Supporting Information

Effect of vanadium valence state on the solution chemistry and the stability of vanadium substituted polyoxometaltes

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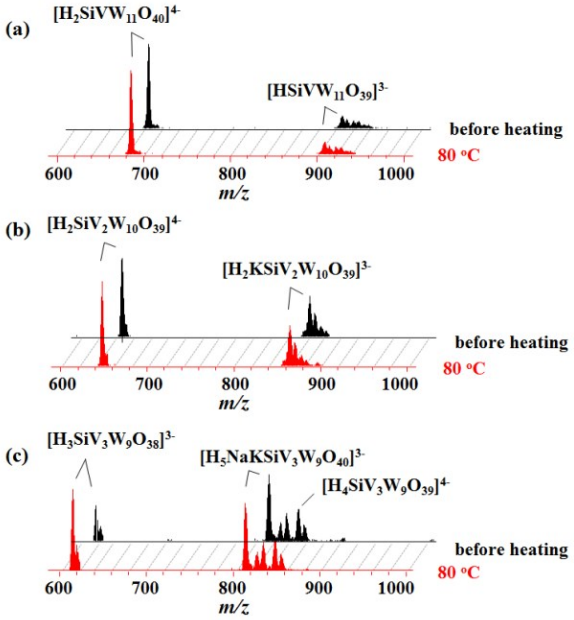

Fig. S1 ESI-MS monitoring of the reaction mixtures at 80 °C: (a) – (c) correspond to mixtures **1** - **3** with concentration of 1.7×10^{-2} M.

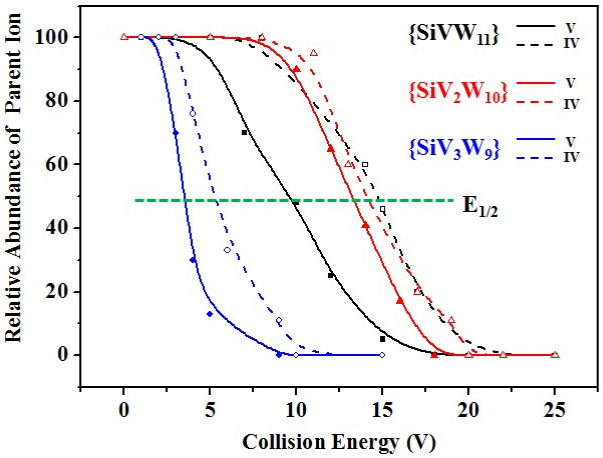

Fig. S2 Dissociation curves for the V-substituted POMs ($\{SiV^{V}W_{11}\}$, black line; $\{SiV^{V}_{2}W_{10}\}$, red line; $\{SiV^{V}_{3}W_{9}\}$, blue line). Solid and dotted lines represent V^{+5}- and V^{+4}-substituted POMs, respectively.

Table S1. Selected bond lengths (in Å) and free energies (in kcal mol^{-1}) for a series of Keggin anions.

Species	V-O_t	V-O_{b1}	V-O_{b2}	Si-O	ΔE[a]	ΔG[a]
β-$[SiW_{11}V(V)O_{40}]^{5-}$	1.59	1.85	1.93	1.63	0.0	0.0
β-$[SiW_{11}V(IV)O_{40}]^{6-}$	1.60	1.99	1.98	1.64	-104.9	-105.8
γ-$[SiW_{10}V(V)_2O_{40}]^{6-}$	1.60	1.82	1.93	1.63	0.0	0.0
γ-$[SiW_{10}V(IV)_2O_{40}]^{8-}$	1.61	1.84	1.90	1.63	-134.1	-134.0
β-$[SiW_9V(V)_3O_{40}]^{7-}$	1.61	1.82	1.99	1.62	0.0	0.0
β-$[SiW_9V(IV)_3O_{40}]^{10-}$	1.64	1.89	2.09	1.62	-177.6	-182.5

a. ΔE and ΔG are the relative energy of V(VI)-containing POM relative to the V(V)-containing POM.

Table S2. Cartesian coordinates and absolute energies for all mono-, di-, and tri-vanadium-substituted Keggin anions in water solution.

β-$[SiW_{11}V^{V}O_{40}]^{5-}$

E = -4119.2935145 a.u
G = -4119.229308 a.u

Si	-0.01396012	0.13815530	0.00000000
W	-2.41767628	2.10705945	1.67490433
W	-0.04933569	0.00218452	-3.56737356
W	2.58335446	1.88928667	-1.65961471
W	-2.47405003	-1.57503032	1.88599638
W	-0.04933569	0.00218452	3.56737356
W	-2.41767628	2.10705945	-1.67490433
W	0.69254043	-2.82503750	1.84970823
W	0.69254043	-2.82503750	-1.84970823
W	2.58335446	1.88928667	1.65961471
W	3.37440336	-0.97873697	0.00000000
W	-2.47405003	-1.57503032	-1.88599638
O	-1.38658088	3.65610903	-1.30582695
O	-3.34502680	2.38542948	-0.00000000
O	-3.59453201	2.76050142	2.75170894
O	-1.07630943	1.49749471	-2.91979352
O	-0.96596458	1.46469337	-0.00000000
O	1.17434943	3.02588391	-1.30980262
O	0.31553557	5.24478150	0.00000000
O	-2.99327355	0.23659881	-1.59602038
O	0.08229458	0.34336559	-5.24959328
O	0.74546601	-1.75123969	-3.47004457
O	-1.74083549	-0.93423538	-3.55339651
O	1.52922543	0.82794841	-2.89512344
O	-0.32756299	-0.76456268	-1.34630241
O	3.73034742	0.27715778	-1.36926268
O	3.56518507	2.76420104	-2.77567987
O	1.57806829	0.55951785	0.00000000
O	-3.92806115	-2.29979806	2.45674764
O	-1.74083549	-0.93423538	3.55339651
O	-2.61668797	-1.91829226	0.00000000
O	-1.22239322	-3.03982471	2.09365111
O	-0.32756299	-0.76456268	1.34630241
O	0.08229458	0.34336559	5.24959328
O	0.74546601	-1.75123969	3.47004457

O	1.52922543	0.82794841	2.89512344
O	-1.07630943	1.49749471	2.91979352
O	-3.59453201	2.76050142	-2.75170894
O	1.17434943	3.02588391	1.30980262
O	1.24847469	-4.32404660	2.48831160
O	2.30388016	-2.00034201	1.28644408
O	0.43312201	-3.27703852	0.00000000
O	1.24847469	-4.32404660	-2.48831160
O	2.30388016	-2.00034201	-1.28644408
O	-1.22239322	-3.03982471	-2.09365111
O	3.56518507	2.76420104	2.77567987
O	3.73034742	0.27715778	1.36926268
O	4.83515931	-1.89129919	0.00000000
O	-2.99327355	0.23659881	1.59602038
O	-3.92806115	-2.29979806	-2.45674764
O	-1.38658088	3.65610903	1.30582695
O	3.38321059	2.46781950	0.00000000
V	-0.07651268	3.70572108	0.00000000

β-[$SiW_{11}V^{IV}O_{40}]^{6-}$

E = -4119.4606667 a.u
G = -4119.397849 a.u

Si	-0.02258879	0.15451466	-0.00000000
W	-2.50291401	2.06115693	1.66857920
W	-0.05811286	-0.00175575	-3.55507530
W	2.52208843	1.98201528	-1.66492088
W	-2.42085848	-1.66071999	1.87798015
W	-0.05811286	-0.00175575	3.55507530
W	-2.50291401	2.06115693	-1.66857920
W	0.79443007	-2.80978242	1.85169552
W	0.79443007	-2.80978242	-1.85169552
W	2.52208843	1.98201528	1.66492088
W	3.41829806	-0.86981839	-0.00000000
W	-2.42085848	-1.66071999	-1.87798015
O	-1.61043454	3.61755515	-1.36251062
O	-3.47951530	2.19051785	0.00000000
O	-3.74384140	2.56424919	2.76492842
O	-1.14230144	1.43830027	-2.92548716
O	-1.00805246	1.46222925	0.00000000
O	1.11443111	3.09031340	-1.37022745
O	0.13248777	5.31787437	-0.00000000
O	-2.98847156	0.08968144	-1.58223284

O	0.06895222	0.34068648	-5.24329891
O	0.81836523	-1.72892218	-3.46414274
O	-1.69548229	-1.03095943	-3.56171162
O	1.50464694	0.86783690	-2.89397528
O	-0.30123422	-0.77151852	-1.34207012
O	3.72990672	0.38115836	-1.36836796
O	3.51234391	2.85018927	-2.78903852
O	1.55734102	0.62977446	-0.00000000
O	-3.84377825	-2.45471018	2.45582851
O	-1.69548229	-1.03095943	3.56171162
O	-2.53428927	-2.06590360	0.00000000
O	-1.09497873	-3.09396228	2.09155568
O	-0.30123422	-0.77151852	1.34207012
O	0.06895222	0.34068648	5.24329891
O	0.81836523	-1.72892218	3.46414274
O	1.50464694	0.86783690	2.89397528
O	-1.14230144	1.43830027	2.92548716
O	-3.74384140	2.56424919	-2.76492842
O	1.11443111	3.09031340	1.37022745
O	1.41278568	-4.28837695	2.49465879
O	2.37752828	-1.93039946	1.28516648
O	0.56205433	-3.28248142	0.00000000
O	1.41278568	-4.28837695	-2.49465879
O	2.37752828	-1.93039946	-1.28516648
O	-1.09497873	-3.09396228	-2.09155568
O	3.51234391	2.85018927	2.78903852
O	3.72990672	0.38115836	1.36836796
O	4.90644683	-1.74835132	-0.00000000
O	-2.98847156	0.08968144	1.58223284
O	-3.84377825	-2.45471018	-2.45582851
O	-1.61043454	3.61755515	1.36251062
O	3.32725944	2.56374179	-0.00000000
V	-0.16384270	3.74395319	-0.00000000

γ-[$SiV^{V}_{2}W_{10}O_{40}$]$^{6-}$

E = -4122.8857249 a.u
G = -4122.823039 a.u

Si	0.00000000	0.00000000	0.19821789
O	0.00000000	1.18572039	3.91169378
O	-0.00000000	-1.18572039	3.91169378
O	1.40174945	-2.91529057	1.14209942
O	-1.40174945	-2.91529057	1.14209942

O	-1.40174945	2.91529057	1.14209942
O	1.40174945	2.91529057	1.14209942
O	0.00000000	-2.04220869	-3.17151581
O	0.00000000	2.04220869	-3.17151581
O	2.80515622	-2.45158724	-3.43820622
O	-2.80515622	-2.45158724	-3.43820622
O	-2.80515622	2.45158724	-3.43820622
O	2.80515622	2.45158724	-3.43820622
O	1.27474400	-3.58253589	-1.40343300
O	-1.27474400	-3.58253589	-1.40343300
O	-1.27474400	3.58253589	-1.40343300
O	1.27474400	3.58253589	-1.40343300
O	2.80276130	-1.60585815	-0.71609191
O	-2.80276130	-1.60585815	-0.71609191
O	-2.80276130	1.60585815	-0.71609191
O	2.80276130	1.60585815	-0.71609191
O	1.74286680	-0.00000000	-2.61251137
O	-1.74286680	0.00000000	-2.61251137
O	2.51343187	1.31622851	3.06521719
O	-2.51343187	1.31622851	3.06521719
O	-2.51343187	-1.31622851	3.06521719
O	2.51343187	-1.31622851	3.06521719
O	4.21364551	2.75644004	1.43189751
O	-4.21364551	2.75644004	1.43189751
O	-4.21364551	-2.75644004	1.43189751
O	4.21364551	-2.75644004	1.43189751
O	0.00000000	5.27934319	0.47501222
O	-0.00000000	-5.27934319	0.47501222
O	-3.89447487	0.00000000	1.16919980
O	3.89447487	-0.00000000	1.16919980
O	-1.35859884	0.00000000	1.09673011
O	1.35859884	-0.00000000	1.09673011
O	0.00000000	-1.36730609	-0.74794004
O	0.00000000	1.36730609	-0.74794004
V	-1.38389794	0.00000000	3.91755548
V	1.38389794	-0.00000000	3.91755548
W	-2.89064240	-1.65012882	1.28014111
W	2.89064240	-1.65012882	1.28014111
W	2.89064240	1.65012882	1.28014111
W	-2.89064240	1.65012882	1.28014111
W	-1.70440925	-1.88408659	-2.23195060
W	1.70440925	-1.88408659	-2.23195060
W	1.70440925	1.88408659	-2.23195060
W	-1.70440925	1.88408659	-2.23195060

W	0.00000000	3.60612140	0.05099794
W	-0.00000000	-3.60612140	0.05099794
O	-1.94032062	0.00000000	5.41669743
O	1.94032062	-0.00000000	5.41669743

γ-[$SiV^{IV}_2W_{10}O_{40}$]$^{8-}$

E = -4123.099367 a.u
G = -4123.036639 a.u

Si	0.00000000	0.00000000	0.16404409
O	0.00000000	1.17410935	4.03295052
O	-0.00000000	-1.17410935	4.03295052
O	1.37469016	-2.91880348	1.18260136
O	-1.37469016	-2.91880348	1.18260136
O	-1.37469016	2.91880348	1.18260136
O	1.37469016	2.91880348	1.18260136
O	0.00000000	-2.07449499	-3.17599874
O	0.00000000	2.07449499	-3.17599874
O	2.80555861	-2.46415010	-3.45524807
O	-2.80555861	-2.46415010	-3.45524807
O	-2.80555861	2.46415010	-3.45524807
O	2.80555861	2.46415010	-3.45524807
O	1.29611898	-3.63527082	-1.35324134
O	-1.29611898	-3.63527082	-1.35324134
O	-1.29611898	3.63527082	-1.35324134
O	1.29611898	3.63527082	-1.35324134
O	2.82043767	-1.67037473	-0.66854518
O	-2.82043767	-1.67037473	-0.66854518
O	-2.82043767	1.67037473	-0.66854518
O	2.82043767	1.67037473	-0.66854518
O	1.79066438	-0.00000000	-2.58868076
O	-1.79066438	0.00000000	-2.58868076
O	2.45163070	1.30962731	3.08289256
O	-2.45163070	1.30962731	3.08289256
O	-2.45163070	-1.30962731	3.08289256
O	2.45163070	-1.30962731	3.08289256
O	4.20866559	2.75296936	1.49400906
O	-4.20866559	2.75296936	1.49400906
O	-4.20866559	-2.75296936	1.49400906
O	4.20866559	-2.75296936	1.49400906
O	0.00000000	5.31845810	0.51284503
O	-0.00000000	-5.31845810	0.51284503
O	-3.87726989	0.00000000	1.22599677

O	3.87726989	-0.00000000	1.22599677
O	-1.36358381	0.00000000	1.04905463
O	1.36358381	-0.00000000	1.04905463
O	0.00000000	-1.37283062	-0.78052671
O	0.00000000	1.37283062	-0.78052671
V	-1.41256569	0.00000000	3.98030200
V	1.41256569	-0.00000000	3.98030200
W	-2.86741830	-1.66128841	1.26573171
W	2.86741830	-1.66128841	1.26573171
W	2.86741830	1.66128841	1.26573171
W	-2.86741830	1.66128841	1.26573171
W	-1.70010490	-1.87870854	-2.25050916
W	1.70010490	-1.87870854	-2.25050916
W	1.70010490	1.87870854	-2.25050916
W	-1.70010490	1.87870854	-2.25050916
W	0.00000000	3.64646319	0.03442312
W	-0.00000000	-3.64646319	0.03442312
O	-2.02793925	0.00000000	5.47248467
O	2.02793925	-0.00000000	5.47248467

β-[$SiV^{V}_{2}W_{10}O_{40}$]$^{8-}$

E = -4122.8938594 a.u
G = -4122.829510 a.u

Si	-0.26817500	0.00355300	0.00000000
V	-3.41874000	-0.12514400	1.58960300
W	-0.31824000	-0.12801800	-3.52406700
W	0.66778200	2.99296200	-1.67226300
W	-1.08253200	-2.90069000	1.86820300
W	-0.31824000	-0.12801800	3.52406700
V	-3.41874000	-0.12514400	-1.58960300
W	2.14705700	-1.82791600	1.88269900
W	2.14705700	-1.82791600	-1.88269900
W	0.66778200	2.99296200	1.67226300
W	3.06340600	1.25370800	0.00000000
W	-1.08253200	-2.90069000	-1.86820300
O	-3.62704900	1.69236700	-1.33814800
O	-4.21157000	-0.48010800	0.00000000
O	-4.59882600	-0.42572600	2.62242800
O	-1.97784800	0.30749100	-2.88859600
O	-1.81714500	0.48854900	0.00000000
O	-1.21498900	2.95244800	-1.32657400
O	-3.41956300	4.11845800	0.00000000

O	-2.58550200	-1.88578100	-1.55862000
O	-0.40241600	0.23045900	-5.21609100
O	1.51548500	-0.93756000	-3.43761400
O	-0.87157600	-1.98067900	-3.55908100
O	0.46602600	1.52813700	-2.87640600
O	0.05460900	-0.90617000	-1.34076200
O	2.51894300	2.55634400	-1.35992200
O	0.81696100	4.31050400	-2.78016600
O	0.72397100	1.32948300	0.00000000
O	-1.70315100	-4.41045300	2.44448400
O	-0.87157600	-1.98067900	3.55908100
O	-0.87815400	-3.30680000	0.00000000
O	0.88247500	-3.22603300	2.08353900
O	0.05460900	-0.90617000	1.34076200
O	-0.40241600	0.23045900	5.21609100
O	1.51548500	-0.93756000	3.43761400
O	0.46602600	1.52813700	2.87640600
O	-1.97784800	0.30749100	2.88859600
O	-4.59882600	-0.42572600	-2.62242800
O	-1.21498900	2.95244800	1.32657400
O	3.56766400	-2.59413100	2.50129500
O	2.90503400	-0.10334000	1.30809300
O	2.28787000	-2.24262500	0.00000000
O	3.56766400	-2.59413100	-2.50129500
O	2.90503400	-0.10334000	-1.30809300
O	0.88247500	-3.22603300	-2.08353900
O	0.81696100	4.31050400	2.78016600
O	2.51894300	2.55634400	1.35992200
O	4.76487800	1.55644300	0.00000000
O	-2.58550200	-1.88578100	1.55862000
O	-1.70315100	-4.41045300	-2.44448400
O	-3.62704900	1.69236700	1.33814800
O	0.77973400	3.96304800	0.00000000
W	-2.60447600	2.58941600	0.00000000

β-[$SiV^{V}_{3}W_{10}O_{40}$]$^{7-}$

E = -4126.4777396 a.u
G = -4126.412513 a.u

Si	-0.00082877	0.41823777	0.00000000
V	0.90548127	3.39272628	-1.56686626
W	0.12033899	0.39729877	3.53009064
W	-3.11598890	0.39806407	1.66098766

W	2.99682057	0.39559064	-1.86907748
W	0.12033899	0.39729877	-3.53009064
V	0.90548127	3.39272628	1.56686626
W	1.08000044	-2.42731050	-1.87359882
W	1.08000044	-2.42731050	1.87359882
W	-3.11598890	0.39806407	-1.66098766
W	-2.16434872	-2.42445841	0.00000000
W	2.99682057	0.39559064	1.86907748
O	-0.75181208	4.08330048	1.30730402
O	1.51211040	4.07975631	-0.00000000
O	1.51816787	4.43745161	-2.62198510
O	0.13415812	2.11078538	2.88731183
O	-0.00079086	2.03458912	0.00000000
O	-2.56023222	2.10874039	1.32615885
O	-3.02784171	4.43384731	0.00000000
O	2.43269386	2.10791698	1.56046893
O	-0.19014672	0.58315725	5.23014099
O	0.41771191	-1.58221336	3.45109672
O	2.05843907	0.44269409	3.56742413
O	-1.67444913	0.08247047	2.90141152
O	0.77534316	-0.16663237	1.34306598
O	-3.20119021	-1.57963675	1.36182517
O	-4.43309833	0.58760547	2.77945508
O	-1.55382027	-0.16311856	0.00000000
O	4.62391190	0.58177723	-2.45137201
O	2.05843907	0.44269409	-3.56742413
O	3.35284148	0.07932199	-0.00000000
O	2.77758091	-1.58228966	-2.09192794
O	0.77534316	-0.16663237	-1.34306598
O	-0.19014672	0.58315725	-5.23014099
O	0.41771191	-1.58221336	-3.45109672
O	-1.67444913	0.08247047	-2.90141152
O	0.13415812	2.11078538	-2.88731183
O	1.51816787	4.43745161	2.62198510
O	-2.56023222	2.10874039	-1.32615885
O	1.43815073	-4.00600775	-2.49831782
O	-0.74946958	-2.66973894	-1.29527053
O	1.49486120	-2.67829766	-0.00000000
O	1.43815073	-4.00600775	2.49831782
O	-0.74946958	-2.66973894	1.29527053
O	2.77758091	-1.58228966	2.09192794
O	-4.43309833	0.58760547	-2.77945508
O	-3.20119021	-1.57963675	-1.36182517
O	-2.88433862	-4.00317486	0.00000000

O	2.43269386	2.10791698	-1.56046893
O	4.62391190	0.58177723	2.45137201
O	-0.75181208	4.08330048	-1.30730402
O	-4.11782498	0.44783883	0.00000000
V	-1.80633799	3.39103634	0.00000000

β-[$SiV^{VI}_3W_{10}O_{40}$]$^{10-}$

E = -4126.7607258 a.u
G = -4126.703264 a.u

Si	-0.45694558	-0.00189812	-0.00000000
V	-3.50429359	-0.90755382	1.55666418
W	-0.38989540	-0.12366808	-3.55363558
W	-0.40209323	3.12599563	-1.67219197
W	-0.37797002	-3.01535459	1.87370405
W	-0.38989540	-0.12366808	3.55363558
V	-3.50429359	-0.90755382	-1.55666418
W	2.44346098	-1.08397890	1.86455915
W	2.44346098	-1.08397890	-1.86455915
W	-0.40209323	3.12599563	1.67219197
W	2.44217737	2.16914090	-0.00000000
W	-0.37797002	-3.01535459	-1.87370405
O	-4.16772021	0.74538836	-1.38481260
O	-4.17433905	-1.56330308	0.00000000
O	-4.47681074	-1.62277997	2.66933577
O	-2.09187452	-0.10171490	-2.96244429
O	-2.07865927	0.00190089	-0.00000000
O	-2.10461366	2.61634651	-1.38019673
O	-4.50391770	3.09491423	-0.00000000
O	-2.07287378	-2.47011061	-1.57676369
O	-0.53898912	0.21092496	-5.27308373
O	1.59197866	-0.39032708	-3.46064813
O	-0.43780114	-2.05952273	-3.61082764
O	-0.07060458	1.70377894	-2.92150505
O	0.16290224	-0.77876552	-1.34230969
O	1.59017681	3.22830785	-1.35169584
O	-0.54731724	4.47241458	-2.79327541
O	0.14022012	1.56060196	-0.00000000
O	-0.55596906	-4.65617282	2.47880552
O	-0.43780114	-2.05952273	3.61082764
O	-0.07336021	-3.40543409	0.00000000
O	1.57737355	-2.80043729	2.11609257
O	0.16290224	-0.77876552	1.34230969

O	-0.53898912	0.21092496	5.27308373
O	1.59197866	-0.39032708	3.46064813
O	-0.07060458	1.70377894	2.92150505
O	-2.09187452	-0.10171490	2.96244429
O	-4.47681074	-1.62277997	-2.66933577
O	-2.10461366	2.61634651	1.38019673
O	4.03691162	-1.44837122	2.48709380
O	2.68586433	0.80906738	1.31953754
O	2.69582573	-1.46347397	0.00000000
O	4.03691162	-1.44837122	-2.48709380
O	2.68586433	0.80906738	-1.31953754
O	1.57737355	-2.80043729	-2.11609257
O	-0.54731724	4.47241458	2.79327541
O	1.59017681	3.22830785	1.35169584
O	4.02969258	2.91278565	-0.00000000
O	-2.07287378	-2.47011061	1.57676369
O	-0.55596906	-4.65617282	-2.47880552
O	-4.16772021	0.74538836	1.38481260
O	-0.44272116	4.14209668	-0.00000000
V	-3.46246890	1.82805972	-0.00000000

$[WO_3(OH)]^-$

E = -369.6562143 a.u
G = -369.665834 a.u

W	-0.03492900	0.00036500	0.00000000
O	-0.62453900	-0.82883000	1.43231900
O	-0.62453900	1.65478800	0.00000000
O	1.89973000	0.09310800	0.00000000
H	2.37587300	-0.74889500	0.00000000
O	-0.62453900	-0.82883000	-1.43231900

$[VO_3(OH)]^{2-}$

E = -373.2286891 a.u
G = -373.236404 a.u

V	0.09238300	-0.00084800	-0.00078000
O	0.59365200	0.84505100	1.35984700
O	0.71699600	-1.55599300	-0.02651100
O	-1.78431400	-0.21421200	0.05902700
H	-2.22236200	0.64603600	0.02165800
O	0.48586100	0.84683700	-1.39282800

Table S3. Cartesian coordinates and absolute energies for all mono-, di-, and tri-V^{5+}-substituted Keggin anions in vacuum.

β-$[SiW_{11}V^{V}O_{40}]^{5-}$

E = -4118.22028 a.u
G = -4118.154721 a.u

Si	-0.00016000	0.01570800	0.13801500
W	-1.67788200	2.42568200	2.10792500
W	3.57306400	0.03999900	0.00427500
W	1.65640100	-2.59032600	1.89690200
W	-1.88388000	2.48494400	-1.57870800
W	-3.57362100	0.05531800	0.00205900
W	1.68543800	2.41663200	2.11087500
W	-1.84958900	-0.69096500	-2.83443700
W	1.84876400	-0.69647900	-2.83252100
W	-1.66864100	-2.58469600	1.89506800
W	-0.00590800	-3.38551800	-0.98416000
W	1.89718000	2.47778200	-1.57607900
O	1.30738200	1.37579500	3.65936900
O	0.00583700	3.33681600	2.39538000
O	-2.74865500	3.60689300	2.78376300
O	2.92348100	1.07180800	1.49855500
O	0.00215100	0.96835600	1.46632500
O	1.30509200	-1.19177800	3.03396700
O	-0.00373700	-0.30275700	5.27474500
O	1.61384600	2.99212300	0.24308100
O	5.26540500	-0.10055500	0.33690500
O	3.46679300	-0.74782200	-1.75128900
O	3.56058700	1.73484500	-0.93103600
O	2.88886400	-1.53094800	0.83026400
O	1.34889100	0.33134800	-0.76521200
O	1.35997100	-3.73345100	0.26548500
O	2.77224700	-3.58901200	2.76899500
O	-0.00139100	-1.57953900	0.55837300
O	-2.46158300	3.94322600	-2.31016600
O	-3.55106400	1.74949600	-0.93428400
O	0.00649800	2.62661500	-1.90476100
O	-2.08979100	1.23309700	-3.03660800
O	-1.34723100	0.33353200	-0.76553100
O	-5.26734400	-0.07678400	0.33133600

O	-3.46847800	-0.73363400	-1.75324500
O	-2.89699900	-1.51696000	0.83147500
O	-2.92347200	1.08818100	1.49694800
O	2.76213600	3.59281800	2.78637600
O	-1.31130300	-1.18851800	3.03371800
O	-2.50104200	-1.23547200	-4.34209800
O	-1.28762900	-2.29691600	-2.01683600
O	0.00029700	-0.42235700	-3.28222700
O	2.49977600	-1.24355500	-4.33944300
O	1.27793700	-2.30154600	-2.01560300
O	2.09861600	1.22597800	-3.03578900
O	-2.78972900	-3.57886400	2.76534900
O	-1.37808800	-3.72582300	0.26276500
O	-0.00836800	-4.85506900	-1.89824200
O	-1.60199100	3.00033700	0.24172100
O	2.48146400	3.93435100	-2.30570500
O	-1.30533400	1.37978900	3.65712800
O	-0.00777500	-3.39599500	2.45512900
V	-0.00286300	0.08173800	3.72723600

β-[SiV$^{V}_{2}$W$_{10}$O$_{40}$]$^{8-}$

E = -4121.3384489 a.u
G = -4121.273417 a.u

Si	-0.27060300	0.00323900	0.00000000
V	-3.45026000	-0.12077300	1.59645700
W	-0.32760200	-0.13200500	-3.53766400
W	0.66869700	3.00304400	-1.68213300
W	-1.08579200	-2.91319900	1.87138400
W	-0.32760200	-0.13200500	3.53766400
V	-3.45026000	-0.12077300	-1.59645700
W	2.16260100	-1.83026400	1.89213100
W	2.16260100	-1.83026400	-1.89213100
W	0.66869700	3.00304400	1.68213300
W	3.07638000	1.25278800	0.00000000
W	-1.08579200	-2.91319900	-1.87138400
O	-3.64539200	1.66951300	-1.33182800
O	-4.21209000	-0.50952700	0.00000000
O	-4.64897700	-0.42837100	2.62070700
O	-1.98741600	0.28846200	-2.90918900
O	-1.82263300	0.49039200	0.00000000
O	-1.23661300	2.95625900	-1.32387000
O	-3.46781800	4.11311100	0.00000000

O	-2.58350100	-1.91026100	-1.58411400
O	-0.40121700	0.21800900	-5.24422400
O	1.52743600	-0.92272800	-3.42841700
O	-0.84643700	-1.99118200	-3.56602200
O	0.43986300	1.54050800	-2.87692600
O	0.05115400	-0.90737400	-1.34462500
O	2.50314800	2.57995100	-1.36100700
O	0.81496600	4.33910300	-2.78815300
O	0.72519800	1.33250500	0.00000000
O	-1.68365300	-4.43895400	2.46684300
O	-0.84643700	-1.99118200	3.56602200
O	-0.87321200	-3.31216100	0.00000000
O	0.90699100	-3.21982400	2.08336100
O	0.05115400	-0.90737400	1.34462500
O	-0.40121700	0.21800900	5.24422400
O	1.52743600	-0.92272800	3.42841700
O	0.43986300	1.54050800	2.87692600
O	-1.98741600	0.28846200	2.90918900
O	-4.64897700	-0.42837100	-2.62070700
O	-1.23661300	2.95625900	1.32387000
O	3.59425800	-2.59424300	2.52249000
O	2.92480700	-0.07872200	1.31005900
O	2.30807800	-2.20949000	0.00000000
O	3.59425800	-2.59424300	-2.52249000
O	2.92480700	-0.07872200	-1.31005900
O	0.90699100	-3.21982400	-2.08336100
O	0.81496600	4.33910300	2.78815300
O	2.50314800	2.57995100	1.36100700
O	4.78244500	1.60130200	0.00000000
O	-2.58350100	-1.91026100	1.58411400
O	-1.68365300	-4.43895400	-2.46684300
O	-3.64539200	1.66951300	1.33182800
O	0.74436800	3.96616800	0.00000000
W	-2.59658100	2.60191900	0.00000000

β-[$SiV^{V}_{3}W_{10}O_{40}$]$^{7-}$

E = -4124.349638 a.u
G = -4124.287976 a.u

Si	-0.42080000	-0.00136800	0.00000000
V	-3.41163200	0.90687700	-1.58013600
W	-0.40096300	0.12078300	3.54805000
W	-0.39786700	-3.13260500	1.67006500

W	-0.40392900	3.01242300	-1.87759500
W	-0.40096300	0.12078300	-3.54805000
V	-3.41163200	0.90687700	1.58013600
W	2.44341900	1.08690200	-1.87853100
W	2.44341900	1.08690200	1.87853100
W	-0.39786700	-3.13260500	-1.67006500
W	2.44448900	-2.16678600	0.00000000
W	-0.40392900	3.01242300	1.87759500
O	-4.08283600	-0.75787400	1.30404900
O	-4.08429100	1.50189900	0.00000000
O	-4.49730800	1.50806500	-2.62039500
O	-2.11467900	0.15047700	2.90932000
O	-2.04220500	-0.00379200	0.00000000
O	-2.11116700	-2.59273000	1.32252600
O	-4.49005200	-3.03444400	0.00000000
O	-2.11526800	2.44108300	1.58412500
O	-0.57455300	-0.18114100	5.26808700
O	1.58311300	0.42046700	3.44755600
O	-0.43535300	2.06269600	3.57366100
O	-0.10291600	-1.67484500	2.90084900
O	0.16083200	0.77841900	1.34807000
O	1.58509400	-3.19590800	1.36077600
O	-0.57358400	-4.47198300	2.79052700
O	0.15974200	-1.55964500	0.00000000
O	-0.58013200	4.65213100	-2.47785700
O	-0.43535300	2.06269600	-3.57366100
O	-0.10549600	3.35296400	0.00000000
O	1.58161600	2.77745300	-2.08721100
O	0.16083200	0.77841900	-1.34807000
O	-0.57455300	-0.18114100	-5.26808700
O	1.58311300	0.42046700	-3.44755600
O	-0.10291600	-1.67484500	-2.90084900
O	-2.11467900	0.15047700	-2.90932000
O	-4.49730800	1.50806500	2.62039500
O	-2.11116700	-2.59273000	-1.32252600
O	4.02864100	1.45992800	-2.52514600
O	2.68008700	-0.74465500	-1.29259800
O	2.68379400	1.49509500	0.00000000
O	4.02864100	1.45992800	2.52514600
O	2.68008700	-0.74465500	1.29259800
O	1.58161600	2.77745300	2.08721100
O	-0.57358400	-4.47198300	-2.79052700
O	1.58509400	-3.19590800	-1.36077600
O	4.03059500	-2.91123500	0.00000000

O	-2.11526800	2.44108300	-1.58412500
O	-0.58013200	4.65213100	2.47785700
O	-4.08283600	-0.75787400	-1.30404900
O	-0.43294700	-4.12649000	0.00000000
V	-3.40617700	-1.83155200	0.00000000

$[WO_3(OH)]^-$

E = -369.5578756 a.u
G = -369.567152 a.u

W	0.04384300	-0.00255400	-0.00000100
O	0.47886800	0.91671200	1.42954700
O	0.82317900	-1.57144100	-0.00004600
O	-1.88695200	-0.30308900	0.00011700
H	-2.39404100	0.51801800	0.00023300
O	0.47860800	0.91668900	-1.42964000

$[VO_3(OH)]^{2-}$

E = -372.8763345 a.u
G = -372.885159 a.u

V	0.11084000	0.00093500	-0.00119600
O	0.43123100	0.88132700	1.39602700
O	0.94789900	-1.45082300	-0.05646100
O	-1.78270800	-0.43747500	0.03249500
H	-2.16493800	0.45091000	0.01141200
O	0.35553000	0.94791900	-1.37004900

Table S4. The pH values recorded before and during the solution reactions

pH of reactant solutions (C_{high}/C_{low})			Reaction Time	pH of reaction mixtures	
				$C_{mix}=5\times10^{-4}$ mol/L	$C_{mix}=1.7\times10^{-2}$ mol/L
1	$K_8[\beta\text{-}SiW_{11}O_{39}]\cdot14H_2O$	6.52/6.44	0 h	3.31	3.10
			1 h	3.23	3.01
	1 equiv $VOSO_4$	2.61/3.20	2 h	3.15	2.93
			24 h	3.06	2.90
2	$K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot12H_2O$	7.01/6.91	0 h	4.04	3.91
			1 h	3.95	3.87
	2 equiv $VOSO_4$	3.11/2.38	2 h	3.86	3.82
			24 h	3.80	3.77
3	$Na_9[\beta\text{-}HSiW_9O_{34}]\cdot23H_2O$	9.02/8.89	0 h	6.92	6.42
			1 h	6.76	6.37
	3 equiv $VOSO_4$	3.02/2.11	2 h	6.59	6.31
			24 h	6.50	6.22