

Geochemical applications of the simple salt approximation to the lattice energies of complex materials

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ABSTRACT

The lattice energies for a variety of compounds that can be classified as double salts are calculated by summing the lattice energies of the constituent simple salts. A comparison with the lattice energies obtained from the Born-Haber or other thermodynamic cycles shows that the simple salt approximation reproduces these values generally to within 1.2%, even for compounds that have considerable covalent character. Application of this method to the calculation of the lattice energies of silicates, using the sum of the lattice energies of the constituent oxides are, on average, within 0.2% of the value calculated from the experimental enthalpies of formation. The implications of the simple salt approximation for the thermodynamics of geochemically important processes are discussed.

INTRODUCTION

The lattice energies of complex salts such as double salts or salts containing complex ions are essential to the estimation of relative stabilities and properties such as solubilities. These energies, obtainable for simple salts through the Born equation using the Madelung constant or more approximately through the Kapustinskii equation, are not easily available by classical closed methods because of the complexity of the crystal lattices. Approximate methods using energy minimization techniques or extensions of the Kapustinskii equation are also available. For example, we have shown that the lattice energies of the apatite series of compounds $[M_3(PO_4)_3X]$, where M is a divalent metal cation and X is hydroxide or halide] obtained with the Glasser-Jenkins approximation are generally within 4% of the experimental (Born-Haber cycle) values (Yoder et al. 2003).

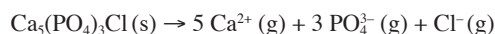
In our attempts to find simple ways to approximate the lattice energies of these complex systems, we have found that the interactions in a generalized double salt $MX_nM'Q_m$ are not too dissimilar to the weighted average interactions in the hypothetical constituent simple salts MX_n and $M'Q_m$. For example, the simple salt constituents of fluoroapatite, $Ca_5(PO_4)_3F$, are CaF_2 and $Ca_3(PO_4)_2$, and the salts contribute $1/2 CaF_2 + 3/2 Ca_3(PO_4)_2$ to the stoichiometry of the compound. Our assumption, then, for fluoroapatite is that the interactions in one mole can be approximated as one-half of the interactions in calcium fluoride plus three-halves of the interactions in calcium phosphate. It is therefore a simple matter to estimate the lattice energy of fluoroapatite by looking up the lattice energies of the simple salts. We have found that this simple assumption allows for excellent estimation of the lattice energies of many diverse complex salts. Though many of the salts are comprised of more than two simple salts, we have chosen to use the term “double salt” because the term “complex” implies covalent interactions, as in “complex ions.” Although silicates are less obviously regarded as “double”

salts, they can be thought of (and for analytical purposes have long been thus regarded) as “double” salts of the constituent oxides. For example, microcline, $KAlSi_3O_8$, can be thought of as a double salt of K_2O , Al_2O_3 , and SiO_2 in the ratio $0.5 K_2O + 0.5 Al_2O_3 + 3 SiO_2$.

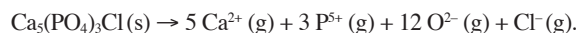
RESULTS

It is important to realize that the lattice energy of many complex salts can be defined in a variety of ways. For example, the lattice energy of chloroapatite, $Ca_5(PO_4)_3Cl$, can be defined as:

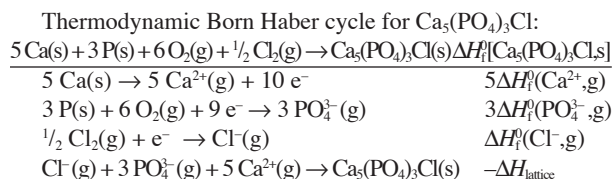
(1) the energy necessary to create the gaseous Ca^{2+} , PO_4^{3-} , and Cl^- ions



(2) the energy necessary to create the gaseous Ca^{2+} , P^{5+} , O^{2-} , and Cl^- ions



The first of these is probably more appropriate because of the well-known existence of the phosphate ion and its structural integrity in the lattice of apatites. The lattice energy calculated from the enthalpy of formation of apatite using these definitions is, of course, vastly different. For the first definition, a value of 16 848 kJ/mol was obtained, whereas for the second definition the lattice energy is almost 80 000 kJ/mol. Both of these values were calculated from the thermodynamic Born-Haber cycle, shown below for the calculation of the lattice energy using the structural entity PO_4^{3-} .



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In some cases the calculation using a structural entity such as an oxy anion is made very difficult by the absence of a value for the heat of formation of that anion. This is the case, for example, with the orthosilicate ion, SiO_4^{4-} . For compounds that contain this ion, as well as other silicate ions (many of which are not discrete, monomeric ions even in the solid phase), the definition involving ionization to the Si^{4+} ion is adopted. [The difference between the two definitions of lattice energy for the SiO_4^{4-} ion—for example, $\text{Ca}_2\text{SiO}_4(\text{s}) \rightarrow 2 \text{Ca}^{2+}(\text{g}) + \text{SiO}_4^{4-}(\text{g})$ vs. $\text{Ca}_2\text{SiO}_4(\text{s}) \rightarrow 2 \text{Ca}^{2+}(\text{g}) + \text{Si}^{4+}(\text{g}) + 4 \text{O}^{2-}(\text{g})$ —is the formation of the gaseous oxy anion from its gaseous components (Glasser and Jenkins 2000).]

Regardless of the definition employed for the lattice energy, the parameter measures the forces within the crystal lattice. The assumption that these forces in a double salt can be estimated as a sum of the forces in the “constituent” salts implies an additivity relationship that at first glance does not seem reasonable because of the additional forces that must exist in the double salt. There are, however, several reported additivity relationships for calculation of heats of formation of complex materials—polyhedral contributions (Chermak and Rimstidt 1989), constituent oxide additivity (Kutolin 1965), and bond and atom additivity (Wilcox and Bromley 1963; Ducros and Sannier 1992).

Table 1 provides enthalpies of formation, lattice energies obtained from the enthalpies of formation using Born-Haber type thermodynamic cycles, lattice energies calculated as the sum of the simple salt constituents, and the percent difference between the “experimental” cycle and simple salt values. The compounds in the table are arranged by anion beginning with the oxy anions carbonate, sulfate, phosphate, and orthosilicate, followed by halide, oxide, and sulfide, and ending with several cyanides, iodate, and nitrate. The lattice enthalpies obtained from the Born-Haber cycle were converted to lattice energies by accounting for vibrational modes of monatomic and polyatomic ions, using the equation $\Delta H_{\text{lattice}} = U_{\text{POT}} + [p(n_{\text{M}}/2-2) + q(n_{\text{X}}/2-2)]RT$, where n_{M} and n_{X} are determined by the ions of the salt M_pX_q and have values of 3, 5, and 6 for monatomic, linear, and polyatomic ions, respectively (Jenkins et al. 2002). The average difference between the Born-Haber experimental values and the simple salt values is 1.2% and the largest difference is 7.0%; 50% of the values have a difference of 0.5% or less.

For double salts that contain two or more cations and two or more anions there is more than one set of simple salt constituents. For example, for alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, the two sets of four simple salt constituents [K_2SO_4 , KOH , $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}(\text{OH})_3$] that provide the correct stoichiometry are $1/2 \text{K}_2\text{SO}_4 + 1/2 \text{Al}_2(\text{SO}_4)_3 + 2 \text{Al}(\text{OH})_3$ and $\text{KOH} + 5/3 \text{Al}(\text{OH})_3 + 2/3 \text{Al}_2(\text{SO}_4)_3$. These sets produce lattice energies of 18216 and 18268 kJ/mol, respectively, for an average of 18242 kJ/mol. In the four cases of this type in Table 1, the averages obtained from the sets are reported in the table. For lazulite, $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$, three combinations are

possible— $2 \text{AlPO}_4 + \text{Mg}(\text{OH})_2$ (18024 kJ/mol), $1/3 \text{Mg}_3(\text{PO}_4)_2 + 4/3 \text{AlPO}_4 + 2/3 \text{Al}(\text{OH})_3$ (17566 kJ/mol), and $1/6 \text{Mg}_3(\text{PO}_4)_2 + 5/3 \text{AlPO}_4 + 1/2 \text{Mg}(\text{OH})_2 + 1/3 \text{Al}(\text{OH})_3$ (17795 kJ/mol)—which produce an average of 17795 kJ/mol. For double salts that contain ions that could generate significant covalent interactions, it would presumably be advantageous to use only the set that contains that pair of ions; for example, in the compound $\text{Ag}_2\text{CaSO}_4\text{Br}_2$ the set $2 \text{AgBr} + \text{CaSO}_4$ would probably provide a better estimate of the lattice energy because of the covalent (and van der Waals) interactions in AgBr . Unfortunately, very few experimental enthalpies of formation are available for comparison.

It is important to understand that our convention for the selection of simple salt constituents was to choose the “salts” of the ions as they appear in the formulas given in Table 1 when the anions exist as discrete entities in the solid phase (and in most cases have known enthalpies of formation in the gaseous state). Thus, for alunite we did not use the simple salt constituents K_2O , H_2O , Al_2O_3 , $\text{Al}_2(\text{SO}_4)_3$ —this choice of simple salts will produce, in the correct combination, the stoichiometry of alunite, but it will result in a lattice energy that corresponds to formation of the ions K^+ , Al^{3+} , SO_4^{2-} , H^+ , and O^{2-} , rather than K^+ , Al^{3+} , SO_4^{2-} , and OH^- in the gaseous phase.

For the silicates the oxides were chosen as simple salt constituents. In these compounds the existence of discrete ions in the solid state may be uncertain and the enthalpies of formation of the gaseous anions (for example, for orthosilicate) are unknown or uncertain. For example, for microcline, KAlSi_3O_8 , the constituents are $1/2 \text{K}_2\text{O} + 1/2 \text{Al}_2\text{O}_3 + 3 \text{SiO}_2$ and the lattice energy corresponds to complete “ionization” as shown below:



Values calculated for the silicates using this convention are listed in Table 2 (the lattice energies of the orthosilicates in Table 1 were calculated using this convention and are included in both tables). Table 2 contains both the Born-Haber cycle

TABLE 1. Lattice energies of selected double salts, kJ/mol

Compound	Name	Constituent simple salts*	ΔH_f° (298K)	LE, BH†	LE, SS‡	% diff.§
$\text{Na}_2\text{Cu}(\text{CO}_3)_2$		$(\text{Na}_2\text{CO}_3) \cdot (\text{CuCO}_3)$	-1712.5	5021	5357	6.7
$\text{K}_2\text{Cu}(\text{CO}_3)_2$		$(\text{K}_2\text{CO}_3) \cdot (\text{CuCO}_3)$	-1733.4	5173	5185	0.2
$\text{CaMg}(\text{CO}_3)_2$	dolomite	$(\text{CaCO}_3) \cdot (\text{MgCO}_3)$	-2331.6	5962	5932	0.5
$\text{CaMn}(\text{CO}_3)_2$	kutnahorite	$(\text{CaCO}_3) \cdot (\text{MnCO}_3)$	-2093.4	5895	5961	1.1
$\text{Cu}_2(\text{OH})_2\text{CO}_3$	malachite	$(\text{CuCO}_3) \cdot (\text{Cu}(\text{OH})_2)$	-1054.7	6552	6564	0.2
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	azurite	$2(\text{CuCO}_3) \cdot (\text{Cu}(\text{OH})_2)$	-1675.1	9905	9891	0.1
$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$	hydrozincite	$2(\text{ZnCO}_3) \cdot 3(\text{Zn}(\text{OH})_2)$	-3584	15989	16020	0.2
$\text{BaCa}(\text{CO}_3)_2$	alstonite	$(\text{BaCO}_3) \cdot (\text{CaCO}_3)$	-2434.6	5376	5364	0.2
$\text{Pb}_2(\text{CO}_3)_2(\text{OH})_2$	hydrocerussite	$2(\text{PbCO}_3) \cdot (\text{Pb}(\text{OH})_2)$	-1906	8093	8123	0.4
$\text{Pb}_3\text{O}(\text{CO}_3)_2$		$(\text{PbO}) \cdot 2(\text{PbCO}_3)$	-1624	8940	8933	0.1
Pb_2OCO_3		$(\text{PbO}) \cdot (\text{PbCO}_3)$	-943	6208	6183	0.4
$\text{Pb}_2\text{O}_2\text{CO}_3$		$2(\text{PbO}) \cdot (\text{PbCO}_3)$	-1127	9606	9616	0.1
$\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$	macphersonite	$2(\text{PbCO}_3) \cdot (\text{PbSO}_4) \cdot (\text{Pb}(\text{OH})_2)$	-2167.9	9969	10657	6.9
$(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$		$((\text{NH}_4)_2\text{SO}_4) \cdot 2(\text{CdSO}_4)$	-3031.7	7255	7559	4.2
$(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$		$((\text{NH}_4)_2\text{SO}_4) \cdot 2(\text{MnSO}_4)$	-3250.2	7266	7427	2.2
$\text{K}_2\text{Cd}_2(\text{SO}_4)_3$		$(\text{K}_2\text{SO}_4) \cdot 2(\text{CdSO}_4)$	-3305.5	7305	7578	3.7
$\text{K}_2\text{Cu}(\text{SO}_4)_2$		$(\text{K}_2\text{SO}_4) \cdot (\text{CuSO}_4)$	-2209.6	4774	4862	1.8
$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$	langbeinite	$(\text{K}_2\text{SO}_4) \cdot 2(\text{MgSO}_4)$	-3953	7402	7544	1.9
$\text{K}_2\text{Zn}_2(\text{SO}_4)_3$		$(\text{K}_2\text{SO}_4) \cdot 2(\text{ZnSO}_4)$	-3406.9	7725	7808	1.1
$\text{K}_3\text{Na}(\text{SO}_4)_2$	aphthitalite	$1.5(\text{K}_2\text{SO}_4) \cdot 0.5(\text{Na}_2\text{SO}_4)$	-2855.8	3492	3663	4.9
$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	alunite	see text	-5026.4	19606	18242	7.0
$\text{Cu}_3\text{SO}_4(\text{OH})_4$	antlerite	$(\text{CuSO}_4) \cdot 2(\text{Cu}(\text{OH})_2)$	-1723.7	9550	9540	0.1
$\text{Cu}_4(\text{SO}_4)(\text{OH})_6$	brochantite	$(\text{CuSO}_4) \cdot 3(\text{Cu}(\text{OH})_2)$	-2053.5	12646	12777	1.0
Cu_2OSO_4		$(\text{CuO}) \cdot (\text{CuSO}_4)$	-936.4	7126	7116	0.1

Continued on the next page.

values and the simple salt approximation values for the lattice energy. [Enthalpies of formation of gaseous ions were taken from Wagman et al. 1992 and Dasent 1982, $\Delta H_f^\circ(\text{O}^{2-})$ was taken at

838 kJ/mol, consistent with the values used to obtain the lattice energies in the compilation of Jenkins 1996]. The compounds in the table are arranged primarily by type of silicate beginning with tectosilicates.

TABLE 1 continued.

Pb ₂ OSO ₄	lanarkite	(PbO)·(PbSO ₄)	-1171.5	5999	5967	0.5
Pb ₃ O ₂ SO ₄		2(PbO)·(PbSO ₄)	-1399.1	9441	9400	0.4
Pb ₄ O ₃ SO ₄		3(PbO)·(PbSO ₄)	-1626.7	12882	12833	0.4
NaFePO ₄	maricite	0.33(Na ₃ PO ₄)·0.33(Fe ₃ (PO ₄) ₂)	-1571.8	5253	5175	1.5
Na ₃ Fe(PO ₄) ₂		(Na ₃ PO ₄)·(FePO ₄)	-3830.8	12015	11210	6.7
Al ₄ (PO ₄) ₃ (OH) ₂	trolleite	(Al(OH) ₃)·3(AlPO ₄)	-6530	28992	28154	2.9
Ca ₂ Al(PO ₄) ₂ OH	bearthite	see text	-4327.3	14160	13969	1.3
MgAl ₂ (PO ₄) ₂ (OH) ₂	lazulite	see text	-4532	18200	17795	2.2
MgAlOPO ₄		see text	-2405	11398	11330	0.6
Ca ₅ (PO ₄) ₃ OH		1.5(Ca ₃ (PO ₄) ₂)·0.5(Ca(OH) ₂)	-6657	17106	17041	0.4
Ca ₅ (PO ₄) ₃ F		1.5(Ca ₃ (PO ₄) ₂)·0.5(CaF ₂)	-6779	17118	17034	0.5
Sr ₅ (PO ₄) ₃ F		1.5(Sr ₃ (PO ₄) ₂)·0.5(SrF ₂)	-6802	16464	16359	0.6
Sr ₅ (PO ₄) ₃ Cl		1.5(Sr ₃ (PO ₄) ₂)·0.5(SrCl ₂)	-6616.5	16301	16191	0.7
Ba ₅ (PO ₄) ₃ Cl		1.5(Ba ₃ (PO ₄) ₂)·0.5(BaCl ₂)	-6623	15657	15509	0.9
Cd ₅ (PO ₄) ₃ F		1.5(Cd ₃ (PO ₄) ₂)·0.5(CdF ₂)	-4397.5	18225	18113	0.6
Cd ₅ (PO ₄) ₃ Cl		1.5(Cd ₃ (PO ₄) ₂)·0.5(CdCl ₂)	-4231.5	18081	17985	0.5
Ca ₄ (PO ₄) ₂ O		(Ca ₃ (PO ₄) ₂)·(CaO)	-4764.1	13951	13880	0.5
Ca ₃ Al ₂ (SiO ₄) ₃	grossular	3(CaO)·(Al ₂ O ₃)·3(SiO ₂)	-6656.7	64771	64427	0.5
Ca ₃ Fe ₂ (SiO ₄) ₃	andradite	3(CaO)·(Fe ₂ O ₃)·3(SiO ₂)	-5764.7	64338	64037	0.5
Fe ₃ Al ₂ (SiO ₄) ₃	almandine	3(FeO)·(Al ₂ O ₃)·3(SiO ₂)	-5272	65858	65817	0.1
LiAlSiO ₄	eucryptite	0.5(Li ₂ O)·0.5(Al ₂ O ₃)·(SiO ₂)	-2123.3	22083	22007	0.3
Ca ₄ F ₂ Si ₂ O ₇	cuspidine	3(CaO)·(CaF ₂)·2(SiO ₂)	-5234	39167	38873	0.8
CaTiOSiO ₄	titanite	(CaO)·(TiO ₂)·(SiO ₂)	-2610.1	28454	28334	0.4
Al ₂ OSiO ₄	andalusite	(Al ₂ O ₃)·(SiO ₂)	-2587.5	28184	28182	0.0
CaMgSiO ₄	monticellite	(CaO)·(MgO)·(SiO ₂)	-2263.1	20328	20212	0.6
K ₂ CuCl ₃		2(KCl)·(CuCl)	-1016.7	2443	2426	0.7
KAgCl ₂		(KCl)·(AgCl)	-563.2	1638	1630	0.5
KCuCl ₃		(KCl)·(CuCl ₂)	-671.5	3547	3526	0.6
K ₂ AgBr ₃		2(KBr)·(AgBr)	-906.2	2307	2268	1.7
KAgBr ₂		(KBr)·(AgBr)	-492.5	1595	1586	0.6
KAgI ₂		(KI)·(AgI)	-382.4	1529	1538	0.6
K ₂ AgI ₃		2(KI)·(AgI)	-686.6	2153	2187	1.6
Cu ₄ (OH) ₆ Cl ₂	atacamite	(CuCl ₂)·3(Cu(OH) ₂)	-1652.7	12542	12522	0.2
Pb ₄ (OH) ₆ Cl ₂		3(Pb(OH) ₂)·(PbCl ₂)	-1682.6	9849	10138	2.9
Pb ₃ O ₂ Cl ₂	mendipite	2(PbO)·(PbCl ₂)	-836	9174	9135	0.4
Pb ₄ O ₂ Cl ₂	damaraite	3(PbO)·(PbCl ₂)	-1060.2	12612	12568	0.3
PbClOH	laurionite	0.5(Pb(OH) ₂)·0.5(PbCl ₂)	-525.9	2524	2446	3.1
PbFCI	matlockite	0.5(PbF ₂)·0.5(PbCl ₂)	-534.7	2423	2396	1.1
Pb ₂ OCl ₂		(PbO)·(PbCl ₂)	-605.4	5730	5702	0.5
Cu ₄ (OH) ₆ Br ₂		(CuBr ₂)·3(Cu(OH) ₂)	-1582	12499	12474	0.2
CaTiO ₃	perovskite	(CaO)·(TiO ₂)	-1660.6	15395	15314	0.5
Ca ₃ Ti ₂ O ₇		3(CaO)·2(TiO ₂)	-3950.5	34186	34029	0.5
MnAl ₂ O ₄	galaxite	(MnO)·(Al ₂ O ₃)	-2099.3	18946	18907	0.2
NiFe ₂ O ₄	trevorite	(NiO)·(Fe ₂ O ₃)	-1078.5	18796	18786	0.1
MgAl ₂ O ₄	spinel	(MgO)·(Al ₂ O ₃)	-2299.9	18975	18953	0.1
CuCo ₂ S ₄	carrollite	(CuS)·(Co ₂ S ₃)	-153.6	17844	17487	2.0
KHgCl(CN) ₂		(KCl)·(Hg(CN) ₂)	-179.9	3425	3468	1.3
KHgBr(CN) ₂		(KBr)·(Hg(CN) ₂)	-148.5	3407	3435	0.8
KHgI(CN) ₂		(KI)·(Hg(CN) ₂)	-91.6	3371	3402	0.9
Cu ₄ (OH) ₆ (IO ₃) ₂	salesite	(Cu(IO ₃) ₂)·3(Cu(OH) ₂)	-1797.0	12729	12730	0.0
Cu ₄ (NO ₃) ₂ (OH) ₆	gerhardtite	(Cu(NO ₃) ₂)·3(Cu(OH) ₂)	-1726	12434	12431	0.0

Notes: Many heats of formation were obtained from Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Harlow, J., Bailey, S.M., Churney, K.L. and Nuttall, R.L. (1982) The NBS Tables of chemical thermodynamic properties. J. Phys. Chem. Ref. Data, 11, Suppl. 2. Others were from Vieillard, P. (1988) Thermochemical properties of the copper compounds. Thermodynamic data file. Sciences Geologiques, Bulletin, 41, 289-308. Other enthalpies of formation values are available from the authors upon request. Heats of formation of gaseous ions obtained from Lide, D.R., Ed. (1996) CRC Handbook of Chemistry and Physics. CRC Press, Boca Raton. 5-1 to 5-4.

* The simple salt constituents for the purpose of calculation of the lattice energy.

† The experimentally based lattice energies were determined using a thermochemical cycle from the heat of formation of the double salt and gaseous ions.

‡ "LE, SS" refers to the lattice energy determined by adding the lattice energies of the constituent simple salts.

|| Experimentally-based lattice energies determined using a thermochemical cycle based on the heat of dissolution of the compound, and the enthalpies of hydration of the ions.

§ Errors are absolute (unsigned).

Two of the minerals in Table 2 are hydrates. The enthalpy of formation of the anhydrous parent of these minerals was obtained by subtracting $n(-298.6 \text{ kJ/mol})$, where n is the number of waters in the formula, from the experimental enthalpy of formation of the hydrate (Jenkins and Glasser 2002). This procedure allows for direct comparison of the cycle lattice energy of the parent with the simple salt approximation. [An alternative procedure, also reported by Jenkins and Glasser (2002), is to obtain the lattice energy of the hydrate and then convert it to the lattice energy of the anhydrous parent using $U_{\text{POT}}(\text{anhydrous}) = U_{\text{POT}}(\text{hydrate}) - n(54.3 \text{ kJ/mol})$.]

For the silicates, the average deviation of the simple salt approximation to the lattice energy from the Born-Haber value is 0.2%, less than the 1.2% average deviation for the 75 double salts in Table 1.

The simple salt lattice energies were taken from the compilation by Jenkins (1996) or were calculated by us from reported enthalpies of formation using the Born-Haber cycle, and are listed in Table 3.

The separation of the compounds in the Table 1 by anion shows that differences between the cycle lattice energies and the simple salt approximations are fairly uniform for all of the anion types—carbonate, sulfate, phosphate, orthosilicate, oxide, halide, etc. The deviations from the experimental values also do not seem to depend markedly on the nature of the cation. The greater covalent character of many transition metal compounds is apparently subsumed by the interactions that occur in the simple salt constituents. The generally excellent agreement and the wide variety of compounds to which the simple salt treatment responds suggests that this is a powerful and accurate method for calculating lattice energies of many complex materials.

As an example of the application of this method to a system for which the lattice energy was obtained by extensive computer calculation (treating the total potential energy as a sum of the Madelung, repulsive, and van der Waals interactions using the Buckingham equation), consider K_2NaGaF_6 and K_2NaScF_6 , for which the lattice energies were calculated as 8713 and 8162 kJ/mol, respectively (Marx 2000). The simple salt method uses the Born-Haber lattice energies as found in the CRC compilation: KF, 821; NaF, 923; GaF₃, 6205;

TABLE 2. Born-Haber and simple salt approximation values of the lattice energies of some silicates, kJ/mol*

Formula	Name	ΔH_f^\ddagger	Born-Haber LE	Simple salt LE	% error [†]
KAlSi ₃ O ₈	microcline	-3967.7	47975	47758	0.45
NaAlSi ₃ O ₈	albite(low)	-3935.1	48037	47880	0.33
CaAl ₂ Si ₂ O ₈	anorthite	-4243.0	44715	44604	0.25
KAlSi ₂ O ₆	leucite	-3038.7	34936	34738	0.57
Na ₆ (Al ₆ Si ₆ O ₂₄)Cl ₂	sodalite	-1618.6	121675	132606	8.98
CaAl ₂ Si ₇ O ₁₈ +6H ₂ O	heulandite	-10575.5	110786 [§]	109707	0.97
NaAlSi ₃ O ₆ +H ₂ O	analcime	-3307.9	35330 [§]	34859	1.33
Mg ₂ Al ₂ (AlSi ₃ O ₁₀)	cordierite	-9161.5	103060	103009	0.05
Fe ₂ Al ₂ Si ₅ O ₁₈	ferrocordierite	-8450.4	103152	103157	0.01
Al ₂ Si ₂ O ₁₀ (OH) ₂	pyrophyllite	-5643.3	71475	71450	0.03
Al ₂ Si ₂ O ₅ (OH) ₄	kaolinite	-4114.9	49634	49615	0.04
Al ₂ Si ₂ O ₅ (OH) ₄	dickite	-4117.5	49636	49615	0.04
Mg ₃ Si ₄ O ₁₀ (OH) ₂	talca	-5915.9	67828	67661	0.25
Mg ₃ Si ₂ O ₅ (OH) ₄	serpentine	-4366.0	45965	45826	0.30
Mg ₃ Si ₂ O ₅ (OH) ₄	chrysotile	-4361.7	45961	45826	0.29
Mg ₃ Al ₂ Si ₃ O ₁₀ (OH) ₈	chlorite	-8901.5	90288	90003	0.32
Ca ₂ Al ₂ Si ₂ O ₁₀ (OH) ₂	prehnite	-6193.2	65448	65232	0.33
KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	muscovite	-5976.7	67377	67127	0.37
KMg ₃ (AlSi ₃ O ₁₀)F ₂	fluorophlogopite	-6392.9	58619	58297	0.55
Ca ₂ Fe ₂ Si ₆ O ₂₂ (OH) ₂	actinolite	-10523.6	134791	134497	0.22
Ca ₂ Mg ₅ (Si ₈ O ₂₂)(OH) ₂	trémolite	-12355.1	134616	134127	0.36
MgSiO ₃	enstatite	-1526.7	16825	16812	0.08
MgSiO ₃	clinoenstatite	-1547.8	16846	16812	0.21
FeMgSi ₂ O ₆	hypersthene	-2755.6	33754	33697	0.17
CaMg(SiO ₃) ₂	diopside	-3210.8	33385	33233	0.46
CaFeSi ₂ O ₆	hedenbergite	-2840.5	33416	33307	0.33
NaAl(SiO ₃) ₂	jadeite	-3029.4	35022	34859	0.46
LiAlSi ₂ O ₆	al-spodumene	-3053.5	35122	35028	0.27
FeSiO ₃	ferrosilite	-1195.0	16895	16886	0.06
MnSiO ₃	rhodonite	-1319.4	16789	16765	0.14
CaSiO ₃	wollastonite	-1635.2	16511	16422	0.54
NaMg ₂ Al ₄ (BO ₃) ₂ Si ₆ O ₁₈ (OH) ₄	dravite	-15437	173128	172727	0.23
Be ₂ Al ₂ Si ₆ O ₁₈	beryl	-9006.6	106651	106614	0.04
Ca ₂ MgSi ₂ O ₇	akermanite	-3876.5	36817	36634	0.50
Ca ₂ Al ₂ SiO ₇	gehlenite	-4007.6	35136	34985	0.43
Ca ₂ Si ₂ F ₂ O ₇	cuspidine	-5234.0	39167	38880	0.73
Ca ₂ SiO ₄	larnite	-2306.0	19948	19823	0.63
Ca ₂ SiO ₄	calcium olivine	-2316.6	19959	19822	0.68

Be ₂ SiO ₄	phenakite	-2143.1	21920	21907	0.06
Zn ₂ SiO ₄	willemitite	-1636.8	20993	20963	0.14
Mg ₂ Al ₂ Si ₂ O ₁₂	pyrope	-6284.6	65667	65597	0.11
Fe ₃ Al ₂ (SiO ₄) ₃	almandine	-5272	65858	65819	0.06
Ca ₃ Al ₂ Si ₂ O ₁₂	grossular	-6656.7	64771	64427	0.53
Ca ₃ Fe ₂ (SiO ₄) ₃	andradite	-5764.7	64338	64038	0.47
Ca ₂ Fe ³⁺ Al ₂ Si ₂ O ₁₂ (OH)	epidote	-6461.8	70736	70516	0.31
ZrSiO ₄	zircon	-2033.4	22757	22735	0.10
BeAlSiO ₄ (OH)	euclase	-2532.9	27173	27148	0.09
Ca ₃ Mg(SiO ₄) ₂	merwinite	-4566.8	40274	40035	0.59
Fe ₂ SiO ₄	fayalite	-1479.4	20770	20751	0.09
Mg ₂ SiO ₄	fosterite	-2170.4	20658	20603	0.27
Mn ₂ SiO ₄	tephroite	-1728.1	20558	20510	0.23
LiAlSiO ₄	eucryptite	-2123.3	22083	22007	0.34
KAlSiO ₄	kaliophyllite	-2121.9	21910	21718	0.88
NaAlSiO ₄	nepheline	-2092.1	21975	21839	0.62
Ba ₂ SiO ₄		-2265.6	19377	19129	1.28
CaMgSiO ₄	monticellite	-2263.1	20328	20213	0.57
Ni ₂ SiO ₄		-1396.6	21050	21044	0.03
Sr ₂ SiO ₄		-2304.5	19676	19467	1.06
Al ₂ OSiO ₄	andalusite	-2587.5	28184	28183	0.00
Al ₂ SiO ₅	sillimanite	-2585.7	28182	28183	0.00
Al ₂ SiO ₅	kyanite	-2591.7	28188	28183	0.02
Fe ₂ Al ₂ Si ₄ O ₂₃ (OH)	staurolite	-12059	130321	130145	0.13
CaTiOSiO ₄	titanite	-2610.1	28454	28334	0.42
CaTiSiO ₅	sphene	-2601.4	20768	20233	2.68
CaAl ₂ SiO ₆	pyroxene	-3280.2	31643	31584	0.19
CaAl ₂ Si ₂ O ₁₀ (OH) ₂	margarite	-6233.3	64099	63973	0.20
KFe ₃ AlSi ₃ O ₁₀ F ₂	annite	-5155.5	58586	58448	0.24
Mg ₄ Al ₁₀ Si ₃ O ₃₁ (OH) ₄	yoderite	-17871	190640	190531	0.06

* Most heats of formation obtained from Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures. Geological Survey Bulletin 1452. United States Government Printing Office, Washington. Some also obtained from Faure, G. (1991) Principles and applications of inorganic geochemistry. Macmillan Publishing Company, New York, or Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Harlow, L., Bailey, S.M., Churney, K.L. and Nutall, R.L. (1982) The NBS Tables of chemical thermodynamic properties. J. Phys. Chem. Ref. Data, 11, Suppl. 2. Other values for enthalpies of formation are available from the authors upon request. Heats of formation of gaseous ions obtained from Lide, D.R., Ed. (1996) CRC Handbook of Chemistry and Physics. CRC Press, Boca Raton. 5-1 to 5-4.

§ Calculated for anhydrous parent, see text.

† Errors are absolute (unsigned).

and ScF₃, 5492 kJ/mol (Jenkins 1996). Thus, the simple salt approximation for K₂NaGaF₆ is 2(821) + 923 + 6205 = 8770 kJ/mol and for K₂NaScF₆, 8057 kJ/mol. The differences between the simple salt values and the reported lattice energies are 0.7% and 1.3% for the gallium and scandium compounds, respectively.

We have also calculated the lattice energies using the versatile Glasser-Jenkins equation, a modification of the Kapustinskii equation (Jenkins et al. 1999; Glasser and Jenkins 2000). These values were obtained from experimental XRD formula unit volumes (when possible) and the equation $U_{\text{POT}} = AI/V_{\text{norm}}^{1/3}$. In this equation $A = 121.39$ kJ/mol nm, $I = 1/2\sum n_i z_i^2$, where n_i is the number of ions of type i per formula unit, each with charge z_i , and V_{norm} is the normalized unit-cell volume ($V_{\text{norm}} = V_m/2I$, where V_m is the unit-cell volume for the molar formula). When experimental unit-cell volumes were unknown, the unit-cell volume was approximated as the sum of the ion volumes as described by Glasser and Jenkins (2000). The volume (0.063 nm³) previously established for the phosphate ion was utilized in these ion volume calculations (Yoder et al. 2003). A selected set of Glasser-Jenkins lattice energies is shown in Table 4, arranged in order of increasing deviation from the Born-Haber lattice energy. Because this approximation is based on the assumption of total ionic character it is not surprising that those compounds that deviate the most contain a transition metal ion such as copper or silver or a polarizable ion such as lead which presumably confers

covalent character to the bonding. The average deviation of the Glasser-Jenkins value for all 75 compounds in Table 1 is 20%, but for compounds without these ions it is 10%. The average deviation of the Glasser-Jenkins approximation for the silicates (7%) is significantly higher than the simple salt approximation. Thus, the simple salt approximation provides a good approximation to the lattice energy, arguably as good as those from extensive calculational methods.

DISCUSSION

There are several important geochemical consequences of the observation that the lattice energy of a "double" salt can be approximated as the sum of the lattice energies of the constituent simple salts.

First, the enthalpies of formation of "double salts" can be approximated as the sum of the enthalpies of formation of their simple salt constituents. The enthalpy of formation of an ionic salt is the sum of the heat of formation of the gaseous cations and anions minus the lattice enthalpy, as shown below for CuCO₃.

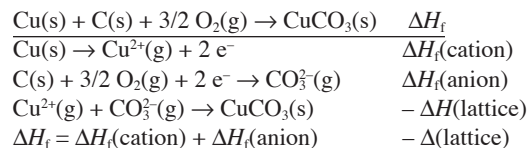


TABLE 3. Simple Salt lattice energies (kJ/mol) used in summation approximation†

Salt	Lattice E	Salt	Lattice E	Salt	Lattice E	Salt	Lattice E
BaCO ₃	2554	Ca ₃ (PO ₄) ₂	10479	MgF ₂	2957	FeO	3865
CaCO ₃	2810	Cd ₃ (PO ₄) ₂	11139‡	PbCl ₂	2269	Fe ₂ O ₃	14774
CuCO ₃	3327	FePO ₄	7303	PbF ₂	2522	H ₂ O	4206§
K ₂ CO ₃	1858	Fe ₃ (PO ₄) ₂	11619*	SrCl ₂	2156	K ₂ O	2232§
MgCO ₃	3122	Mg ₃ (PO ₄) ₂	11407	SrF ₂	2492	Li ₂ O	2811§
MnCO ₃	3151	Na ₃ PO ₄	3907			MgO	3791
Na ₂ CO ₃	2030	Sr ₃ (PO ₄) ₂	10075	Al(OH) ₃	5627	MnO	3745
PbCO ₃	2750			Ca(OH) ₂	2645	Na ₂ O	2475§
ZnCO ₃	3273	AgCl	915	Cd(OH) ₂	2918	NiO	4012
		AgBr	904	Cu(OH) ₂	3237	PbO	3433§
Al ₂ (SO ₄) ₃	12128§	AgI	889	Fe(OH) ₃	6103§	SiO ₂	13020§
CdSO ₄	2891	BaCl ₂	2056	KOH	804	SrO	3223
CuSO ₄	3066	CaF ₂	2630	Mg(OH) ₂	3006	TiO	3811
Fe ₂ (SO ₄) ₃	12486§	CdCl ₂	2552	NaOH	900	TiO ₂	11913§
K ₂ SO ₄	1796	CdF ₂	2809	Pb(OH) ₂	2623	ZnO	3971
MgSO ₄	2874§	CuBr ₂	2763	Sr(OH) ₂	2483	ZrO ₂	9714§
MnSO ₄	2825	CuCl	996	Zn(OH) ₂	3158		
(NH ₄) ₂ SO ₄	1777	CuCl ₂	2811			Co ₂ S ₃	13863§
Na ₂ SO ₄	1938	FeF ₂	2952§	Al ₂ O ₃	15162§	CuS	3624§
PbSO ₄	2534	KBr	682	B ₂ O ₃	18730§	Hg(CN) ₂	2753§
ZnSO ₄	3006	KCl	715	BaO	3054	KSCN	616
		KI	649	BeO	4443	Cu(IO ₃) ₂	3019§
AlPO ₄	7509	NaCl	786	CaO	3401	KHCO ₃	736
Ba ₃ (PO ₄) ₂	9654	NaF	923	CuO	4050	Cu(NO ₃) ₂	2720

* Lattice energy calculated from Born-Haber cycle using the heat of formation obtained from Kaell (1984).

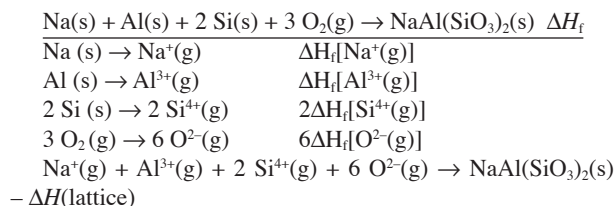
† All lattice energies except those indicated were obtained from Jenkins (1996). The values correspond to "Thermochemical Cycle Values" ($U_{\text{TOT}}^{\text{BHC}}$) rather than "Calculated Values" in that listing, except Al(OH)₃ and CdSO₄ (which were "Calculated Values"). Lattice energies were calculated for the oxides from heats of formation[§] and use of 838 kJ/mol for the heat of formation of the gaseous oxide ion.

‡ Lattice energy calculated from Born-Haber cycle using the heat of formation obtained from Cherifa (2001).

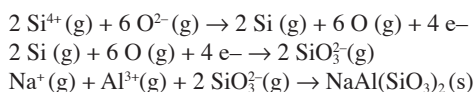
§ Lattice energy calculated from Born-Haber cycle using heats of formation obtained from Wagman (1982). In a few cases, where enthalpies of formation of the gaseous ion were not available, the cycle involved enthalpies of dissolution, also obtained from the same source.

|| Lattice energy calculated by Glasser-Jenkins equation using ion volumes obtained from Landolt-Börnstein (1973) and H.D.B. Jenkins, private communication.

If the "salt" has considerable covalent character, as is the case with silicates, the heat of formation can still be written using this ionic Born-Haber cycle. Because most silicates do not contain discrete, monomeric anions and because it is very difficult to obtain the heat of formation of gaseous silicate ions (such as SiO₄⁴⁻) that could be treated as discrete monomeric ions, the cycle must be written in terms of the complete "dissociation" into gaseous Si⁴⁺ and O²⁻ ions, even though these ions do not exist as such in the compound. For example, for jadeite, NaAl(SiO₃)₂ (a member of the pyroxene group), the cycle is written:

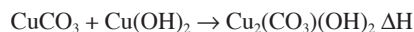


In this case the lattice energy contains all of the information about the bonding interactions in the silicate. For example, if the bonding in the metasilicate ion in jadeite is of interest, the lattice energy step above could be further decomposed into the steps:



where the second step in particular is more typical of covalent interactions, specifically the formation of covalent bonds in the metasilicate ion.

In the formation of a double salt from its simple salt constituents, the same cations and anions appear on both sides of the equation and therefore the enthalpies of formation of these cancel in the calculation of the enthalpy of formation of the double salt. The enthalpy change is therefore simply the lattice enthalpies of the two (or more) simple salts minus the lattice enthalpy of the double salt. For example, for the formation of malachite, Cu₂(CO₃)(OH)₂, from copper carbonate and copper hydroxide



$$\Delta H = \Delta H_{\text{lattice}}(\text{CuCO}_3) + \Delta H_{\text{lattice}}[\text{Cu(OH)}_2] - \Delta H_{\text{lattice}}[\text{Cu}_2(\text{CO}_3)(\text{OH})_2]$$

But, because the lattice enthalpy of the double salt is approximately equal to the sum of the lattice enthalpies of the simple salts; that is,

$$\Delta H_{\text{lattice}}[\text{Cu}_2(\text{CO}_3)(\text{OH})_2] \sim \Delta H_{\text{lattice}}(\text{CuCO}_3) + \Delta H_{\text{lattice}}[\text{Cu(OH)}_2]$$

then, ΔH for the formation of a double salt from its constituent simple salts is approximately zero. The RT difference between lattice enthalpy and lattice energy also cancels in the formation of the double salt from its simple salt constituents and hence the relationship can also be expressed in terms of the lattice energies.

If $\Delta H \sim 0$ for the formation of a double salt from its constituent simple salts, it must be the case that the enthalpy of formation of the double salt is approximately equal to the sum

TABLE 4. Glasser-Jenkins lattice energies (kJ/mol) of selected double salts

Compound	Name	Vm nm ³	LE, BH*	LE, G-J†	% error‡
Ca ₃ Al ₂ (SiO ₄) ₃	grossular	0.2080	64771	64708	0.1
Al ₂ OSiO ₄	andalusite	0.08554	28184	28116	0.2
MgAl ₂ O ₄	spinel	0.06602	18975	19185	1.1
Ca ₅ (PO ₄) ₃ F	fluorapatite	0.2404	17118	16554	3.3
Ca ₂ Al(PO ₄) ₂ OH	bearthite	0.1498	14160	13585	4.1
CaTiO ₃	perovskite	0.05595	15395	16122	4.7
Ca ₄ (PO ₄) ₂ O		0.1990	13951	13281	4.8
Cd ₅ (PO ₄) ₃ F		0.2334	18225	16846	7.6
K ₃ Na(SO ₄) ₂	aphthitalite	0.2047	3492	3156§	9.6
Al ₄ (PO ₄) ₃ (OH) ₃	trolleite	0.2386	28992	26102	10.0
MgAl ₂ (PO ₄) ₂ (OH) ₂	lazulite	0.1622	18200	16249	10.7
CaMg(CO ₃) ₂	dolomite	0.1070	5962	5155	13.5
BaCa(CO ₃) ₂	alstonite	0.1545	5376	4560	15.2
Na ₂ Cu(CO ₃) ₂		0.1315	5021	4205	16.3
Pb ₃ (CO ₃) ₂ (OH) ₂	hydrocerussite	0.1877	8093	6535	19.3
K ₂ Cd ₂ (SO ₄) ₃		0.2669	7305	5811	20.5
K ₂ Cu(SO ₄) ₂		0.2033	4774	3689§	22.7
KAgCl ₂		0.1183	1638	1241§,†	24.2
KAgI ₂		0.1683	1529	1115§,†	27.1
Cu ₄ (SO ₄) ₂ (OH) ₆	brochantite	0.1891	12646	8145	35.6
Cu ₄ (OH) ₆ Cl ₂	atacamite	0.1877	12542	7339	41.5

* The experimentally based lattice energies were determined using a thermochemical cycle from the heat of formation of the double salt and gaseous ions.

† Unless otherwise noted, "LE, G-J" determined using the approximation $U_{TOT} = Al(2l/V)^{1/3}$. See Glasser and Jenkins (2000). Unit cell volumes were obtained from the International Center for Diffraction Data (ICDD) PDF-2 Sets 1-44 Inorganics (includes zeolites and minerals) (1994).

‡ No experimental unit cell volume was available. Volumes determined by ion summation.

§ Lattice energy was estimated to be less than 5000 and was determined by $U_{TOT} = 2l(\alpha/V_m^{1/3} + \beta)$. See Glasser and Jenkins (2000).

†† Errors are absolute (unsigned).

TABLE 5. Experimental and simple salt approximations of the enthalpies of formation of selected compounds, kJ/mol*

Double Salt	H _f , experimental	H _f , simple salt	% error‡
Zn ₅ (OH) ₆ (CO ₃) ₂	-3584	-3552.2	0.89
Cu ₃ (SO ₄) ₂ (OH) ₄	-1723.7	-1671.0	3.06
Cu ₄ (OH) ₆ Cl ₂	-1652.7	-1569.5	5.03
Fe ₃ Al ₂ (SiO ₄) ₃	-5272	-5224.5	0.90
K ₂ Zn ₂ (SO ₄) ₃	-3406.9	-3403.4	0.10
Al ₄ (PO ₄) ₃ (OH) ₃	-6530	-6477.4	0.81
KAgBr ₂	-492.5	-494.2	0.34
MnAl ₂ O ₄	-2099.3	-2060.9	1.83
CaMn(CO ₃) ₂	-2093.4	-2101.0	0.36
Pb ₃ (CO ₃) ₂ (OH) ₂	-1906	-1912.8†	0.36
K ₂ Cu(CO ₃) ₂	-1733.4	-1746.0†	0.73
Cu ₂ (OH) ₂ CO ₃	-1054.7	-1044.8†	0.94
Na ₂ Cu(CO ₃) ₂	-1712.5	-1725.6†	0.77
Cu ₃ (OH) ₂ (CO ₃) ₂	-1675.1	-1639.7†	2.11
Al ₂ OSiO ₄	-2587.5	-2586.6	0.03
Fe ₃ Al ₂ (SiO ₄) ₃	-5272	-5224.5	0.90
MgAl ₂ O ₄	-2299.9	-2277.4	0.98
KAgI ₂	-382.4	-389.7	1.92
Ca ₃ Al ₂ (SiO ₄) ₃	-6656.7	-6313.8	5.15
Ca ₂ Fe ₂ (SiO ₄) ₃	-5764.7	-5462.3	5.25
CaMgSiO ₄	-2263.1	-2147.7	5.10
Ca ₂ F ₂ Si ₂ O ₇	-5234	-4946.8	5.49
MgAlPO ₄	-2405	-2335.5	2.89
Pb ₂ OCO ₃	-943	-916.4	2.82
Pb ₂ OSO ₄	-1171.5	-1137.3	2.82
PbOPbCl ₂	-605.4	-576.7	4.74
Pb ₃ O ₂ CO ₃	-1127	-1133.7	0.60
Mg ₃ Al ₂ Si ₃ O ₁₂	-6284.6	-6213.6	1.13
CaAl ₂ SiO ₆	-3280.2	-3221.7	1.78
MgSiO ₃	-1547.8	-1512.6	2.27

* Unless otherwise indicated, all values for heats of formation were obtained from Wagman et al. (1982).

† Values for ΔH_f° of Pb(OH)₂ and CuCO₃ were obtained from Rossini et al. (1952).

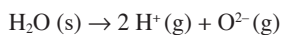
‡ Errors are absolute (unsigned).

of the enthalpies of formation of the constituent simple salts. For malachite, then,

$$\Delta H_f(\text{malachite}) \sim \Delta H_f(\text{CuCO}_3) + \Delta H_f[\text{Cu}(\text{OH})_2]$$

In fact, the experimental enthalpy of formation of malachite is -1054.7 kJ/mol, whereas the enthalpy of formation obtained from the enthalpies of formation of the simple salts is -1044.8 kJ/mol.

Geochemists frequently define enthalpy of formation in terms of the constituent oxides, which for silicates are SiO₂ plus metal oxides such as MgO, Al₂O₃, and, frequently, H₂O. The simple salt approximation assumes that the lattice energy of any complex silicate is approximately equal to the sum of the lattice energies of the constituent oxides. For example, for talc, Mg₃Si₄O₁₀(OH)₂, the simple salt constituents are 3MgO + 4SiO₂ + H₂O. The use of H₂O as a simple salt constituent requires comment. As for all of the silicate simple salt "constituents" the lattice energy of water is defined as the enthalpy change for complete dissociation of the solid to the appropriately charged gaseous monatomic ions,



and was calculated from the enthalpies of formation of each of the species (Wagman et al. 1982; Lide 1966). This definition is not more problematic than the similar definition for SiO₂, which is also covalent but not molecular. [When water appears as a reactant or product in a geochemical reaction it usually appears as a liquid (at least at 25 °C). Because the difference in enthalpy change for the formation of the gaseous ions from liquid water at

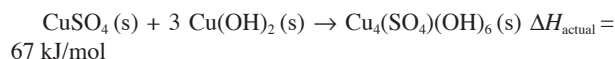
25 °C and the enthalpy change from solid water is less than 10 kJ/mol (the heat of fusion of water is 6.0 kJ/mol), this difference in state can be ignored in approximate calculations.]

The experimental and simple salt approximations for the enthalpies of formation of several double salts and silicates are shown in Table 5. The average percent error in the enthalpy of formation as calculated from the enthalpies of formation of the simple salts is 2.1%, with a high of 5%. Kutolin (1965) made a similar observation concerning additivity of the enthalpies of formation of oxides and found an error of approximately 3% for a series of about 30 silicate minerals. Although the fact has received little attention, the relatively small (generally less than 60 kJ/mol) enthalpies of formation of silicates from the oxides can be thought of as a manifestation of the simple salt observation. Interestingly, the simple salt approximation in general appears to slightly underestimate the enthalpy of formation, while the approximation gives lattice energies that show no definite tendency to over- or underestimate.

Although the percent error in estimation of the enthalpy of formation appears to be small, this can result in a large absolute error. Grossular, for example, has an experimental enthalpy of formation of -6656.7 kJ/mol. The estimated enthalpy of formation using the enthalpies of formation of the simple salt is -6313.8 kJ/mol (a 5.2% difference). The difference between the values is almost 350 kJ/mol, more than ten times the error involved in an experimental determination of enthalpy of formation. The estimated enthalpy of formation using the simple salt lattice energies is -6337 kJ/mol. This large error is a result of the large

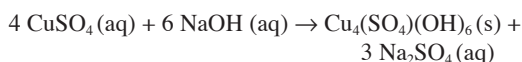
absolute (but small percentage) error in the estimated lattice energy. Thus, the simple salt approximation can rarely be used as a substitute for an experimental enthalpy of formation.

Second, the formation of a double salt from its simple salt constituents will have an enthalpy change of close to zero. For example, the enthalpy of formation of brochantite, $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$, can be approximated as the enthalpy of formation of CuSO_4 plus three times the enthalpy of formation of $\text{Cu}(\text{OH})_2$. Thus, the formation of brochantite, $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$, from the simple salts in the solid state should have an enthalpy change of approximately zero (the actual enthalpy change is 67 kJ/mol).



Based upon the approximation that the enthalpy change for these reactions is approximately zero, one might expect that room temperature formation would be of somewhat uncertain favorability. A brief comparison of absolute entropies of double salts and their single salt constituents (Table 6) shows that at least for this small sample the entropy change for formation of double salts from their single salt constituents is small. For 37 double salts, including 21 silicates, the difference in absolute entropy between the "salt" and its simple salt constituents ranged from -39.2 to 43.9 J/K mol, with an average of 3.1 J/K mol. Consequently, in general, the standard free energy change for the formation of double salts from their simple salts will be approximately zero.

Of course, double salts are usually not prepared by simply mixing the simple salt constituents. In fact, the formation of double salts often occurs, both geologically and in the laboratory, from aqueous solution and the enthalpy of solution of one or more components must then also be considered. For example, brochantite can be made in the laboratory by adding an aqueous solution of sodium hydroxide to an aqueous solution of copper sulfate:



and for this reaction $\Delta H^\circ = -168$ kJ/mol and the standard free energy change is negative.

In reactions that do not contain the same simple salt constituents on both sides of the equation, the enthalpy change will not necessarily be approximately zero. For example, in the formation of brochantite from copper sulfate and sodium hydroxide, the simple salt constituents on the left side of the equation are CuSO_4 and NaOH , but on the right side they are CuSO_4 , $\text{Cu}(\text{OH})_2$ and Na_2SO_4 . The ΔH for the reaction, whether in solid state or aqueous solution cannot therefore be assumed to be approximately zero. Table 7 gives a few equations of geological significance for which the simple salt approximation predicts zero enthalpies, while Table 8 contains several processes for which the enthalpy change cannot be assumed to be zero. As expected, the values of ΔH° (determined from experimental enthalpies of formation) in Table 7 are generally considerably smaller than those in Table 8.

Finally, we provide an example of a thermochemical prediction made possible by the simple salt approximation. Consider

TABLE 6. Entropy change for formation of some double salts from their simple salt constituents in the solid state

Double salt	Name	$S^\circ(\text{DS})$ J/(mol·K)	Sum $S^\circ(\text{SS})$ J/(mol·K)	ΔS° J/(mol·K)
MgAl ₂ O ₄	spinel	80.63	77.86	2.77
Ca ₃ (PO ₄) ₃ OH	hydroxyapatite	390.35	395.69	-5.34
Ca ₃ (PO ₄) ₃ F	fluorapatite	387.85	388.43	-0.58
PbFCl	matlockite	121.8	123.25	-1.45
Pb ₂ OCO ₃		204.2	199.7	4.5
Pb ₂ OSO ₄	lanarkite	206.7	217.27	-10.57
CaAl ₂ Si ₂ O ₈	anorthite	199.3	173.67	25.63
MgSiO ₃	clinoenstatite	67.86	68.5	-0.64
CaMgSi ₂ O ₆	diopside	142.9	149.75	-6.85
NaAl(SiO ₃) ₂	jadeite	133.47	145.99	-12.52
CaSiO ₃	wollastonite	82.01	81.25	0.76
Ca ₂ Al ₂ SiO ₇	gehlenite	209.8	171.92	37.88
Ca ₃ Al ₂ Si ₃ O ₁₂	grossular	255.5	294.67	-39.17
Fe ₂ SiO ₄	fayalite	148.32	156.48	-8.16
Al ₂ OSiO ₄	andalusite	93.22	92.42	0.8
CdSiO ₃		97.5	96.3	1.2
BeAl ₂ O ₄		66.3	65.06	1.24
Mg ₃ Si ₂ O ₇ (OH) ₄	chrysotile	221.3	236.3	-15.0
Mg ₂ Al ₂ Si ₂ O ₁₀	cordierite	407.1	363.22	43.88
Mg ₂ SiO ₄	fosterite	95.1	95.38	-0.28
CaTiSiO ₅	titanite	129.2	131.17	-1.97
Ca ₃ MgSi ₂ O ₈	merwinite	253.1	229.19	23.91
LiAlSi ₃ O ₆	al-spodumene	129.3	127.24	2.05
LiAlSiO ₄	eucryptite	103.8	85.74	18.05
PbFCl	matlockite	121.8	123.25	-1.45
FeAl ₂ O ₄		106.3	108.41	-2.11
ZnFe ₂ O ₄		151.7	131.04	20.66
CuFeO ₂		88.7	100.12	-11.42
CuFe ₂ O ₄		141	130.03	10.97
Al ₆ Si ₂ O ₁₃		255	235.76	19.24
Zn ₃ SiO ₄	willemitite	131.4	128.78	2.62
(NH ₄) ₂ Cd ₂ (SO ₄) ₃		485.7	466.18	19.52
Na ₂ Si ₂ O ₅		164.05	158.06	5.99
Na ₂ SiO ₃		113.85	116.56	-2.71
NaFeO ₂		88.3	95.02	-6.72
KAl(SO ₄) ₂		204.6	207.43	-2.83
CsCuCl ₃		213.4	209.24	4.16
	Average			3.14

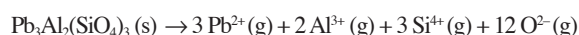
* All values for S° are in J/(mol·K) and are obtained from Wagman (1982). Simple salt constituents are as given in Tables 1 and 2.

the conversion of grossular, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$, to the lead garnet $\text{Pb}_3\text{Al}_2(\text{SiO}_4)_3$. Conventional wisdom would probably predict that the larger size of Pb^{2+} relative to Ca^{2+} (119 vs. 100 pm) would make substitution unlikely. The thermodynamic translation of this argument is that the larger size of the lead ion should presumably result in a lower lattice energy for $\text{Pb}_3\text{Al}_2(\text{SiO}_4)_3$, which in turn should lead ultimately to a more positive enthalpy and free energy change for the substitution. On the other hand, lead compounds often exhibit considerable covalent character, which would increase the lattice energy.

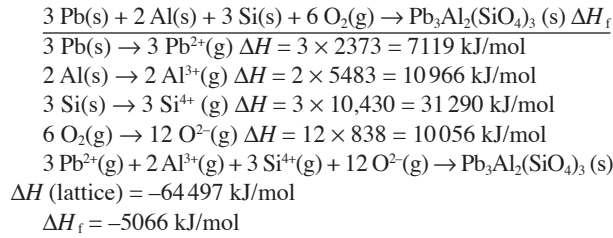
Although the heat of formation of grossular is known (-6656.7 kJ/mol), there is no experimental value for the unknown lead garnet. Hence, our calculation begins with the determination of the heat of formation of $\text{Pb}_3\text{Al}_2(\text{SiO}_4)_3$. First, we determine the lattice energy using the simple salt approximation as:

$$\text{LE}[\text{Pb}_3\text{Al}_2(\text{SiO}_4)_3] = 3 \text{LE}(\text{PbO}) + \text{LE}(\text{Al}_2\text{O}_3) + 3 \text{LE}(\text{SiO}_2) \\ 3(3433) + 15162 + 3(13020) = 64522 \text{ kJ/mol.}$$

It is important to remember that this is an approximation, probably good to about 0.2%, for the energy required for the reaction:



After correction for the RT term, this translates to a lattice enthalpy of 64 497 kJ/mol. Next we write a thermodynamic cycle for the formation of the lead garnet:



Summation of the enthalpies of formation of gaseous cations and the gaseous oxide ion and subtraction of the lattice energy produces an enthalpy of formation of -5066 kJ/mol. This value is higher (more positive) than the enthalpy of formation of grossular in spite of the slightly larger estimated lattice energy of the lead derivative because the energy required to form Pb^{2+} from solid lead is greater than the energy required to form Ca^{2+} from solid calcium (2373 kJ/mol vs. 1926 kJ/mol for Pb^{2+} and Ca^{2+} , respectively). Although the difference in the lattice energies of $\text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ and $\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ (64522 and 64427 kJ/mol, respectively) is not greater than the average deviation for the simple salt method, the somewhat larger lattice energy for $\text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ is consistent with the slightly larger lattice energy of PbO relative to CaO. According to our approximation, then, the substitution of Pb^{2+} for Ca^{2+} is not prohibited by a decrease in the potential energy of the lattice structure due to the larger size of the lead ion.

Estimation of the enthalpy of formation of $\text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ could also be approached by using the difference in enthalpies of formation of compounds of calcium and lead with the same anion. Because this tactic attributes the differences in enthalpies of formation strictly to the cation, it is important to use compounds that contain an anion the same as or at least similar to SiO_4^{4-} . This procedure takes into account the difference in enthalpies

TABLE 7.* Some reactions for which simple salt approximation predicts $\Delta H_{\text{rxn}} = 0$

Reaction	ΔH_{rxn} (kJ/mol)
$\text{Ca}_2\text{MgSi}_2\text{O}_7 + \text{Al}_2\text{O}_3 \rightarrow \text{Ca}_2\text{Al}_2\text{SiO}_7 + \text{MgO} + \text{SiO}_2$	30.66
$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 \rightarrow \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$	49.87
$\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4 + 2 \text{SiO}_2 \rightarrow \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + \text{H}_2\text{O}$	8.05
$2 \text{MgSiO}_3 + 2 \text{Al}_2\text{SiO}_5 + \text{SiO}_2 \rightarrow \text{Mg}_2\text{Al}_2\text{Si}_2\text{O}_{18}$	-25.06
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \rightarrow 3 \text{MgSiO}_3 + \text{SiO}_2 + \text{H}_2\text{O}$	138.23
$\text{NaAlSi}_3\text{O}_8 + \text{SiO}_2 \rightarrow \text{NaAlSi}_2\text{O}_8$	4.94
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}_2\text{O} \rightarrow 2 \text{Al}(\text{OH})_3 + 2 \text{SiO}_2$	26.95

* All states are solid unless otherwise indicated. H_2O is liquid.

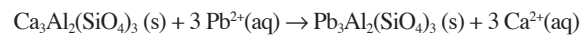
TABLE 8.* Some reactions for which ΔH_{rxn} cannot be assumed to be zero

Reaction	ΔH_{rxn} (kJ/mol)
$2 \text{NaAlSi}_3\text{O}_8 + 2 \text{H}^+(\text{aq}) \rightarrow \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + 2 \text{Na}^+(\text{aq}) + 2 \text{SiO}_2$	-75.12
$2 \text{NaAlSi}_3\text{O}_8 + 2 \text{H}_2\text{SO}_4 \text{ (aq, 1M)} \rightarrow \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + 2 \text{Na}_2\text{SO}_4 \text{ (aq, 1M)} + 2 \text{SiO}_2$	-555.36
$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + 5 \text{Mg}^{2+}(\text{aq}) + 8 \text{H}_2\text{O} \rightarrow \text{Mg}_5\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_8 + \text{SiO}_2 + 10 \text{H}^+(\text{aq})$	450.95
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+(\text{aq}) \rightarrow 3 \text{Mg}^{2+}(\text{aq}) + 2 \text{SiO}_2 + 5 \text{H}_2\text{O}$	-289.58
$\text{Fe}_2\text{SiO}_4 + 1/2 \text{O}_2 \text{ (g)} + 3 \text{H}_2\text{O} \rightarrow 2 \text{Fe}(\text{OH})_3 + \text{SiO}_2$	-219.55
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6 \text{H}^+(\text{aq}) \rightarrow 3 \text{Mg}^{2+}(\text{aq}) + 4 \text{SiO}_2 + 4 \text{H}_2\text{O}$	-271.63

* All states are solid unless otherwise indicated. H_2O is liquid.

of formation of the cation and, if the anion is well-chosen, will also at least partly compensate for differences in lattice energy. Fortunately, the enthalpy of formation of Pb^{2+} orthosilicate has been reported (-1363.1 kJ/mol, Wagman et al. 1982). Subtraction of the heat of formation of Pb_2SiO_4 from the enthalpy of formation of Ca_2SiO_4 (-2306.0 kJ/mol) should then give a reasonable approximation to the difference in the enthalpy of formation caused by substitution of two lead ions for two calcium ions in an orthosilicate compound. This difference [-1363.1 kJ/mol - (-2306.0 kJ/mol) = 943 kJ/mol] can then be used to obtain the difference in the enthalpy of formation of $\text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ relative to $\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ by multiplying by 3/2 to account for the substitution of three ions. Thus, by this method the enthalpy of formation of $\text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ should be -6656.7 kJ/mol + 3/2(943 kJ/mol) = -5242 kJ/mol. The use of other relatively large oxy anions such as sulfate, oxalate, and carbonate gives a somewhat lower value (ca. -5100 kJ/mol)

Substitution of Pb^{2+} for Ca^{2+} could occur in the reaction of grossular and a lead-containing mineral in the solid state or in aqueous solution. The enthalpy changes for several reactions calculated using the simple salt estimation for $\text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3$ and literature enthalpies of formation for the other reactants and products are shown in Table 9. Because the simple salt approximation underestimates the lattice energies of the garnets in Table 2 by an average of 0.6%, a more accurate value for the enthalpy change can be obtained by using the simple salt approximation for the enthalpy of formation of grossular (-6337 kJ/mol). (Assuming underestimation of the lattice energy of the lead garnet, this procedure should allow cancellation of some of the errors in the lattice energies of both compounds.) The enthalpy changes obtained in this way are given in parentheses in Table 9. The enthalpy changes were also calculated using the enthalpy of formation of the lead garnet obtained by subtraction of the enthalpies of formation (-5242 kJ/mol) and the experimental enthalpy of formation of grossular (-6656.7 kJ/mol) and are given in Table 9 in brackets. The values in the table suggest that substitution in aqueous solution is likely to have a negative enthalpy change.



The entropy change for this reaction is almost surely slightly negative because the more negative entropy of aqueous Ca^{2+} (-53 J/K-mol) relative to Pb^{2+} (10 J/K-mol) is not counterbalanced by the difference in entropies of the solids (Latimer contributions of 39 and 65 J/K-mol, for Ca and Pb, respectively). It is likely, therefore, that the free energy change at 25 °C for substitution of Pb^{2+} for Ca^{2+} is slightly favorable. However, the rate of sub-

TABLE 9.* Estimated enthalpy changes for some lead substitution reactions, kJ/mol

Reaction	ΔH_{rxn} (kJ/mol)
$\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{PbO} \rightarrow \text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{CaO}$	342 (23) [166]
$\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{PbS} \rightarrow \text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{CaS}$	445 (125) [269]
$\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{PbSO}_4 \rightarrow \text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{CaSO}_4$	48 (-272) [-128]
$\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{PbSO}_4 \rightarrow \text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{CaSO}_4(\text{aq})$	-6 (-326) [-182]
$\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{Pb(NO}_3\text{)}_2(\text{aq}) \rightarrow \text{Pb}_3\text{Al}_2\text{(SiO}_4\text{)}_3 + 3 \text{Ca(NO}_3\text{)}_2(\text{aq})$	-33 (-353) [-209]

* All states are solid unless otherwise indicated. See text for method of calculation.

stitution is almost surely very slow at room temperature, and at higher temperatures the free energy change would be less favorable if ΔH is negative.

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