics.

Table S3. Published Te(IV) acid-base and TeO<sub>2</sub>(s) solubility constants.

Reaction	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	I electrolyte	Te concentration <sup>b</sup> <i>pH</i> range	Technique	Reference	Comments
TeO <sub>2</sub> (s) + H <sub>2</sub> O = H <sub>2</sub> TeO <sub>3</sub>		-4.64 ± 0.15	25	0	-0.30–13.6	Solubility and potentiometry for p <i>K</i> <sub>3</sub> only	Grundler et al. 2013	Coarse TeO <sub>2</sub> powder 99+% acquired from Aldrich. No further characterisation
		-3.79 ± 0.04	80					
		-2.72 ± 0.05	200					
H <sub>3</sub> TeO <sub>3</sub> <sup>+</sup> = H <sub>2</sub> TeO <sub>3</sub> + H <sup>+</sup>		-2.81 ± 0.20	25					
		-2.22 ± 0.09	80					
H <sub>2</sub> TeO <sub>3</sub> = HTeO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>		-1.08 ± 0.18	200					
		-5.18 ± 0.19	25					
		-5.95 ± 0.06	80					
HTeO <sub>3</sub> <sup>-</sup> = TeO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup>		-6.63 ± 0.11	200					
		-10.02 ± 0.01	Other <i>T</i>					
TeO <sub>2</sub> (s) + H <sub>2</sub> O + H <sup>+</sup> = H <sub>3</sub> TeO <sub>3</sub> <sup>+</sup>		-2.20	25	0	0–8	Estimation from solubility data + data from other sources	McPhail 1995	No experimental details given Values calculated at other <i>T</i> (0.01 to 350 C) Origin of solubility data: the author refers to a manuscript in preparation, apparently never published
TeO <sub>2</sub> (s) + H <sub>2</sub> O = H <sub>2</sub> TeO <sub>3</sub>		-5.03	25					
TeO <sub>2</sub> (s) + H <sub>2</sub> O = HTeO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>		-11.41	25					
H <sub>3</sub> TeO <sub>3</sub> <sup>+</sup> = H <sub>2</sub> TeO <sub>3</sub> + H <sup>+</sup>		-2.83	25					
HTeO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> = H <sub>2</sub> TeO <sub>3</sub>		6.38	25					
TeO <sub>3</sub> <sup>2-</sup> + 2 H <sup>+</sup> = H <sub>2</sub> TeO <sub>3</sub>		15.94	25					
			values at other <i>T</i>					

Reaction	$K$	$\log K^a$	$T / ^\circ\text{C}$	I electrolyte	Te concentration <sup>b</sup> <i>pH range</i>	Technique	Reference	Comments
$\text{Te}^{4+} + \text{OH}^- = \text{Te}(\text{OH})^{3+}$ $\text{Te}^{4+} + 2 \text{OH}^- = \text{Te}(\text{OH})_2^{2+}$ $\text{Te}^{4+} + 3 \text{OH}^- = \text{Te}(\text{OH})_3^+$ $\text{Te}^{4+} + 4 \text{OH}^- = \text{Te}(\text{OH})_4$	$0.909 \times 10^{-12}$ $0.336 \times 10^{-24}$ $0.683 \times 10^{-35}$ $0.709 \times 10^{-46}$	11.96 23.53 34.83 45.85	28	0.1 M $\text{KNO}_3$  Values also at 0.3, 0.5, 0.7 and 1.0 M	0 to 4?	Spectrophotometry with competing ligand	Nazarenko et al. 1977	
$\text{HTeO}_3^- = \text{TeO}_3^{2-} + \text{H}^+$ $\text{H}_2\text{TeO}_3 = \text{HTeO}_3^- + \text{H}^+$ $\text{H}_3\text{TeO}_3^+ = \text{H}_2\text{TeO}_3 + \text{H}^+$		$-9.56 \pm 0.02$ $-6.08 \pm 0.06$ $-2.8 \pm 0.2$	20	0		Potentiometry + MINIQUAD (pK1) and solubility (the other two)	Masson 1976	$\text{TeO}_2$ Koch-Light electronic grade, 99.998% pure, no further characterization  Table with most previous values; comments on many studies  Solubility values found dependent on equilibration time; different values when starting with $\text{TeO}_2(\text{s})$ or $\text{H}_2\text{TeO}_3(\text{s})$
$\text{Te}^{4+} + 2 \text{OH}^- = \text{Te}(\text{OH})_2^{2+}$ $\text{Te}(\text{OH})_2^{2+} + \text{OH}^- = \text{Te}(\text{OH})_3^+$ $\text{Te}(\text{OH})_3^+ + \text{OH}^- = \text{Te}(\text{OH})_4$	$6.3 \times 10^{28}$ $1.0 \times 10^{14}$ $1.7 \times 10^{12}$	28.8 14.0 12.2	20	2.5 M $\text{HClO}_4$ 1.0 M $\text{HClO}_4$ 0.5 M $\text{NaClO}_4$	$2.5 \times 10^{-4}$ –0.1 M	Comparative electro dialysis + Bjerrum method	Nabivanets et al. 1974	Polymerisation when $[\text{Te}(\text{IV})] > 5 \times 10^{-3} \text{ g-atom L}^{-1}$  Masson (1976): $\text{Te}(\text{IV})$ solubility exceeded

Reaction	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	I electrolyte	Te concentration <sup>b</sup> <i>pH</i> range	Technique	Reference	Comments
$\text{H}_2\text{TeO}_3 = \text{HTeO}_3^- + \text{H}^+$  $\text{HTeO}_3^- = \text{TeO}_3^{2-} + \text{H}^+$		-6.92 ± 0.05 -6.50 ± 0.05 -6.56 ± 0.05 -6.36 ± 0.05 -6.18 ± 0.05 -9.43 ± 0.06 -9.36 ± 0.06 -9.00 ± 0.06 -8.60 ± 0.06 -8.48 ± 0.06	20	0 0.1 M NaClO <sub>4</sub> 0.5 1.0 1.5 0 0.1 M NaClO <sub>4</sub> 0.5 1.0 1.5	3–10	Potentiometry with competing ligand+ Bjerrum method	Nazarenko et al. 1973	Masson (1976): Te(IV) solubility exceeded; Bjerrum not applicable
$\text{H}_2\text{TeO}_3 = \text{HTeO}_3^- + \text{H}^+$ $\text{HTeO}_3^- = \text{TeO}_3^{2-} + \text{H}^+$		-6.27 ± 0.02 -8.43 ± 0.02	25	1.5 M NaCl	$2 \times 10^{-2}$ M Na <sub>2</sub> TeO <sub>3</sub> 3.5–10.5	Potentiometry and solubility+ Bjerrum method	Ganelina and Borgoyakov 1971	Masson (1976): Te(IV) solubility exceeded; Bjerrum not applicable
$\text{TeO}(\text{OH})^+ + \text{H}_2\text{O} = \text{TeO}(\text{OH})_2 + \text{H}^+$	$(2.1 \pm 0.7) \times 10^{-2}$	-1.68	18	0.5 M NaClO <sub>4</sub>	0.5–2	Solubility	Nabivanets and Kapantsyan 1968	“Freshly prepared tellurium hydroxide TeO(OH) <sub>2</sub> ” but reactions are between dissolved species
$\text{H}_2\text{TeO}_3 = \text{HTeO}_3^- + \text{H}^+$  $\text{H}_3\text{TeO}_3^+ = \text{H}_2\text{TeO}_3 + \text{H}^+$		-2.46 -3.07 -3.16 -4.17	25	0.1 M NaClO <sub>4</sub> 3.0 M NaClO <sub>4</sub> 0.1 M NaClO <sub>4</sub> 3.0 M NaClO <sub>4</sub>		Solvent extraction	Sekine et al. 1968	These values do not make sense

Reaction	<i>K</i>	<i>logK</i> <sup>a</sup>	<i>T</i> / °C	I electrolyte	Te concentration <sup>b</sup> <i>pH range</i>	Technique	Reference	Comments
Kbasic <i>K</i> <sub>b</sub> '(TeO <sub>2</sub> plus acid) Kacid <i>K</i> <sub>a</sub> ' (TeO <sub>2</sub> plus base)	3.1x10 <sup>-11</sup> 2.51x10 <sup>-6</sup>	-10.5 -5.6	25		0.1-2.5 7-8	Solubility + Rossotti and Rossotti method	Issa and Awad 1954	TeO <sub>2</sub> prepared as in Schuhmann (1925) but not characterised  Paper difficult to interpret: equations never written
TeO <sub>2</sub> (s) + H <sup>+</sup> = TeO(OH) <sup>+</sup>		-2.1	25	Various HClO <sub>4</sub>		This value does not appear in the publication. It corresponds to the log of the mean value of tree ΣTe/[H <sup>+</sup> ] ratios	Schuhmann 1925	TeO <sub>2</sub> not characterised but proved to be anhydrous
TeO <sub>2</sub> (s) + 4 H <sup>+</sup> H <sub>2</sub> TeO <sub>3</sub> (s) + 4 H <sup>+</sup> Te <sup>4+</sup> + 6 OH <sup>-</sup> = TeO <sub>3</sub> <sup>2-</sup> + 3 H <sub>2</sub> O H <sub>2</sub> TeO <sub>3</sub> (s) = Te(O <sub>2</sub> (s) + H <sub>2</sub> O	300 0.021 1.3x10 <sup>-64</sup> 5550 ± 500 cal	2.5 -1.7 -63.9	18	Various HCl		The first two constants correspond to [Te <sup>4+</sup> ]/[H <sup>+</sup> ] <sup>4</sup> ratios	Kasarnowsky 1924	H <sub>2</sub> TeO <sub>3</sub> (s) and TeO <sub>2</sub> (s) have different solubilities
Tellurite + acid Tellurite + base	2.7x10 <sup>-3</sup> 1.8x10 <sup>-6</sup>	-2.6 -7.7			0.0075 M Na <sub>2</sub> TeO <sub>3</sub>	Conductimetry	Blanc 1920	These values quoted as 'recommended values' by Dutton (1966)

<sup>a</sup>Value in italics calculated from original *K* value. If not in italics, *logK* value is as published.

<sup>b</sup>Values in italics are pH.



Table S4. Published Te(VI) acid-base constants.

Reaction <sup>a</sup>	K	logK <sup>a</sup>	T / °C	I electrolyte	Te concentration <i>pH range</i>	Technique	Reference	Comments
$\text{Te(OH)}_6 = \text{TeO(OH)}_5^- + \text{H}^+$ $\text{TeO(OH)}_5^- = \text{TeO}_2(\text{OH})_4^{2-} + \text{H}^+$ $2 \text{Te(OH)}_6 = \text{Te}_2\text{O(OH)}_{11}^- + \text{H}^+$ $\text{Te}_2\text{O(OH)}_{11}^- = \text{Te}_2\text{O}_2(\text{OH})_{10}^{2-} + \text{H}^+$		$-7.166 \pm 0.004$ $-10.090 \pm 0.005$ $-6.222 \pm 0.036$ $-7.050 \pm 0.020$	25	1.0 m NaClO <sub>4</sub>	0.005-0.100 mol kg <sup>-1</sup> <i>5-11</i>	Glass electrode	Marhold et al. 1988	
$\text{Te(OH)}_6 = \text{TeO(OH)}_5^- + \text{H}^+$		$-7.586 \pm 0.008$	25	0.1 M KCl	0.001-0.005 M	Glass electrode SCOGS	Purokoski et al. 1987	
$\text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te(OH)}_6(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + 2 \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})_2^{2-} + 2 \text{H}^+$ $\text{Te(OH)}_6 + 2 \text{H}_2\text{O} = \text{Te(OH)}_6(\text{OH})_2^{2-} + 2 \text{H}^+$ $2 \text{Te(OH)}_6 + 3 \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})_3^{3-} + 3 \text{H}^+$		$-7.28 \pm 0.02$ $-6.31 \pm 0.03$ $-13.45 \pm 0.03$ $-17.74 \pm 0.03$ $-22.93 \pm 0.03$	25 Also values at 35, 40 and 45 and $\Delta H$	1.0 M KCl	Te fixed all along the titrations at 0.020 M	Glass electrode	Kaehler et al. 1975a	Data at 25 are from previous publications but seems to be recalculated here
$\text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te(OH)}_6(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + 2 \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})_2^{2-} + 2 \text{H}^+$		$\Delta H$ in kcal mol <sup>-1</sup> $7.0 \pm 0.2$ $6.2 \pm 0.3$ $13.1 \pm 0.3$	25	1.0 M KCl	0-0.0970 M	calorimetry	Kaehler et al. 1975b	I 1 M in the title and 3 M in the abstract
$\text{H}_6\text{TeO}_6 = \text{H}_5\text{TeO}_6^- + \text{H}^+$ $\text{H}_5\text{TeO}_6^- = \text{H}_4\text{TeO}_6^{2-} + \text{H}^+$	$(3.4 \pm 0.12) \times 10^{-8}$ $(4.6 \pm 0.3) \times 10^{-10}$	$-7.47$ $-9.34$	22	dilute	1-100 mM	Glass electrode	Biryukov and Ganelina 1971	Telluric acid does not polymerise on standing, Na and K tellurites do

Reaction <sup>a</sup>	K	logK <sup>a</sup>	T / °C	I electrolyte	Te concentration <i>pH range</i>	Technique	Reference	Comments
$\text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te(OH)}_6(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + 2 \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})_2^{2-} + 2 \text{H}^+$		-7.31 ± 0.01 -6.24 ± 0.03 -13.28 ± 0.02	25	1 M NaCl	0.005-0.2 M	Glass electrode	Kaehler and Brito 1971	
$\text{Te(OH)}_6 = \text{TeO(OH)}_5^- + \text{H}^+$ $\text{TeO(OH)}_5^- = \text{TeO}_2(\text{OH})_4^{2-} + \text{H}^+$		-7.65 -11.15	25	dilute	0.01 M	Glass electrode	Kawassiadis et al., 1968	No reaction written
$\text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te(OH)}_6(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})^- + \text{H}^+$ $2 \text{Te(OH)}_6 + 2 \text{H}_2\text{O} = \text{Te}_2(\text{OH})_{12}(\text{OH})_2^{2-} + 2 \text{H}^+$		-7.33 ± 0.02 -6.25 ± 0.03 -13.23 ± 0.03	25	1 M NaCl	5-200 mM	Glass electrode	Brito 1966	
$\text{H}_6\text{TeO}_6 = \text{H}_5\text{TeO}_6^- + \text{H}^+$  $\text{H}_5\text{TeO}_6^- = \text{H}_4\text{TeO}_6^{2-} + \text{H}^+$		-8.03 ± 0.02 -7.70 ± 0.1 -7.59 ± 0.01 -7.28 ± 0.02 $\Delta H$ 5.8 ± 0.2 -11.45 ± 0.03 -10.95 ± 0.02 -10.80 ± 0.02 -10.27 ± 0.03 $\Delta H$ 9.4 ± 0.4	5 25 35 61  5 25 35 61	→0	5.22x10 <sup>-3</sup> M	Glass electrode	Ellison et al. 1962	McPhail (1995): concentrations low enough to avoid polymerisation

Reaction <sup>a</sup>	K	logK <sup>a</sup>	T / °C	I electrolyte	Te concentration <i>pH range</i>	Technique	Reference	Comments
$\text{H}_6\text{TeO}_6 = \text{H}_5\text{TeO}_6^- + \text{H}^+$ $\text{H}_5\text{TeO}_6^- = \text{H}_4\text{TeO}_6^{2-} + \text{H}^+$ $\text{H}_4\text{TeO}_6^{2-} = \text{H}_3\text{TeO}_6^{3-} + \text{H}^+$	$2.0 \times 10^{-8}$ $9.2 \times 10^{-12}$ $3 \times 10^{-15}$	$-7.70 \pm 0.01$ $-11.04 \pm 0.05$ $-14.5$	25	$\rightarrow 0$  $> 1 \text{ M KOH}$	highest conc. used 0.03 M (see comment)	Glass electrode  Spectrophotometry	Earley et al. 1959	“Solutions containing more than 0.04 M of $\text{KHTeO}_6$ were observed to form opalescent suspensions on standing”
mononuclear  $2 \text{ HT} = \text{H}^+ + \text{T}_2^-$  $3 \text{ HT} = \text{H}^+ + \text{T}_3^-$		7.611 7.356 7.522 7.116 -6.838 -6.796 -6.409 6.910 6.764 6.168	25	0 M 0.315 M KCl 0.315 M $\text{NaClO}_4$ 1.725 M $\text{NaClO}_4$ 0 M 0.315 M $\text{NaClO}_4$ 1.725 M $\text{NaClO}_4$ 0 M 0.315 M $\text{NaClO}_4$ 1.725 M $\text{NaClO}_4$		Glass electrode	Antikainen and Tevanen 1960	Only mononuclear species are present in solution below 0.01 molar in telluric acid
$2 \text{ HT} = \text{H}^+ + \text{T}_2^-$ $3 \text{ HT} = \text{H}^+ + \text{T}_3^-$	$1.45 \times 10^{-7}$ $1.23 \times 10^{-7}$	-6.84 -6.91	25	Not given, probably 0		Quinhydrone electrode	Antikainen 1957a	No new data. Data from Antikainen (1955) and other previous publications of the author

Reaction <sup>a</sup>	K	logK <sup>a</sup>	T / °C	I electrolyte	Te concentration <i>pH range</i>	Technique	Reference	Comments
Telluric acid ionization		-8.187 -7.975 -7.427 -7.120	0 10 35 45	→0 In KCl	0.01 M	Glass electrode	Antikainen 1957b	Chemical reaction not written  Reason of logK changes with T: polymerisation  They calculate ΔH at each T but the meaning is not clear
Telluric acid ionization		-6.53 -5.80 -5.60 -6.75 -5.90	room <i>T</i>	NaCl NaClO <sub>4</sub> LiNO <sub>3</sub> MgSO <sub>4</sub> mannitol	0.1/5 M	Glass electrode	Antikainen 1956	Chemical reactions not written  Mg and Li tellurates probably precipitated at basic pH values
Orthotelluric acid: HT = H <sup>+</sup> + T <sup>-</sup>  dimer		-7.611  -6.570	25	KCl used  Extrapolated to 0 (Debye-Hückel)	In solutions less than 0.01 M  In 1 M solutions	Quinhydrone electrode	Antikainen 1955	Chemical reactions not written
TeO <sub>4</sub> H <sub>2</sub> + OH <sup>-</sup> = TeO <sub>4</sub> H <sup>-</sup> + H <sub>2</sub> O		7.45	?	2 M Li <sub>2</sub> SO <sub>4</sub>		Potentiometry	Lourijsen- Teyssèdre 1955	
Te(OH) <sub>6</sub> = TeO(OH) <sub>5</sub> <sup>-</sup> + H <sup>+</sup>  pK <sub>2</sub>	1.0x10 <sup>-11</sup> 1.55x10 <sup>-11</sup> 2.36x10 <sup>-11</sup> 3.31x10 <sup>-11</sup> 4.23x10 <sup>-11</sup> 4.7x10 <sup>-11</sup>	-8.00 -7.81 -7.63 -7.48 -7.37 -10.3	12 22 32 42 50 18	?	0.06 M Te(OH) <sub>6</sub>	Conductivity     potentiometry	Fouasson 1948	Effect of temperature on polymerisation

Reaction <sup>a</sup>	K	logK <sup>a</sup>	T / °C	I electrolyte	Te concentration <i>pH range</i>	Technique	Reference	Comments
$\text{Te(OH)}_6 = \text{TeO(OH)}_5^- + \text{H}^+$ $\text{TeO(OH)}_5^- = \text{TeO}_2(\text{OH})_4^{2-} + \text{H}^+$		-7.68 -11.19	18	various	0.04 M telluric acid	Glass electrode	Britton and Robinson 1932	Equation from Baes Mesmer (1972); no equation in paper
$\text{Te(OH)}_6 = \text{TeO(OH)}_5^- + \text{H}^+$ $\text{Te(OH)}_6 = \text{TeO}_2(\text{OH})_4^{2-} + \text{H}^+$		-7.84 ca. -12.5	18	various	0.025 M	Sb electrode	Britton et al. 1931b	Equation from Baes Mesmer (1972); no equation in paper
$\text{Te(OH)}_6 = \text{TeO(OH)}_5^- + \text{H}^+$		-7.35	18	various		W electrode	Britton and Robinson 1931a	Equation from Baes Mesmer (1972); no equation in paper
Tellurate + acid Tellurate + base	$6.8 \times 10^{-7}$ $4.1 \times 10^{-11}$	-6.2 <i>-10.4</i>	?	?		Conductimetry	Blanc 1920	
H <sub>6</sub> TeO <sub>6</sub> deprotonation		8.8	20	?		Hydrogen electrode	Rosenheim and Jander 1918	

<sup>a</sup>Value in italics calculated from original *K* value. If not in italics, log*K* value is as published.

<sup>b</sup>Values in italics are pH.

Table S5. Published tellurium-halogenide stability constants.

Reaction <sup>a</sup>	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	<i>I</i> electrolyte	Technique	Reference
Fluoride						
$\text{TeF}_4\text{OH}^- + \text{HF} = \text{TeF}_5^- + \text{H}_2\text{O}$	$2.5 \times 10^3$ <sup>b</sup>	2.4	22	HF aqueous	IR and Raman spectroscopy	Milne and Moffett 1974
Chloride						
$\text{TeCl}_6^{2-} = \text{TeCl}_4(\text{OH})^- + \text{HCl} + \text{Cl}^-$	$(3.78 \pm 0.01) \times 10^4$	4.58	25	6.5–10 M HCl	Spectrophotometry	Milne 1991
	$(2.21 \pm 0.16) \times 10^4$	4.34		3–10 M HCl	Raman	
	$(1.92 \pm 0.07) \times 10^4$	4.28		7 M HCl	<sup>125</sup> Te NMR	
$\text{TeCl}_4(\text{OH})^- = \text{TeCl}_2(\text{OH})_2 + \text{HCl} + \text{Cl}^-$	$442 \pm 57$	2.64				
	$450 \pm 24$	2.66		6.5–10 M HCl	Spectrophotometry	
$\text{TeO}(\text{OH})\text{Cl} + \text{H}_2\text{O} = \text{TeO}(\text{OH})_2 + \text{H}^+ + \text{Cl}^-$	$(6.4 \pm 0.9) \times 10^{-3}$	-2.2	18	0.50 M NaClO <sub>4</sub>	Solubility	Nabivanets and Kapantsyan 1968
$\text{TeOCl}_2 = \text{TeO}(\text{OH})\text{Cl} + \text{Cl}^- + \text{H}^+$	0.5	-0.3				
$\text{TeOCl}_3^- = \text{TeOCl}_2 + \text{Cl}^-$	3.0	0.48				
$\text{TeOCl}_4^{2-} = \text{TeOCl}_3^- + \text{Cl}^-$	3.7	0.57				
$\text{TeCl}_5(\text{H}_2\text{O})^- + \text{Cl}^- = \text{TeCl}_6^{2-} + \text{H}_2\text{O}$	$(6.4 \pm 0.7) \times 10^{-3}$	-2.2		5–10 M HCl	Spectrophotometry	Shikheeva 1968
$\text{TeCl}_4(\text{H}_2\text{O})_2 + \text{Cl}^- = \text{TeCl}_5(\text{H}_2\text{O})^-$	$(1.48 \pm 0.08) \times 10^{-2}$	-1.83				
$\text{TeO}(\text{OH})\text{Cl}_3^{2-} + \text{Cl}^- + \text{H}^+ = \text{TeOCl}_4^{2-} + \text{H}_2\text{O}$	$(4.8 \pm 0.8) \times 10^{-4}$	-3.3				
$\text{TeOCl}_4^{2-} + 2 \text{H}^+ + \text{H}_2\text{O} = \text{TeCl}_4(\text{H}_2\text{O})_2$	$(6.3 \pm 1.3) \times 10^{-3}$	-2.2				

Reaction <sup>a</sup>	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	<i>I</i> electrolyte	Technique	Reference
$\text{Te}^{4+} + \text{Cl}^- = \text{TeCl}^{3+}$ $\text{Te}^{4+} + 2\text{Cl}^- = \text{TeCl}_2^{2+}$ $\text{Te}^{4+} + 3\text{Cl}^- = \text{TeCl}_3^+$ $\text{Te}^{4+} + 4\text{Cl}^- = \text{TeCl}_4$ $\text{Te}^{4+} + 5\text{Cl}^- = \text{TeCl}_5^-$ $\text{Te}^{4+} + 6\text{Cl}^- = \text{TeCl}_6^{2-}$	1.75x10 <sup>3</sup> 1.02x10 <sup>6</sup> 2.19x10 <sup>8</sup> 1.53x10 <sup>10</sup> 5.75x10 <sup>12</sup> 1.99x10 <sup>15</sup>	3.24 6.01 8.34 10.2 12.8 15.3	25	7.0 M (HCl + LiCl, HCl + HClO <sub>4</sub> )	Solvent extraction	Shitareva and Nazarenko 1968
$\text{H}_2\text{TeCl}_6 = \text{H}_2\text{TeCl}_4^{2+} + 2 \text{Cl}^-$	(2.9 ± 0.1)x10 <sup>-2</sup> (5.5 ± 0.2)x10 <sup>-1</sup>	1.54 0.26	?	8.0 M HClO <sub>4</sub> 6.0 M HClO <sub>4</sub>	Spectrophotometry	Ripan and Marc 1966
Bromide						
$\text{TeBr}_6^{2-} = \text{Te}^{4+} + 6 \text{Br}^-$	1.38x10 <sup>-11</sup>	-10.9		H <sub>2</sub> SO <sub>4</sub> variable (7 M ?); no I control	Spectrophotometry	Bakunina and Murashova 1970
$\text{Te}^{4+} + \text{Br}^- = \text{TeBr}^{3+}$ $\text{Te}^{4+} + 2\text{Br}^- = \text{TeBr}_2^{2+}$ $\text{Te}^{4+} + 3\text{Br}^- = \text{TeBr}_3^+$ $\text{Te}^{4+} + 4\text{Br}^- = \text{TeBr}_4$ $\text{Te}^{4+} + 5\text{Br}^- = \text{TeBr}_5^-$ $\text{Te}^{4+} + 6\text{Br}^- = \text{TeBr}_6^{2-}$	9.4 38. 90.8 141.4 160.5 134.3	0.97 1.58 1.96 2.15 2.21 2.13	25	3.0 M NaClO <sub>4</sub>	Solvent extraction	Shitareva and Nazarenko 1967
$\text{H}_2\text{TeBr}_6 = \text{H}_2\text{TeBr}_4^{2+} + 2 \text{Br}^-$	(2.8 ± 0.2)x10 <sup>-4</sup> (2.8 ± 0.2)x10 <sup>-2</sup>	3.6 1.6		6.0 M HClO <sub>4</sub> 4.0M HClO <sub>4</sub>	Spectrophotometry	Ripan and Marc 1966

Reaction <sup>a</sup>	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	<i>I</i> electrolyte	Technique	Reference
Iodide						
$\text{TeI}_6^{2-} = \text{Te}^{4+} + 6 \text{I}^-$	4.49x10 <sup>-8</sup>	-7.35		1 M HCl	Spectrophotometry	Murashova 1966

<sup>a</sup>Value in italics calculated from original *K* value. If not in italics, log*K* value is as published.

<sup>b</sup>IUPAC quotes -0.4 which is the log of 2.5 but units in the article are mL<sup>-1</sup>. Thus, this constant is 2.5x10<sup>3</sup>.



Table S6. Published tellurium- inorganic ligands (other than halides) equilibrium constants

Te	Reaction <sup>a</sup>	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	<i>I</i> electrolyte	Te concentration <i>pH</i>	Technique	Reference
	Nitrate							
Te(IV)	$\text{Te}^{4+} + \text{NO}_3^- = \text{TeNO}_3^{3+}$ $\text{TeNO}_3^{3+} + \text{NO}_3^- = \text{Te}(\text{NO}_3)_2^{2+}$ $\text{Te}(\text{NO}_3)_2^{2+} + \text{NO}_3^- = \text{Te}(\text{NO}_3)_3^+$ $\text{Te}(\text{NO}_3)_3^+ + \text{NO}_3^- = \text{Te}(\text{NO}_3)_4$ $\text{Te}(\text{NO}_3)_4 + \text{NO}_3^- = \text{Te}(\text{NO}_3)_5^-$ $\text{Te}(\text{NO}_3)_5^- + \text{NO}_3^- = \text{Te}(\text{NO}_3)_6^{2-}$	0.52 0.35 0.29 0.27 0.23 0.15	-0.28 -0.46 -0.54 -0.58 -0.64 -0.82	20	3.00 M HClO <sub>4</sub> + HNO <sub>3</sub>	2x10 <sup>-4</sup> M	Ionic exchange Bjerrum method	Oganesian et al 1982
	Sulfate							
Te(IV)	$\text{Te}^{4+} + \text{SO}_4^{2-} = \text{TeSO}_4^{2+}$ $\text{TeSO}_4^{2+} + \text{SO}_4^{2-} = \text{Te}(\text{SO}_4)_2$ $\text{Te}(\text{SO}_4)_2 + \text{SO}_4^{2-} = \text{Te}(\text{SO}_4)_3^{2-}$	6.5x10 <sup>2</sup> 3.6x10 <sup>2</sup> 2.0x10 <sup>2</sup>	2.8 2.6 2.3	22	3.00 M HClO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub>	2x10 <sup>-4</sup> M	Ionic exchange Bjerrum method	Nabivanets et al 1980
	Molybdate							
Te(VI)	$6 \text{H}^+ + 6 \text{MoO}_4^{2-} + \text{Te}(\text{OH})_6 = \text{H}_6(\text{MoO}_4)_6[\text{Te}(\text{OH})_6]$ $7 \text{H}^+ + 6 \text{MoO}_4^{2-} + \text{Te}(\text{OH})_6 = \text{H}_7(\text{MoO}_4)_6[\text{Te}(\text{OH})_6]$ $8 \text{H}^+ + 6 \text{MoO}_4^{2-} + \text{Te}(\text{OH})_6 = \text{H}_8(\text{MoO}_4)_6[\text{Te}(\text{OH})_6]$	50.40 ± 0.02 53.68 ± 0.07 55.47 ± 0.07		25	1.0 M NaCl	4.5–17.2 mM 2.0–7.2	Glass potentiometry	Yagasaki and Sasaki 1987

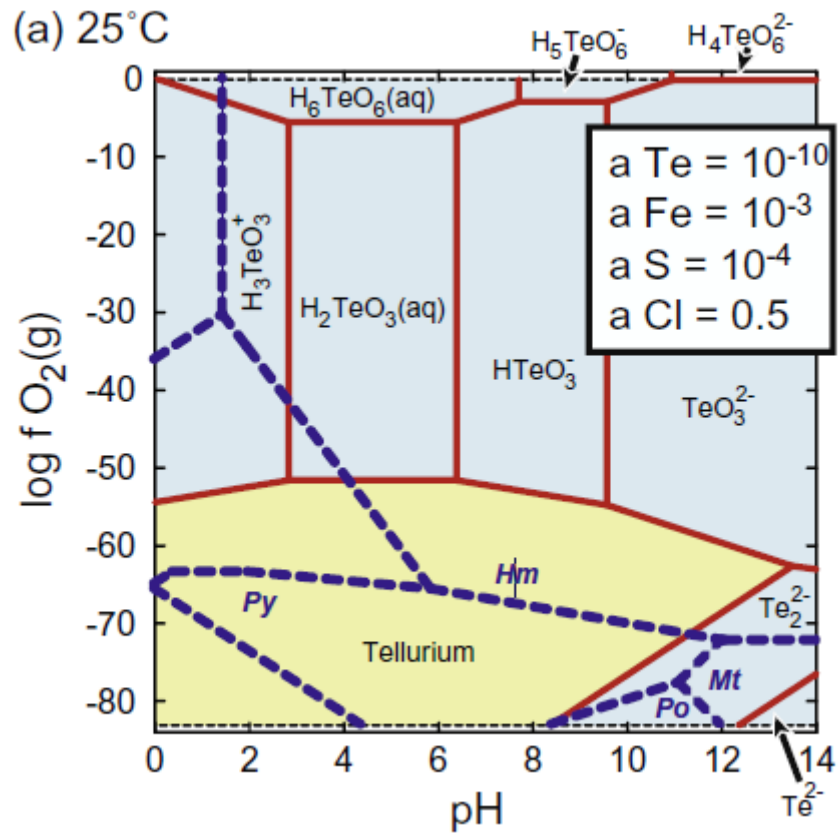
Te	Reaction <sup>a</sup>	<i>K</i>	log <i>K</i> <sup>a</sup>	<i>T</i> / °C	<i>I</i> electrolyte	Te concentration <i>pH</i>	Technique	Reference
	Tungstate							
Te(VI)	$\text{H}_2[\text{TeO}_2(\text{OH})_4] + 4 \text{H}_2\text{WO}_4 = \text{H}_6\text{TeO}_6 \cdot 4(\text{H}_3\text{WO})$	$(2.9 \pm 1.3) \times 10^{18}$	18.5		Probably, no inert electrolyte, <i>I</i> not constant	$1.68 \times 10^{-4}$ M 1.5–6.5	Spectrophotometry	Ganelina and Bubnova 1973
	Peroxide							
Te(VI)	$\text{H}_5\text{TeO}_6^- + \text{H}_2\text{O}_2 = \text{H}_6\text{TeO}_7^- + \text{H}_2\text{O}$	$0.08 \pm 0.02$	<i>-0.17</i>	25	0.10 M KCl		Glass potentiometry	Earley et al. 1959
Te(IV)	K1		4.50	18		<i>Alkaline medium</i>	Spectrophotometry; Te electrode	Greiver and Zaitsev 1972
	K2		8.21					
	K3		7.11					
	K4		3.97					
	K5		2.55					
	K6		2.00					
Te(VI)	K1		7.39					
	K2		11.45					
	K3		5.04					
	K4		4.35					
	K5		2.90					
	K6		2.49					
	Reactions not given, unclear							

<sup>a</sup>Value in italics calculated from original *K* value. If not in italics, log*K* value is as published.

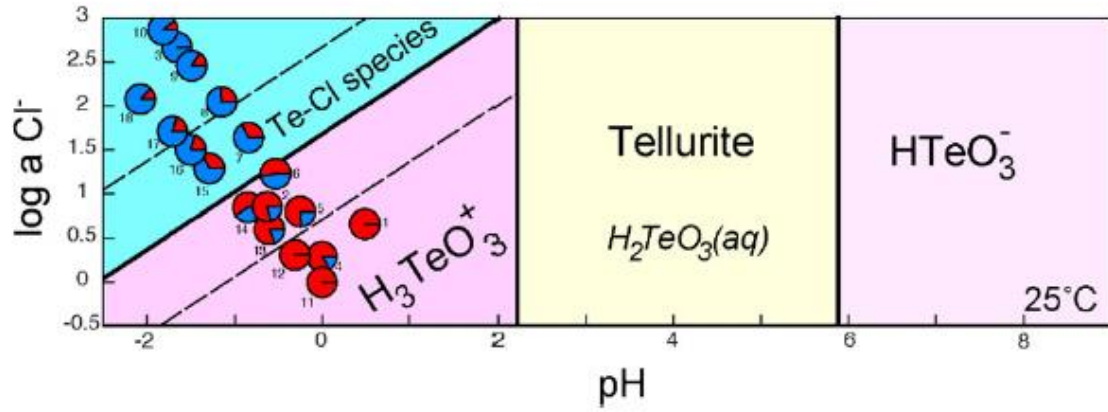
<sup>b</sup>Values in italics are pH

Figure S1 Published tellurium Eh-pH diagrams. Texts in italics copied from original captions.

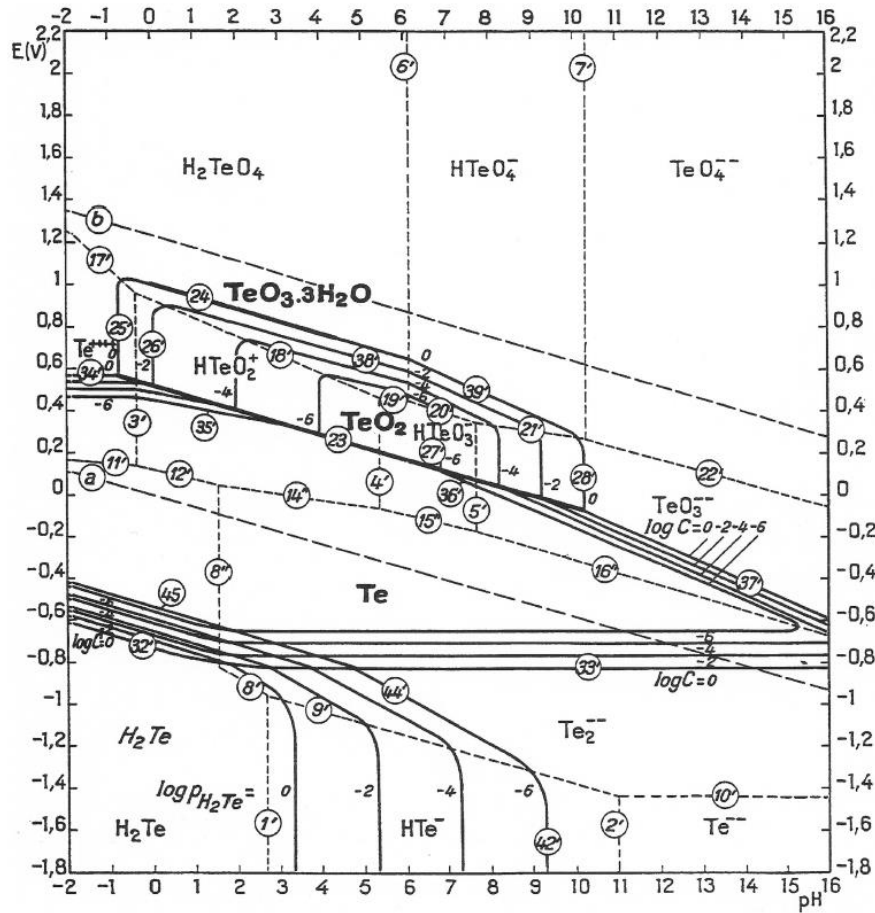
Grundler et al. (2013). Reproduced with permission from Elsevier.



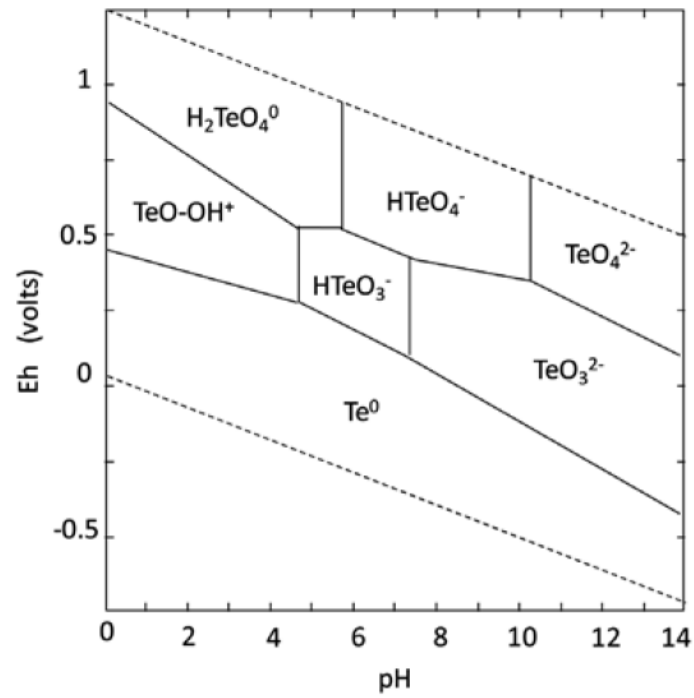
Etschmann et al. (2016): Solubility contour of tellurite ( $10^{-4}$  m) and predominant Te(IV) complexes as a function of activity of chloride ion and pH. The solubility contours and predominance fields for aqueous Te(IV) species were calculated from thermodynamic data from Grundler et al. (2013). Reproduced with permission from Elsevier.



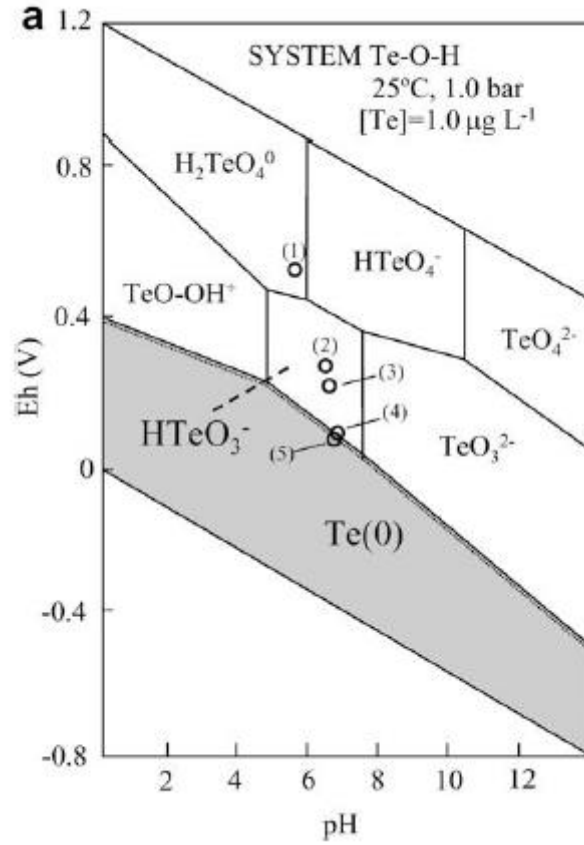
Bouroushian (2010): *Potential–pH equilibrium diagram for the system tellurium–water, at 25 °C. Reproduced from Pourbaix M (1974) Atlas of electrochemical equilibria in aqueous solutions. National association of corrosion engineers (2nd English Edn.) USA. Reproduced with permission from NACE International.*



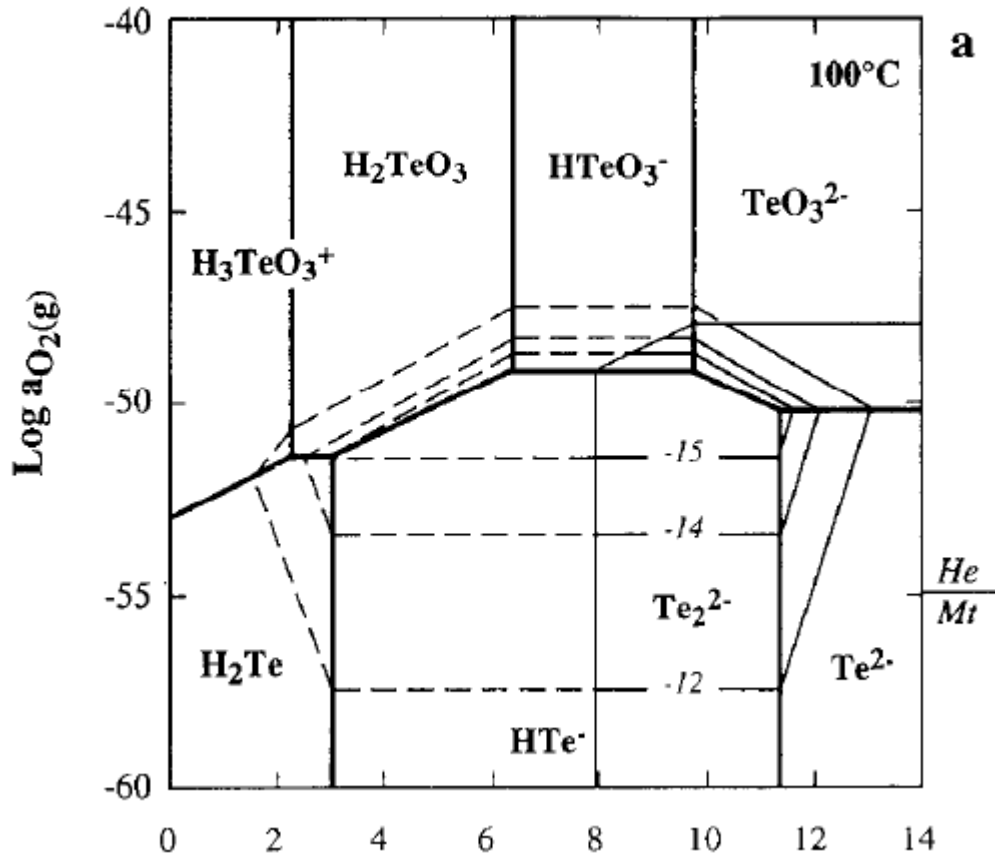
Lombi and Holm (2010): Te concentration not give. *Adapted from Harada and Takahashi. (2008).* Reproduced with permission from Elsevier.



Harada et al. (2008): Diagram at 25 C and 1.0 bar calculated based on the constants summarized Brookins (1988). The total dissolved concentration of Te used for the calculations was  $1.0 \mu\text{g L}^{-1}$ . The circles correspond to the conditions in our experimental systems for  $W_s = 60\%$ . Reproduced with permission from Elsevier.

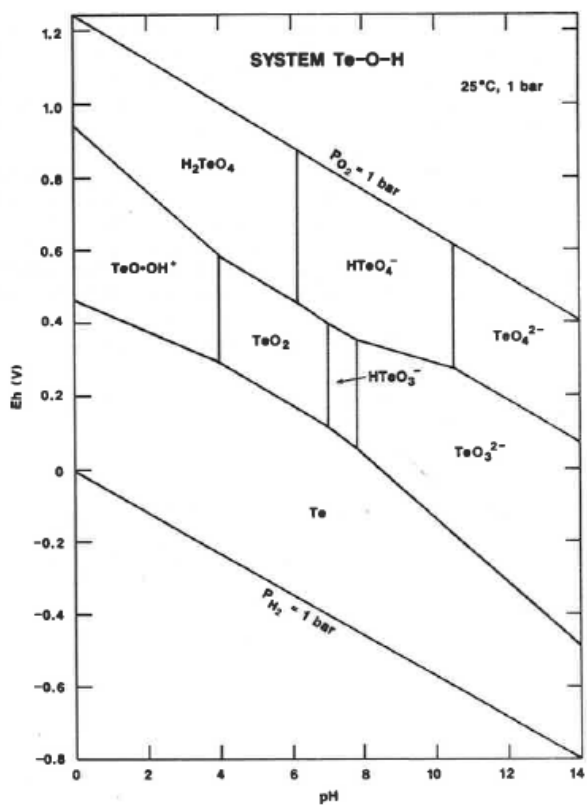


McPhail (1995): *Predominance area diagrams for aqueous Te species at 100 °C. The area for  $\text{Te}_2^{2-}$  is contoured for constant log activity of all Te species (labelled). Dashed portions of the contours are metastable with respect to native Te and solid portions are stable. The thin lines bounding the lower left hand corners of the figures represent the maximum stability limits of Te in equilibrium with native Te.* Reproduced with permission from Elsevier.





Brookins (1987): *The activity of dissolved Te = 10<sup>-6</sup> M*. Reproduced with permission from Springer.



D'yachkova and Khodakovskiy (1968): *Eh-pH* at  $\Sigma S = 10^{-1} M$  and  $\Sigma Te = 10^{-7} M$ .  
 Temperature  $25^{\circ}C$ ,  $P = 1 atm$ .

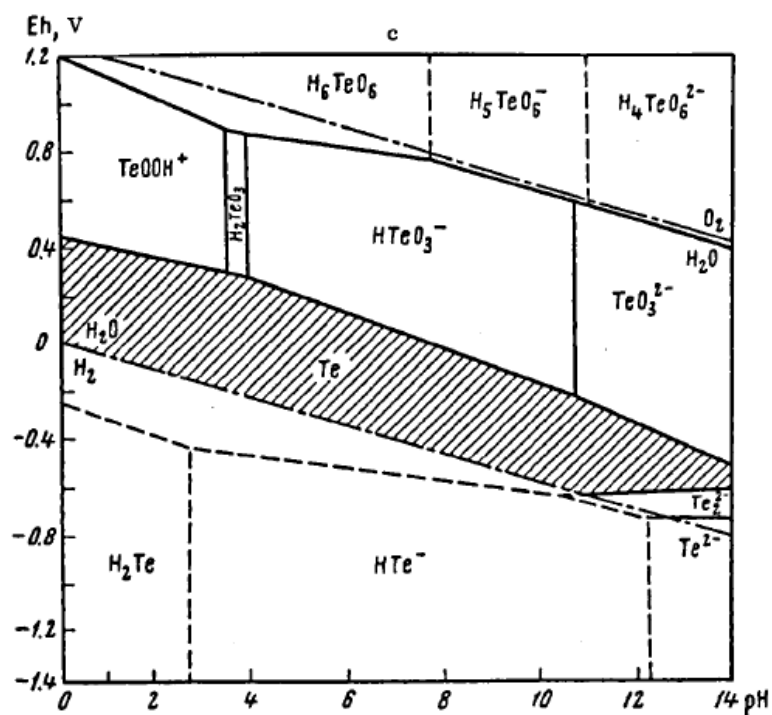


Fig. 2c

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