TABLE II. Quadrupole splitting vs pressure Fe(III) quadrupole splitting.[a] Pressure (kbar).

Derivative		20	40	60	80	100	120	140	160	180
					Class A					
ACA(1)	S [b]	0.775	0.896	1.049	1.191	1.308	1.396	1.458	1.503	1.534
BA(4)	A	0.771	0.957	1.172	1.347	1.469	1.558	1.612	1.649	1.662
TFACA(5)	A	0.675	0.827	0.982	1.156	1.340	1.483	1.562	1.593	1.605
MACA(9)	S	0.820	0.923	1.030	1.136	1.231	1.314	1.378	1.409	1.420
NACA(11)	S	0.825	0.944	1.082	1.238	1.397	1.509	1.558	1.579	1.591
EACA(12)	S	0.921	1.056	1.172	1.276	1.358	1.419	1.460	1.480	1.488
					Class B					
FTFA(6)	A		0.822	0.948	1.169	1.408	1.600	1.714	1.761	1.775
TTFA(7)	A	0.781	0.943	1.110	1.279	1.446	1.591	1.697	1.741	1.750
BTFA(8)	A		0.873	1.109	1.330	1.521	1.671	1.776	1.832	1.845
PACA(10)	S	0.660	0.872	1.033	1.150	1.250	1.329	1.378	1.400	1.409
					Class C					
DBM(2)	S		0.921	1.022	1.174	1.370	1.538	1.619	1.649	1.660
DPM(3)	S		0.721	0.939	1.158	1.319	1.411	1.447	1.453	1.453

Fe(II) Quadrupole splitting. Pressure (kbar).

Derivative	40	60	80	100	120	140	160	180
				Class A				
ACA(1)	2.002	1.954	1.926	1.916	1.922	1.934	1.942	1.945
BA(4)	2.050	1.977	1.935	1.916	1.916	1.929	1.946	1.966
TFACA(5)	2.248	2.123	2.055	2.046	2.068	2.094	2.115	2.122
MACA(9)	2.180	2.180	2.180	2.189	2.206	2.220	2.224	2.224
NACA(11)	2.081	2.147	2.202	2.248	2.289	2.321	2.338	2.342
EACA(12)	2.275	2.191	2.148	2.129	2.122	2.120	2.120	2.120
				Class B				
FTFA(6)	2.225	2.132	2.095	2.102	2.130	2.144	2.148	2.149
TTFA(7)		1.982	1.990	2.017	2.044	2.060	2.065	2.065
BTFA(8)	2.365	2.175	2.040	2.003	2.018	2.051	2.075	2.082
PACA(10)	2.305	2.215	2.148	2.107	2.088	2.080	2.074	2.070
				Class C				
DBM(2)	2.190	2.078	2.028	2.015	2.014	2.014	2.014	2.014
DPM(3)	2.486	2.447	2.412	2.384	2.375	2.395	2.418	2.423

[a] In mm/sec.   [b] S-symmetric substitution, A-asymmetric substitution.

ency for electron attraction than hydrogen. The σ values reflect a combination of inductive and resonance effects and are sensitive to the position of substitution. Brown and Okamoto[18] have shown that better correlations can be obtained for electrophilic reactions using slightly modified σ values. Both sets of substituent values work equally well for the compounds, so the σ^+ set has been used here.

The third chemical parameter which can be related to the electronic behavior of the ligand derivatives is the appearance potential from electron impact mass spectrometry. The technique involves bombarding the substance in the gas phase with electrons and monitoring the ion current produced as the range of accelerating voltages is scanned. The appearance potential of interest in the metal β-diketonate systems corresponds to that voltage at which the singly ionized ML_3^+ species appears. Here M refers to the metal and L to the ligand.

Numerous examinations of the β-diketonate derivatives of the first transition series metals[19-24] have indicated that the appearance potentials depend predominantly on the ligand and only slightly on the metal.
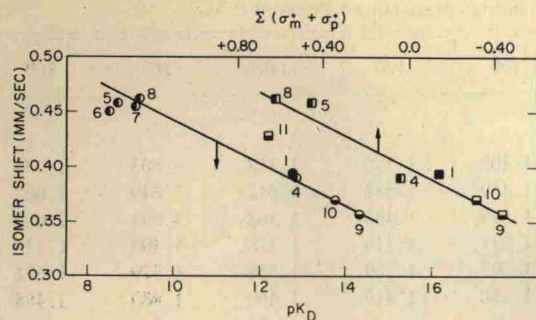
Fig. 5. Fe(III) isomer shift vs pk_D and Hammett σ.

Thus, data for the homologous series of Cu(II) chelates have been used because data for the Fe(III) chelates were incomplete.

Still another chemical parameter from which electronic information may be deduced is the half wave potential $E_{1/2}$ from polarography. Electron donating groups on the chelate ring will tend to increase the basicity of the oxygen atoms and impart strong covalent character to the metal–oxygen bond. This will result in a large negative value of the half-wave potential. Withdrawing groups lead to more ionic metal–oxygen bonds and a less stable chelate with a less negative half wave potential. As was previously the case, no literature data were available for the iron series derivatives. However, several investigations of the copper series[25-29] have been made and are used here.

Variations in the order of electron donor ability among the derivatives, as predicted by these different chemical correlations, do exist. However, three rough groupings of compounds are readily apparent. These are, in decreasing order of electron donor ability: [DPM(3), MACA(9), PACA(10), EACA(12)]> [ACA(1),DBM(2),BA(4)]>[TFACA(5),FTFA(6), TTFA(7), BTFA(8), NACA(11)] where the members of each general group have been arbitrarily arranged in order of their reference code.

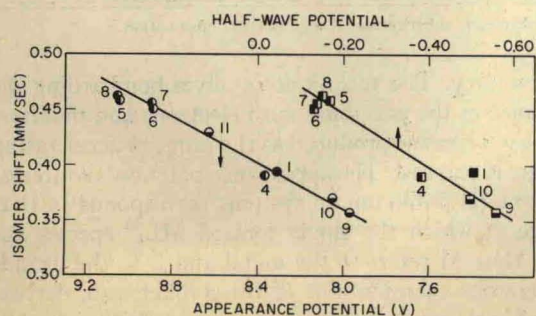Figures 5 and 6 show the correlation between atmos-

Fig. 6. Fe(III) isomer shift vs half wave potential and appearance potential.

pheric Fe(III) isomer shifts determined in this work, and the various atmospheric chemical measurements obtained from the literature. The isomer shift is given relative to *bcc* iron and the chemical parameters have been plotted so that movement to the right corresponds to an increase in electron donor tendency. The numbers refer to the reference codes given in Fig. 1. The same general correlation is observed in all cases, i.e., the smaller isomer shift, or greater *s* electron density at the iron nucleus, may be associated with a greater tendency for donation of the ligand electrons to the metal. It is important to realize, however, that the absolute value of the isomer shift depends on several contributions, as has been pointed out by Erickson.[30] The isomer shift is affected by metal orbital expansion
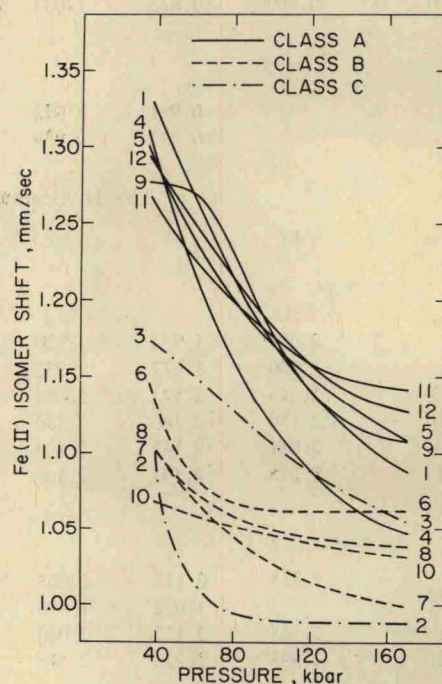

Fig. 7. Fe(II) isomer shifts vs pressure.

due to a reduction of effective nuclear charge associated with the overlap of the metal electron cloud with the negative ligand charge, and by $4s$ orbital augmentation, which constitute central field covalency. In addition, metal d_π backbonding to vacant ligand π^* orbitals or $3s$ shielding because of overlap of ligand electron density in the bond region, which constitute symmetry restricted covalency, are important factors to consider. Since these contributions may well exhibit different pressure behavior, the fact that the correlations of isomer shifts and measures of electron donor tendencies at atmospheric pressure are fairly consistent does not necessarily imply that such a correlation of absolute isomer shifts with degrees of conversion will be as good at high pressures.