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Study Notes on Carbides

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Carbides

The formation of various binary compounds of carbon with metals and metalloids is known as the carbides. These can be classified as follows:

Saline carbides: These are largely ionic solids and are formed by the elements of Groups 1 and 2 and by aluminium.

Metallic carbides: These have a metallic conductivity and lustre and are formed by the d-block elements.

Metalloid carbides: These are hard covalent solids which are formed by boron and silicon.

Let's discuss two types of carbides in detail.

(a) Saline carbides: These are the metal- carbon compounds in which metals have high electropositive character. Non-metal carbides are generally hard and are semiconductors. For group 1 and 2, these carbides can be divided into three categories:

Graphite intercalation compounds are formed by the group 1 metals. Their formation takes place by the reaction between graphite and alkali metal vapor or between graphite and metal-ammonia solution. Example: KC_8, dicarbides (or 'acetylides'), which contain the C_2^{2-} anion, and methides, which formally contain the C^{4-} anion. A series of alkali metal-graphite intercalation compounds can be prepared with different metal: carbon ratios, including KC_8 and KC_{16}.

The formation of dicarbides takes place by a broad range of electropositive metals, including those from Groups 1 and 2 and the lanthanoids. The C_2^{2-} ion has a very short CC distance in some dicarbides which is consistent with it being a triply bonded $[C\equiv C]^{2}$ ion isoelectronic with $[C\equiv N]^{-}$ and $N\equiv N$. The structures of some dicarbides are related to rock salt, but replacement of the spherical Cl^{-} ion by the elongated $[C\equiv C]^{2-}$ ion leads to an elongation of the crystal along one of the axes, and a resulting tetragonal symmetry. In lanthanoid dicarbides, CC bond is significantly longer which suggests that for them the simple triply bonded structure is not a good approximation. Carbides like Be_2C and Al_4C_3 are borderline between saline and metalloid, and the isolated C ion is only formally C^{4-}. The presence of directional bonding in carbides is indicated by the crystal structures of methides, which are not those expected for the simple packing of spherical ions.

The principal synthetic routes to the saline carbides and acetylides of Groups 1 and 2 are very straightforward. These can be formed by the direct reaction of the elements at high temperatures.

$$Ca(l) + 2C(s) \xrightarrow{>2000°C} CaC_2(s)$$

The formation of graphite intercalation compounds is another example of a direct reaction, but is carried out at much lower temperatures.

Reaction of a metal oxide and carbon at a high temperature is given below.

$$CaO(s) + 3C(s) \xrightarrow{2000°C} CaC_2(s) + CO(g)$$

Crude calcium carbide is prepared in electric arc furnaces by this method. The carbon acts both as a reducing agent to remove the oxygen and as a source of carbon to form the carbide.

Reaction of ethyne (acetylene) with a metal-ammonia solution:

$$2\ Na(am) \mid C_2H_2(g) \rightarrow Na_2C_2(s) \mid H_2(g)$$

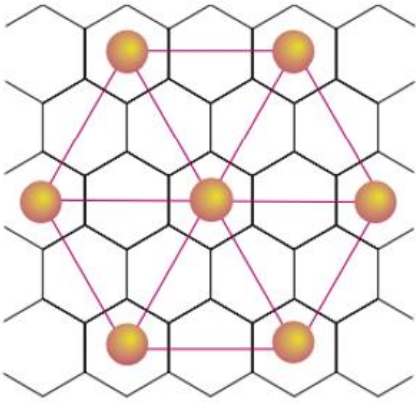
The above reaction takes place under mild conditions and leaves the carbon-carbon bonds of the starting material intact. As the ethyne molecule acts a very weak Bronsted acid ($pK_2 = 25$), the reaction can be regarded as a redox reaction between a highly active metal and a weak acid to yield H_2 (with H^+ the oxidizing agent) and the metal dicarbide.

The saline carbides have high electron density on the C atom, so they can be readily oxidized and protonated. For example, calcium carbide reacts with the weak acid water which results in the formation of ethyne.

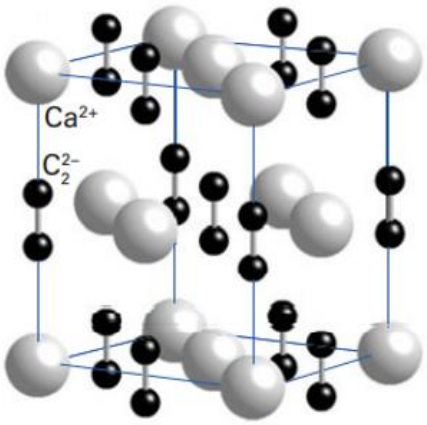
$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + HC{\equiv}CH(g)$$

This reaction is readily understood as the transfer of a proton from a Bronsted acid (H_2O) to the conjugate base (C_2^{2-}) of a weaker acid ($HC{\equiv}CH$). Similarly, the controlled hydrolysis or oxidation of the graphite intercalation compound KC_8 restores the graphite and produces a hydroxide or oxide of the metal:

$$2KC_8(s) + 2H_2O(g) \rightarrow 16\ C(graphite) + 2\ KOH(s) + H_2(g)$$



In KC_8, which is a graphite intercalation compound, the potassium atoms lie in a symmetrical array between the sheets.



The above structure is of the calcium carbide structure. Because C_2^{2-} is not spherical, the cell is elongated along one axis. This crystal is therefore tetragonal rather than cubic (Fig. 14.14).

(b) Metallic carbides: Generally, d-Metal carbides are hard materials with the carbon atom octahedrally surrounded by metal atoms. The d metals provide the largest class of carbides. Examples are Co_6Mo_6C and Fe_3Mo_3C. They are also referred to as **interstitial carbides** because it was long thought that the structures were the same as those of the metals and that they were formed by the insertion of C atoms in octahedral holes. In fact, the structure of the metal and the metal carbide often differ. The presence of the hardness and other properties of metallic carbides indicates the strong metal-carbon bonding is present in them. Some of these carbides are economically and technologically useful materials. Tungsten carbide (WC), for example, is used to cut tools and high-pressure apparatus such as that used to produce diamond. Cementite, Fe_3C, is a major constituent of steel and cast iron.

Metallic carbides with composition MC have an FCC or hcp arrangement of metal atoms with the C atoms present in the octahedral holes. The FCC arrangement results in a rock-salt structure. The C atoms in carbides of composition M_2C occupy only half the octahedral holes between the close-packed metal atoms. A C atom in an octahedral hole is formally **hyper coordinate** (untypically high coordination number) because it is surrounded by six metal atoms.

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