Supplementary Information

Cohesive Energies and Enthalpies:

Complexities, Confusions, and Corrections

Leslie Glasser[a,*] and Drew Sheppard[b]

[a]*Nanochemistry Research Institute, Department of Chemistry*

Curtin University, GPO Box U1987, Perth, WA 6845, Australia

[b]*Hydrogen Storage Research Group, Fuels and Energy Technology Institute,*

Department of Physics and Astronomy,

Curtin University, GPO Box U1987, Perth, WA 6845, Australia

4 Figures

3 Tables

[*]Corresponding author

L. Glasser: Telephone: + 61 8 9848-3334 Fax: + 61 8 9266-4699

E-mail: l.glasser@curtin.edu.au

Table S1: Published "experimental" cohesive energies (column 2) in the energy units listed in column 1, followed by the formation enthalpy of the ionic solid and the enthalpies of the contributing atoms, finally summed in the column headed "Sum". This result is to be compared with the cohesive energy converted[a] to "kJ mol^{-1} per formula unit" in the penultimate column.[1] The integer factor *n* corrects from the particular formula unit used in column 2. The final column compares the thermodynamic summation with the published "experimental" cohesive energy. The data have been sorted into alphabetical order of the chemical formula (column 3).

Energy unit[ref]	**Cohes. E.**	**Material**	**$\Delta_f H$**	**Atom Contributions / kJ mol^{-1}**				**Enthalpy Sum**	**Cohes. E.**	***n***	***n*·Cohes. E.**	**Enthalpy Sum /*n*·Cohes E.**
			/kJ mol^{-1}	**M(g)**	**$\Delta_f H$(M,g)**	**X(g)**	**$\Delta_f H$(X,g)**	**/kJ mol^{-1}**				
eV[2]	10.65	Al_2O_3	-1675.7	Al(g)	660.0	O(g)	747.5	3083.2	1027.6	3	3082.8	1.00
kcal[3]	178.9	AlAs	-116.3	Al(g)	330.0	As(g)	278.4	724.7	748.5	1	748.5	0.97
kcal[3]	198.0	AlP	-111.7	Al(g)	330.0	P(g)	316.4	758.1	828.4	1	828.4	0.92
kcal[3]	165.0	AlSb	-50.4	Al(g)	330.0	Sb(g)	262.3	642.7	690.4	1	690.4	0.93
kJ[4]	3079	BaO	-553.8	Ba(g)	180.1	O(g)	249.2	983.0	983.0	1	983.0	1.00
eV[2]	10.18	BaO	-553.8	Ba(g)	180.1	O(g)	249.2	983.0	982.2	1	982.2	1.00
kJ[5]	351.0	$CaAl_2$	-73.2	Ca(g)	177.8	Al(g)	330.0	911.0	351.0	3	1053.0	0.87
kJ[4]	3475	CaO	-634.9	Ca(g)	177.8	O(g)	249.2	1061.9	1061.9	1	1061.9	1.00
eV[2]	11.01	CaO	-634.9	Ca(g)	177.8	O(g)	249.2	1061.9	1062.3	1	1062.3	1.00
kcal[3]	131.6	CdS	-161.9	Cd(g)	111.8	S(g)	278.8	552.5	550.6	1	550.6	1.00
kcal[3]	113.6	CdSe	-144.8	Cd(g)	111.8	Se(g)	227.1	483.7	475.3	1	475.3	1.02

kcal[3]	95.8	CdTe	-100.8	Cd(g)	111.8	Te(g)	209.5	422.1	400.8	1	400.8	1.05
kJ[5]	411.1	$CeAl_2$	-54.4	Ce(g)	423.0	Al(g)	330.0	1137.4	411.1	3	1233.3	0.92
kJ[5]	660.3	$CeIr_2$	-73.8	Ce(g)	423.0	Ir(g)	665.3	1827.3	660.3	3	1980.9	0.92
kJ[4]	3996	CoO	-237.9	Co(g)	424.7	O(g)	249.2	911.8	911.8	1	911.8	1.00
eV[2]	9.26	Cr_2O_3	-1137.3	Cr(g)	794.3	O(g)	747.5	2679.2	893.5	3	2680.4	1.00
eV[2]	7.74	CrO_2	-581.6	Cr(g)	397.1	O(g)	498.3	1477.1	746.8	2	1493.6	0.99
eV[2]	8.28	Fe_2O_3	-824.8	Fe(g)	830.7	O(g)	747.5	2403.0	798.9	3	2396.7	1.00
eV[2]	8.69	Fe_3O_4	-1115.5	Fe(g)	1246.0	O(g)	996.7	3358.2	838.5	4	3353.9	1.00
kJ[4]	3928	FeO	-265.1	Fe(g)	415.3	O(g)	249.2	929.6	929.6	1	929.6	1.00
eV[2]	9.68	FeO	-265.1	Fe(g)	415.3	O(g)	249.2	929.6	934.0	1	934.0	1.00
eV[6]	6.52	GaAs	-71.0	Ga(g)	272.0	As(g)	278.4	621.4	629.1	1	629.1	0.99
kcal[3]	154.7	GaAs	-71.0	Ga(g)	272.0	As(g)	278.4	621.4	647.3	1	647.3	0.96
kcal[7]	76	GaAs	-71.0	Ga(g)	272.0	As(g)	278.4	621.4	318.0	2	636.0	0.98
eV[6]	8.96	GaN	-156.8	Ga(g)	272.0	N(g)	472.7	901.5	864.5	1	864.5	1.04
kcal[3]	173.8	GaP	-114.6	Ga(g)	272.0	P(g)	316.4	703.0	727.2	1	727.2	0.97
kcal[3]	138.6	GaSb	-41.8	Ga(g)	272.0	Sb(g)	262.3	576.1	579.9	1	579.9	0.99
kcal[7]	69	GaSb	-41.8	Ga(g)	272.0	Sb(g)	262.3	576.1	288.7	2	577.4	1.00
kcal[3]	144.3	InAs	-58.6	In(g)	243.3	As(g)	278.4	580.3	603.8	1	603.8	0.96
kcal[7]	66	InAs	-58.6	In(g)	243.3	As(g)	278.4	580.3	276.1	2	552.3	1.05

kcal[3]	158.6	InP	-69.3	In(g)	243.3	P(g)	316.4	629.0	663.6	1	663.6	0.95
kcal[7]	77	InP	-69.3	In(g)	243.3	P(g)	316.4	629.0	322.2	2	644.3	0.98
kcal[3]	128.5	InSb	-30.5	In(g)	243.3	Sb(g)	262.3	536.1	537.6	1	537.6	1.00
kcal[7]	64	InSb	-30.5	In(g)	243.3	Sb(g)	262.3	536.1	267.8	2	535.6	1.00
eV[2]	8.17	K_2O	-363.2	K(g)	178.0	O(g)	249.2	790.4	788.3	1	788.3	1.00
Hartree[8]	0.248	KCl	-436.7	K(g)	89.0	Cl(g)	121.3	647.0	651.1	1	651.1	0.99
Hartree[8]	0.283	KF	-567.4	K(g)	89.0	F(g)	79.4	735.7	743.0	1	743.0	0.99
kJ[5]	657.5	$LaIr_2$	-6.9	La(g)	425.9	Ir(g)	665.3	1763.3	657.5	3	1972.5	0.89
Hartree[8]	0.266	LiCl	-408.3	Li(g)	159.3	Cl(g)	121.3	688.9	698.4	1	698.4	0.99
Hartree[8]	0.331	LiF	-616.9	Li(g)	159.3	F(g)	79.4	855.6	869.0	1	869.0	0.98
kJ[5]	284.7	$MgCu_2$	-11.7	Mg(g)	147.1	Cu(g)	338.0	834.8	284.7	3	854.1	0.98
kJ[5]	353.4	$MgNi_2$	-18.8	Mg(g)	147.1	Ni(g)	430.0	1025.9	353.4	3	1060.2	0.97
kJ[4]	3898	MgO	-601.6	Mg(g)	147.1	O(g)	249.2	997.9	997.9	1	997.9	1.00
eV[2]	10.34	MgO	-601.6	Mg(g)	147.1	O(g)	249.2	997.9	997.7	1	997.7	1.00
kJ[5]	142.5	$MgZn_2$	-10.9	Mg(g)	147.1	Zn(g)	130.4	418.8	142.5	3	427.5	0.98
kJ[4]	3813	MnO	-385.2	Mn(g)	282.4	O(g)	249.2	916.8	916.8	1	916.8	1.00
eV[2]	9.05	MoO_2	-587.9	Mo(g)	659.0	O(g)	498.3	1745.2	873.2	2	1746.4	1.00
Rydberg[9]	0.6442	Na_2O	-415.1	Na(g)	107.5	O(g)	249.2	771.8	845.7	1	845.7	0.91
eV[2]	9.1	Na_2O	-415.1	Na(g)	107.5	O(g)	249.2	771.8	878.0	1	878.0	0.88

Hartree	0.246	NaCl	-411.1	Na(g)	107.5	Cl(g)	121.3	639.9	645.9	1	645.9	0.99
Hartree	0.294	NaF	-576.6	Na(g)	107.5	F(g)	79.4	763.5	771.9	1	771.9	0.99
eV[2]	9.51	Nb_2O_5	-1898.3	Nb(g)	1445.7	O(g)	1245.9	4589.8	917.6	5	4588.0	1.00
kJ[5]	517.5	$NbCr_2$	-7	Nb(g)	722.8	Cr(g)	397.1	1524.1	517.5	3	1552.5	0.98
kJ[5]	543.6	$NbFe_2$	-15.5	Nb(g)	722.8	Fe(g)	415.3	1569.0	543.6	3	1630.8	0.96
eV[10]	8.26	NiO	-239.7	Ni(g)	430.0	O(g)	249.2	918.9	797.0	1	797.0	1.15
kJ[4]	4083	NiO	-239.7	Ni(g)	430.0	O(g)	249.2	918.9	918.9	1	918.9	1.00
eV[11]	15.07	RuO_2	-305.0	Ru(g)	642.7	O(g)	498.3	1446.1	1454.1	1	1454.1	0.99
kJ[5]	434.9	$ScCo_2$	-26.7	Sc(g)	377.7	Co(g)	424.7	1253.8	434.9	3	1304.7	0.96
kJ[5]	412.0	$ScFe_2$	-11.2	Sc(g)	377.7	Fe(g)	415.3	1219.6	412.0	3	1236.0	0.99
eV[11]	14.4	SnO_2	-577.4	Sn(g)	301.2	O(g)	498.3	1376.9	1389.4	1	1389.4	0.99
kJ[4]	3262	SrO	-592.0	Sr(g)	164.0	O(g)	249.2	1005.2	1005.2	1	1005.2	1.00
eV[2]	10.41	SrO	-592.0	Sr(g)	164.0	O(g)	249.2	1005.2	1004.4	1	1004.4	1.00
kJ[5]	531.7	$TaCr_2$	-9	Ta(g)	782.5	Cr(g)	397.1	1585.8	531.7	3	1595.1	0.99
eV[2]	11.11	Ti_2O_3	-1520.9	Ti(g)	939.7	O(g)	747.5	3208.1	1072.0	3	3215.9	1.00
eV[2]	12.88	TiO	-542.7	Ti(g)	469.9	O(g)	249.2	1261.7	1242.8	1	1242.8	1.02
eV[11]	19.9	TiO_2	-944.7	Ti(g)	469.9	O(g)	498.3	1913.0	1920.1	1	1920.1	1.00
eV[2]	9.93	TiO_2	-944.7	Ti(g)	469.9	O(g)	498.3	1913.0	958.1	2	1916.2	1.00
kJ[5]	464.3	UFe_2	-10.8	U(g)	533.0	Fe(g)	415.3	1374.5	464.3	3	1392.9	0.99

eV[2]	10.35	V_2O_3	-1218.8	V(g)	1028.4	O(g)	747.5	2994.7	998.6	3	2995.9	1.00
eV[11]	18.17	VO_2	-713.6	V(g)	514.2	O(g)	498.3	1726.1	1753.2	1	1753.2	0.98
kcal[3]	146.6	ZnS	-203.0	Zn(g)	130.4	S(g)	278.8	612.2	613.4	1	613.4	1.00
kcal[3]	124.5	ZnSe	-177.0	Zn(g)	130.4	Se(g)	227.1	534.5	520.9	1	520.9	1.03
kcal[3]	106.3	ZnTe	-117.0	Zn(g)	130.4	Te(g)	209.5	456.9	444.8	1	444.8	1.03
eV[2]	11.4	ZrO_2	-1100.3	Zr(g)	608.8	O(g)	498.3	2207.4	1100.0	2	2199.9	1.00

[a] Conversion factors applied[1]: 1 hartree = 2 Ry = 2625.5 kJ mol^{-1}; 1 eV = 96.4869 kJ mol^{-1}; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}

Table S2: Lattice energies, U_{pot}, derived from tables of incorrectly identified cohesive energies, sorted alphabetically by chemical formula. The U_{pot} values in the penultimate column are from Jenkins and Roobottom.[12]

Apparent Cohes. E.	Material	Apparent Cohes. E.	U_{pot}(calc)	Upot(calc) /Apparent Cohes. E.
/kcal mol^{-1}		/kJ mol^{-1}		
179	AlAs	748.9		
198	AlP	828.4		
165	AlSb	690.4		
786	BaO	3288.6	3029	0.92
679	BaS	2840.9		
660	BaSe	2761.4	2611	0.95
629	BaTe	2631.7		
839	CaO	3510.4	3414	0.97
764	CaS	3196.6		
726	CaSe	3037.6	2858	0.94
679	CaTe	2840.9	2721	0.96
132	CdS	552.3		
114	CdSe	477.0		
96	CdTe	401.7		
155	GaAs	648.5		
174	GaP	728.0		
139	GaSb	581.6		
144	InAs	602.5		
159	InP	665.3		
129	InSb	539.7		
163	KBr	682.0	671	0.98
170	KCl	711.3	701	0.99
194	KF	811.7	808	1.00
154	KI	644.3	632	0.98
194	LiBr	811.7	788	0.97
203	LiCl	849.4	834	0.98
247	LiF	1033.4	1030	1.00
180	LiI	753.1	730	0.97
932	MgO	3899.5	3795	0.97
896	MgS	3748.9		
780	MgSe	3263.5	3071	0.94
179	NaBr	748.9	732	0.98
187	NaCl	782.4	769	0.98
220	NaF	920.5	910	0.99
167	NaI	698.7	682	0.98
157	RbBr	656.9	651	0.99
164	RbCl	686.2	680	0.99

186	RbF	778.2	774	0.99
149	RbI	623.4	617	0.99
796	SrO	3330.5	3217	0.97
720	SrS	3012.5		
693	SrSe	2899.5	2736	0.94
667	SrTe	2790.7		
147	ZnS	615.0		
125	ZnSe	523.0		
106	ZnTe	443.5		

Table S3: Cohesive energies of alkaline-earth halides calculated via thermodynamic enthalpy summation.[13] Von Szentpaly[14] has a more extensive list for these and related materials.

Material	$\Delta_f H$	Atom Contributions / kJ mol^{-1}						Cohesive Energy
	/kJ mol^{-1}	M(g)	$\Delta_f H$(M,g)	Moles of M	X(g)	$\Delta_f H$(X,g)	Moles of X	/kJ mol^{-1}
MgF_2	-1124.2	Mg(g)	147.1	1	F(g)	79.4	2	1430.1
$MgCl_2$	-641.3	Mg(g)	147.1	1	Cl(g)	121.3	2	1031.0
$MgBr_2$	-524.3	Mg(g)	147.1	1	Br(g)	111.9	2	895.1
MgI_2	-364.0	Mg(g)	147.1	1	I(g)	106.8	2	724.6
CaF_2	-1228.0	Ca(g)	177.8	1	F(g)	79.4	2	1564.6
$CaCl_2$	-795.4	Ca(g)	177.8	1	Cl(g)	121.3	2	1215.8
$CaBr_2$	-683.8	Ca(g)	177.8	1	Br(g)	111.9	2	1085.3
CaI_2	-536.4	Ca(g)	177.8	1	I(g)	106.8	2	927.7
SrF_2	-1217.1	Sr(g)	164.0	1	F(g)	79.4	2	1539.9
$SrCl_2$	-833.8	Sr(g)	164.0	1	Cl(g)	121.3	2	1240.5
$SrBr_2$	-718.0	Sr(g)	164.0	1	Br(g)	111.9	2	1105.7
SrI_2	-561.5	Sr(g)	164.0	1	I(g)	106.8	2	939.0
BaF_2	-1208.8	Ba(g)	180.1	1	F(g)	79.4	2	1547.6
$BaCl_2$	-855.2	Ba(g)	180.1	1	Cl(g)	121.3	2	1277.9
$BaBr_2$	-757.3	Ba(g)	180.1	1	Br(g)	111.9	2	1161.1
BaI_2	-605.4	Ba(g)	180.1	1	I(g)	106.8	2	999.0

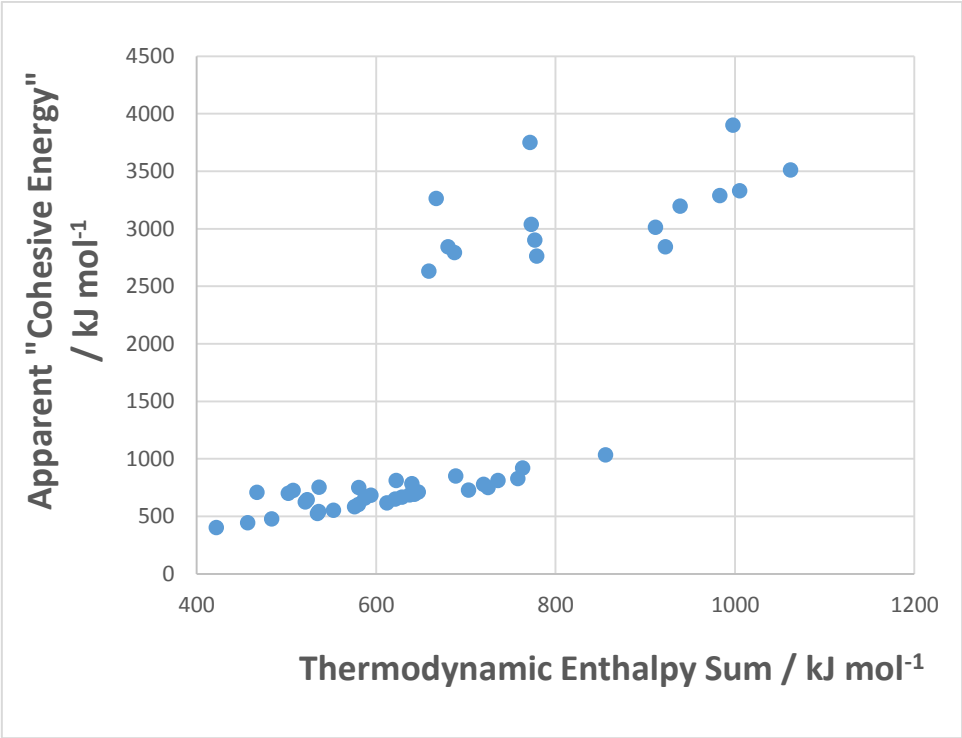

Figure S1: Plot of apparent "cohesive energy" (data listed in Tables 2 and S2) *versus* thermodynamic enthalpy sum (calculations not shown), showing lack of correlation; that is, this confirms that the listed apparent "cohesive energy" is not a cohesive energy, but actually a lattice enthalpy.

References

(1) Cohen, E. R.; Cvitaš, T.; Frey, J. G.; Holmström, B.; Kuchitsu, K.; Marquardt, R.; Mills, I.; Pavese, F.; Quack, M.; Stohner, J.; Strauss, H. L.; Takami, M.; Thor, A. J., *Quantities, Units and Symbols in Physical Chemistry - the IUPAC Green Book*. 3rd ed.; IUPAC: RSC Publishing: Cambridge, UK, 2007.

(2) Shinzato, Y. Energy expression for the chemical bond between atoms in hydrides and oxides. Nagoya University, 2008.

(3) Yadav, D. S.; Singh, D. V., *Phys. Scr.* **2012,** *85*, 015701.

(4) Jog, K. N.; Singh, R. K.; Sanyal, S. P., *Physical Review B* **1985,** *31*, 6047-6057.

(5) Li, C.; Lim Hoe, J.; Wu, P., *J. Phys. Chem. Solids* **2003,** *64*, 201-212.

(6) Palummo, M.; Bertoni, C. M.; Reining, L.; Finocchi, F., *Physica B: Condensed Matter* **1993,** *185*, 404-409.

(7) Hilsum, C.; Rose-Innes, A. C., *Semiconducting III-V compounds*. Pergamon Press: New York, 1961.

(8) Doll, K.; Stoll, H., *Physical Review B* **1997,** *56*, 10121-10127.

(9) Thompson, M.; Shen, X.; Allen, P. B., *Physical Review B* **2009,** *79*, 113108.

(10) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P., *Physical Review B* **1998,** *57*, 1505-1509.

(11) Hamad, B. A., *European Physical Journal B* **2009,** *70*, 163-169.

(12) Jenkins, H. D. B.; Roobottom, H. K., Lattice Energies. In *CRC Handbook of Chemistry and Physics*, Haynes, W. M., (Editor-in-Chief), Ed. CRC Press: Boca Raton, FL, 2015.

(13) Outotec HSC Chemistry 8. http://www.outotec.com/en/Products--services/HSC-Chemistry/ (April, 2016),

(14) von Szentpaly, L., *J. Am. Chem. Soc.* **2008,** *130*, 5962-5973.