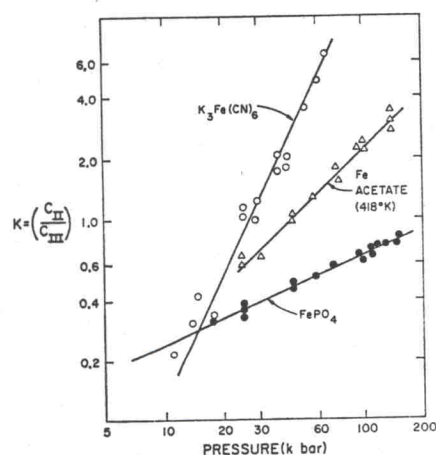
FIG. 23. $\ln K$ versus $\ln P$ — FeCl_3 , FeBr_3 and KFeCl_4 .FIG. 24. $\ln K$ versus $\ln P$ — FePO_4 , $\text{K}_3\text{Fe}(\text{CN})_6$ and basic ferric acetate.

transfer peak normally has an energy of 3–6 eV, with a long low energy tail which may extend through the visible and even into the infrared part of the spectrum. As indicated earlier, a red shift (shift to lower energy) of one-half to 1 eV in 100 kb is observed experimentally, and can be explained theoretically; however this is of course not sufficient to move the optical peak to zero energy. The high pressure transition observed by the Mössbauer studies is, however, a thermal transition which takes place sufficiently slowly so that the atomic coordinates can assume their new equilibrium values, whereas an optical transition must take place vertically on a configuration diagram, according to the Franck-Condon principle. The situation is illustrated in a typical diagram in Fig. 25. The horizontal configuration coordinate is typically some vibrational mode of the system (metal plus ligands) which

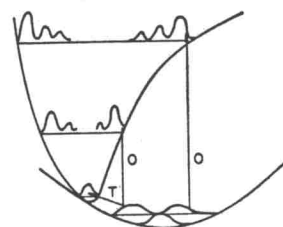


FIG. 25. Schematic configuration coordinate diagram. O = optical transition, T = thermal transition.

permits the rearrangement. The observed tail on the charge transfer peak is consistent with a very steep slope of the side of the excited-state potential well above the centre of the ground-state well, and accounts for the small thermal energy necessary for the transition. The diagram also explains the temperature coefficient of the equilibrium constant, as there is a thermal distribution for transfer of electrons from the ground to the excited electronic level, and in addition a distribution of electrons among the vibrational levels of the ground state with increasing temperature.

There remains the problem of the pressure dependence of the conversion. Qualitatively, one can see why the conversion does not go to completion at a given pressure as follows. When electron transfer takes place, one creates a ferrous ion in a ferric site plus a free radical or radical ion. (The excitation may also be smeared out over the nearest neighbour ligands.) There is thus a transfer of charge, a change of