

The parameter c has been evaluated for XY_2 type molecules like SeO_2 , ClO_2 , SO_2 , OF_2 and OCl_2 and for XY_4 type molecules like GeF_4 , $GeCl_4$, VCl_4 , $TiCl_4$ and CF_4 using published force fields based on vibrational frequencies and other experimental data. Plots of c versus m_y/m_x have been drawn and are found to be linear (Fig. 1). Values of c as well as m_y/m_x are collected in Table I.

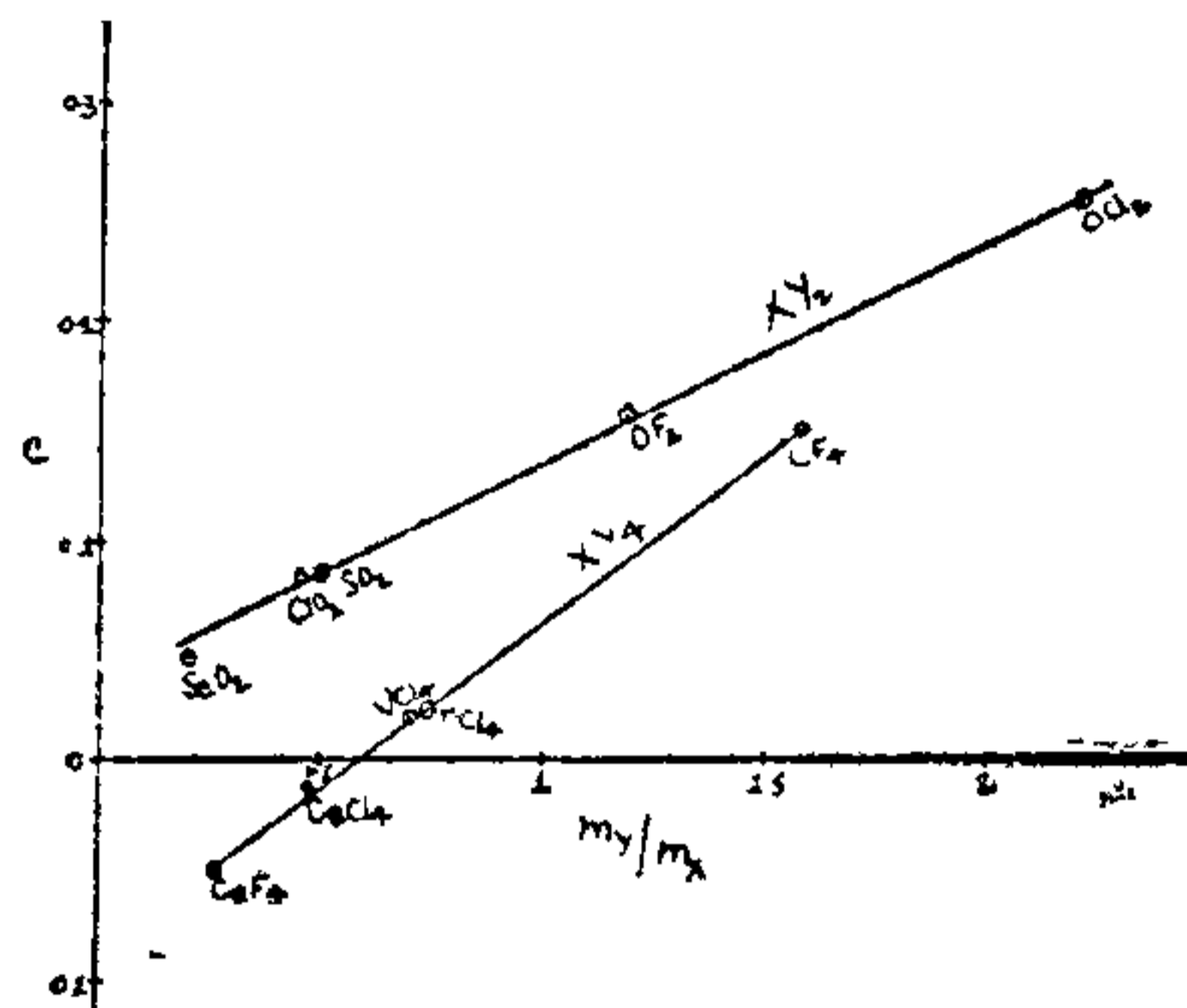


FIG. 1. Plots of parameter c vs. mass-ratio m_y/m_x .

With the help of the parameter-mass-ratio graphs an attempt has been made to determine the force fields and Coriolis constants of several XY_2 and XY_4 type molecules. The results of the investigation (Table II) are seen to be in good agreement with force fields and experimental Coriolis constants reported in the literature. In the light of the results reported here, it is highly plausible that smooth relationships may exist between the parameter and mass-ratio in other XY_n systems also. Such relationships will be of value in the elimination of spurious force fields and the correct assignment of frequencies. These aspects of the problem are being looked into.

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ON THE Z-DEPENDENCE OF TOTAL TO K-SHELL PHOTOELECTRIC CROSS SECTION RATIOS AT K-THRESHOLD

THERE have been very few studies on the total to K-shell photoelectric cross section ratios (T/K) at the K-edges. In the absence of reliable theoretical predictions, till recently, some empirical thumb rule of '5/4' law was used¹. Later, Davisson² deduced the values of the total to K-shell ratios from the data of Kirchner for the first time systematically. From such deduced data Z-dependence of the ratio is found. The value is found to vary from 1.09 for aluminum to 1.235 for uranium. Based on the measurements of such ratios, empirical expressions were proposed by Allen³ and Hubbell⁴ to express the Z-dependence. However, recent theoretical^{5,6} as well as experimental^{7,8} data at higher energies show that deduced values at K-threshold are under estimated specially in high Z-elements. Hence, it is of interest to measure and study the Z-dependence of these ratios at K-threshold. In the recent investigations in these laboratories, the total photon attenuation coefficients above and below the K-edges are measured in the elements Cu, Zr, Ag, Sn, Ta, Pb, Th and U using proportional counters and Ge (Li) systems on a good geometry set-up^{9,10}. Using these attenuation coefficients the photoelectric cross sections are deduced by subtracting the coherent and incoherent scattering contributions. The deduced photoelectric cross sections are fitted to log-log curves using IBM 1130

computer facility and the total to K-shell photoelectric cross section ratios at the respective K-edges in the elements are deduced. In the present note, a study of the Z-dependence of these ratios is made using the measured values.

The measured ratios are fitted to a polynomial expression using the IBM 1130 computer. The best fit is obtained as:

$$T/K = 1 + 7.819 \times 10^{-3} Z - 1.8 \times 10^{-4} Z^2 + 7.625 \times 10^{-7} Z^3.$$

The values obtained from this expression are plotted in Fig. 1 alongwith those for the expressions of Allen³ and Hubbell⁴ and the recent theoretical values of Scofield.

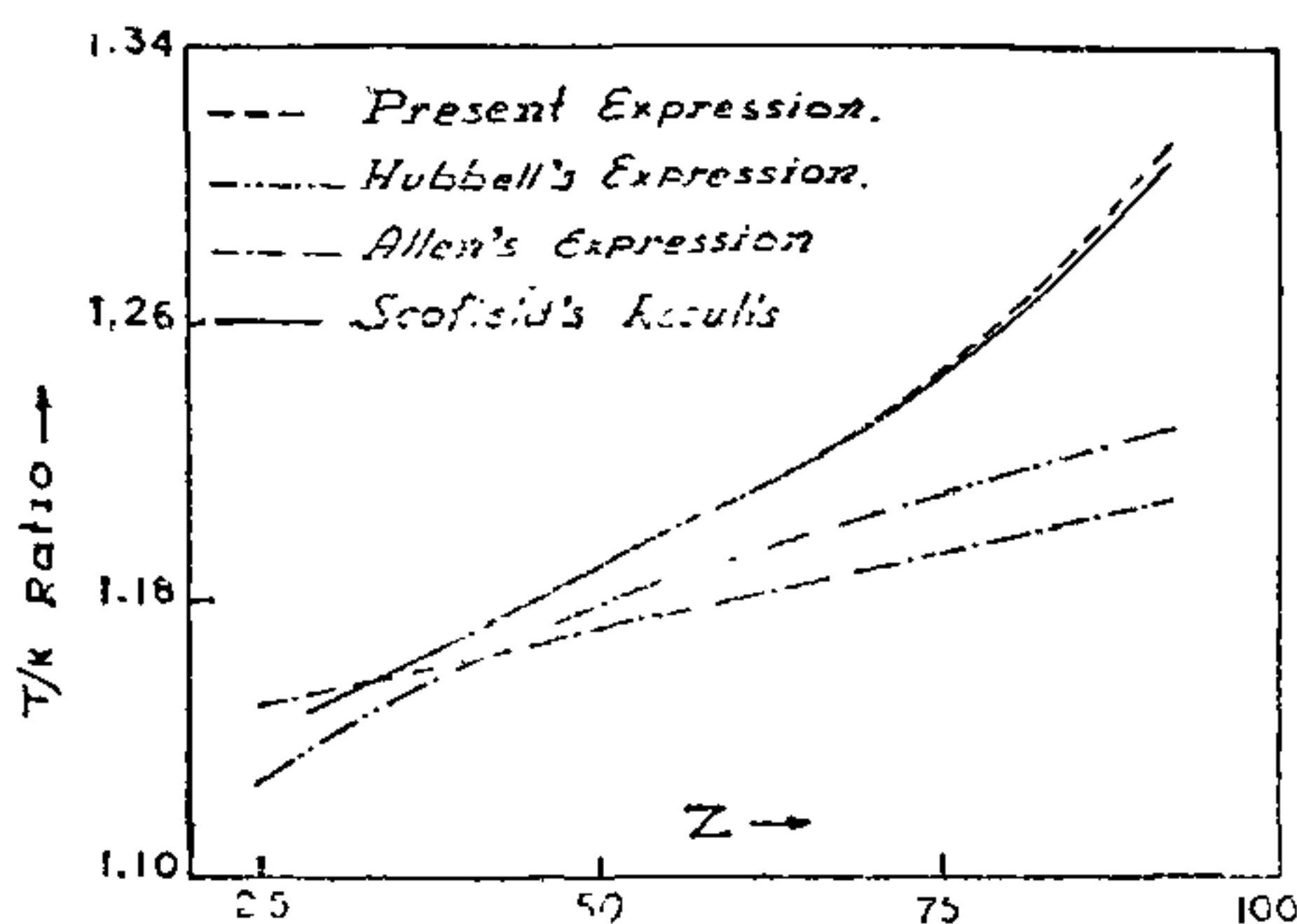


FIG. 1

It can be seen from the figure that the present trend differs from those of Allen and Hubbell in the high Z-region significantly. It can also be seen that the present values are in excellent agreement with the recent theoretical values of Scofield.

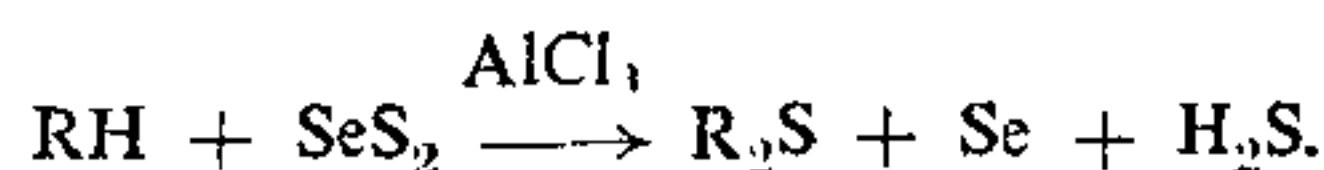
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FRIEDEL-CRAFTS REACTION OF SELENIUM SULPHIDE

NUCLEOPHILIC addition of sulphur into the organic moiety under Friedel-Crafts condition is known only in the case of benzene¹ while addition of selenium under similar conditions towards the synthesis of diaryl selenides has not been reported. The ditolyl and xylyl sulphides are synthesised by reduction of sulphoxides² or by the reaction of diorganomercury compounds with sulphur³ or from the reaction of lead salts of organothio compounds with aryl halides⁴. The methods of introducing selenium into the organic moiety are summarised in literature^{5,6}. It would be desirable to have the synthesis of both diaryl sulphide and selenide in one step and towards this end selenium sulphide as a starting material offers an advantage.

In the course of our studies on the synthesis and reactivity of selenium sulphides it has been found that octatomic species, $Se_n S_{8-n}$, are inert towards many reactions though they possess interesting structures. The selenium sulphide, SeS_2 , synthesised by published method⁷, undergoes a variety of reactions and we wish to report here some of our results. The SeS_2 reacts with benzene, toluene and *p*-xylene in presence of anhydrous $AlCl_3$ to form diaryl sulphides in nearly quantitative amounts. No undesirable disulphide formation has been noticed. The course of the reaction can easily be monitored by the evolution of H_2S and quantitative precipitation of elemental selenium is observed at the completion of the reaction. The products are found to be pure from their bp/mp, elemental analysis, chromatographic and spectral methods. The reaction can be represented as:



No formation of diaryl selenides has been noticed though different reaction conditions such as varying mole proportions of the reactants, reaction time and temperature are employed.

In the case of toluene the GLC data showed that the product contained a mixture of three isomers. The major component (53%) has been characterised as the *para* substituted derivative since the infrared spectrum showed two absorptions at 1890 and 1780 cm^{-1} ⁸. The minor components (35% and 12%) in the product, however, could not be identified by spectroscopic method nor the separation of the isomers was possible on account of their close boiling points. The minor components are recognised as di *ortho* and *ortho-para* substituted sulphides based on reactivity considerations.

The reaction seems to proceed through the formation of a reactive intermediate complex of the type,