that the lithium salt at 4900 atm forms only loose pairs. From its absorption curve (see fig. 3) $r_2$ is calculated to be 0.35 and 0.31 for the sodium and lithium salts, respectively.

The plots of log $K$ against $P$ are shown in fig. 4. Their initial slopes give $\Delta V$ of $-24.4$ ml/mol for the sodium salt and $-15.6$ ml/mol for lithium fluorenyl.

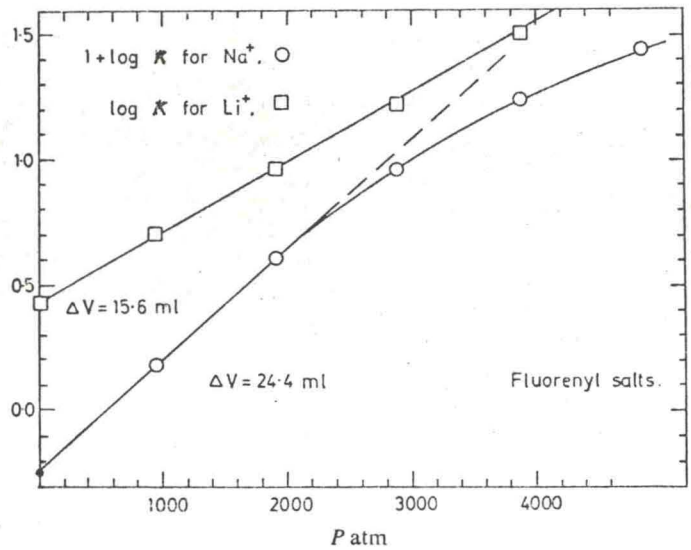


FIG. 4.—Plots of log $K$ against pressure for lithium and sodium fluorenyls in THF at ~22°C. $K$ is the equilibrium constant of the conversion of a tight ion-pair into a loose one.

## DISCUSSION

We have established that the conversion of tight ion-pairs into loose ones decreases the volume of the system. This result resembles the phenomenon of electrostriction viz., as a tight pair is transformed into a loose one more solvent molecules are bound to it and this accounts for the observed contraction of volume.

The magnitude of $\Delta V$ is related to the number of solvent molecules which become attached to the loose pair during its formation. The solvent molecules are mainly clustered around the cation and our results indicate that the formation of the loose sodium salt binds more THF molecules ($\Delta V = -24.4$ ml/mol) than the formation of the lithium pair ($\Delta V = -15.6$ ml/mol). Apparently, the degree of solvation of the *tight* lithium pair is greater than that of the sodium one, and consequently the further gain in solvation arising from the formation of the loose pairs is larger for the latter than the former. Judging from their mobility [4] the free $Na^+$ and $Li^+$ cations are equally bulky in THF.

Freezing of solvent molecules around loose ion-pairs accounts also for the decrease in the entropy of the system accompanying the process; tight ion-pairs→loose ion-pairs. The relevant $\Delta S$ were $-33$ and $-22$ cal/mol K for sodium and lithium fluorenyls, respectively, in THF.[1, 5] The correlation of $\Delta S$ with $\Delta V$ is remarkable—both increase by about 50 % as sodium is substituted for lithium. Assuming that the binding of 1 mol of solvent decreases its (mainly translational) entropy by ~11 cal/mol K, we conclude that the compression arising from packing of 1 mol of THF into the solvation shells of the loose pairs contracts the volume of the system