Table II: Negative Logarithm of the Conventional Ionization Constant, K, for the Dissociation of NaI into Na^+ and I^-. Standard State Is the Hypothetical 1 M Solution

T, °C	Density, g cm^{-3}								
	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75
400	3.24	2.68	2.39	2.01	1.54	1.23	0.85	0.67	0.16
450	3.46	2.93	2.54	2.11	1.63	1.32	0.92	0.63	0.43
500	3.63	3.10	2.66	2.19	1.73	1.33	1.04	0.75	0.53
550	3.76	3.23	2.77	2.27	1.81	1.45	1.19	0.85	0.64
600	3.88	3.33	2.86	2.34	1.91	1.54	1.22	0.99	0.70
650	3.97	3.42	2.93	2.44	2.02	1.68	1.34	1.02	0.83
700	4.06	3.50	3.01	2.52	2.13	1.79	1.48	1.18	0.83
750	4.16	3.58	3.08	2.62	2.24	1.89	1.60		
800	4.25	3.65	3.14	2.73	2.36	2.00	1.72		

numbers of NaI, Na^+, and I^-, respectively, while k denotes the net change in waters of solvation resulting from the ionization of one mole of NaI. Over the complete density range from 400 to 800°, values of the conventional ionization constant (K) were obtained from the experimental data using the Shedlovsky equation,[12] with Λ_0(NaI) values calculated from eq 1. With this procedure the Shedlovsky equation contains only one parameter, the conventional ionization constant. Table II gives the calculated negative logarithms of the conventional constants at temperatures from 400 to 800° and densities from 0.35 to 0.75 g cm^{-3}. These ionization constants are based on the standard state of unit molarity at each temperature and density. The average uncertainty associated with the values in Table II is approximately 0.03 pK unit, with the greatest uncertainties occurring at the highest densities at all temperatures.
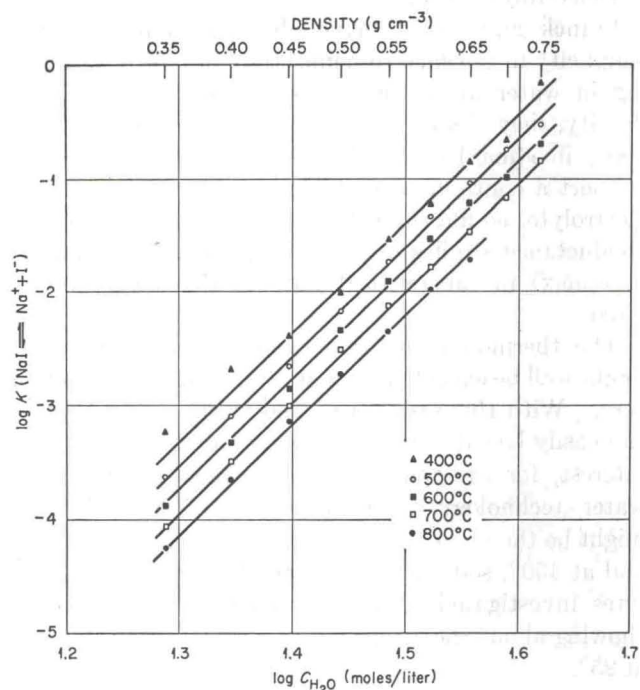

Figure 5. Log K(molar units) for the equilibrium NaI $\rightleftharpoons$ $Na^+ + I^-$ as a function of the logarithm of the molar concentration of water at temperatures from 400 to 800°.

With the concept of the complete ionization constant (including hydration),[7,8] where a_{H_2O} is replaced by the molar concentration of water (C_{H_2O}) with a hypothetical standard state of unit molarity at the particular density (or pressure), isothermal plots of log K against log C_{H_2O} provided linear relationships at the several temperatures as shown in Figure 5. The slope k for NaI was independent of temperature in the range 400 to 800°, having an average least-squared value of 9.67 $\pm$ 0.08. Corresponding least-squared values for NaCl and NaBr are included in Table IV. These values have been proposed to represent the net changes in waters of solvation on ionization of one mole of each electrolyte. From the value of $k = 9.67$ for NaI (Figure 5), together with the data of Table II, values of log K^0(NaI) have been calculated and are given in Table III. Cor-

Table III: Values of the Logarithm of the Complete Ionization Constants (K^0) and the Complete Free Energy Changes $(\Delta G°$, kcal mol^{-1}) for the NaCl, NaBr, and NaI Equilibria

T, °C	NaCl		NaBr		NaI	
	log K^0	$\Delta G°$	log K^0	$\Delta G°$	log K^0	$\Delta G°$
400	−17.10	52.7	−16.49	50.8	−15.87	48.9
450	−17.23	57.0	−16.58	54.9	−16.01	53.0
500	−17.31	61.2	−16.73	59.2	−16.12	57.0
550	−17.42	65.6	−16.90	63.7	−16.23	61.1
600	−17.52	70.0	−17.04	68.1	−16.32	65.2
650	−17.62	74.4	−17.16	72.5	−16.43	69.4
700	−17.70	78.8	−17.27	76.9	−16.52	73.6
750	−17.77	83.2	−17.35	81.2	−16.61	77.8
800	−17.83	87.6	−17.38	85.3	−16.71	82.1

responding values for NaCl[4] and NaBr[5] have also been included for comparison.

Comparative Thermodynamic Behavior of the Alkali Halides. Over the entire range of temperature (T) and density (d) studied, the order of association at constant T and d, is NaCl > NaBr > NaI. This behavior can be observed from a comparison of both the conventional ionization constants, presented in Table II for NaI and previously for the other two halides,[4,5] and the complete constants, presented in Table III for the
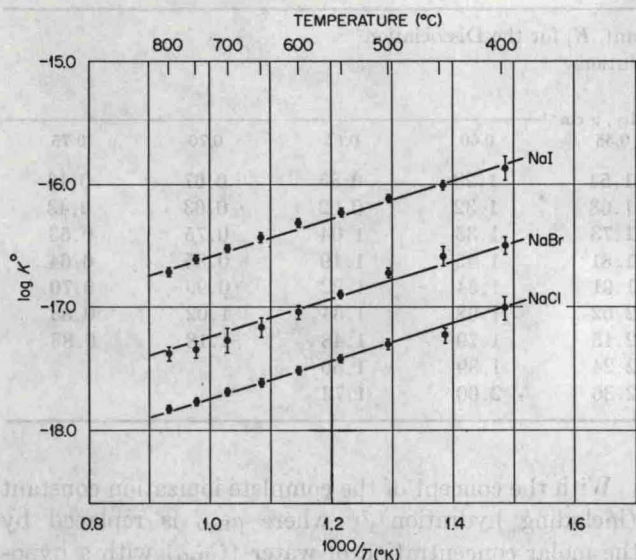
Figure 6. Log K^0 (molar units) for the equilibrium $NaX(H_2O)_j + kH_2O \rightleftharpoons Na(H_2O)_m{}^+ + X(H_2O)_n{}^-$ as a function of T^{-1}(°K) for NaCl, NaBr, and NaI.

three alkali halides. Thus, NaI is the most highly ionized electrolyte, while NaCl is the most highly associated electrolyte, with NaBr occupying an intermediate position. This pattern observed over an extreme range of temperature and density implies strongly that the halogen ion sizes, independent of the degree of hydration, remain in the order, $I^- > Br^- > Cl^-$, where the extent of association is expected to be inversely proportional to the ion sizes. The comparative values of $\Delta G°$ for the complete equilibria, tabulated in Table III at 400–800°, show the relatively small differences in standard free energy changes among the three halides.

The approximate constancy of k (the net change in waters of solvation) between 400 and 800° allows a simple comparison of the thermodynamic functions over this range of temperature, since for each electrolyte the respective equilibrium does not change in stoichiometry. Plots of the log K^0 data in Table III against T^{-1} (°K) are shown in Figure 6 for the three sodium halides. Least-squares analysis of the data indicated an average slope of 1540 ± 160 for each of the electrolytes, within the precision of the measurements. This value of the slope yielded a single value of −7.0 kcal mol^{-1} for $\Delta H°$ for the complete equilibrium for each of the three electrolytes. With this value of $\Delta H°$ and the $\Delta G°$ values in Table III, values for $\Delta S°$ for the complete reactions were calculated, and were found, within the precision of the measurements, to be independent of both density and temperature (400–800°). Comparative values for k, $\Delta H°$, and $\Delta S°$ are given in Table IV for the three electrolytes. For the complete equilibria

$$(\partial \ln K^0 / \partial P)_T = -\Delta V° / RT = 0 \qquad (9)$$

Thus $\Delta H° = \Delta E° + P\Delta V° = \Delta E°$. The negative values of $\Delta S°$, approximately proportional to k, show

Table IV: Thermodynamic Values ($\Delta H°$, $\Delta S°$) and k for the NaCl, NaBr, and NaI Equilibria, 400–800°

Electrolyte	k	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}
NaCl	10.20 ± 0.15	-7.0 ± 0.7	-88.3 ± 0.1
NaBr	9.94 ± 0.48	-7.0 ± 0.7	-86.2 ± 0.3
NaI	9.67 ± 0.08	-7.0 ± 0.7	-82.9 ± 0.1

that increase in solvation upon ionization of the ion pairs provides greater order in the respective systems.

Simple Description of Alkali Halide Behavior. By obtaining complete ionization constants, it has been found that at high temperatures not only does k become constant with temperature and density, but also $\Delta H°$ and $\Delta S°$. Since $\Delta H°$ is a constant, independent of density and temperature (400–800°) within the precision of the measurements for all three 1–1 salts, only $\Delta S°$ needs to be known for the particular salt in order to specify K^0 or $\Delta G°$. To specify the fraction ionized at a particular temperature and pressure, we must know the additional single value for k.

The closeness in values of k and $\Delta S°$ and the essentially identical value of $\Delta H°$ for these three alkali halides suggest that the degrees of ionization for most 1–1 salts are similar in this high-temperature range, and can be specified approximately by the above relationships and averaged values of $\Delta S°$ and k from those in Table IV. This similar behavior has been observed from a conductance study of many 1–1 electrolytes,[9] and also in the observed linear relationships of Λ_0 vs. density, where the intercept and slope of eq 1–4 are approximately the same for the several 1–1 electrolytes studied.[3-5]

Franck and Roth[13] have observed some apparent simplicity in the spectroscopic study of hydrogen bonding in water at temperatures to 400°. At constant density, they observe an approach to constancy (above 400°) in ν(max) of an absorption band considered to support a continuum model for water. The observed electrolyte equilibrium behavior in water from the conductance studies and this approach to constancy of ν(max) in supercritical water perhaps may be related.

The thermodynamic relationships presented herein might well be expected to exist at pressures approaching zero. With this assumption the fraction of ionization can easily be calculated for cases of immediate, applied interest, for example, in geochemistry or pressurized water technology where pressures of 200–400 bars might be the range to be considered. Thus at 200 bars and at 400°, sodium iodide (and the other 1–1 electrolytes investigated) is an extremely weak electrolyte, showing about the same extent of dissociation as water at 25°.

(13) E. U. Franck and K. Roth, *Discussions Faraday Soc.*, **43**, 108 (1967).