XCI.—*The Absorption Spectra of Chlorobenzene, the Dichlorobenzenes, and the Chlorotoluenes.*

By EDWARD CHARLES CYRIL BALLY.

IN two previous papers (Baly and Collie, Trans., 1905, **87**, 1332, and Baly and Ewbank, *ibid.*, 1355) the absorption spectra were described of chlorobenzene and the three dichlorobenzenes and chlorotoluenes. I am indebted to Mr. J. E. Purvis for pointing out that these substances exhibit more absorption bands than were described in the above papers. I have now repeated the examination of the seven compounds with the help of a larger and more accurate spectrograph than was available at that time, and the new results are given in Figs. 1 and 2, solutions in alcohol being used. The present results have been obtained by using as the source of light the condensed spark between cadmium electrodes, and also carbon electrodes well impregnated with molybdenum and uranium oxides. There is no doubt that whilst the small spectrograph employed in the first investigation was unsuited for the detection of the narrow absorption bands given by these compounds, the sources of light now made use of are far more adapted for the purpose than the iron arc which was originally used. At the same time, it must be pointed out that there is considerable danger in using only the cadmium spectrum, since it is possible that one or more of the absorption bands might be missed owing

FIG. 1.
Oscillation frequencies.

Upper curves : o-Dichlorobenzene.
Middle curves : p-Dichlorobenzene.
Lower curves : o-Chlorotoluene.

m-Dichlorobenzene.
Chlorobenzene.
m-Chlorotoluene.

FIG. 2.

p-Chlorotoluene.

to their falling exactly in the position occupied by strong cadmium lines. Chlorobenzene is a case in point, for the band at $1/\lambda = 3878$ would not have been detected at all unless the uranium and molybdenum spark had also been used, for there is a very bright cadmium line at $1/\lambda = 3885$.

The oscillation frequencies of the heads of the bands are as follows:

Chlorobenzene	3682	3777	3825	3878	3920	3975	4072
<i>o</i> -Dichlorobenzene	3605	3708	3810	3880	—	—	—
<i>m</i> -Dichlorobenzene ...	3590	3698	3803	3900	—	—	—
<i>p</i> -Dichlorobenzene	3560	3660	3765	3875	3930	—	—
<i>o</i> -Chlorotoluene	3660	3758	3870	—	—	—	—
<i>m</i> -Chlorotoluene	3640	3740	3850	—	—	—	—
<i>p</i> -Chlorotoluene	3610	3705	3813	—	—	—	—

In *p*-chlorotoluene there is evidence of an incipient band at about $1/\lambda = 3900$.

It is interesting to note the progressive shift of the absorption bands towards the longer wave-lengths in passing from the ortho- through the meta- to the para-isomeride, and also the existence of one additional band in *p*-dichlorobenzene. *p*-Chlorotoluene also would appear to have one additional band, but in this case it is not so decisive. It is thus evident that none of the conclusions drawn in the previous papers are invalidated.

THE UNIVERSITY,
LIVERPOOL