

TABLE 2. *Heats of reaction.*

Material (kb)	$H$ (ev)	
	325°K	375°K
Acetyl acetate		
60	0.15	0.25
100	0.105	0.15
150	0.065	0.085
200	0.032	0.037
Basic acetate		398°K
75		0.93
100		0.60
150		0.44
Oxalate	315°K	360°K
25	0.19	0.34
70	0.23	0.39
100	0.26	0.42
150	0.29	—
Strontium ferric oxalate		333°K
20		0.11
50		0.15
100		0.20
200		0.24

tures can probably be associated with thermal relaxation of the strains. The heat of reaction decreases markedly with increasing pressure.

On the other hand, the oxalates exhibit a value of  $B(P\Delta V/RT)$  and a heat of formation of the Fe(II) site which increases with pressure, i.e., the work to perform the reduction is greater at high than at low temperature. It is known that oxalates tend to reduce photochemically,<sup>12, 13</sup> and when heated in the dark, they undergo a series of reactions; first reduction, then oxidation.<sup>14</sup> In both cases CO<sub>2</sub> is evolved and the process is irreversible.

As indicated earlier, the high-pressure reduction is reversible and involves a lowering of energy of metal antibonding levels with respect to ligand nonbonding  $p$ -orbitals, so it is not necessary to postulate formation of CO<sub>2</sub> in the lattice. Nevertheless, the radical formed in the process quite possibly has a volume in the lattice that is rather temperature-dependent. It is of interest to note that the slope  $B$ , and therefore the volume difference ( $V^{\text{III}} - V^{\text{II}}$ ), is noticeably smaller for the strontium salt than for the ferric oxalate, although the number and gross symmetry of the ligands is apparently the same for both compounds. This illustrates the important effect of the ability to redistribute the strain to next-nearest neighbors and beyond on the conversion equilibrium.

While the main interest in this study was the conversion of Fe(III) to Fe(II), isomer shift and quadrupole splitting data were obtained both for the Fe(III) and for the Fe(II) formed at high pressure. These results appear in Tables 3 and 4. Isomer shift data are shown only at room temperature, for it was necessary to change the source location slightly with increasing pressure, which caused a slight change in its temperature. Peak locations established with changing amounts of Fe(III) and Fe(II) present are necessarily less accurate than those obtained in nonreacting systems, but one can comment on two trends of interest whose magnitude are well beyond any experimental error.

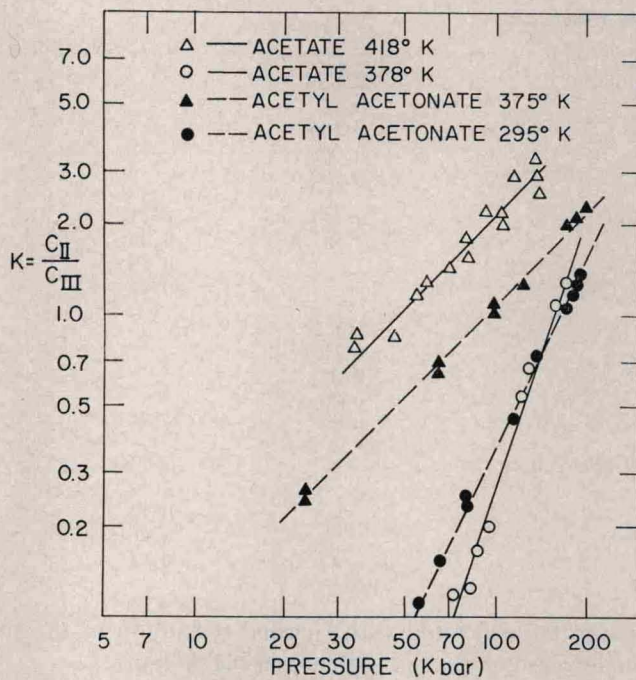


FIG. 1.— $\ln K$  vs.  $\ln P$ —acetate and acetyl acetate.

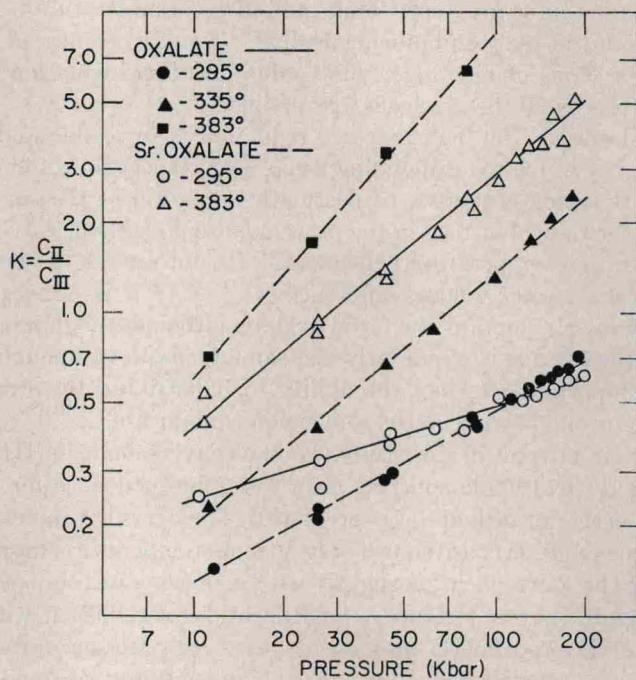


FIG. 2.— $\ln K$  vs.  $\ln P$ —ferric oxalate and strontium ferric oxalate.