The equation giving K is based on the following assumptions. (i) The extinction coefficients of the two types of pairs at their respective maxima are equal at all pressures. (ii) The shape of the absorption curve of the loose pairs is independent of pressure and of the nature of cation (whether Li^+ or Na^+). (iii) The absorption curves of the tight pairs derived from the lithium or sodium salts are identical in shape but one is displaced with respect to the other by 6 nm. Moreover, their shape is again assumed not to be affected by pressure. It follows then that r_1 and r_2 are also independent of pressure. A critical examination of these assumptions is given in the appendix.

TABLE 2.—FLUORENYL LITHIUM IN THF AT ~22°C

expt.	pressure atm	O.D. (350)	O.D. (374)	R	K
1	1	0.658	0.988	1.502	2.7
2	1	0.833	1.281	1.538	2.8
3	1	0.818	1.243	1.520	2.7
4	1	0.290	0.431	1.486	2.6
			average	1.509	2.7
1	940	0.617	1.225	1.985	4.9
2	940	0.812	1.679	2.068	5.5
3	940	0.785	1.574	2.005	5.0
4	940	0.288	0.571	1.983	4.9
			average	2.010	5.1
1	1920	0.598	1.423	2.380	8.7
2	1920	0.813	1.986	2.443	9.6
3	1920	0.770	1.886	2.450	9.8
4	1920	0.269	0.638	2.372	8.6
			average	2.406	9.2
1	2920	0.595	1.575	2.647	14.2
2	2920	0.801	2.19	2.734	17.3
3	2920	0.751	2.08	2.770	18.9
4	2920	0.265	0.715	2.698	15.8
			average	2.712	16.5
1	3900	0.578	1.646	2.848	23
2	3900	0.794	2.35	2.960	35
3	3900	0.734	2.19	2.984	38
4	3900	0.261	0.765	2.961	31
			average	2.938	32
3	4900	0.719	2.28	3.17	—
4	4900	0.258	0.793	3.07	—

O.D. corrected for the solvent absorption at the appropriate pressure.

The absorption curve of the sodium salt at 1 atm is assumed to represent the spectrum of the pure tight-pairs. From it we determined r_1 to be 0.24 for the sodium salt and 0.10 for the lithium salt (the latter is given by $\text{O.D.}_{380}/\text{O.D.}_{356}$). The validity of these results was confirmed by determining the spectrum of sodium fluorenyl in a flat quartz cell (optical path ~0.01 cm) attached to the storage ampoule. For example, $\text{O.D.}_{374}/\text{O.D.}_{356} = 0.242$ in the flat cell while the average of 4 experiments performed in the pressure vessel led to the ratio 0.238 (see table 1). It is assumed 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 ΔV of -24.4 ml/mol for the sodium salt and -15.6 ml/mol for lithium fluorenyl.

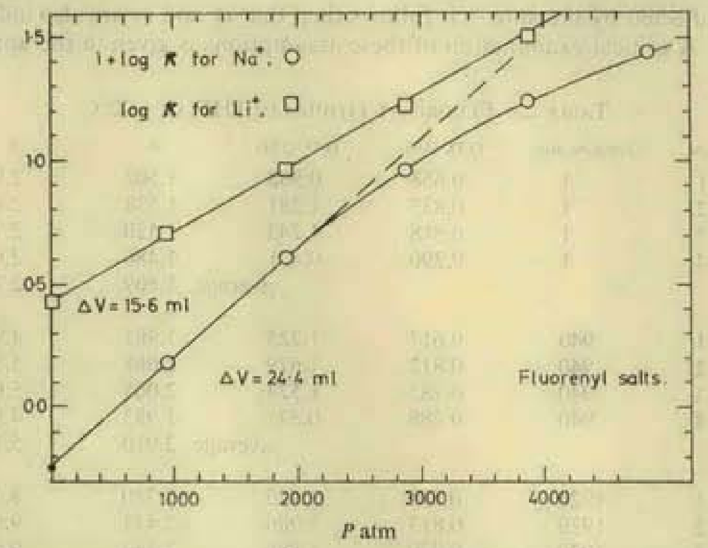

FIG. 4.—Plots of log K against pressure for lithium and sodium fluorenyls in THF at ~22°C. K is the equilibrium constant of the conversion of a tight ion-pair into a loose one.

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 ΔV 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 ΔS were -33 and -22 cal/mol K for sodium and lithium fluorenyls, respectively, in THF.[1, 5] The correlation of ΔS with ΔV 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