Bureau International des Poids et Mesures

Guide to the Realization of the ITS-90

Fixed Points: Influence of Impurities

APPENDIX 3: *Data on precipitation*

Consultative Committee for Thermometry
under the auspices of the
International Committee for Weights and Measures

APPENDIX 3

Data on precipitation

Tables A3.1 and A3.2 are taken from [Fahr and Rudtsch 2009]. They provide a ranking concerning the precipitation of undissolved oxides. The ranking is based on maximum estimates max(ln(a_i)) for the natural logarithm of the (chemical) activity a_i of the atoms of impurity *i* in the liquid hosts (fixed-point substances of the ITS-90) if the pure oxides listed in the first column precipitate. These estimates have been deduced in [Fahr and Rudtsch 2009] from fundamental thermodynamic relations making several key assumptions. In ideal solutions, the activity is equal to the concentration c_1^i. But in reality, a_i may strongly deviate from c_1^i. The ranking should be applied with caution because, among other reasons, it is not conclusive due to the key assumptions and the lack of reliable thermodynamic data for many systems. For Ag, Au, and Cu, the calculations have been performed for the O_2 partial pressures of 10^{-1} Pa and 10^{-7} Pa, respectively, as examples since the partial pressure of oxygen in the gas phase is not known in general.

The colours of the numbers in the tables indicate the classification in [Fahr and Rudtsch 2009]:

- **Red colour**: max(ln(a_i)) ≤ –30, i.e. $a_i < 10^{-13}$: The impurity has a very high affinity for oxygen and will not be found dissolved in relevant amounts in the fixed-point metal.
- **Blue colour**: max(ln(a_i)) ≥ 0: This (rather noble) impurity is unlikely to build oxide in the fixed-point cell, hence its solubility is not restricted by the formation of oxides, i.e. the small amount of impurity contained in the cell will (probably) be dissolved in the metal. (ln(c_1^i) values larger than zero are not possible of course.)
- **Black colour**: –30 < max(ln(a_i)) < 0: Due to the uncertainties and assumptions of the calculations and the unknown activity factor (ratio of activity to concentration) of the dissolved impurity, the values in the table are only a rough indication of what the behaviour of the impurity might be.

If the activity would be equal to the concentration c_1^i, the values in the tables would indicate the following concentrations:

- ln(c_1^i) < –14: The equilibrium concentration of dissolved impurity in the metal is < 1 ppm.
- ln(c_1^i) < –21: The equilibrium concentration of dissolved impurity in the metal is < 1 ppb.
- ln(c_1^i) < –60: The equilibrium concentration of dissolved impurity in the metal is < 0.01 atoms/mol, thus not even one atom statistically stays in solution in the metal (a customary fixed-point cell contains about 250 ml of metal, corresponding to up to 20 mol).

References

Fahr M, Rudtsch S 2009 *Metrologia* **46** 423-438

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Table A3.1: Maximum estimates max(ln(a_i)) for the natural logarithm of the (chemical) activity a_i of the atoms of impurity i in the liquid metallic fixed-point materials of the ITS-90. The possible oxides of the impurities are listed in the first column. Gaseous oxides are marked by "(g)". T_{90} is the fixed-point temperature.

	Fixed-point material											
	Hg	Ga	In	Sn	Zn	Al	Ag	Ag	Au	Au	Cu	Cu
T_{90} / K	234	303	430	505	693	933	1235	1235	1337	1337	1358	1358
Oxygen donor	HgO	Ga_2O_3	In_2O_3	SnO_2	ZnO	Al_2O_3	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa
H_2O (g)	–46.7	19.1	6.6	3.9	9.4	21.1	–0.6	2.8	0.4	3.9	0.6	4.1
Li_2O	–129.3	–45.3	–39.5	–35.6	–20.1	–1.4	–18.3	–14.8	–16.0	–12.6	–15.6	–12.2
BeO	–267.4	–98.2	–85.2	–77.0	–45.2	–7.3	–40.6	–33.7	–36.1	–29.2	–35.3	–28.3
B_2O_3	–260.5	–38.9	–51.9	–51.2	–21.4	23.0	–35.7	–25.3	–30.9	–20.6	–30.1	–19.7
CO (g)	–33.9	77.3	31.9	19.2	18.8	34.4	–14.6	–7.7	–13.8	–6.9	–13.6	–6.7
CO_2 (g)	–135.1	107.3	36.7	18.5	28.9	67.8	–24.9	–11.0	–21.9	–8.1	–21.4	–7.6
Na_2O	–81.7	–8.4	–13.4	–13.3	–3.8	10.8	–8.9	–5.4	–7.3	–3.9	–7.1	–3.6
MgO	–262.2	–93.9	–81.8	–73.9	–42.7	–5.1	–38.7	–31.8	–34.2	–27.3	–33.4	–26.5
Al_2O_3	–360.8	–115.9	–105.3	–96.2	–53.5	0.0	–52.4	–42.0	–46.1	–35.8	–45.0	–34.6
SiO_2	–378.3	–75.8	–85.8	–82.3	–38.6	23.4	–52.9	–39.1	–46.1	–32.3	–44.9	–31.1
PO (g)	9.5	111.1	56.1	40.0	34.3	46.2	–5.4	1.5	–5.2	1.7	–5.1	1.8
PO_2 (g)	–77.2	152.1	68.1	45.3	48.2	82.0	–14.1	–0.3	–12.1	1.8	–11.7	2.1
SO_2 (g)	–86.5	144.7	62.8	40.6	44.7	79.3	–16.4	–2.6	–14.2	–0.4	–13.8	0.0
SO_3 (g)	–92.3	248.7	120.0	84.7	87.6	137.2	–7.8	12.9	–4.9	15.9	–4.3	16.4
K_2O	–69.2	1.0	–7.0	–8.0	–0.1	13.3	–7.3	–3.8	–5.9	–2.5	–5.7	–2.2
K_2O_2	–79.2	47.8	18.4	11.5	19.9	41.6	–3.2	3.7	–1.3	5.6	–1.0	5.9
KO_2	–60.6	169.2	85.8	63.2	66.5	100.5	4.5	18.3	6.6	20.4	7.0	20.8
CaO	–279.6	–107.4	–91.4	–82.1	–48.7	–9.6	–42.2	–35.3	–37.4	–30.5	–36.6	–29.7
Sc_2O_3	–421.5	–163.0	–138.7	–124.8	–74.5	–15.8	–64.6	–54.2	–57.4	–47.1	–56.1	–45.8
TiO	–223.2	–64.4	–61.9	–57.4	–31.4	2.5	–33.7	–26.8	–29.8	–22.9	–29.1	–22.2
Ti_2O_3	–322.5	–86.6	–85.0	–79.2	–41.4	8.6	–46.2	–35.9	–40.6	–30.2	–39.5	–29.2
Ti_3O_5	–345.8	–86.5	–87.7	–82.3	–42.0	12.4	–49.3	–37.7	–43.1	–31.6	–42.0	–30.5
VO	–176.9	–28.4	–36.1	–35.4	–15.1	14.9	–24.0	–17.1	–20.8	–13.9	–20.2	–13.3
V_2O_3	–246.3	–28.0	–44.1	–44.6	–16.6	26.7	–32.9	–22.6	–28.4	–18.0	–27.5	–17.2
V_2O_5	–287.5	48.5	–6.6	–17.4	13.8	75.1	–31.8	–14.5	–26.0	–8.7	–25.0	–7.7
V_3O_5	–257.2	–18.4	–40.2	–42.1	–13.1	33.5	–33.7	–22.2	–28.9	–17.4	–28.1	–16.5
Cr_2O_3	–225.6	–11.9	–32.6	–34.8	–9.3	32.2	–28.7	–18.3	–24.4	–14.0	–23.6	–13.3
MnO	–155.1	–12.0	–25.2	–26.4	–9.1	18.8	–21.6	–14.7	–18.7	–11.8	–18.2	–11.3
MnO_2	–177.6	79.6	23.8	10.9	29.4	73.9	–14.7	–0.9	–10.8	3.0	–10.1	3.7
Mn_2O_3	–180.0	23.2	–8.1	–14.0	5.6	43.0	–20.6	–10.3	–17.0	–6.7	–16.4	–6.0
Mn_3O_4	–178.6	6.3	–17.3	–21.0	–1.2	33.7	–21.8	–12.6	–18.3	–9.1	–17.7	–8.5
Fe_2O_3	–144.6	50.8	11.6	2.9	18.1	52.5	–13.2	–2.9	–10.2	0.2	–9.6	0.8
Fe_3O_4	–132.7	41.8	7.6	0.2	14.2	45.0	–13.2	–4.0	–10.5	–1.2	–9.9	–0.7
CoO	–78.9	47.1	16.6	9.2	17.0	38.3	–6.7	0.2	–4.9	2.0	–4.6	2.3

Table A3.1: (Continued)

	Fixed-point material											
	Hg	Ga	In	Sn	Zn	Al	Ag	Ag	Au	Au	Cu	Cu
T_{90} / K	234	303	430	505	693	933	1235	1235	1337	1337	1358	1358
Oxygen donor	HgO	Ga_2O_3	In_2O_3	SnO_2	ZnO	Al_2O_3	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa
Co_3O_4	–91.7	74.0	30.9	20.3	29.4	56.9	–3.8	5.4	–1.5	7.7	–1.1	8.1
NiO	–77.1	48.7	17.9	10.4	18.1	39.3	–5.8	1.1	–4.0	2.9	–3.7	3.2
CuO	–35.9	80.7	40.8	30.1	32.7	50.3	2.8	9.7	4.0	10.9	4.2	11.1
Cu_2O	–21.9	37.1	17.8	12.6	14.3	23.4	–0.2	3.3	0.4	3.9	0.6	4.0
ZnO	–134.2	4.9	–12.4	–15.1	0.0	26.3	–15.1	–8.2	–12.5	–5.6	–12.1	–5.1
Ga_2O_3	–210.8	0.0	–23.7	–26.9	–3.1	37.2	–24.4	–14.0	–20.3	–9.9	–19.6	–9.2
GeO	–90.8	38.0	10.3	4.0	13.4	35.7	–8.5	–1.6	–6.6	0.3	–6.2	0.7
GeO_2	–206.9	57.2	8.5	–1.9	20.5	67.7	–19.0	–5.2	–14.7	–0.9	–13.9	–0.1
As_2O_5	–124.7	175.0	83.2	59.4	70.4	117.7	1.0	18.2	4.4	21.7	5.0	22.3
SeO_2 (g)	–15.8	201.6	105.7	78.6	75.1	104.3	4.9	18.7	6.2	20.0	6.5	20.3
SeO (g)	23.2	123.6	67.3	50.8	44.4	55.9	4.0	10.9	4.1	11.0	4.1	11.0
RbO_2	–238.9	35.5	–2.8	–9.4	18.7	69.9	–14.1	–0.2	–9.1	4.7	–8.2	5.7
SrO	–257.9	–90.7	–79.7	–72.3	–41.6	–4.5	–38.3	–31.4	–33.9	–27.0	–33.1	–26.2
Y_2O_3	–420.7	–162.5	–138.4	–124.5	–74.4	–15.8	–64.5	–54.2	–57.4	–47.1	–56.1	–45.8
ZrO_2	–474.5	–149.8	–137.6	–126.2	–70.3	0.3	–70.1	–56.3	–61.9	–48.0	–60.4	–46.6
NbO	–163.8	–18.3	–29.1	–29.4	–10.8	18.0	–21.7	–14.8	–18.7	–11.7	–18.1	–11.2
NbO_2	–319.0	–29.8	–53.2	–54.5	–18.2	38.7	–41.2	–27.4	–35.3	–21.5	–34.2	–20.4
Nb_2O_5	–376.6	–20.3	–54.9	–58.4	–16.0	53.1	–48.3	–31.0	–41.2	–23.9	–39.9	–22.6
MoO_2	–212.5	52.6	4.9	–5.1	17.9	65.5	–21.0	–7.2	–16.6	–2.8	–15.8	–2.0
MoO_3	–250.6	131.1	43.3	22.6	48.1	113.3	–20.7	0.0	–15.2	5.6	–14.2	6.6
RuO_2	–68.1	163.6	82.1	60.2	64.5	99.3	3.7	17.6	6.0	19.8	6.4	20.2
RuO_4	46.7	467.9	262.5	203.4	188.7	242.0	39.5	67.1	41.3	68.9	41.6	69.2
RhO_2	–37.4	182.5	89.0	62.8	60.6	90.8	–8.0	5.8	–6.5	7.3	–6.2	7.6
Rh_2O_3	–30.0	139.4	73.9	55.9	56.7	81.1	8.3	18.6	9.7	20.0	9.9	20.3
PdO	–12.0	99.3	53.9	41.3	40.9	56.5	7.5	14.4	8.4	15.3	8.5	15.4
Ag_2O	12.8	63.8	36.4	28.4	25.7	31.7	5.9	9.4	6.1	9.5	6.1	9.5
Ag_2O_2	37.8	137.5	80.6	63.8	57.1	68.3	16.2	23.1	16.2	23.2	16.3	23.2
Ag_2O_3	76.7	222.3	132.7	106.1	93.7	108.9	29.6	40.0	29.5	39.9	29.5	39.8
CdO	–87.1	41.3	13.2	6.7	15.9	38.1	–6.3	0.6	–4.4	2.6	–4.0	2.9
In_2O_3	–168.0	33.3	0.0	–6.6	12.0	48.7	–15.5	–5.2	–12.1	–1.7	–11.4	–1.1
SnO	–98.9	32.1	6.6	1.1	11.7	34.9	–8.8	–1.9	–6.7	0.2	–6.3	0.6
SnO_2	–204.4	59.5	10.4	0.0	22.2	69.3	–17.5	–3.7	–13.2	0.6	–12.4	1.4
Sb_2O_5	–136.6	165.7	76.8	53.9	66.4	114.7	–1.2	16.0	2.4	19.7	3.0	20.3
TeO_2	–77.3	156.9	78.0	56.9	62.6	98.3	3.5	17.3	5.9	19.7	6.3	20.2
BaO	–236.5	–74.5	–68.6	–63.0	–35.2	0.0	–35.3	–28.4	–31.2	–24.3	–30.5	–23.5

Table A3.1: (Continued)

	Fixed-point material											
	Hg	Ga	In	Sn	Zn	Al	Ag	Ag	Au	Au	Cu	Cu
T_{90} / K	234	303	430	505	693	933	1235	1235	1337	1337	1358	1358
Oxygen donor	HgO	Ga_2O_3	In_2O_3	SnO_2	ZnO	Al_2O_3	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa	O_2 at 10^{-1}Pa	O_2 at 10^{-7}Pa
La_2O_3	–392.3	–140.5	–123.0	–111.4	–64.9	–8.8	–59.3	–48.9	–52.6	–42.2	–51.4	–41.0
CeO_2	–465.8	–142.6	–131.7	–120.8	–65.6	4.4	–66.4	–52.6	–58.3	–44.4	–56.8	–43.0
Ce_2O_3	–392.5	–140.6	–122.9	–111.3	–64.7	–8.5	–59.0	–48.6	–52.3	–41.9	–51.1	–40.7
Nd_2O_3	–396.1	–143.4	–125.1	–113.2	–66.2	–9.8	–60.1	–49.7	–53.4	–43.0	–52.1	–41.8
Sm_2O_3	–399.7	–146.2	–127.0	–114.8	–67.3	–10.5	–60.6	–50.3	–53.8	–43.5	–52.6	–42.2
Eu_2O_3	–354.4	–110.9	–101.6	–93.1	–51.1	1.8	–51.0	–40.6	–44.8	–34.5	–43.7	–33.3
Eu_3O_4	–326.4	–107.2	–96.3	–87.7	–48.9	–0.8	–47.0	–37.7	–41.3	–32.1	–40.3	–31.1
Dy_2O_3	–409.2	–153.4	–131.8	–118.8	–70.0	–12.3	–61.8	–51.4	–54.8	–44.5	–53.6	–43.2
Ho_2O_3	–414.3	–157.4	–134.8	–121.4	–72.1	–14.0	–63.2	–52.8	–56.2	–45.8	–54.9	–44.5
Er_2O_3	–418.8	–160.9	–137.3	–123.6	–73.7	–15.2	–64.1	–53.7	–57.0	–46.7	–55.7	–45.4
Tm_2O_3	–415.4	–158.0	–134.9	–121.4	–71.8	–13.6	–62.6	–52.2	–55.6	–45.2	–54.3	–43.9
Yb_2O_3	–397.6	–144.6	–125.9	–113.9	–66.7	–10.1	–60.3	–49.9	–53.5	–43.2	–52.3	–41.9
Lu_2O_3	–413.6	–156.9	–134.4	–121.2	–71.9	–13.9	–63.1	–52.7	–56.1	–45.7	–54.8	–44.4
HfO_2	–497.6	–167.8	–150.4	–137.2	–78.4	–5.9	–74.9	–61.1	–66.3	–52.5	–64.8	–51.0
Ta_2O_5	–413.9	–49.1	–75.1	–75.6	–28.5	43.9	–55.1	–37.9	–47.5	–30.2	–46.1	–28.8
WO_3	–300.1	93.0	16.6	0.0	31.8	101.4	–29.6	–8.8	–23.3	–2.5	–22.1	–1.4
WO_2	–213.0	52.3	4.6	–5.3	17.7	65.4	–21.1	–7.3	–16.7	–2.9	–15.9	–2.1
Re_2O_7	–165.5	250.8	119.1	84.6	98.2	163.2	–1.0	23.1	3.6	27.8	4.4	28.6
OsO_4	–31.9	407.3	220.0	167.3	162.6	222.8	25.2	52.9	28.2	55.8	28.7	56.3
OsO_2	–60.0	170.4	87.6	65.2	68.8	103.1	7.2	21.0	9.4	23.2	9.8	23.6
IrO_2	–32.5	191.4	102.1	77.3	77.4	109.1	11.5	25.3	13.2	27.0	13.5	27.3
HgO	0.0	108.9	61.2	47.7	46.0	60.7	11.1	18.0	11.8	18.7	11.9	18.8
Tl_2O	–22.8	36.8	18.1	13.2	15.2	24.5	1.1	4.5	1.7	5.2	1.9	5.3
Pb_3O_4	–62.4	96.6	46.9	33.8	39.2	64.1	1.7	10.9	3.4	12.7	3.8	13.0
PbO_2	–51.0	178.0	93.7	70.8	73.6	107.3	11.0	24.8	13.1	26.9	13.5	27.3
PbO	–66.1	57.5	24.6	16.4	22.9	43.3	–2.4	4.5	–0.8	6.1	–0.5	6.4
PbO	–66.7	57.1	24.4	16.3	22.9	43.3	–2.3	4.6	–0.7	6.3	–0.4	6.6
Bi_2O_3	–80.7	100.2	46.3	32.3	39.6	68.3	–1.4	9.0	0.8	11.1	1.2	11.5
ThO_2	–539.3	–200.0	–173.0	–156.4	–92.3	–16.1	–82.6	–68.7	–73.4	–59.6	–71.8	–57.9
UO_2	–468.3	–145.5	–135.1	–124.3	–69.4	0.5	–70.4	–56.6	–62.3	–48.5	–60.8	–47.0
UO_3	–495.9	–58.6	–90.3	–91.0	–34.7	52.0	–67.0	–46.2	–57.8	–37.1	–56.2	–35.5
U_3O_7	–483.2	–120.9	–123.3	–115.9	–59.8	16.2	–70.4	–54.2	–61.8	–45.7	–60.3	–44.2
U_3O_8	–494.5	–93.7	–109.7	–106.0	–49.2	32.5	–70.0	–51.6	–61.1	–42.7	–59.5	–41.1
U_4O_9	–479.5	–127.1	–126.3	–118.1	–62.3	12.1	–70.5	–55.0	–62.1	–46.6	–60.6	–45.0

Table A3.2: Maximum estimates max(ln(a_i)) for the natural logarithm of the (chemical) activity a_i of the atoms of impurity i in the liquid metallic fixed–point materials of the ITS–90. The possible gaseous oxides of the impurities are listed in the first column. Compared with Table A3.1, the values are corrected to account for the dilute concentration of the gaseous oxides in the relatively pure atmosphere within the fixed–point cell. (For gases, the activity is replaced by the fugacity.) Since the partial pressures of the gases in fixed–point cells are not known in general, pressures p of $p_0 \cdot 10^{-6}$ and $p_0 \cdot 10^{-12}$ are taken as examples (p_0 = 100 kPa). Copper and gold have been intentionally left out of Table A3.2, because their values lie very close to those of silver, and can be easily calculated using Table A3.1. T_{90} is the fixed–point temperature.

	Fixed-point material													
	Hg		Ga		In		Sn		Zn		Al		Ag	
T_{90} / K	234		303		430		505		693		933		1235	
Oxygen donor	HgO		Ga_2O_3		In_2O_3		SnO_2		ZnO		Al_2O_3		O_2 at $10^{-9} \cdot p_0$	
p / p_0	10^{-6}	10^{-12}	10^{-6}	10^{-12}	10^{-6}	10^{-12}	10^{-6}	10^{-12}	10^{-6}	10^{-12}	10^{-6}	10^{-12}	10^{-6}	10^{-12}
H_2O	–53.6	–60.6	12.1	5.2	–0.3	–7.2	–3.0	–9.9	2.5	–4.4	14.2	7.3	–5.8	–12.7
CO	–47.7	–61.5	63.5	49.7	18.1	4.3	5.4	–8.4	5.0	–8.8	20.6	6.8	–25.0	–38.8
CO_2	–149.0	–162.8	93.5	79.7	22.8	9.0	4.7	–9.1	15.1	1.2	53.9	40.1	–31.8	–45.6
PO	–4.4	–18.2	97.3	83.5	42.3	28.5	26.2	12.4	20.5	6.7	32.4	18.6	–15.7	–29.6
PO_2	–91.0	–104.8	138.2	124.4	54.3	40.5	31.4	17.6	34.4	20.6	68.2	54.4	–21.1	–34.9
SO_2	–100.3	–114.1	130.9	117.1	49.0	35.1	26.8	13.0	30.9	17.1	65.4	51.6	–23.3	–37.1
SO_3	–106.2	–120.0	234.9	221.1	106.2	92.3	70.9	57.0	73.8	60.0	123.4	109.6	–11.3	–25.1