The vaporization of CrCl₃ has been studied over the past years and relative references can be found elsewhere⁴⁵. Thermodynamic functions of vaporization and vapor pressures have been measured and critically evaluated. Monomeric trigonal planar species CrCl₃(g) are formed but the simultaneous appearance of CrCl₄(g) and CrCl₅(g) has been argued to exist ⁴⁶. At elevated temperatures many molten binary halide systems are known to enhance their "apparent" volatility by forming gaseous complex molecules which have been useful in a variety of applications ¹⁷,1₈. Many trivalent rare earth halides increase their volatility by reacting with alkali halides and forming vapor molecules with a predominant stoichiometry 1:1 (i.e ALnX₃). In the present work high temperature electronic absorption spectroscopy is used in the temperature range 800-1300 K in order to study the vapors over solid CrCl₃ and molten CrCl₃-ACl (A=C₃,Li) mixtures. A reverse optics Perkin Elmer Model L-900 spectrophotometer equipped with fiber optics and a three zone cylindrical kanthal furnace capable of handling optical cells up to 10 cm have been used for measuring the spectra. Figure 1 shows typical vapor spectra over solid CrCl₃ and over molten CrCl₃-CsCl. Measurements of spectra over CrCl₃(s) in the temperature range 800-1300 K have shown no bands due to Cl₂(g) and/or CrCl₂(g). Bands were seen at temperatures above 950 K and their position remained unchanged with temperature. These bands (Fig.1a) were assigned to monomeric CrCl₃(g). The 750 nm band with molar absorptivity ε = 20 lit.mol⁻¹.cm⁻¹ is presumably a Cr(III) d→π transition of the trigonal CrCl₃(g) and the 385 nm band a charge transfer (CT) transition of the same species. Spectra of the CrCl₃/CsCl vapor complex could be measured even at temperatures below 950 K indicating an "apparent" vapor pressure enhancement of the CrCl₃(s). A d→π Cr (III) broad band near 800 nm with ε = 21 lit.mol⁻¹.cm⁻¹ and a high intensity band CT band near 375 nm were observed. These bands are assigned to the CsCrCl₄ vapors species. Temperature dependent measurements in cells having no solid or liquid phases present show both the CrCl₃(g) and CsCrCl₄(g) bands which indicates that these vapor species are in equilibrium: CsCrCl₄(g) ⇌ CrCl₃(g)+CsCl (g).

The data permit the estimation of the volatility enhancement of the CrCl₃ due to the comparison reaction. Values above 10 were measured at temperature below 1000 K.

**References**