APPENDIX 3: THERMODYNAMIC PROPERTIES

Table 3A. $\overline{G}_f^0$, $\overline{H}_f^0$, and $\overline{S}^0$ Values for Common Chemical Species in Aquatic Systems:[a] Valid at 25°C, 1 atm Pressure, and Standard States[b]

Species	Formation from the Elements		Entropy	
	$\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	$\overline{S}^0$ (J mol^{-1} K^{-1})	Reference[c]
Ag (Silver)				
Ag (Metal)	0	0	42.6	NBS
Ag^+(aq)	77.12	105.6	73.4	NBS
AgBr	−96.9	−100.6	107	NBS
AgCl	−109.8	−127.1	96	NBS
AgI	−66.2	−61.84	115	NBS
Ag_2S(α)	−40.7	−29.4	14	NBS
AgOH(aq)	−92			NBS
$Ag(OH)_2^-$(aq)	−260.2			NBS
AgCl(aq)	−72.8	−72.8	154	NBS
$AgCl_2^-$(aq)	−215.5	−245.2	231	NBS
Al (Aluminum)				
Al	0	0	28.3	R
Al^{3+}(aq)	−489.4	−531.0	−308	R
$AlOH^{2+}$(aq)	−698			S
$Al(OH)_2^+$(aq)	−911			S
$Al(OH)_3$(aq)	−1115			S
$Al(OH)_4^-$(aq)	−1325			S
$Al(OH)_3$ (amorph)	−1139			R
Al_2O_3 (Corundum)	−1582	−1676	50.9	R

AlOOH (Boehmite)	−922	−1000	17.8	R
$Al(OH)_3$ (Gibbsite)	−1155	−1293	68.4	R
$Al_2Si_2O_5(OH)_4$ (Kaolinite)	−3799	−4120	203	R
$KAl_3Si_3O_{10}(OH)_2$ (Muscovite)	−1341			R
$Mg_5Al_2Si_3O_{10}(OH)_8$ (Chlorite)	−1962			R
$CaAl_2Si_2O_8$ (Anorthite)	−4017.3	−4243.0	199	R
$NaAlSi_3O_8$ (Albite)	−3711.7	−3935.1		R
As (Arsenic)				
As (α-Metal)	0	0	35.1	NBS
H_3AsO_4(aq)	−766.0	−898.7	206	NBS
$H_2AsO_4^-$(aq)	−748.5	−904.5	117	NBS
$HAsO_4^{2-}$(aq)	−707.1	−898.7	3.8	NBS
AsO_4^{3-}(aq)	−636.0	−870.3	−145	NBS
$H_2AsO_3^-$(aq)	−587.4			NBS
Ba (Barium)				
Ba^{2+}(aq)	−560.7	−537.6	9.6	R
$BaSO_4$ (Barite)	−1362	−1473	132	R
$BaCO_3$ (Witherite)	−1132	−1211	112	R
Be (Beryllium)				
Be^{2+}(aq)	−380	−382	−130	NBS
$Be(OH)_2(\alpha)$	−815.0	−902	51.9	NBS
$Be_3(OH)_3^{3+}$	−1802			NBS
B (Boron)				
H_3BO_3(aq)	−968.7	−1072	162	NBS
$B(OH)_4^-$(aq)	−1153.3	−1344	102	NBS

Table 3A. (*Continued*)

Species	Formation from the Elements $\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	Entropy $\overline{S}^0$ (J mol^{-1} K^{-1})	Reference[c]
Br (Bromide)				
Br_2(l)	0	0	152	NBS
Br_2(aq)	3.93	−259	130.5	NBS
Br^-(aq)	−104.0	−121.5	82.4	NBS
HBrO(aq)	−82.2	−113.0	147	NBS
BrO^-(aq)	−33.5	−94.1	42	NBS
C (Carbon)				
C (Graphite)	0	0	152	NBS
C (Diamond)	3.93	−2.59	130.5	NBS
CO_2(g)	−394.37	−393.5	213.6	NBS
$H_2CO_3^*$(aq)	−623.2	−699.6	187.0	R[d]
H_2CO_3(aq) ("true")	~ −607.1			S
HCO_3^-(aq)	−586.8	−692.0	91.2	S
CO_3^{2-}(aq)	−527.9	−677.1	−56.9	NBS
CH_4(g)	−50.79	−74.80	186	NBS
CH_4(aq)	−34.39	−89.04	83.7	NBS
CH_3OH(aq)	−175.4	−245.9	133	NBS
HCOOH(aq)	−372.3	−425.4	163	NBS
$HCOO^-$(aq)	−351.0	−425.6	92	NBS
CH_2O(aq)	−129.7			
CH_2O(g)	−110.0	−116.0	218.6	S
HCN(aq)	112.0	105.0	129	NBS
CN^-(aq)	166.0	151.0	118	NBS
COS(g)	−169.2	−137.2	234.5	NBS

CNS^-(aq)	88.7	72.0		S
$H_2C_2O_4$(aq)	−697.0	−818.26		S
$HC_2O_4^-$(aq)	−690.86	−818.8		S
$C_2O_4^{2-}$(aq)	−674.04	−818.8	45.6	S
Ca (Calcium)				
Ca^{2+}(aq)	−553.54	−542.83	−53	R
$CaOH^+$(aq)	−718.4			NBS
$Ca(OH)_2$(aq)	−868.1	−1003	−74.5	NBS
$Ca(OH)_2$ (Portlandite)	−898.4	−986.0	83	R
$CaCO_3$ (Calcite)	−1128.8	−1207.4	91.7	R
$CaCO_3$ (Aragonite)	−1127.8	−1207.4	88.0	R
$CaMg(CO_3)_2$ (Dolomite)	−2161.7	−2324.5	155.2	R
$CaSiO_3$ (Wollastonite)	−1549.9	−1635.2	82.0	R
$CaSO_4$ (Anhydrite)	−1321.7	−1434.1	106.7	R
$CaSO_4 \cdot 2\ H_2O$ (Gypsum)	−1797.2	−2022.6	194.1	R
$Ca_5(PO_4)_3OH$ (Hydroxyapatite)	−6338.4	−6721.6	390.4	R
Cd (Cadmium)				
Cd (γ-Metal)				
Cd^{2+}(aq)	−77.58	−75.90	−73.2	R
$CdOH^+$(aq)	−284.5			R
$Cd(OH)_3^-$(aq)	−600.8			R
$Cd(OH)_4^{2-}$(aq)	−758.5			R
$Cd(OH)_2$(aq)	−392.2			R
CdO (s)	−228.4	−258.1	54.8	
$Cd(OH)_2$ (precip.)	−473.6	−560.6	96.2	R
$CdCl^+$(aq)	−224.4	−240.6	43.5	R
$CdCl_2$(aq)	−340.1	−410.2	39.8	R

Table 3A. *(Continued)*

Species	Formation from the Elements		Entropy	
	$\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	$\overline{S}^0$ (J mol^{-1} K^{-1})	Reference[c]
$CdCl_3^-$(aq)	−487.0	−561.0	203	R
$CdCO_3$(s)	−669.4	−750.6	92.5	R
Cl (Chlorine)				
Cl^-(aq)	−131.3	−167.2	56.5	NBS
Cl_2(g)	0	0	223.0	NBS
Cl_2(aq)	6.90	−23.4	121	NBS
HClO(aq)	−79.9	−120.9	142	NBS
ClO^-(aq)	−36.8	−107.1	42	NBS
ClO_2(aq)	117.6	74.9	173	NBS
ClO_2^-(aq)	17.1	−66.5	101	NBS
ClO_3^-(aq)	−3.35	−99.2	162	NBS
ClO_4^-(aq)	−8.62	−129.3	182	NBS
Co (Cobalt)				
Co (Metal)	0	0	30.04	R
Co^{2+}(aq)	−54.4	−58.2	−113	R
Co^{3+}(aq)	134	−92	−305	R
$HCoO_2^-$(aq)	−407.5			NBS
$Co(OH)_2$(aq)	−369	−518	134	NBS
$Co(OH)_2$ (blue precip.)	−450			NBS
CoO(s)	−214.2	−237.9	53.0	R
Co_3O_4 (Cobalt Spinel)	−725.5	−891.2	102.5	R

Cr (Chromium)				
Cr (Metal)	0	0	23.8	NBS
Cr^{2+}(aq)		−143.5		NBS
Cr^{3+}(aq)	−215.5	−256.0	308	NBS
Cr_2O_3 (Eskolaite)	−1053	−1135	81	R
$HCrO_4^-$(aq)	−764.8	−878.2	184	R
CrO_4^{2-}(aq)	−727.9	−881.1	50	R
$Cr_2O_7^{2-}$(aq)	−1301	−1490	262	R
$Cr(OH)_3$ (hydrous)	−858	−984	(1051)	Bard et al.
$Cr(OH)^{2+}$	−430	−495	(−156)	Bard et al.
$Cr(OH)_2^+$	−653	−748	(−27)	Bard et al.
$Cr(OH)_4^-$	−1013	−1169	(238)	Bard et al.
Cu (Copper)				
Cu (Metal)	0	0	33.1	NBS
Cu^+(aq)	50.0	71.7	40.6	NBS
Cu^{2+}(aq)	65.5	64.8	−99.6	NBS
$Cu(OH)_2$(aq)	−249.1	−395.2	−121	NBS
$HCuO_2^-$(aq)	−258			
CuS (Covellite)	−53.6	−53.1	66.5	NBS
Cu_2S (α)	−86.2	−79.5	121	NBS
CuO (Tenorite)	−129.7	−157.3	43	NBS
$CuCO_3 \cdot Cu(OH)_2$ (Malachite)	−893.7	−1051.4	186	NBS
$2\ CuCO_3 \cdot Cu(OH)_2$ (Azurite)		−1632		NBS
F (Fluorine)				
F_2(g)	0	0	202	NBS
F^-(aq)	−278.8	−332.6	−13.8	NBS

Table 3A. (*Continued*)

Species	Formation from the Elements		Entropy	Reference[c]
	$\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	$\overline{S}^0$ (J mol^{-1} K^{-1})	
HF(aq)	−296.8	320.0	88.7	NBS
HF_2^-(aq)	−578.1	−650	92.5	NBS
Fe (Iron)				
Fe (Metal)	0	0	27.3	NBS
Fe^{2+}(aq)	−78.87	−89.10	−138	NBS
$FeOH^+$(aq)	−277.4	324.7	29	NBS
$Fe(OH)_2$(aq)	−441.0	—	—	NBS
Fe^{3+}(aq)	−4.60	−48.5	−316	NBS
$FeOH^{2+}$(aq)	−229.4	−324.7	−29.2	NBS
$Fe(OH)_2^+$(aq)	−438	250.8	142.0	NBS
$Fe(OH)_3$(aq)	−659.4	—	—	NBS
$Fe(OH)_4^-$(aq)	−842.2	—	34.5	NBS
$Fe_2(OH)_2^{4+}$(aq)	−467.27	612.1	356.0	NBS
FeS_2 (Pyrite)	−160.2	−171.5	52.9	R
FeS_2 (Marcasite)	−158.4	−169.4	53.9	R
FeO(s)	−251.1	−272.0	59.8	R
$Fe(OH)_2$ (precip.)	−486.6	−569	87.9	NBS
α-Fe_2O_3 (Hematite)[e]	−742.7	−824.6	87.4	R
Fe_3O_4 (Magnetite)	−1012.6	−1115.7	146	R
α-FeOOH (Goethite)[e]	−488.6	−559.3	60.5	R
FeOOH (amorph)[e]	−462			S
$Fe(OH)_3$ (amorph)[e]	−699(−712)			S
$FeCO_3$(Siderite)	−666.7	−737.0	105	R
Fe_2SiO_4 (Fayalite)	−1379.4	−1479.3	148	R

H (Hydrogen)				
$H_2(g)$	0	0	130.6	NBS
$H_2(aq)$	17.57	−4.18	57.7	NBS
$H^+(aq)$	0	0	0	NBS
$H_2O(l)$	−237.18	−285.83	69.91	NBS
$H_2O(g)$	−228.57	−241.8	188.72	R
$H_2O_2(aq)$	−134.1	−191.17	143.9	NBS
$HO_2^-(aq)$	−67.4	−160.33	23.8	NBS
Hg (Mercury)				
Hg(l)	0	0	76.0	NBS
$Hg_2^{2+}(aq)$	153.6	172.4	84.5	NBS
$Hg^{2+}(aq)$	164.4	171.0	−32.2	NBS
Hg_2Cl_2 (Calomel)	−210.8	265.2	192.4	NBS
HgO(red)	−58.5	−90.8	70.3	NBS
HgS (Metacinnabar)	−43.3	−46.7	96.2	NBS
HgI_2 (red)	−101.7	−105.4	180	NBS
$HgCl^+(aq)$	−5.44	−18.8	75.3	NBS
$HgCl_2(aq)$	−173.2	−216.3	155	NBS
$HgCl_3^-(aq)$	−309.2	−388.7	209	NBS
$HgCl_4^{2-}(aq)$	−446.8	−554.0	293	NBS
$HgOH^+(aq)$	−52.3	−84.5	71	NBS
$Hg(OH)_2(aq)$	−274.9	−355.2	142	NBS
$HgO_2^-(aq)$	−190.3			NBS
I (Iodine)				
I_2 (Crystal)	0	0	116	NBS
$I_2(aq)$	16.4	22.6	137	NBS
$I^-(aq)$	−51.59	−55.19	111	NBS

Table 3A. (*Continued*)

Species	Formation from the Elements $\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	Entropy $\overline{S}^0$ (J mol^{-1} K^{-1})	Reference[c]
I_3^-(aq)	−51.5	−51.5	239	NBS
HIO(aq)	−99.2	−138	95.4	NBS
IO^-(aq)	−38.5	−107.5	−5.4	NBS
HIO_3(aq)	−132.6	−211.3	167	NBS
IO_3^-	−128.0	−221.3	118	NBS
Mg (Magnesium)				
Mg (Metal)	0	0	32.7	R
Mg^{2+}(aq)	−454.8	−466.8	−138	R
$MgOH^+$(aq)	−626.8			S
$Mg(OH)_2$(aq)	−769.4	−926.8	−149	NBS
$Mg(OH)_2$ (Brucite)	−833.5	−924.5	63.2	R
Mn (Manganese)				
Mn (Metal)	0	0	32.0	R
Mn^{2+}(aq)	−228.0	−220.7	−73.6	R
$Mn(OH)_2$ (precip.)	−616			S
Mn_3O_4 (Hausmannite)	−1281			S
MnOOH (α-Manganite)	−557.7			S
MnO_2 (Manganate) (IV) ($MnO_{1.7}$–MnO_2)	−453.1			S
MnO_2 (Pyrolusite)	−465.1	−520.0	53	R
$MnCO_3$ (Rhodochrosite)	−816.0	−889.3	100	R
MnS (Albandite)	−218.1	−213.8	87	R
$MnSiO_3$ (Rhodonite)	−1243	−1319	131	R

N (Nitrogen)				
$N_2(g)$	0	0	191.5	NBS
$NO(g)$	86.57	90.25	210.6	S
$NO_2(g)$	51.3	33.2	240.0	S
$N_2O(g)$	104.2	82.0	220	NBS
$NH_3(g)$	−16.48	−46.1	192	NBS
$NH_3(aq)$	−26.57	−80.29	111	NBS
$NH_4^+(aq)$	−79.37	−132.5	113.4	NBS
$HNO_2(aq)$	−42.97	−119.2	153	NBS
$NO_2^-(aq)$	−37.2	−104.6	140	NBS
$HNO_3(aq)$	−111.3	−207.3	146	NBS
$NO_3^-(aq)$	−111.3	−207.3	146.4	NBS
Ni (Nickel)				
$Ni^{2+}(aq)$	−45.6	−54.0	−129	R
NiO (Bunsenite)	−211.6	−239.7	38	R
NiS (Millerite)	−86.2	−84.9	66	R
O (Oxygen)				
$O_2(g)$	0	0	205	NBS
$O_2(aq)$	16.32	−11.71	111	NBS
$O_3(g)$	163.2	142.7	239	NBS
$O_3(aq)$		125.9		NBS
$O_2^{\cdot -}$	31.84			NBS
$HO_2^{\cdot}(aq)$	4.44			NBS
$H_2O_2(g)$	−105.6	−136.31	232.6	NBS
$H_2O_2(aq)$	−134.1	−191.17	143.9	NBS
$HO_2^-(aq)$	−67.4	−160.33	23.8	NBS
$OH^{\cdot}(g)$	34.22	38.95	183.64	NBS

Table 3A. ***(Continued)***

Species	Formation from the Elements $\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	Entropy $\overline{S}^0$ (J mol^{-1} K^{-1})	Reference[c]
$OH^{\bullet}$(aq)	7.74			NBS
OH^-(aq)	−157.29	−230.0	−10.75	NBS
P (Phosphorus)				
P (α, white)	0	0	41.1	
PO_4^{3-}(aq)	−1018.8	−1277.4	−222	NBS
HPO_4^{2-}(aq)	−1089.3	−1292.1	−33.4	NBS
$H_2PO_4^-$(aq)	−1130.4	−1296.3	90.4	NBS
H_3PO_4(aq)	−1142.6	−1288.3	158	NBS
Pb (Lead)				
Pb (Metal)	0	0	64.8	NBS
Pb^{2+}(aq)	−24.39	−1.67	10.5	NBS
$PbOH^+$(aq)	−226.3			NBS
$Pb(OH)_3^-$(aq)	−575.7			NBS
$Pb(OH)_2$ (precip.)	−452.2			NBS
PbO (yellow)	−187.9	−217.3	68.7	NBS
PbO_2	−217.4	−277.4	68.6	NBS
Pb_3O_4	−601.2	−718.4	211	NBS
PbS	−98.7	−100.4	91.2	NBS
$PbSO_4$	−813.2	−920.0	149	NBS
$PbCO_3$ (Cerussite)	−625.5	−699.1	131	NBS
S (Sulfur)				
S (rhombic)	0	0	31.8	NBS
SO_2(g)	−300.2	−296.8	248	NBS

$SO_3(g)$	−371.1	−395.7	257	NBS
$H_2S(g)$	−33.56	−20.63	205.7	NBS
$H_2S(aq)$	−27.87	−39.75	121.3	NBS
$S^{2-}(aq)$	85.8[f]	33.0	−14.6	NBS
$HS^-(aq)$	12.05	−17.6	62.8	NBS
$SO_3^{2-}(aq)$	−486.6	−635.5	−29	NBS
$HSO_3^-(aq)$	−527.8	−626.2	140	NBS
$H_2SO_3^*$	−537.9	−608.8	232	NBS[g]
$H_2SO_3(aq)$ ("true")	~ −534.5			S
$SO_4^{2-}(aq)$	−744.6	−909.2	20.1	NBS
$HSO_4^-(aq)$	−756.0	−887.3	132	NBS
Se (Selenium)				
Se (black)	0	0	42.4	NBS
$SeO_3^{2-}(aq)$	−369.9	−509.2	12.6	NBS
$HSeO_3^-(aq)$	−431.5	−514.5	135	NBS
$H_2SeO_3(aq)$	−426.2	−507.5	208	NBS
$SeO_4^{2-}(aq)$	−441.4	−599.1	54.0	NBS
$HSeO_4^-(aq)$	−452.3	−581.6	149	NBS
Si (Silicon)				
Si (Metal)	0	0	18.8	NBS
SiO_2 (α, Quartz)	−856.67	−910.94	41.8	NBS
SiO_2 (α, Cristobalite)	−855.88	−909.48	42.7	NBS
SiO_2 (α, Tridymite)	−855.29	−909.06	43.5	NBS
SiO_2 (amorph)	−850.73	−903.49	46.9	NBS
$H_4SiO_4(aq)$	−1308.0[h]	−1468.6	180	NBS

Table 3A. (*Continued*)

Species	Formation from the Elements		Entropy	
	$\overline{G}_f^0$ (kJ mol^{-1})	$\overline{H}_f^0$ (kJ mol^{-1})	$\overline{S}^0$ (J mol^{-1} K^{-1})	Reference[c]
Sr (Strontium)				
Sr^{2+}(aq)	−559.4	−545.8	−33	R
$SrOH^+$(aq)	−721			NBS
$SrCO_3$ (Strontianite)	−1137.6	−1218.7	97	R
$SrSO_4$ (Celestite)	−1341.0	−1453.2	118	R
Zn (Zinc)				
Zn (Metal)	0	0	29.3	NBS
Zn^{2+}(aq)	−147.0	−153.9	112	NBS
$ZnOH^+$(aq)	−330.1			NBS
$Zn(OH)_2$(aq)	−522.3			NBS
$Zn(OH)_3^-$(aq)	−694.3			NBS
$Zn(OH)_4^{2-}$(aq)	−858.7			NBS
ZnO (solid)	−318.32	−348.28	43.64	NBS
$Zn(OH)_2$ (solid β)	−553.6	−641.9	81.2	NBS
$ZnCl^+$(aq)	−275.3			NBS
$ZnCl_2$(aq)	−403.8			NBS
$ZnCl_3^-$(aq)	−540.6			NBS
$ZnCl_4^{2-}$(aq)	−666.1			S
$ZnCO_3$ (Smithsonite)	−731.6	−812.8	82.4	NBS

[a]The quality of the data is highly variable; the authors do not claim to have critically selected the ''best'' data. For information on precision of the data and for a more complete compendium, which includes less common substances, the reader is referred to the references. For research work, the original literature should be consulted.

[b]Thermodynamic properties taken from Robie, Hemingway, and Fisher are based on a reference state of the elements in their standard states at 1 bar (10^5 P = 0.987 atm). This change in reference pressure has a negligible effect on the tabulated values for the condensed phases. [For gas phases only data from NBS (reference state = 1 atm) are given.]

[c]NBS: D. D. Wagman et al., Selected Values of Chemical Thermodynamic Properties, U.S. National Bureau of Standards, Technical Notes 270-3 (1968), 270-4 (1969), 270-5 (1971). R: R. A. Robie, B. S. Hemingway, and J. R. Fisher, *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures*, Geological Survey Bulletin No. 1452, Washington, DC, 1978. Bard et al.: Bard, A. J., R. Parsons and D. L. Parkhurst, *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York (1985). S: Other sources (e.g., computed from data in *Stability Constants*).

[d]$[H_2CO_3^*] = [CO_2(aq)] +$ "true" $[H_2CO_3]$.

[e]The thermodynamic stability of oxides, hydroxides, or oxyhydroxides of Fe(III) depends on mode of preparation, age, and molar surface. Reported solubility products ($K_{s0} = \{Fe^{3+}\}\{OH^-\}^3$) range from $10^{-37.3}$ to $10^{-43.7}$. Correspondingly, FeOOH may have G_f° values between -452 J mol^{-1} (freshly precipitated amorphous FeOOH) and -489 J mol^{-1} (aged goethite). If the precipitate is written as $Fe(OH)_3$, its G_f° values vary from -692 to -729 J mol^{-1}.

[f]The value for this species appears too low, on the basis of recently reported pK_2 values for $H_2S(aq)$.

[g]$[H_2SO_3^*] = [SO_2(aq)] +$ "true" $[H_2SO_3]$.

[h]R value yields a solubility constant for quartz more in accord with observation.