sodium hydroxide solution, and the pK_s values of 3.38 and 3.65 were found for mannuronic and guluronic acid, respectively. The differences observed in the pK_s' values for polymers with different uronic acid composition are thus in good agreement with the pK_s values found for the monomeric units.

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Experimental Determination of Br f Values by Electron Diffraction

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A study of the electron diffraction pattern of the Br_2 molecule was carried out in conjunction with a Fulbright research grant to Norway. From data taken on the Oslo diffraction unit, it had appeared that there existed an anomaly in the intensity of the electron scattering from bromine compounds. For the compounds ordinarily studied, usually hydrocarbons and chlorine substituted hydrocarbons, it was always possible to bring the observed atomic scattering into almost exact coincidence with that calculated theoretically¹. This could not be done for bromine containing com-

pounds. Since the Br_2 molecule is the simplest of bromine compounds, and since it also exhibits the apparent anomaly, the diffraction pattern from this molecule was studied in detail.

Except for constants, the total intensity observed in electron scattering by a diatomic molecule is given by

$$I \propto \frac{1}{s^4} \left[g^2(s) + ZS + g^2(s)e^{-ds} \frac{\sin sr}{sr} \right]$$

where the first two terms in brackets constitute the atomic scattering, and the third term is the molecular effect. The term ZS is the incoherent atomic scattering which is usually relatively small; s is equal to $(4\pi/\lambda) \sin \Theta/2$; d is the damping factor; and $g(s)$ is the amplitude of the coherently scattered wave. Within the limits of the Born approximation, $g(s)$ is equal to $(Z-f)$, where f is the ordinary X-ray atomic form factor. The data is recorded photographically, and since a flat plate plus a rotating sector are employed, suitable correction must be made. Since the sector effectively compensates for the well known $\csc^4 \Theta/2$ effect, the over-all variation in intensity is sufficiently small that recording the intensity photographically introduces little error.

It was established that the difficulty of calculating the atomic scattering lay mainly in the use of the bromine f values obtained from statistical atomic models. For small values of s , the intensity is highly sensitive

Fig. 1. Intensity in electron diffraction pattern from Br_2 : (a) Observed atomic scattering; (b) predicted atomic scattering from Thomas-Fermi atom with exchange; (c) predicted atomic scattering from Thomas-Fermi atom without exchange.

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Fig. 2. Experimental f values for bromine with various theoretical curves.

to the f values employed as is shown by the easily obtained approximate relation,

$$\frac{dI}{I} = \frac{2df}{Z-f}$$

When f approaches Z , as it does for small s , one sees that a small error in f will produce a large discrepancy between the calculated and the observed intensity. One can observe the effect of this sensitivity in Fig. 1. The observed intensity is plotted with the atomic scattering to the expected on the basis of the Thomas-Fermi and Thomas-Fermi-Dirac models. In addition, the obvious relation that exists between the molecular scattering and the total atomic scattering makes it possible to determine the amount of the noise that comes with the signal, and thus to establish what the atomic scattering actually must be; the latter is also shown in Fig. 1.

The sensitivity of the calculated atomic scattering to the f values implies that one possesses a suitable technique for measuring the f values experimentally. One knows, however, that the Born approximation is inadequate to describe the scattering at the voltages commonly employed in

electron diffraction². By making the reasonable assumption that the relation between $g(s)$ and $(Z-f)$ in a Thomas-Fermi atom is preserved in the bromine atom proper, one obtains the f values shown in Fig. 2. Several theoretical curves are also shown.

The question still remains as to the reliability of the results. The general shape of the curve is quite reasonable; it retains vestigial features of the curves of lighter elements and it has much in common with the f values of Rb^+ for which Hartree calculations exist³. By normalization to a computed value of $f = 2.42$ at $s = 40$, where the hydrogen-like inner orbitals play the major role⁴, one finds good agreement with the Thomas-Fermi results for $s = 11$ to $s = 23$. A hump in the region of $s = 4$ to $s = 11$ is predicted by Pauling-Sherman as is the slight hump at $s = 30$. The high values for $s < 4$ may be due to (1) the enhanced possibility for error due to the sector correction, (2) the failure to consider the polarization of the atom and the uncertainty of the incoherent scattering term, or (3) a real effect. If the latter is the case, it indicates that the charge cloud due to the outer electrons is held somewhat closer to the nucleus than the statistical models predict. This would be consistent with the fact that the f values found here are the effective values for a bonded atom. In any event, electron diffraction techniques offer a sensitive method for obtaining f values. By considering the scattering from sufficiently simple molecules, it should be possible to compile experimental f values which are superior to the theoretical values which are known to be in error.

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