Fig. 1.   Variation of enthalpy of formation (ΔH_f°) of Al_2MgO_4 (spinel) with K_T.

that if the structure is known our estimates will not be extremely low even if non-ionic bonding is important.

The enthalpy calculated for α-quartz is in much poorer agreement with the observed heat of formation than any of the above compounds. This possibly arises from its low bulk modulus (which may in itself result from covalency). If however the 160 kcal/mole covalent contribution of Si–O bond determined from the silicate

spinels is valid for tectosilicates then very little of the almost 900 kcal/mole discrepancy in quartz can be attributed to covalency. We conclude that the lattice energy calculated as we have done it is not valid for oxides in fourfold coordination which are as compressible as quartz.

Table 3 lists the differences between calculated and measured enthalpies of formation for several of the compounds. There are five cases in which a particular coordination is represented by more than one compound: $Al-O_6$, $Ti-O_6$ $Fe^{2+}-O_4$, $Fe^{3+}-O_6$ and $Si-O_4$. For both corundum and spinel ($MgAl_2O_4$) the apparent enthalpy of covalency is about 50 kcal/mole, for three silicate spinels it is about 160 kcal/mole and for rutile and two titanites it is about 235 kcal/mole. The second case shows that for different compounds in the same structure the same ion pairs have nearly identical enthalpies of covalency. The other cases show us that this holds even for different structures if the coordination is the same. However, comparison of stishovite and the silicate spinels shows that this is now true if there is a coordination change. Therefore the following list of enthalpies of covalency can be inferred for future use:

$Al-O_6$ -25 ± 5 kcal/mole;
$Ti-O_6$ -217 ± 10 kcal/mole ($CaTiO_3$ omitted because of an unreliable bulk modulus);
$Si-O_4$ -154 ± 9 kcal/mole;
$Si-O_6$ ≈ -105 kcal/mole);

TABLE 3

Apparent enthalpies of covalency

Compound	Structure	Enthalpy of formation (kcal/mole) observed	calculated	Apparent enthalpy of covalency (kcal/mole)	Predominant covalent bond
Al_2O_3	corundum	-399	-344	-55	$Al-O_6$
Al_2MgO_4	spinel	-553	-507	-46	$Al-O_6$
Mg_2SiO_4	spinel	-512	-349	-163	$Si-O_4$
Ni_2SiO_4	spinel	-328	-176	-152	$Si-O_4$
Fe_2SiO_4	spinel	-350	-204	-146	$Si-O_4$
SiO_2	rutile	-206	-101	-105	$Si-O_6$
Fe_2O_3	corundum	-197	-45	-80^*	$Fe^{3+}-O_6$
TiO_2	rutile	-226	-1	-225	$Ti-O_6$
$SrTiO_3$	perovskite	-397	-189	-208	$Ti-O_6$
$CaTiO_3$	perovskite	-397	-130	-267	$Ti-O_6$
Cr_2O_3	corundum	-273	-287	$+14$	$Cr-O_6$
$FeCr_2O_4$	spinel	-342	-259	-83	$Fe^{2+}-O_4$
Fe_2TiO_4	spinel	-356	-46	-310	$Ti-O_6, Fe^{2+}-O_4$
Fe_3O_4	spinel	-267	-108	-159	$Fe^{3+}-O_6, Fe^{3+}-O_4$

* See text.