THERMODYNAMICS OF METAL AGENT FIRE EXTINGUISHMENT

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ABSTRACT

The thermodynamics of oxides, carbonates, halides and related metal compounds involved in extinguishment by dry chemicals and metal agents has been analyzed. It is shown that lattice energies play an important role in determining the extinguishment activities and properties of metallo fire extinguishants. In particular, lattice energies can explain why some metallic compounds are inactive as fire extinguishing compounds and others reach a saturation point where additional agent give little improvement in performance.

INTRODUCTION

For some scenarios, certain metal compounds appear to be more effective suppressants than halons. Three types of mechanisms have been proposed for flame extinguishment by solid agents — (1) thermal (temperature lowering), (2) heterogeneous chemical, and (3) homogeneous chemical. Studies indicate that thermal mechanisms, such as radiation and heat absorption by decomposition, and heterogeneous mechanisms are insufficient to account for observed suppression characteristics. Homogeneous reactions (e.g., Equations 1 and 2) are believed by most to be the primary suppression mechanism.

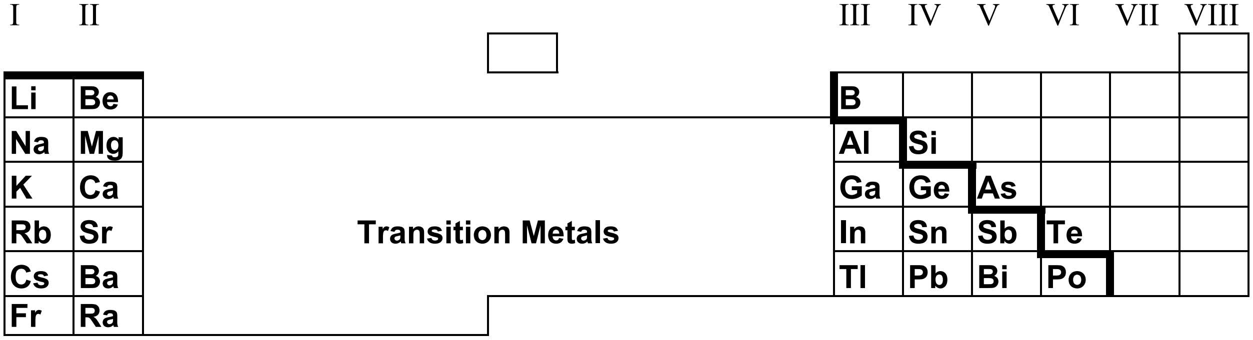


Figure 1. Metals and Metalloids.

$$\mathrm{MOH} + \bullet\mathrm{H} \rightarrow \bullet\mathrm{M} + \mathrm{H_2O} \quad (1)$$
$$\mathrm{MOH} + \cdot\mathrm{H}\bullet \rightarrow \cdot\mathrm{MO} + \mathrm{H_2} \quad (2)$$

Three phenomena must be explained:

1. For some main group metals, suppression ability increases with increasing atomic mass. For example, extinguishment ability appears to increase in the order Li < Na < K < Rb and Si < Sn.
2. Some metal and metalloid compounds, e.g. compounds of Group II, show no suppression characteristics.
3. Some transition metal compounds are exceedingly effective, but show saturation.

It appears that many of these characteristics might be explained from thermodynamic considerations:

1. Bond strengths often decrease with increasing atomic weight. Since activation energy often increases with increasing bond strength, reaction rates for suppression chemical steps may increase with increasing molecular mass.
2. Large lattice energies may enhance particulate formation and decrease agent volatilization, leading to inactive suppression and to saturation. Since lattice energies often decrease with increasing atomic weight, lattice effects could also explain the increase in fire suppression activity for higher atomic weight elements.

As examples of changes with atomic weight, note the trends for alkali metal and alkaline earth hydrides in Table 1 and Figure 2.

Table 1. Thermodynamics of Alkali Metal Hydrides

Metal	M—H Bond Energy, kJ/mol	MH(s) Atomization Energy, kJ/mol
Li	238	470
Na	202	382
K	184	365

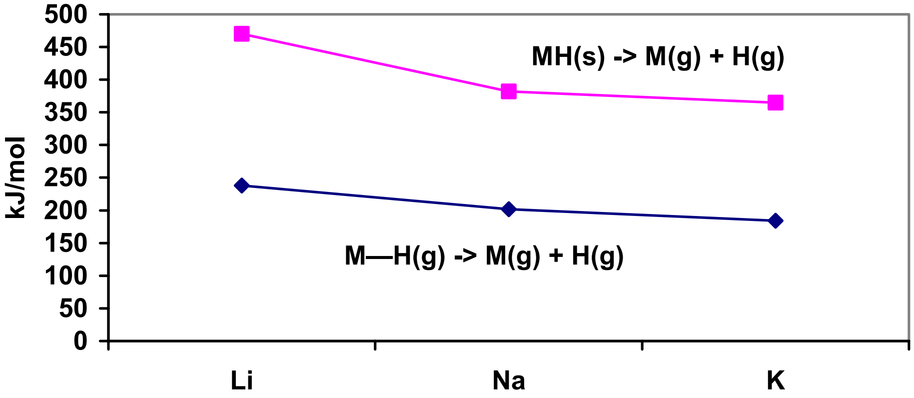


Figure 2. Atomization and Bond Energy for Alkali Metal Hydrides

Here we investigate these factors. Thermodynamic data are taken from Reference 1 and 2.

MAIN GROUP METALS AND METALLOIDS

Alkali Metals

For alkali metal compounds, the primary suppression reactions proposed [3] are

$$MOH + \bullet H \rightarrow \bullet M + H_2O \qquad (1)$$
$$\bullet M + \bullet OH + m \rightarrow MOH + m^* \qquad (3)$$

This can be compared with the principal reactions for halon fire suppression, which are believed to be

$$RBr + H \rightarrow \bullet R + HBr \qquad (4)$$
$$\bullet H + HBr \rightarrow H_2 + \bullet Br \qquad (5)$$
$$\bullet Br + \bullet H + m \rightarrow HBr + m^* \qquad (6)$$

For both mechanisms, hydrogen atoms are removed from the free-radical pool. Kinetic modeling [4] shows sodium compounds to be better than lithium compounds for Reactions 1 and 3, in agreement with experimentation, but fails to explain the improved performance of potassium compounds. (Although it is proposed that Reaction 3 is faster for potassium.)

The thermodynamics for Reaction 1 are surprising. As expected, the reaction is exothermic for all of the alkali metals for which data are available (data are unavailable for cesium), and is least exothermic for lithium. What is surprising is that the reaction exothermicity decreases from sodium to potassium to cesium (Table 2 and Figure 3). Moreover, one would predict that the M-OH bond strength would significantly decrease in the order Na > K > Cs, but this is not the case.

Table 2.Thermodynamics for Alkali Metal Compounds

Metal	$MOH(g)+H(g) \rightarrow M(g)+H_2O(g)$ ΔH_f, kJ/mol	M—OH Bond Energy, kJ/mol
Li	-53	447
Na	-141	358
K	-139	361
Cs	-124	376

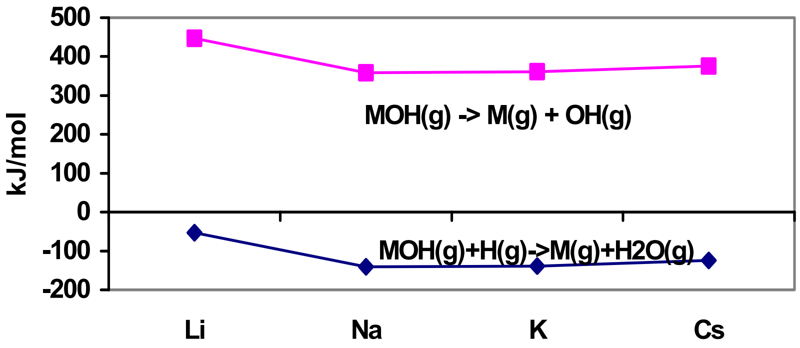


Figure 3. Thermodynamics for Alkali Metal Compounds

Thus, like kinetic calculations, thermodynamic considerations of the reaction involved do not correctly predict effectiveness. The question is, why are the results different than expected? The problem is almost certainly that we have failed to take into account the possibility of multiple bonding. Hydrogen, used in the first examples, has no surplus electrons; however, oxygen does, so that there is a real possibility of dπ-pπ bonding for the heavier elements Figure 4.

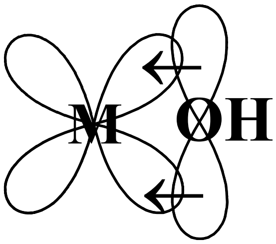


Figure 4. pπ→dπ Bonding.

Are there other things that should be considered? One of these is lattice energy. Excluding lithium, there is relatively little difference in the dissociation energies of the chloride salts (used as dry powder extinguishing agent). The correct trend is, however, observed for the oxides, which are a likely product (Table 3 and Figure 5). Thus, there is a possibility that particulate formation may be removing more sodium than potassium from flames.

Table 3. Atomization Energies for Alkali Metal Compounds

Metal	MCl(s), kJ/mol	M_2O(s), kJ/mol of M
Li	690	602
Na	640	442
K	647	396
Cs	641	

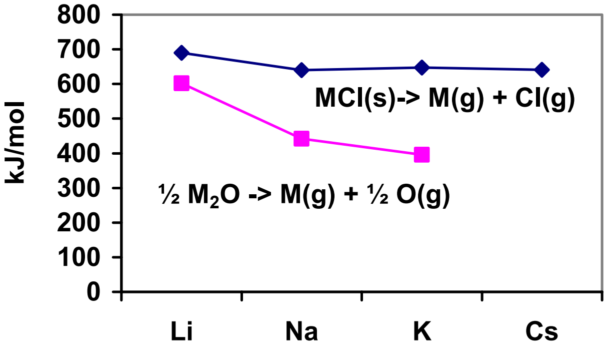


Figure 5. Atomization Energies for Alkali Metal Compounds

Alkali Metals

Compounds of the alkaline earths show little if any extinguishing ability other than that attributable to thermal effects. Examination of the thermodynamics shows that Reaction 1 is exothermic for the alkaline earths, as for the alkali metals, but considerably less so (Table 4 and

Figure 6). This decrease in exothermicity may explain, at least in part, the decreased suppression ability of the alkaline earth compounds.

Table 4. Thermodynamics for Alkaline Earth Compounds

Metal	$MOH(g)+H(g) \rightarrow M(g)+H_2O(g)$ ΔH_f, kJ/mol	M—OH Bond Energy, kJ/mol
Be	-28	472
Mg	-95	405
Ca	-57	442
Sr	-54	415
Ba	-90	379

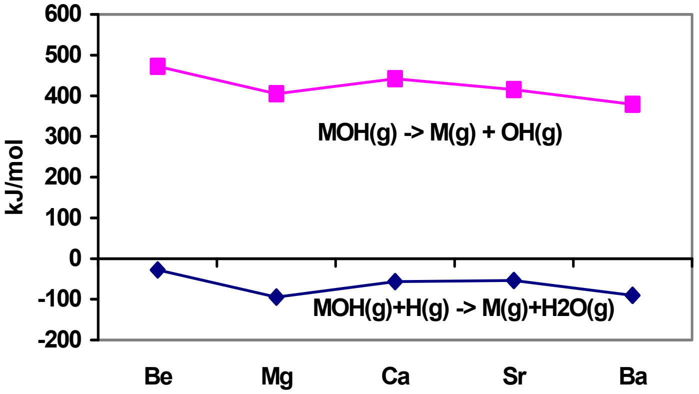


Figure 6. Thermodynamics for Alkaline Earth Compounds.

Due to their higher oxidation states (larger number of bonds and/or ionic charge), the atomization energies of alkaline metal compounds in the solid state are considerably higher for than atomization energies for corresponding compounds of the alkali metals (per mole of metal released, Table 5 and Figure 7). The higher lattice energies for the alkaline earths most likely explains their lack of chemical suppression activity.

Table 5. Atomization Energies for Two Alkaline Earth Compounds

Metal	$MCl_2(s)$, kJ/mol	MO(s), kJ/mol
Be	1066	1176
Mg	1032	999
Ca	1218	1064
Sr	1281	977
Ba	1236	1006

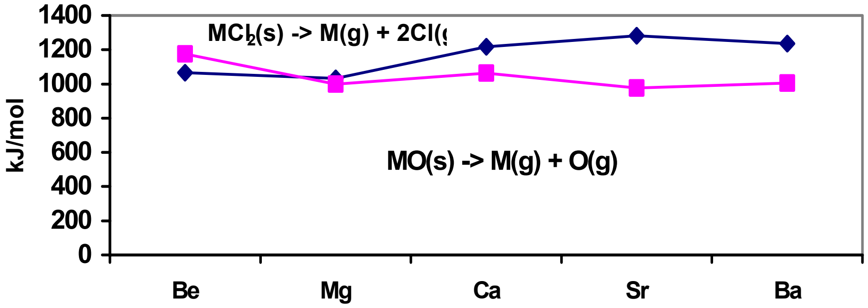


Figure 7. Atomization Energies for Two Alkaline Earth Compounds

Group III Compounds

None of the Group III elements appear to have an intrinsic fire suppression ability. Neither aluminum nor boron form a stable M—OH species, so that reactions similar to that shown in Reactions 1 and 3 are impossible. The only species formed are O=M—H. This behavior is not surprising for elements that have higher coordination numbers. The thermodynamics for a reaction similar to that in Reaction 1 are shown in Table 6. The reactions are strongly exothermic, due to the large affinity of Group III

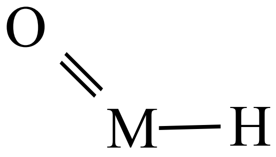


Figure 8. Structure of Oxyhydrides for Group III Elements

Table 6. Reaction Enthalpy for Reaction of Group III Oxyhydrides with Hydrogen Atoms

Metal	$O{=}MH(g)+H(g)\rightarrow M(g)+H_2O(g)$ ΔH_f, kJ/mol
B	180
Al	47

Moreover, the Group III compounds have large lattice energies (Table 7}. Certainly aluminum compounds are likely to give refractory aluminum oxide, rather than gas phase species that could be involved in suppression.

Table 7. Atomization Energies for Some Group III Compounds

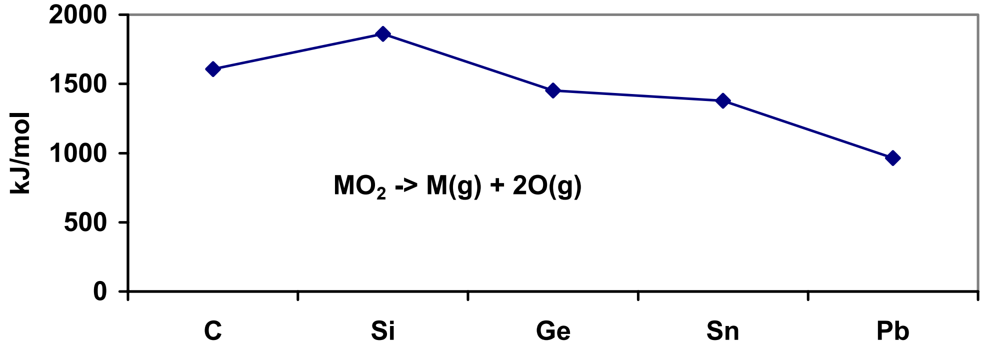
Metal	$MCl_3(s)$, kJ/mol	$M_2O_3(s)$, kJ/mol of M
B	1323	1566
Al	1396	1539

Group IV Compounds

There is significant evidence of chemical suppression activity for tin compounds. There is also evidence that silicon has no inherent fire suppression capability. Insufficient data are available to make a judgment for germanium or lead compounds. Almost certainly Si—OH would rearrange to O=Si-H due to the great affinity of silicon for multiple bonding to oxygen. In any respect, highly refractory SiO_2 would form almost immediately. The dissociation energies for oxides of the Group IV compounds are shown below. (Note that CO_2 is a gas, not a solid.) Although the lattice energy for SnO_2 is relatively high, a lower oxidation state is available and the product SnO has an atomization energy of only 551 kJ/mol. The lower oxidation state is more stable at higher temperatures.

Table 8. Atomization Energies for Group IV Oxides

Metal	MO_2(g,s), kJ/mol
C	1608
Si	1861
Ge	1452
Sn	1378
Pb	965



TRANSITION METALS

There are three transition metals that are known or believed to exhibit significant catalytic fire suppression capabilities — chromium, iron, and, possibly, manganese. The reason that these specific metals possess catalytic capabilities, while others do not (or are believed to not exhibit such capabilities) is unknown. The saturation observed with iron pentacarbonyl, however, is likely to be observed for any metal that has a very high melting (low volatility) solid oxide.

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