

Supporting Information

Calculating Atomization Energies

Converting from one standard state to another is straightforward if the conversion is based on the atomization energies. It is quite difficult if the actual standard state species are used since some standard states are solids, e.g. graphite for carbon. Consider for example, the atomization reaction of MMA(V)



The atomization energy of MMA(V) is

$$\begin{aligned} \Delta G_f^a(g)[MMA(V)] = & \Delta G_f^{qc}(g)[MMA(V)] - \Delta G_f^{qc}(g)[As] \\ & - \Delta G_f^{qc}(g)[C] - 5\Delta G_f^{qc}(g)[H] - 3\Delta G_f^{qc}(g)[O] \end{aligned} \quad (S2)$$

where the superscript “a” refers to the atomization energy and “qc” refers to the quantum chemical standard state. The atomization energy can also be computed using the NBS standard states

$$\begin{aligned} \Delta G_f^a(g)[MMA(V)] = & \Delta G_f^0(g)[MMA(V)] - \Delta G_f^0(g)[As] \\ & - \Delta G_f^0(g)[C] - 5\Delta G_f^0(g)[H] - 3\Delta G_f^0(g)[O] \end{aligned} \quad (S3)$$

where the superscript “0” refers to the NBS standard state. Since thermodynamic quantities do not depend on the standard states used for the components, the two atomization energies are equal. Equating Eqs. (S2) and (S3) and solving for

$\Delta G_f^0(g)[MMA(V)]$ yields

$$\begin{aligned} \Delta G_f^0(g)[MMA(V)] = & \Delta G_f^a(g)[MMA(V)] + \Delta G_f^0(g)[As] \\ & + \Delta G_f^0(g)[C] + 5\Delta G_f^0(g)[H] + 3\Delta G_f^0(g)[O] \end{aligned} \quad (S4)$$

where $\Delta G_f^a(g)[MMA(V)]$ is computed using Eq.(S2) and the formation energies of the atoms using the NBS standard state are known (Table 1F).

Calculating the Free Energies for Ions

For MMA(V) $pK_{a1}= 4.1$ and $pK_{a2}=8.7$, and for DMA(V) $pK_a = 6.2$ (16), where $pK_a = -\log_{10}[K_a]$ for the equilibrium constant, K_a . For example, for the deprotonation reaction



the reaction free energy is

$$\Delta G_{rxn}^0 = -RT \ln(K_a) = -1.364 \log(K_a) = 1.364 pK_a \quad (S6)$$

and the free energy of formation for the anion is

$$\Delta G_f^0(aq)[MMA(V)] = \Delta G_f^0(aq)[MMA(V)] - 1.364 pK_a \quad (S7)$$

Table S1. Percentage of the total methyl arsenic detected in various media

Source	MMA(V)	MMA(III)	DMA(V)	DMA(III)	Reference
Human					
Hepatocytes	5.1	33.1	25.2	36.6	9
Human Blood					
Plasma	40.9	0	42.4	0	10
Hamster Liver					
Tissue	15.4	18.9	41.1	24.5	22
Tosa Bay, Japan	7.1	2.4	88.9	1.6	16
Lake Biwa, Japan	12.4	0.2	85.9	1.5	17

Table S2. Methyl arsenic species in human urine

As _T ingested μg/L	As _T in urine μg/L	IAs %	MMA %	DMA %	Location	Ref.
600	583	18	15	67	Chile	25
15	61	15	11	75	Chile	26
-	19.1	14	16	69	-	27 ^a
161	-	7	19	74	Romania	27 ^b
Air	-	17	11	72	China	33 ^c
Ranges		10-30	10-20	55-80		16,21,25,28

^aReported that all iAs is iAs(III)^bTotal MMA as 13% MMA(V) and 7% MMA(III)^cAir only exposure to arsenic

Table S3 - Methyl arsenic species in human urine

As _T ingested μg/L	As _T in urine μg/L	iAs(V) %	iAs(III) %	MMA(V) %	MMA(III) %	DMA(V) %	DMA(III) %	Location	Ref.
510-660	475	0	12	16	0	71	0	China	7,8,30
30-1100	370	11	13	19	1	48	9	Mexico	9
33	50	10	14	8	5	45	19	India	10
148	195	13	13	10	4	46	11	India	10
210	242	8	13	10	5	44	21	India	10
248	1487	2	8	11	2	74	4	India	10
-	-	7.3	12.2	12.3	2.8	54.7	10.6	Average	