

## 9.11: The Strange Case of the Alkali Oxides

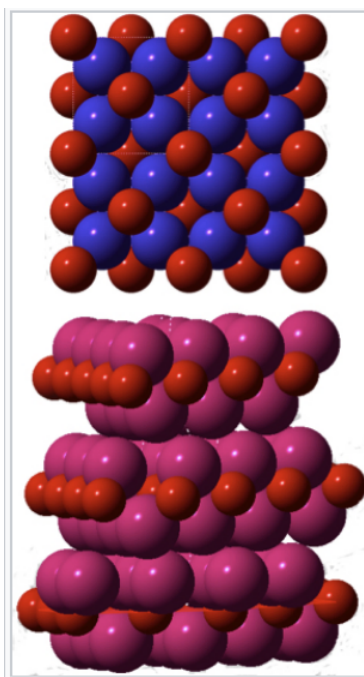
The alkali oxides, made by reacting alkali metals (Li, Na, K, Rb, Cs) with oxygen, show an unusual trend. When lithium reacts with oxygen we obtain the binary oxide  $\text{Li}_2\text{O}$ , as expected from combining an element in group I with one in group VI. Curiously, the oxide that forms most readily when sodium metal is oxidized is not  $\text{Na}_2\text{O}$ , but is instead the peroxide  $\text{Na}_2\text{O}_2$ , which we can formulate as  $(\text{Na}^+)_2(\text{O}_2^{2-})$ . With potassium, rubidium, and cesium we obtain the superoxides  $\text{MO}_2$ , which contain the superoxide radical anion ( $\text{O}_2^-$ ) and should be formulated as  $(\text{M}^+)(\text{O}_2^-)$ . While it is possible to make  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ , and  $\text{Cs}_2\text{O}$  by reaction of the appropriate metal nitrate ( $\text{MNO}_3$ ) with elemental alkali metal  $\text{M}$ ,<sup>[16]</sup> it is curious that these "normal valent" compounds do not form by direct reaction of the metal with oxygen.



Sodium metal is oxidized in air to sodium peroxide,  $\text{Na}_2\text{O}_2$

Because the alkali metals are all very electropositive ( $\chi = 0.8\text{--}1.0$ ), and oxygen is very electronegative ( $\chi = 3.5$ ), we expect all the compounds we make by combining them to be reliably ionic. Consistent with this picture we find that  $\text{Li}_2\text{O}$  (along with  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$ ) adopts the antifluorite structure (8:4 coordination - see problem 8.8.2), which we expect to find with relatively ionic  $\text{M}_2\text{X}$  compounds. Strangely however,  $\text{Cs}_2\text{O}$  crystallizes in the anti- $\text{CdCl}_2$  structure. This is odd because  $\text{CdCl}_2$  has a layered structure that we normally associate with polar covalent  $\text{MX}_2$  compounds (see section 8.4). In  $\text{Cs}_2\text{O}$ , six  $\text{Cs}^+$  cations surround each  $\text{O}^{2-}$  anion in an octahedron. Each  $\text{Cs}^+$  is coordinated to three  $\text{O}^{2-}$  ions, and the  $\text{Cs}^+$  ions contact each other across a van der Waals gap. The juxtaposition of  $\text{Cs}^+$  ions near each other is clearly electrostatically unfavorable, so why does  $\text{Cs}_2\text{O}$  prefer the anti- $\text{CdCl}_2$  structure to antifluorite?

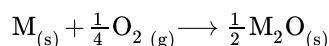
The answer has to do with the crowding of alkali ions around oxygen, as illustrated for  $\text{K}_2\text{O}$  at the right. Because eight large  $\text{K}^+$  ions surround each  $\text{O}^{2-}$  ion in the structure, the cations are essentially in contact. Indeed, the metal-oxygen bonds are "stretched" in  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$  relative to M-O bonds with the same bond order in other structures.<sup>[17]</sup> The situation is so extreme for  $\text{Cs}_2\text{O}$  that it finds an (electrostatically unfavorable) structure in which the coordination is lowered to 6:3. This packing problem is relieved somewhat in the peroxides, where the coordination is still 8:4 but the anion is larger, and especially in the superoxides where the cation:anion ratio is 1:1 and the coordination is 6:6. Thus the larger alkali ions ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) tend to form superoxides.



Space-filling models of the crystal structures of  $K_2O$  (top) and  $Cs_2O$  (bottom). Oxygen atoms are red, potassium ions are blue, and cesium ions are magenta

Another way that we can rationalize this trend is through the energetics of forming the oxides, peroxides, and superoxides.

Let's calculate the enthalpy change (per mole of metal) for forming a metal oxide  $M_2O$  from the metal and oxygen:

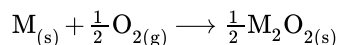


We can use Hess' law to write this as a sum of reactions:

Reaction	$\Delta H$
$M_{(s)} \longrightarrow M_{(g)} \longrightarrow M_{(g)}^+$	$\Delta_s + IE = \Delta_{f,M^+(g)}$
$\frac{1}{4} O_{2(g)} \longrightarrow \frac{1}{2} O_{(g)} \longrightarrow \frac{1}{2} O_{2(g)}^{2-}$	$\frac{1}{4} \Delta H_d + \frac{1}{2} EA_1 + \frac{1}{2} EA_2 = \frac{1}{2} \Delta H_{f,O^{2-}(g)}$
$M_{(g)}^+ + \frac{1}{2} O_{(g)}^{2-} \longrightarrow \frac{1}{2} M_2O_{(s)}$	$\frac{1}{2} E_{L,M_2O} - \frac{3}{2} RT$
<b>Overall:</b>	
$M_{(s)} + \frac{1}{4} O_{2(g)} \longrightarrow \frac{1}{2} M_2O_{(s)}$	$\Delta H_{f,M^+(g)} + \frac{1}{2} \Delta H_{f,O^{2-}(g)} + \frac{1}{2} E_{L,M_2O} - \frac{3}{2} RT$

To get the enthalpy change for the overall reaction (the heat of formation of 1/2 mole of  $M_2O$ ) we will need the heats of formation of  $M^+(g)$  and  $O^{2-}(g)$ , which are available from tabulated values, and  $E_L$ , which we can calculate from Kapustinskii's equation.

Similarly, we can write for the formation of the alkali peroxides:

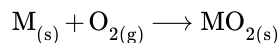


Reaction

Reaction	$\Delta H$
$M_{(s)} \longrightarrow M_{(g)} \longrightarrow M_{(g)}^+$	$\Delta H_{f,M^+(g)}$
$\frac{1}{2} O_{2(g)} \longrightarrow \frac{1}{2} O_{2(g)}^{2-}$	$\frac{1}{2} \Delta H_{f,O_2^{2-}(g)}$

$M_{(g)}^+ + \frac{1}{2}O_{2(g)}^{2-} \longrightarrow \frac{1}{2}M_2O_{2(s)}$	$\frac{1}{2}E_{L,M_2O_2} - \frac{3}{2}RT$
<b>Overall:</b>	
$M_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow \frac{1}{2}M_2O_{2(s)}$	$\Delta H_{f,M^+(g)} + \frac{1}{2}\Delta H_{f,O_2^{2-}(g)} + \frac{1}{2}E_{L,M_2O_2} - \frac{3}{2}RT$

and for the superoxides:



Reaction	$\Delta H$
$M_{(s)} \longrightarrow M_{(g)} \longrightarrow M_{(g)}^+$	$\Delta H_{f,M^+(g)}$
$O_{2(g)} \longrightarrow O_{2(g)}^-$	$\Delta H_{f,O_2^-(g)}$
$M_{(g)}^+ + O_{2(g)}^- \longrightarrow MO_{2(s)}$	$E_{L,MO_2} - 2RT$
<b>Overall:</b>	
$M_{(s)} + O_{2(g)} \longrightarrow MO_{2(s)}$	$\Delta H_{f,M^+(g)} + \Delta H_{f,O_2^-(g)} + E_{L,MO_2} - 2RT$

For the gaseous anions and cations, we have the following heats of formation and ionic radii (CN=6):

Ion	$\Delta H_f$ , kJ	ionic radius, Å
$Li^+$	678	0.76
$Na^+$	602	1.02
$K^+$	506	1.38
$Rb^+$	485	1.52
$Cs^+$	473	1.67
$O^{2-}$	500	1.20
$O_2^{2-}$	519	1.59
$O_2^-$	-88	1.49

Now using Kapustinski's equation, we can calculate the lattice energies for each compound; these have been converted to lattice enthalpies by subtracting 2 RT or 3 RT as appropriate:

$$E_L = \frac{1213.8z_+z_-n}{r_+ + r_-} \left(1 - \frac{0.345}{r_+ + r_-}\right) \quad (9.11.1)$$

Metal	$\Delta H_{L,M_2O}$	$\Delta H_{L,M_2O_2}$	$\Delta H_{L,MO_2}$
Li	-3,065 kJ	-2,651 kJ	-918 kJ
Na	-2,776	-2,433	-838
K	-2,454	-2,178	-751
Rb	-2,345	-2,090	-721
Cs	-2,241	-2,007	-678

As expected, the lattice energies for  $M_2O$  and  $M_2O_2$  are comparable, the latter being somewhat smaller in magnitude because of the larger size of the  $O_2^{2-}$  anion. The lattice energies of the superoxides,  $MO_2$ , are about 1/3 those of the corresponding peroxides because both the anion and cation are singly charged, and there are only two ions per formula unit.

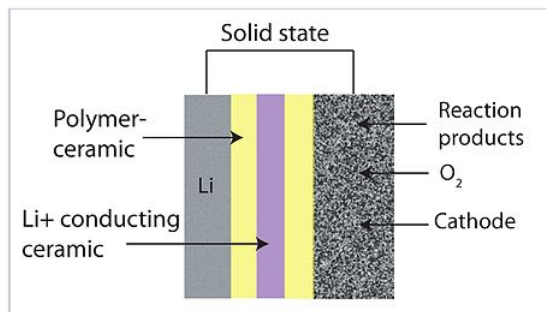
Now, putting it all together, we can use the lattice energies and heats of formation of the individual ions to compare the heats of formation (per mole of metal) of each of the oxides:

Metal	$1/2 \Delta H_f M_2O$	$1/2 \Delta H_f M_2O_2$	$\Delta H_f MO_2$
Li	<b>-404 kJ</b>	-388 kJ	-328 kJ
Na	-338	<b>-354</b>	-324
K	-271	-321	<b>-328</b>
Rb	-241	-300	<b>-324</b>
Cs	-53	-70	<b>-81</b>

We can see that for Li, the formation of  $Li_2O$  is favored over  $Li_2O_2$  or  $LiO_2$  because of the very favorable lattice energy of  $Li_2O$ . As the lattice energy becomes less negative with increasing cation size, the peroxide becomes the most stable at Na. For the heavier alkalis,  $M_2O$  becomes quite unstable and the superoxides  $MO_2$  are the most stable. This is consistent with our observations of the chemistry of the group I oxides.

### Metal-air batteries

The alkali oxides are quite interesting in the context of metal-air batteries because of their potential for extremely high energy storage on a mass basis. Such batteries have alkali metal (typically Li) or Zn anodes and utilize oxygen from the air at the cathode. Although lithium is the lightest and therefore the most energy-dense alkali metal, there are materials problems associated with the formation of Li dendrites when the battery is recharged, and also with the slow kinetics of the four-electron interconversion between  $O_2(g)$  and  $2 O^{2-}$  at the cathode. For this reason, superoxide batteries are currently being studied as alternatives. The one-electron cathode reaction  $O_2 + e^- = O_2^-$  is kinetically fast, and potassium<sup>[18]</sup> and sodium<sup>[19]</sup> represent potentially viable alternatives to lithium for the anode of these air-breathing batteries. Recently, it has been shown that  $LiO_2$  can be kinetically stabilized by template growth on iridium nanoparticles, potentially opening the door to very high energy density lithium-air batteries.<sup>[20]</sup>



Schematic of an air-breathing lithium battery

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