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Supporting information for article:

Towards a quantitative bond valence description of coordination spheres – the concepts of valence entropy and valence diversity coordination numbers

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Supporting information

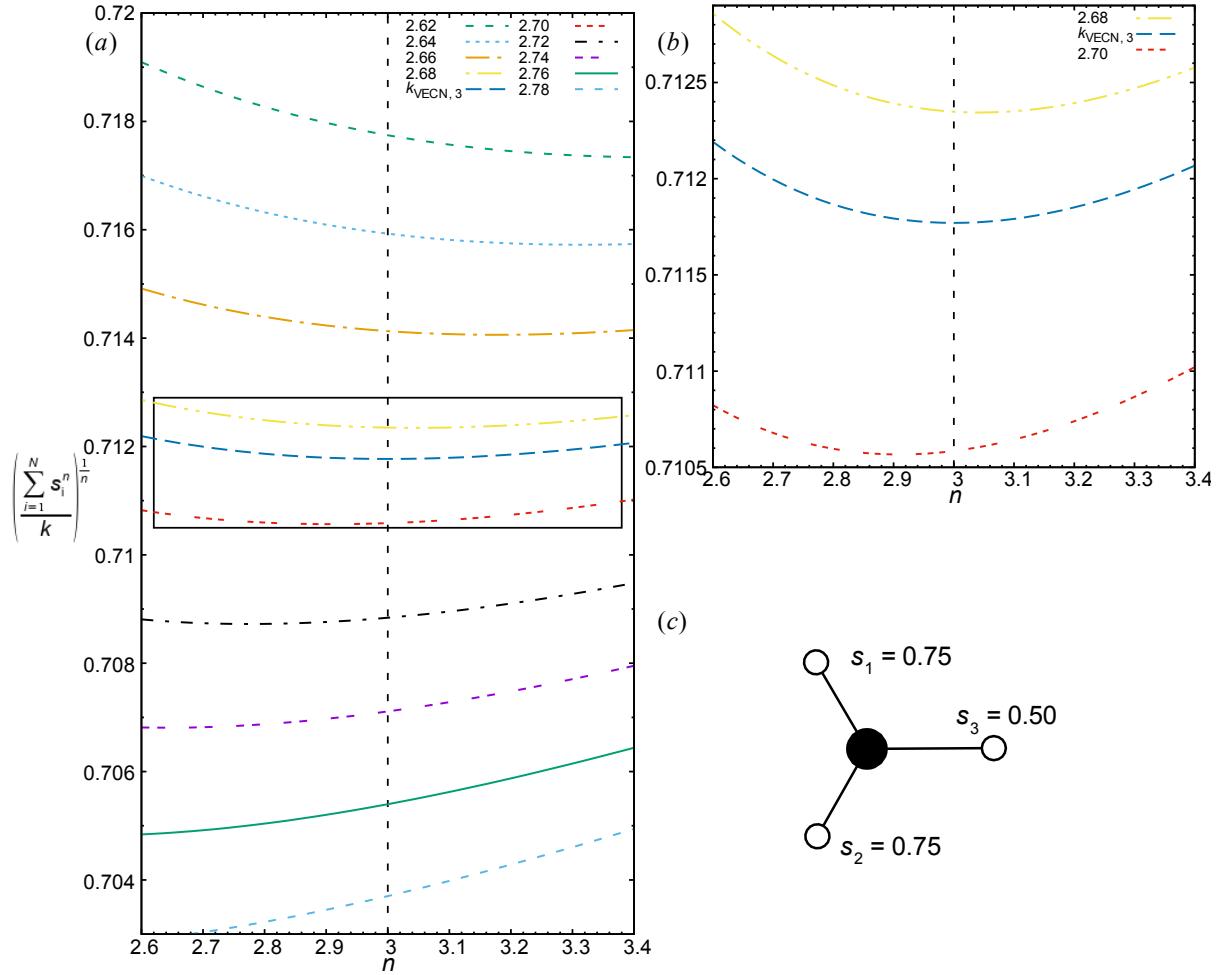


Figure S1 $\left(\frac{\sum_{i=1}^N s_i^n}{k}\right)^{\frac{1}{n}}$ plotted as a function of n for various values of k indicated in the legend (a).

The area of graph marked with a rectangle is enlarged in (b). The coordination sphere for which the calculations were carried out is shown in (c).

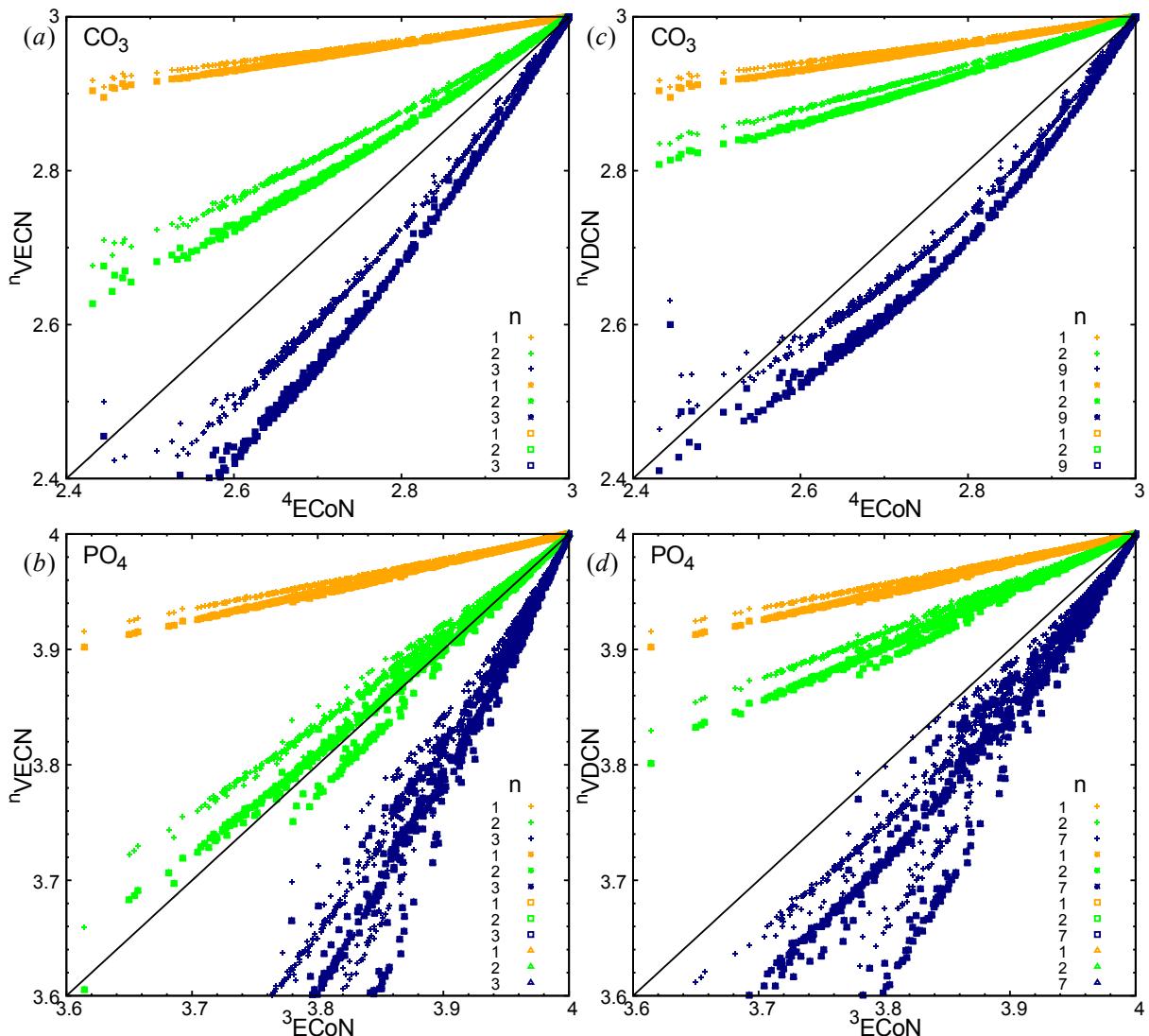


Figure S2 The correlation between iterative $nECoN$ and $nVECN$ as well as $nVDCN$ of various orders for (a, c) CO₃ and (b, d) PO₄ moieties and for various bond valence parameters. Crosses correspond to CNs calculated using bond valence parameters taken from “Gagné, O. C. & Hawthorne, F. C. (2015). *Acta Crystallogr. Sect. B*. **71**, 562–578”, stars to “Brown, I. D. & Altermatt, D. (1985). *Acta Crystallogr. Sect. B*. **41**, 244-247 (empirical)”, squares to “Yu, D. & Xue, D (2006). *Acta Crystallogr. Sect. B*. **62**, 702-709” and triangles to ‘Brese, N. E. & O’Keeffe, M. (1991). *Acta Crystallogr. Sect. B*. **47**, 192-197 (extrapolated)” in case of phosphates. The bond valence parameters for C–O bonds from “Allmann, R. (1975). *Monats. Chem.* **106**, 779-793” were not used as bond valence sums for carbon atoms deviate significantly from 4 for all the CO₃ fragments found in the CSD. Black lines denote the $y = x$ function.

Table S1 Aluminium, gallium and indium coordination numbers in various polymorphs of their oxides, sulphides and selenides.

Compound	ICSD	Space group	Coordination centre	¹ VECN	⁴ VDCN	² ECoN	Source of bond valence parameters
Al_2O_3	9770	$R\bar{3}c$	Al1	5.9	5.7	5.8	a
Al_2O_3	82504	$C2/m$	Al1	4.0	3.9	3.9	a
			Al2	5.8	5.4	5.4	
Al_2O_3	84375	$Pna2_1$	Al1	5.9	5.5	5.7	a
			Al2	5.8	5.4	5.4	
			Al3	4.0	4.0	4.0	
			Al4	5.8	5.3	5.3	
Al_2S_3	300213	$P6_1$	Al1	4.0	3.8	3.9	b
			Al2	3.9	3.8	3.9	
Al_2S_3	73220	$P6_1$	Al1	4.0	4.0	4.0	b
			Al2	4.8	4.4	4.7	
Al_2Se_3	14373	Cc	Al1	4.0	4.0	4.0	b
			Al2	4.0	4.0	4.0	
Al_2Se_3	25661	$P6_3mc$	Al1	4.0	4.0	4.0	b
Ga_2O_3	27431	$R\bar{3}c$	Ga1	5.9	5.5	5.7	a
Ga_2O_3	83645	$C2/m$	Ga1	4.0	4.0	4.0	a
			Ga2	5.9	5.7	5.8	
Ga_2S_3	202408	$P6_1$	Ga1	3.9	3.7	3.8	c
			Ga2	3.8	3.4	3.7	
			Ga3	3.7	3.3	3.4	
Ga_2S_3	202409	$P6_3mc$	Ga1	4.0	4.0	4.0	c
Ga_2Se_3	635359	$F\bar{4}3m$	Ga1	4.0	4.0	4.0	b
Ga_2Se_3	37168	$B11b$	Ga1	3.9	3.8	3.9	b
			Ga2	3.9	3.7	3.9	

Compound	ICSD	Space group	Coordination centre	¹ VECN	⁴ VDCN	² ECoN	Source of bond valence parameters
In_2O_3	14387	$Ia\bar{3}$	In1	6.0	6.0	6.0	a
			In2	6.0	5.9	5.9	
In_2O_3	425685	$Pbcn$	In1	5.9	5.7	5.8	a
In_2O_3	16086	$R\bar{3}c$	In1	5.9	5.5	5.8	a
In_2S_3	76757	$I\bar{4}3m$	In1	4.0	4.0	4.0	c
In_2S_3	151644	$I4_1/amd$	In1	6.0	6.0	6.0	c
			In2	5.7	5.0	5.6	
			In3	4.0	3.9	4.0	
In_2Se_3	151644	$I4_1/amd$	In1	6.0	6.0	6.0	b
			In2	5.7	5.0	5.6	
In_2Se_3	82203	$P6_1$	In1	4.6	4.1	4.4	b
			In2	4.0	4.0	4.0	

^a Gagné, O. C. & Hawthorne, F. C. (2015). *Acta Crystallogr. Sect. B*. **71**, 562–578; ^b Brese, N. E. & O'Keeffe, M. (1991). *Acta Crystallogr. Sect. B*. **47**, 192–197 (extrapolated); ^c Brown, I. D. & Altermatt, D. (1985). *Acta Crystallogr. Sect. B*. **41**, 244–247 (empirical).

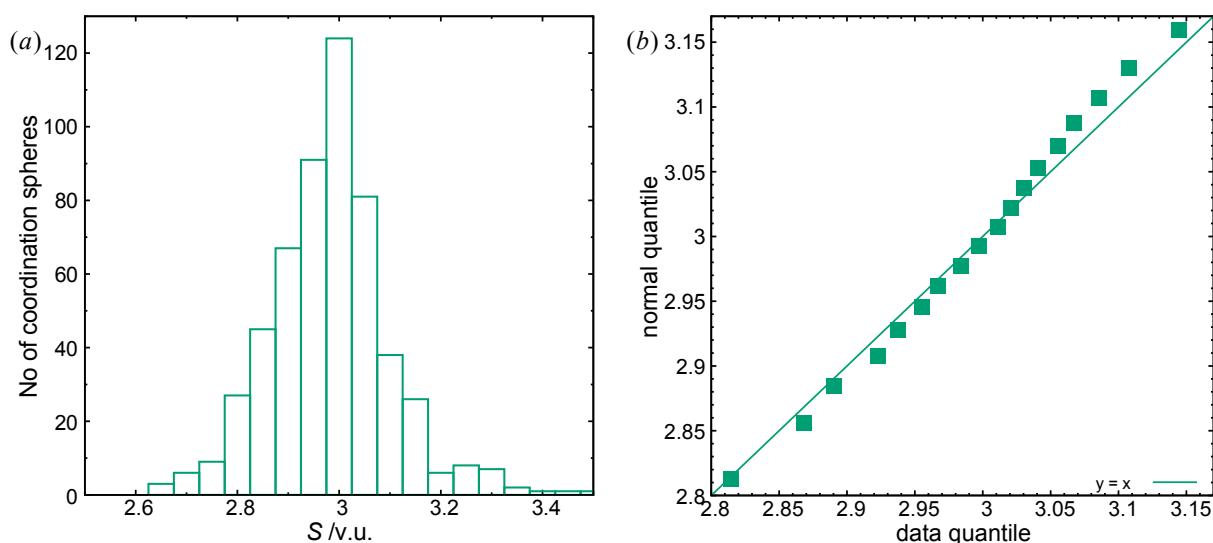


Figure S3 (a) The histogram of bond valence sums S distribution for As(III) coordination spheres and (b) normal probability plot for the distribution.

Table S2 Arsenic and oxygen iterative effective coordination numbers ${}^2\text{ECoN}$ and first-order entropic coordination numbers ${}^1\text{VECN}$ together with their ratios in arsenolite crystal structures under various pressures.

p /GPa	${}^2\text{ECoN(As/O)}$	${}^2\text{ECoN(O/As)}$	$\frac{{}^2\text{ECoN(As/O)}}{{}^2\text{ECoN(O/As)}}$	${}^7\text{ECoN(As/As)}$	${}^1\text{VECN}_{\text{As}}$	${}^1\text{VECN}_O$	$\frac{{}^1\text{VECN}_{\text{As}}}{{}^1\text{VECN}_O}$
0.0001	3.0000	2.0000	1.5000	5.7265	3.6544	2.4363	1.5000
0.07	3.0000	2.0000	1.5000	6.0523	3.6870	2.4580	1.5000
0.49	3.0000	2.0000	1.5000	6.6359	3.7564	2.5043	1.5000
1.26	3.0000	2.0000	1.5000	7.3830	3.8393	2.5596	1.5000
2.46	3.0000	2.0000	1.5000	8.1991	3.9580	2.6387	1.5000
3.28	3.0000	2.0000	1.5000	8.5990	3.9991	2.6660	1.5000
4.64	3.0001	2.0001	1.5000	9.2213	4.1010	2.7340	1.5000
6.01	3.0003	2.0002	1.5000	9.7073	4.1926	2.7951	1.5000
7.71	3.0007	2.0005	1.5000	10.1510	4.2743	2.8495	1.5000
9.27	3.0016	2.0011	1.5000	10.5003	4.3489	2.8993	1.5000
11.08	3.0030	2.0020	1.5000	10.7970	4.4161	2.9441	1.5000
12.96	3.0065	2.0043	1.5000	11.0441	4.5040	3.0026	1.5000
15.16	3.0108	2.0072	1.5000	11.2677	4.5714	3.0476	1.5000
17.59	3.0189	2.0126	1.5000	11.4725	4.6488	3.0992	1.5000
20.07	3.0258	2.0172	1.5000	11.6152	4.6971	3.1314	1.5000
22.27	3.0391	2.0261	1.5000	11.7209	4.7614	3.1743	1.5000
25.02	3.0492	2.0328	1.5000	11.8024	4.8026	3.2018	1.5000
27.48	3.0658	2.0439	1.5000	11.8755	4.8529	3.2353	1.5000
29.83	3.0752	2.0501	1.5000	11.9108	4.8797	3.2531	1.5000
24.78	3.0487	2.0325	1.5000	11.8004	4.8001	3.2001	1.5000
20.04	3.0270	2.0180	1.5000	11.6194	4.7028	3.1352	1.5000
14.3	3.0087	2.0058	1.5000	11.1975	4.5429	3.0286	1.5000
10.13	3.0022	2.0015	1.5000	10.6637	4.3833	2.9222	1.5000
5.16	3.0001	2.0001	1.5000	9.4128	4.1405	2.7603	1.5000

p /GPa	${}^2\text{ECoN(As/O)}$	${}^2\text{ECoN(O/As)}$	$\frac{{}^2\text{ECoN(As/O)}}{{}^2\text{ECoN(O/As)}}$	${}^7\text{ECoN(As/As)}$	${}^1\text{VECN}_{\text{As}}$	${}^1\text{VECN}_{\text{O}}$	$\frac{{}^1\text{VECN}_{\text{As}}}{{}^1\text{VECN}_{\text{O}}}$
0.02	3.0000	2.0000	1.5000	5.7723	3.6618	2.4412	1.5000
0.0001	3.0000	2.0000	1.5000	5.7815	3.6594	2.4396	1.5000

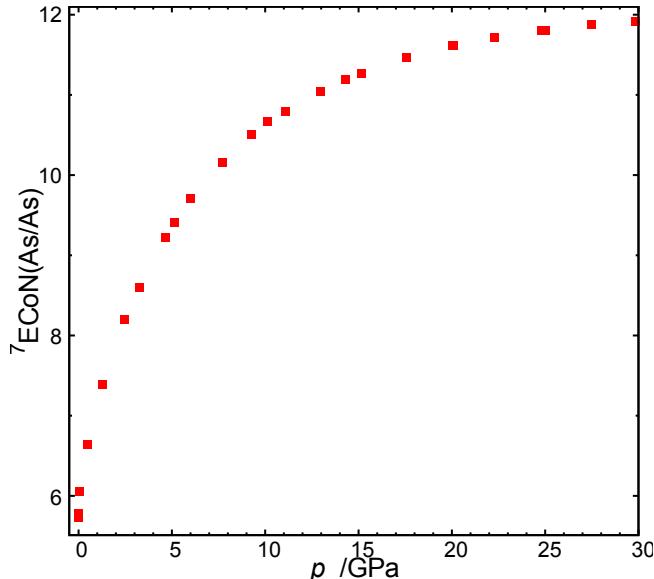


Figure S4 ${}^7\text{ECoN(As/As)}$ plotted as a function of pressure for arsenolite crystal structure.

S1. How to import the functions to calculate ${}^n\text{VECN}$, ${}^n\text{VDCN}$ and ${}^n\text{ECoN}$ to Libreoffice Calc?

LibreOffice Calc is the part of package LibreOffice freely available at <https://www.libreoffice.org/>

In order to use the provided functions:

- Open LibreOffice Calc.
- Choose **Tools - Macros - Edit Macros**. You will now see the Basic IDE.
- Copy the functions source code from the *lo5042sup2.txt* file available in the Supplementary materials.
- Paste the clipboard contents in the Basic-IDE of the document above the *Main* procedure. You may have to restart LibreOffice Calc in order to for it to recognise the pasted functions.
- You may apply the VECN, VDCN and ECON functions in the same way as the built-in functions of LibreOffice Calc. The use and arguments of the functions are described in the code.