EFFECT OF PRESSURE UPON EQUILIBRIUM

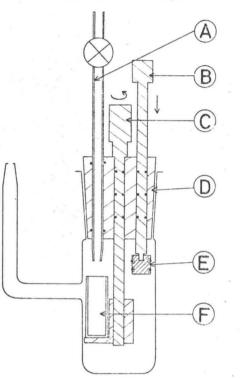


FIG. 1.-The device used for filling the cell in vacuum and closing it with a piston.

The ampoule containing the solution to be investigated was sealed to tube A above the Teflon stopcock marked in fig. 1 by a cross. The unit was evacuated, the Teflon stopcock closed and the break-seal broken. Thereafter, the cell was filled in vacuum by manipulating the stopcock; then it was placed under the piston by turning rod C. The piston was pushed into it by shifting the rod B which was eventually disengaged from the piston by unscrewing. After letting air into the vessel, stopper D was lifted and the filled and closed cell removed. The cell was inserted in the high pressure steel vessel, as described in the preceding paper,² and the spectrum investigated under the desired pressure. A Zeiss M4 QIII spectrophotometer, with accuracy better than 0.01 units of O.D., was used.

In a typical run the spectrum of each solution was recorded at normal pressure, then the pressure was gradually increased, the spectrum being recorded at each increment (940, 1920, 2920, 3900 and 4900 atm). The optical densities were corrected for the absorption of the solvent and of glycerol that filled the space between the sapphire windows and the cell. These corrections were determined for all the required wave-lengths and pressures.

A direct check of the reversibility of the process was not feasible because some carbanions are destroyed when the pressure is reduced. This is caused by contact of the solution with the walls of the cell which were wetted by glycerol when the pressure was high. Nevertheless, reversibility was demonstrated by showing that the ratio of optical densities of the two peaks is the same whether the required pressure was attained from below or from above. The pressure gauge was calibrated from compression measurements on water using piezometers of the type described by Andersson.³ The compressibility of the solvent was determined by the same technique.

RESULTS

Four independently-prepared solutions of sodium and lithium fluorenyl in THF were investigated. Typical spectra of these salts recorded at various pressures are

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