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Density-functional theory calculations of aqueous redox potentials of fourth-period transition metals

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Supporting information

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Table S1: Components of calculated redox potentials using different models.

System	Model	IP(g)	E_{sol}	$T\Delta S$	ΔE_{SHE}	E_{redox} calc.	E_{redox} expt.
Sc^{3+}/Sc^{2+}	ion	25.72	0	0.48	-4.43	21.77	-2.3
	ion + contin.	25.72	-15.89	0.48	-4.43	5.88	-2.3
	ion + 6 H_2O	13.19	0	0.48	-4.43	9.24	-2.3
	ion + 6 H_2O + contin.	13.19	-9.99	0.48	-4.43	-0.75	-2.3
	ion + 18 H_2O	9.11	0	0.48	-4.43	5.16	-2.3
	ion + 18 H_2O + contin.	9.11	-6.77	0.48	-4.43	-1.61	-2.3
Ti^{3+}/Ti^{2+}	ion	28.65	0	0.45	-4.43	24.67	-0.9
	ion + contin.	28.65	-15.87	0.45	-4.43	8.80	-0.9
	ion + 6 H_2O	14.18	0	0.45	-4.43	10.20	-0.9
	ion + 6 H_2O + contin.	14.18	-10.11	0.45	-4.43	0.09	-0.9
	ion + 18 H_2O	10.05	0	0.45	-4.43	6.07	-0.9
	ion + 18 H_2O + contin.	10.05	-6.82	0.45	-4.43	-0.75	-0.9
V^{3+}/V^{2+}	ion	30.00	0	0.45	-4.43	26.02	-0.255
	ion + contin.	30.00	-15.70	0.45	-4.43	10.33	-0.255
	ion + 6 H_2O	15.21	0	0.45	-4.43	11.23	-0.255
	ion + 6 H_2O + contin.	15.21	-10.23	0.45	-4.43	1.00	-0.255
	ion + 18 H_2O	10.61	0	0.45	-4.43	6.63	-0.255
	ion + 18 H_2O + contin.	10.61	-6.80	0.45	-4.43	-0.17	-0.255

Table S1 (continued)

System	Model	IP(g)	E_{sol}	$T\Delta S$	ΔE_{SHE}	E_{redox} calc.	E_{redox} expt.
Cr^{3+}/Cr^{2+}	ion	31.10	0	0.42	-4.43	27.09	-0.42
	ion + contin.	31.10	-15.90	0.42	-4.43	11.19	-0.42
	ion + 6 H_2O	15.10	0	0.42	-4.43	11.09	-0.42
	ion + 6 H_2O + contin.	15.10	-10.37	0.42	-4.43	0.72	-0.42
	ion + 18 H_2O	10.42	0	0.42	-4.43	6.41	-0.42
	ion + 18 H_2O + contin.	10.42	-6.91	0.42	-4.43	-0.50	-0.42
Mn^{3+}/Mn^{2+}	ion	33.95	0	0.54	-4.43	30.06	1.54
	ion + contin.	33.95	-15.91	0.54	-4.43	14.15	1.54
	ion + 6 H_2O	16.95	0	0.54	-4.43	13.06	1.54
	ion + 6 H_2O + contin.	16.95	-10.35	0.54	-4.43	2.70	1.54
	ion + 18 H_2O	11.96	0	0.54	-4.43	8.07	1.54
	ion + 18 H_2O + contin.	11.96	-6.85	0.54	-4.43	1.21	1.54
Fe^{3+}/Fe^{2+}	ion	31.97	0	0.35	-4.43	27.89	0.77
	ion + contin.	31.97	-15.91	0.35	-4.43	11.98	0.77
	ion + 6 H_2O	16.16	0	0.35	-4.43	12.08	0.77
	ion + 6 H_2O + contin.	16.16	-10.16	0.35	-4.43	1.92	0.77
	ion + 18 H_2O	11.63	0	0.35	-4.43	7.55	0.77
	ion + 18 H_2O + contin.	11.63	-6.83	0.35	-4.43	0.73	0.77

Table S1 (continued)

System	Model	IP(g)	E_{sol}	$T\Delta S$	ΔE_{SHE}	E_{redox} calc.	E_{redox} expt.
Co^{3+}/Co^{2+}	ion Co^{3+} Mult=1	38.25	0	0.37	-4.43	34.19	1.92
	ion + contin.	38.25	-15.91	0.37	-4.43	18.27	1.92
	ion + 6 H_2O	17.34	0	0.37	-4.43	13.28	1.92
	ion + 6 H_2O + contin.	17.34	-10.78	0.37	-4.43	2.50	1.92
	ion + 18 H_2O	12.15	0	0.37	-4.43	8.09	1.92
	ion + 18 H_2O + contin.	12.15	-6.99	0.37	-4.43	1.10	1.92
	ion Co^{3+} Mult=5	34.68	0	0.37	-4.43	30.62	1.92
	ion + contin.	34.68	-15.91	0.37	-4.43	14.70	1.92
	ion + 6 H_2O	17.30	0	0.37	-4.43	13.24	1.92
	ion + 6 H_2O + contin.	17.30	-10.16	0.37	-4.43	3.09	1.92
	ion + 18 H_2O	12.59	0	0.37	-4.43	8.53	1.92
	ion + 18 H_2O + contin.	12.59	-6.78	0.37	-4.43	1.75	1.92

Table S1 (continued)

System	Model	IP(g)	E_{sol}	$T\Delta S$	ΔE_{SHE}	E_{redox} calc.	E_{redox} expt.
Ni^{3+}/Ni^{2+}	ion Ni^{3+} Mult=2	37.58	0	0.33	-4.43	33.48	2.3
	ion + contin.	37.58	-16.07	0.33	-4.43	17.40	2.3
	ion + 6 H_2O	18.21	0	0.33	-4.43	14.11	2.3
	ion + 6 H_2O + contin.	18.21	-10.53	0.33	-4.43	3.58	2.3
	ion + 18 H_2O	12.94	0	0.33	-4.43	8.84	2.3
	ion + 18 H_2O + contin.	12.94	-6.90	0.33	-4.43	1.94	2.3
	ion Ni^{3+} Mult=4	36.06	0	0.33	-4.43	31.96	2.3
	ion + contin.	36.06	-15.92	0.33	-4.43	16.04	2.3
	ion + 6 H_2O	18.15	0	0.33	-4.43	14.05	2.3
	ion + 6 H_2O + contin.	18.15	-10.08	0.33	-4.43	3.97	2.3
	ion + 18 H_2O	13.21	0	0.33	-4.43	9.11	2.3
	ion + 18 H_2O + contin.	13.21	-6.87	0.33	-4.43	2.24	2.3
Cu^{3+}/Cu^{2+}	ion	37.25	0	0.45	-4.43	33.27	2.4
	ion + contin.	37.25	-15.91	0.45	-4.43	17.36	2.4
	ion + 6 H_2O	17.87	0	0.45	-4.43	13.89	2.4
	ion + 6 H_2O + contin.	17.87	-10.24	0.45	-4.43	3.66	2.4
	ion + 18 H_2O	13.20	0	0.45	-4.43	9.22	2.4
	ion + 18 H_2O + contin.	13.20	-6.91	0.45	-4.43	2.32	2.4

Table S2: Energies (in Hartrees) of the calculated complexes

File name	DFT energy	ZPE	DFT + COSMO
Co2+4_18h2o-B	-2759.36073712962	0.4600947	-2759.59860464513
Co2+4_6h2o_Ci	-1841.37279961073	0.1506025	-1841.67640649466
Co3+1_18h2o_B	-2758.90643828562	0.4522624	-2759.40109982296
Co3+1_6h2o_Ci-S6	-1840.7378651951	0.1527856	-1841.43776157991
Co3+5_18h2o_B	-2758.88786065228	0.4498065	-2759.37484142234
Co3+5_6h2o_Ci	-1840.7348580429	0.1486141	-1841.41181059629
Cr2+5_18h2o_B	-2421.00676825432	0.4597885	-2421.24246386843
Cr2+5_6h2o_Ci	-1503.02356706988	0.1527509	-1503.32479569343
Cr3+4_18h2o_B	-2420.6228571273	0.4586323	-2421.11248792614
Cr3+4_6h2o_Ci	-1502.46863864339	0.1526725	-1503.15088439102
Cu2+2_18h2o_B	-3017.08357220928	0.4533696	-3017.3208927676
Cu2+2_6h2o_Ci	-2099.09430037235	0.1526605	-2099.40302157408
Cu3+3_18h2o_B	-3016.59352524424	0.4485229	-3017.08465534058
Cu3+3_6h2o_S6	-2098.43274297809	0.1479696	-2099.11759175564
Fe2+5_18h2o_B	-2640.28194134509	0.4603861	-2640.5187532962
Fe2+5_6h2o_Th	-1722.29892191805	0.1533699	-1722.60062506233
Fe3+6_18h2o_B	-2639.84583695427	0.4518076	-2640.33354858166
Fe3+6_6h2o_Th	-1721.70085490852	0.1492306	-1722.37584713244
Mn2+6_18h2o_B	-2527.5717524337	0.4593741	-2527.80830703874
Mn2+6_6h2o_S6	-1609.59433466649	0.1492925	-1609.8935103822
Mn3+5_18h2o_B	-2527.12685374226	0.4538615	-2527.61523417017
Mn3+5_6h2o_Ci	-1608.9709480721	0.1487114	-1609.65060616763

Table S2 (continued)

File name	DFT energy	ZPE	DFT + COSMO
Ni2+3_18h2o_B	-2884.9276736991	0.4594282	-2885.16497860186
Ni2+3_6h2o_Ci	-1966.94121003378	0.1490518	-1967.2486833776
Ni3+2_18h2o_B	-2884.44396041621	0.45123	-2884.9347869568
Ni3+2_6h2o_Ci	-1966.27371060827	0.1508481	-1966.96814571138
Ni3+4_18h2o_B	-2884.43163642505	0.4489186	-2884.92153090864
Ni3+4_6h2o_Ci	-1966.27155027146	0.1463166	-1966.94929439065
Sc2+2_18h2o_B	-2137.22707904021	0.4524503	-2137.46260886423
Sc2+2_6h2o_S6	-1219.25171047355	0.149348	-1219.54924138581
Sc3+1_18h2o_B	-2136.89787028186	0.4580003	-2137.38232241375
Sc3+1_6h2o_S6	-1218.76588934351	0.1481795	-1219.43054256129
Ti2+3_18h2o_A	-2226.21751491347	0.4576389	
Ti2+3_18h2o_B	-2225.98130109708	0.4595017	-2226.21751491347
Ti2+3_6h2o_Ci	-1307.99611427094	0.1564788	-1308.29575366238
Ti3+2_18h2o_A	-2225.61108435018	0.4614265	
Ti3+2_18h2o_B	-2225.61336589405	0.4629661	-2226.10027082681
Ti3+2_6h2o_C3	-1307.47027762032	0.1517658	-1308.14157633931
V2+4_18h2o_A	-2320.51091309617	0.4576923	
V2+4_18h2o_B	-2225.98130109708	0.4614265	-2226.21751491347
V2+4_6h2o_Th	-1307.99611427094	0.1564788	-1308.29575366238
V3+3_18h2o_A	-2320.13443774941	0.4537294	
V3+3_18h2o_B	-2225.61336589405	0.4629661	-2226.10027082681
V3+3_6h2o_Ci	-1307.47027762032	0.1517658	-1308.14157633931