

The Dissociation of Metal Halides in Electrical Discharges

F. K. McTaggart

Division of Mineral Chemistry, C.S.I.R.O. Box 124, Fort
Melbourne, Victoria, Australia.

Introduction. The effect of the energetic electrons produced in electrical discharges in dissociating gas molecules is well known, and is the basis of the chemical reactions that are observed in plasma systems. Since gases such as O_2 , N_2 , N_2O and Cl_2 , as well as vapours of organic and other compounds have been dissociated to atoms and/or radicals, it appears logical to suppose that many other molecules would behave similarly. This paper describes the dissociation of the halides of the Group I, II and III, and rare earth metals.

Experimental. Ideally, the halides should be introduced into the discharge tube in the form of vapours at suitable pressures. Due to the wide range of volatilities occurring in the above compounds and to other experimental difficulties it proved more convenient to use carrier gases, and to volatilize the halides from small boats contained within the reaction tube by heating these boats to suitable temperatures. It was usually possible to make use of the heat generated in the plasma itself for this purpose. Samples were placed upstream from, or within the central plasma region, in positions where heat sufficient to give the desired rate of volatilization was produced. Since heating of solids due to atomic recombination is largely a surface effect it was also possible to vary the sublimation rate of samples by changing the surface area exposed to the plasma.

Both inert gases (in particular He and N_2) and hydrogen have been used and certain reactions which are discussed below appear to involve H atoms as well as dissociative effects. These gases were of commercial purity, the He and H_2 being purified by passing them over zirconium powder heated to $800^\circ C$; although no essential differences between the cylinder gases and the purified gases were observed. Pressures of the carrier gases were varied between 0.5 and 2.3 mm. Halides used were of A.R. grade, but in certain cases impure compounds were deliberately used in order to determine the effects of impurities on the dissociation and on the purity of the metal obtained.

Extensive use was made of a 2450 mC magnetron generator (Mullard JN2/2.5A) which although capable of an output in excess of 2 kW continuous wave power, was seldom operated at inputs higher than 600 watts. Radio-frequency energy from the magnetron was fed via a 50 ohm air dielectric coaxial line, to a section of waveguide operated as a resonant cavity by means of a sliding plunger inserted into the open end. The discharge tube passed transversely through the guide at a point of maximum electrostatic field. Some investigations, involving the chlorides of Li, Be, and Al, which dissociate very readily, were made using an "rf" generator consisting of a 4-125A vacuum tube at a frequency of 30 mC, the power of which could be varied from close to zero to about 400 watts. In these

cases the reaction tube passed through the "tank coil" of the output circuit.

Conventional methods of analysis were used to determine a/ the amount of metal deposited, b/ the undissociated halide sublimed onto the reaction tube, and c/ the halogen or hydrogen halide collected in the liquid air trap which followed the reaction tube in the flow system.

Results. From all the halides studied it was possible to separate metals, often in good yields.

The lithium group compounds¹ dissociated in both inert carrier gases and in H₂ to give metals and the relative reaction rates were determined for the iodides, bromides, chlorides and fluorides of Li, Na, K and Cs. Some of these are shown in Table 1. It will be noted that for any one metal

Table 1

Relative Reaction Rates for the Halides of Li and Na

Compound	Bond Energy	Rel. React. Rate	Compound	Bond Energy	Rel. React. Rate
LiI	82	232.5	NaI	72	26.0
LiBr	102	101.5	NaBr	89	15.0
LiCl	115	66.5	NaCl	99	10.0
LiF	138	19.0	NaF	108	5.0

the rate is greatest for the iodide and least for the fluoride as might be expected from the bond energies (also quoted). However in going from one metal to another it is seen that bond energy is not the main factor involved since, for example, the rates for LiI and NaI are 232.5 and 26.0 while the bond energies are 82 and 72 respectively. The rates presumably depend largely on the energy levels to which the molecules must be raised before dissociation will occur. Not a great deal is known about these energies and they appear to depend more on the nature of the metal atom present than on the halogen.

The effect of variation of sublimation rate (partial pressure) for NaCl is shown in Figure 1 for several input powers. All the Group I halides gave curves of similar shape. As the sublimation rate decreased the percentage dissociation increased to a maximum beyond which there were insufficient halide molecules to "use up" the electrons having sufficient energy to dissociate them. For any one power the amount of halide dissociated was almost independent of sublimation rate (see Table 2). As expected, an increase in power resulted in increased dissociation and an empirical relationship $\text{Rate} = KP^{1.7}$ was found to apply throughout. The highest yield of metal obtained during the experiments was 70% lithium from LiI.

1. McTaggart, F. K. Aust. J. Chem. 18, 936, 949 (1965).

Table 2

Dissociation of NaCl in H₂ at 1.0 mm for Various Input Powers

Sublm. Rate mmole/hour	mmole/hour Na produced			
	168W	220W	270W	320W
0.5	0.11	0.160	-	-
1.0	0.11	0.158	0.225	0.280
1.5	0.105	0.145	0.223	0.255
2.0	0.12	0.156	0.230	0.270
2.5	-	0.175	0.250	0.287
3.0	-	-	0.264	0.291
4.0	-	-	0.240	0.280
Mean	0.111	0.159	0.239	0.277

Figure 2 shows the effect of carrier gas pressure at constant power. A maximum in metal production occurred at about 1.5 mm pressure. For H₂ this pressure coincides closely with the highest concentration of H atoms, and is probably related to the concentration of electrons having sufficient energy to cause dissociation. The reaction rates appeared to be substantially independent of the nature of the carrier gas.

The fact that considerable quantities of highly reactive metals are deposited in atmospheres of even more highly reactive gases, namely halogen atoms, suggests that these halogen species may be in the form of negatively charged ions. Such ions, having a complete outer shell of eight electrons, would be non-reactive chemically, and if neutralization of their charges is delayed until they are swept clear of the metal deposit, an explanation of the apparent absence of appreciable back reaction would be afforded. Mass spectroscopic studies are being made on the nature of the species in these discharges to elucidate this matter.

The Group II compounds. The majority of the halides of Be, Mg, Ca, Sr and Ba were investigated. Rates of dissociation did not appear to vary as widely as those of Group I. As optimum conditions were approached for each compound, all the halide vapourized was dissociated and deposits were formed on the walls of the reaction tube in which metals and dihalides were found in equi-molar proportions. This points strongly to the formation of unstable monohalide molecules in the discharge, which disproportionate to yield the observed products. Again the dissociations were not dependent on the carrier gas employed. BeCl₂, one of the more volatile halides in this group, and one of the most easily dissociated of all the compounds studied, may be broken down in the lower frequency apparatus mentioned previously.

Metals could be separated from the dihalides in the deposits by means of suitable solvents for the latter, or in some cases by vacuum sublimation of the dihalide.

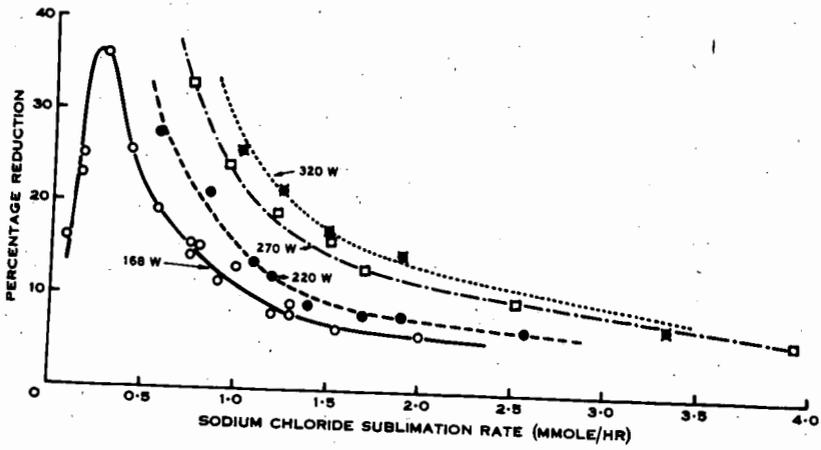


Figure 1

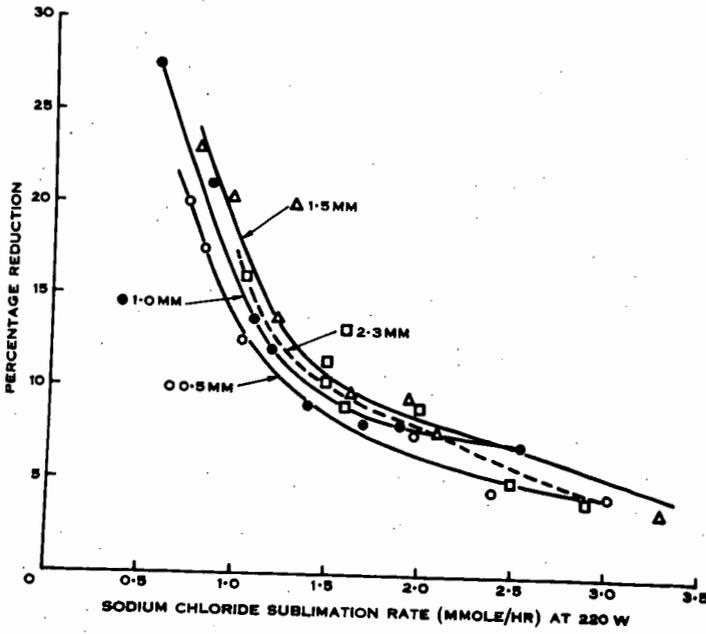


Figure 2

Group III compounds. No investigations have been made on the compounds of boron. Markovskii et al.² reported in 1958 that BCl_3 was reduced to elemental boron by H atoms, and the present work on aluminium halides supports this claim.

When inert carrier gases were used there was a very limited deposition of metal from Al and Sc halides amounting to only a few per cent of the vapour passed through the discharge, but when hydrogen was employed much higher yields of metals were obtained. It would appear, therefore, that at least one step in the decomposition involves a H atom reaction, and the process may well be, for AlCl_3 :— initial dissociation of AlCl_3 to AlCl_2 ; H atom reduction of AlCl_2 to AlCl ; disproportionation of AlCl to Al and AlCl_3 . A mass spectrometric examination of the species present in the discharge revealed AlCl in readily detectable quantities but no AlCl_2 was observed. Yields of up to 55% Al metal have been obtained from AlCl_3 in a single pass through a 2450 mC plasma, and if a second discharge was produced downstream more Al deposited. The rate at which AlCl_3 decomposes, with comparatively low power, and with its intense blue plasma makes this reaction one of the most spectacular of those studied. The relatively involatile AlF_3 also dissociated quite readily to give the metal, although it is not easily handled in the experimental apparatus described. The chloride and fluoride of scandium behaved in a similar manner to the corresponding aluminium compounds.

AlCl_3 also dissociated readily in the lower frequency apparatus. It should be mentioned here that the chief difference between the waveguide and the coil-coupled apparatus appears to be that in the former the electrons are accelerated to higher energies since the electrostatic field is concentrated between the resonator walls where a high potential gradient exists in a direction axial to the discharge tube. By comparison the E field in a coil is much more randomly distributed.

Rare Earth Compounds. We have not as yet had an opportunity of studying these halides systematically, but preliminary experiments have shown that they behave in a manner similar to AlCl_3 . That is, there is only limited dissociation to metal in an inert carrier gas, but with hydrogen satisfactory yields of metals are obtained. Thus Ce and La result from CeF_3 , CeCl_3 , LaF_3 and LaCl_3 . If, for example, chlorides containing appreciable quantities of oxychloride are used for the dissociation this impurity is left in the sample boat and a highly pure metal is deposited. Such reactions may therefore prove of use in the preparation of certain metals.

2. Markovskii, L. V., Lvova, V. I., Kondrashev, Y. D., Ber. Tr. Konf. po Khim. Bora i Ego Svedin, 36 (1958).