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# Electrical Conductances of Aqueous Sodium Iodide and the Comparative Thermodynamic Behavior of Aqueous Sodium Halide Solutions to 800° and 4000 Bars

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# Electrical Conductances of Aqueous Sodium Iodide and the Comparative Thermodynamic Behavior of Aqueous Sodium Halide Solutions to 800° and 4000 Bars[1]

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From electrical conductance measurements on dilute (0.001–0.10 $m$) aqueous solutions, the ionization behavior of NaI was studied in the temperature range 0–800° and at pressures to 4000 bars. Both the conventional ($K$) and complete ($K^0$) ionization constants were calculated for comparison with published values for NaCl and NaBr. As expected, NaI ionized to a greater extent than either NaBr or NaCl, the order being directly proportional to the anion size. The net change ($k$) in waters of solvation on ionization decreased from 10.2 for NaCl to 9.7 for NaI. For the temperature range 400–800°, the van't Hoff isochore yielded standard thermodynamic functions for the complete equilibrium, $\mathrm{NaX(solvated)} + k\mathrm{H_2O} \rightleftharpoons \mathrm{Na^+(solvated)} + \mathrm{X^-(solvated)}$. The $\Delta H°$ obtained, approximately constant with temperature, was essentially the same as found for NaBr and NaCl. With the calculated values of $\Delta G°$ and an average value for $\Delta H°$ of $-7.0$ kcal mol$^{-1}$, standard entropy changes of $-88.3$, $-86.2$, and $-82.9$ cal mol$^{-1}$ deg$^{-1}$ for the complete reactions were obtained for NaCl, NaBr, and NaI, respectively. The negative values of $\Delta S°$ show that order is increased by additional solvation on ionization of the electrolyte. Thus, at high temperatures, inclusion of the solvent as a reactant provides a simple description whereby each equilibrium can be described by only three values ($k$, $\Delta H°$, and $\Delta S°$) which are essentially independent both of temperature and pressure. The closeness in values of $k$ and $\Delta S°$ for the three halides suggests that averaged values from these salts may be used to estimate the equilibrium properties of most 1–1 salts between 400 and 800°.

## Introduction

The properties of aqueous electrolyte solutions at high temperatures and pressures, particularly in the supercritical region, are amenable to investigation by conductance techniques. This method has been applied in several recent publications from this laboratory to the study of the behavior of dilute aqueous solutions of $\mathrm{KHSO_4}$,[3] NaCl,[4] NaBr,[5] and HBr[6] to 800° and to pressures of 4000 bars. The results from these studies have indicated that, at high temperatures and pressures, aqueous electrolyte solutions exhibit a simplified behavior not evident at lower temperatures. It was found that the isothermal limiting equivalent conductances of these salts in the temperature range 100–800°

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[3] A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **70**, 3714 (1966).

[4] A. S. Quist and W. L. Marshall, *ibid.*, **72**, 684 (1968).

[5] A. S. Quist and W. L. Marshall, *ibid.*, **72**, 2100 (1968).

[6] A. S. Quist and W. L. Marshall, *ibid.*, **72**, 1545 (1968).

are linear functions of the solvent density.[3-6] Moreover, at temperatures from 400 to 800°, the limiting equivalent conductances for a particular electrolyte were found to be independent of the temperature at constant solvent density.[3-6]

This paper presents conductance measurements of dilute (0.001–0.10 *m*) aqueous NaI solutions at temperatures from 0 to 800° and at pressures to 4000 bars. From these measurements limiting equivalent conductances of NaI were obtained at integral temperatures and densities. Ionization constants ($K$) for the conventional equilibrium, $\mathrm{NaI} \rightleftarrows \mathrm{Na^+} + \mathrm{I^-}$, were also obtained where NaI behaves as a weak electrolyte. From these values the complete ionization constants ($K^0$) for NaI were calculated at each temperature.[7,8] These results were used for calculation of thermodynamic quantities for NaI for comparison with the previously published results for NaCl and NaBr.

For NaCl, NaBr, and NaI a unified behavior has been observed between 400 and 800° in the attainment of an essentially constant value of $\Delta H°$, independent both of pressure and temperature, that describes the behavior of all three electrolytes. Similarly constant values of $\Delta S°$ and of the net change in waters of solvation ($k$) for each electrolyte have also been calculated.

## Experimental Section

A detailed description of the high-pressure conductance equipment and procedures used has been given previously.[4] The conductance cell with no pressure seals in the high-temperature region was used exclusively in this work. All solutions were prepared by weight from reagent grade NaI (Mallinckrodt Chemical Works) and conductivity water. The salt was dried for 24 hr at 120° before use. The conductivity water was obtained by passing distilled water through an ion-exchange column and then redistilling it twice from a fused quartz distillation unit. Conductivity measurements were made to 800° and 4000 bars on four solutions of NaI: 0.0009996, 0.005001, 0.05000, and 0.1000 *m*. Previous data of Quist and Marshall[9] for 0.01000 *m* NaI solutions under the same conditions have been included in the calculations. Four different inner electrodes were used for the conductance measurements. Their cell constants ranged from 0.495 to 2.104 cm$^{-1}$, as determined fron 0.01 and 0.10 demal KCl solutions at 25.00 ± 0.01°.

## Results and Discussion

Specific conductances and equivalent conductances were calculated from the experimental data in the manner described previously.[4] An example of isothermal specific conductances of NaI solutions as a function of pressure at the temperatures of the measurements is shown in Figure 1. From comparable figures for all five molalities of NaI, specific conductances at integral pressures were obtained by interpolation. Isobaric specific conductances for 0.05000 *m* NaI solutions *vs.* temperature are shown in Figure 2, and isothermal equivalent conductances *vs.* solvent density in Figure 3. The other solutions of NaI exhibit similar behavior except that the density at which the equivalent conductance maximum occurs increases with increasing electrolyte molality. For 0.0009996 *m* NaI the maximum occurs near 0.50 g cm$^{-3}$, while it occurs at about 0.70 g cm$^{-3}$ for 0.1000 *m* NaI solutions. Similar behavior has been observed for NaCl[4] and NaBr[5] solutions.

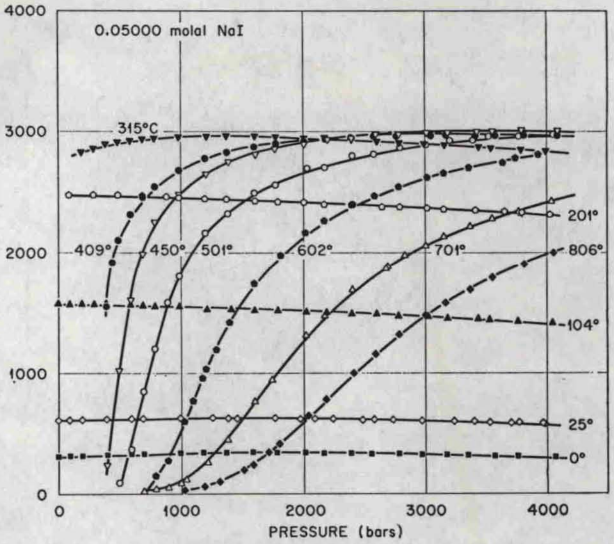

Figure 1. Specific conductances of 0.05000 *m* NaI solutions as a function of pressure at several temperatures.

From plots like Figure 3 equivalent conductances at integral densities were obtained for each molality of NaI at the experimental temperatures. These values were then plotted against temperature at constant solvent density, and from smoothed curves through the data, equivalent conductances at various temperatures and densities were obtained. These are presented in Table I for temperatures from 100 to 800°, and include equivalent conductances for 0.01000 *m* NaI calculated from the specific conductances given elsewhere.[9] Data obtained at 0 and 25° have been used only for comparative purposes as shown in Figures 1–3, and have not been included in Table I. The values in parentheses represent equivalent conductances at saturation vapor pressure at that temperature.

*Calculation of Limiting Equivalent Conductances.* From the conductance values in Table I limiting equivalent conductances were calculated by the several methods described previously,[4] and with the computer programs developed earlier.[3-6] At low temperatures and high densities the Robinson–Stokes equation,[10] the

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[7] W. L. Marshall and A. S. Quist, *Proc. Natl. Acad. Sci., U. S.*, **58**, 901 (1967).

[8] A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968).

[9] A. S. Quist and W. L. Marshall, *ibid.*, in press.

[10] R. A. Robinson and R. H. Stokes, *J. Amer. Chem. Soc.*, **76**, 1991 (1954).

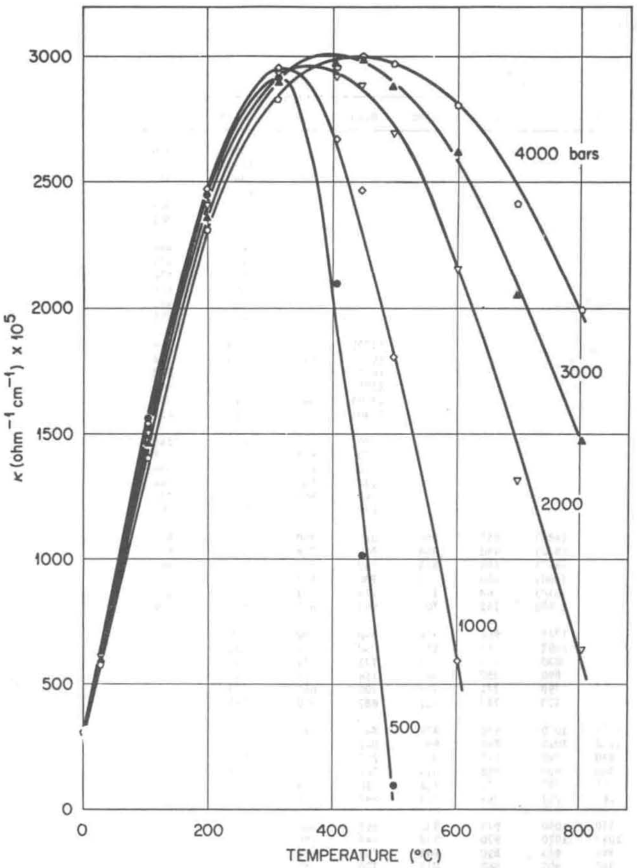

Figure 2. Isobaric variation of the specific conductances of 0.05000 *m* NaI solutions as a function of temperature at pressures from 500 to 4000 bars.

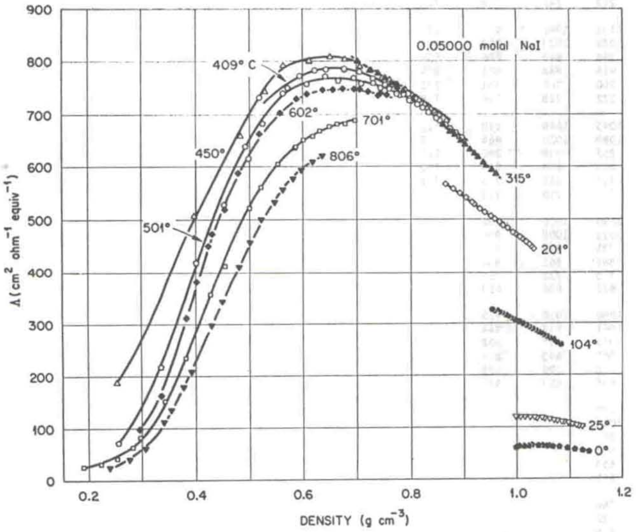

Figure 3. Equivalent conductances of 0.05000 *m* NaI solutions as a function of density at several temperatures.

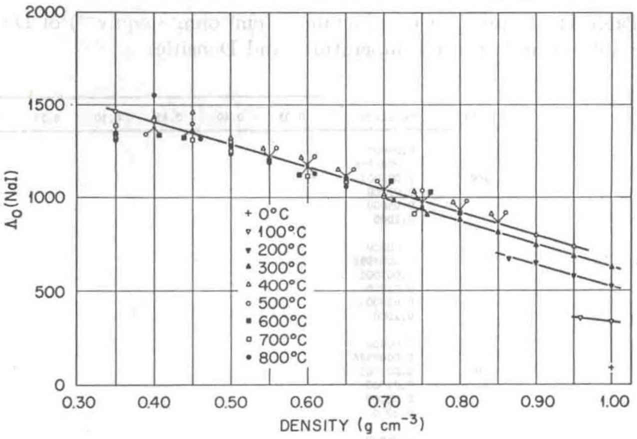

Figure 4. Limiting equivalent conductances of NaI as a function of density at temperatures to 800°.

Fuoss–Onsager–Skinner equation,[11] and the Shedlovsky equation (including an ionization constant)[12] gave essentially identical limiting equivalent conductances. As found previously for NaCl[4] and NaBr,[5] at densities below 0.70 g cm$^{-3}$ the Robinson–Stokes equation did not represent the data as well as the other equations, while below about 0.60 g cm$^{-3}$ only the Shedlovsky equation, which includes an ionization constant, fitted the data satisfactorily.

Limiting equivalent conductances calculated for NaI at the various temperatures and densities are included in Table I, where the (limiting) molality of NaI is set equal to zero. At densities of 0.65 g cm$^{-3}$ and above, the standard errors associated with the $\Lambda_0$(NaI) values of Table I are less than 1%. Below this density the uncertainty in the limiting equivalent conductances increases with increasing temperature and decreasing density. Figure 4 shows the linear relationship observed when isothermal values of $\Lambda_0$(NaI) from Table I are plotted against the density of the solvent. As found previously with NaCl[4] and NaBr,[5] the limiting equivalent conductance of NaI at constant density increases steadily with temperature, reaching a maximum, constant value at about 400° and above. The deviations from linearity (Figure 4) at high temperatures and at densities below 0.45 g cm$^{-3}$ may be due to difficulty in making accurate experimental measurements at sufficiently low electrolyte concentrations for reliable extrapolation to infinite dilution. The limitation under these conditions is the relatively high solvent conductance.[3]

A linear equation describing the variation of the limiting equivalent conductance of NaI with solvent density ($d$) in the temperature range 400–800° is given as

$$\Lambda_0(\mathrm{NaI}) = 1897 - 1210d \qquad (1)$$

Similar relationships were found previously for $KHSO_4$ (considered as a 1–1 electrolyte),[3] NaCl,[4] NaBr,[5] and HBr.[6]

$$\Lambda_0(\mathrm{KHSO_4}) = 1740 - 1100d \qquad (2)$$

$$\Lambda_0(\mathrm{NaCl}) = 1876 - 1160d \qquad (3)$$

$$\Lambda_0(\mathrm{NaBr}) = 1880 - 1180d \qquad (4)$$

$$\Lambda_0(\mathrm{HBr}) = 1840 - 560d \qquad (5)$$

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[11] R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

[12] T. Shedlovsky, *J. Franklin Institute*, **225**, 739 (1938); R. M. Fuoss and T. Shedlovsky, *J. Amer. Chem. Soc.*, **71**, 1496 (1949).

**Table I:** Equivalent Conductances (cm² ohm⁻¹ equiv⁻¹) of Dilute Aqueous NaI Solutions at Various Temperatures and Densities

| | | Density, g cm⁻³ | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T(°C) | Molality | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 | 0.60 | 0.65 | 0.70 | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 | 1.00 |
| 100 | 0.00000 | | | | | | | | | | | | | (356) | 336 |
| | 0.0009996 | | | | | | | | | | | | | (345) | 329 |
| | 0.005001 | | | | | | | | | | | | | (340) | 320 |
| | 0.01000 | | | | | | | | | | | | | (336) | 315 |
| | 0.05000 | | | | | | | | | | | | | (322) | 309 |
| | 0.1000 | | | | | | | | | | | | | (315) | 301 |
| 150 | 0.00000 | | | | | | | | | | | | | 496 | 444 |
| | 0.0009996 | | | | | | | | | | | | | 481 | 434 |
| | 0.005001 | | | | | | | | | | | | | 472 | 424 |
| | 0.01000 | | | | | | | | | | | | | 457 | 414 |
| | 0.05000 | | | | | | | | | | | | | 438 | 402 |
| | 0.1000 | | | | | | | | | | | | | 432 | 391 |
| 200 | 0.00000 | | | | | | | | | | | (670) | 653 | 583 | 526 |
| | 0.0009996 | | | | | | | | | | | (655) | 645 | 563 | 512 |
| | 0.005001 | | | | | | | | | | | (630) | 602 | 554 | 502 |
| | 0.01000 | | | | | | | | | | | (595) | 589 | 545 | 488 |
| | 0.05000 | | | | | | | | | | | (570) | 548 | 512 | 469 |
| | 0.1000 | | | | | | | | | | | (540) | 540 | 507 | 458 |
| 250 | 0.00000 | | | | | | | | | | | 780 | 708 | 644 | 586 |
| | 0.0009996 | | | | | | | | | | | 770 | 698 | 621 | 569 |
| | 0.005001 | | | | | | | | | | | 720 | 656 | 610 | 559 |
| | 0.01000 | | | | | | | | | | | 694 | 640 | 602 | 544 |
| | 0.05000 | | | | | | | | | | | 640 | 605 | 562 | 516 |
| | 0.1000 | | | | | | | | | | | 629 | 596 | 556 | 505 |
| 300 | 0.00000 | | | | | | | | (986) | 955 | 888 | 815 | 750 | 687 | 632 |
| | 0.0009996 | | | | | | | | (970) | 950 | 868 | 805 | 738 | 666 | 611 |
| | 0.005001 | | | | | | | | (920) | 884 | 822 | 747 | 694 | 645 | 600 |
| | 0.01000 | | | | | | | | (860) | 840 | 780 | 730 | 677 | 638 | 586 |
| | 0.05000 | | | | | | | | (810) | 768 | 722 | 678 | 641 | 593 | 550 |
| | 0.1000 | | | | | | | | (760) | 742 | 707 | 665 | 631 | 585 | 538 |
| 350 | 0.00000 | | | | | | | | 1013 | 964 | 910 | 840 | 780 | 718 | |
| | 0.0009996 | | | | | | | | 1002 | 960 | 888 | 830 | 767 | 701 | |
| | 0.005001 | | | | | | | | 930 | 888 | 838 | 772 | 721 | 666 | |
| | 0.01000 | | | | | | | | 890 | 850 | 802 | 754 | 702 | 659 | |
| | 0.05000 | | | | | | | | 798 | 771 | 733 | 700 | 661 | 609 | |
| | 0.1000 | | | | | | | | 773 | 748 | 717 | 687 | 650 | 599 | |
| 400 | 0.00000 | 1320 | 1430 | 1460 | 1310 | 1220 | 1180 | 1115 | 1030 | 970 | 934 | 867 | 799 | 739 | |
| | 0.0009996 | 1076 | 1175 | 1190 | 1200 | 1180 | 1155 | 1102 | 1015 | 968 | 907 | 847 | 785 | 724 | |
| | 0.005001 | 825 | 1000 | 1045 | 1030 | 1025 | 1020 | 990 | 940 | 890 | 846 | 790 | 735 | 679 | |
| | 0.01000 | 695 | 820 | 920 | 925 | 940 | 965 | 945 | 900 | 858 | 814 | 766 | 716 | 669 | |
| | 0.05000 | 495 | 655 | 645 | 705 | 760 | 792 | 798 | 795 | 770 | 738 | 710 | 668 | 613 | |
| | 0.1000 | 475 | 600 | 590 | 655 | 720 | 755 | 765 | 767 | 749 | 724 | 697 | 658 | 604 | |
| 450 | 0.00000 | 1440 | 1420 | 1440 | 1300 | 1220 | 1170 | 1110 | 1040 | 975 | 936 | 869 | 806 | | |
| | 0.0009996 | 935 | 1100 | 1145 | 1185 | 1175 | 1152 | 1097 | 1020 | 970 | 908 | 848 | 790 | | |
| | 0.005001 | 695 | 875 | 980 | 1005 | 1015 | 1010 | 988 | 945 | 890 | 846 | 789 | 738 | | |
| | 0.01000 | 575 | 715 | 860 | 900 | 930 | 955 | 940 | 905 | 860 | 817 | 770 | 719 | | |
| | 0.05000 | 400 | 550 | 590 | 680 | 745 | 780 | 790 | 788 | 768 | 740 | 712 | 666 | | |
| | 0.1000 | 380 | 500 | 545 | 630 | 705 | 741 | 758 | 758 | 746 | 726 | 698 | 658 | | |
| 500 | 0.00000 | 1430 | 1380 | 1400 | 1290 | 1220 | 1170 | 1110 | 1040 | 975 | 934 | 863 | | | |
| | 0.0009996 | 825 | 1010 | 1100 | 1165 | 1170 | 1150 | 1092 | 1025 | 971 | 906 | 838 | | | |
| | 0.005001 | 590 | 780 | 925 | 980 | 1005 | 1000 | 980 | 945 | 890 | 844 | 784 | | | |
| | 0.01000 | 480 | 630 | 800 | 880 | 920 | 942 | 930 | 900 | 856 | 811 | 764 | | | |
| | 0.05000 | 320 | 465 | 550 | 655 | 725 | 762 | 778 | 775 | 762 | 738 | 706 | | | |
| | 0.1000 | 305 | 425 | 500 | 610 | 685 | 722 | 743 | 742 | 738 | 724 | 694 | | | |
| 550 | 0.00000 | 1390 | 1370 | 1380 | 1290 | 1220 | 1179 | 1105 | 1040 | 975 | 927 | | | | |
| | 0.0009996 | 730 | 945 | 1060 | 1150 | 1160 | 1145 | 1088 | 1023 | 968 | 899 | | | | |
| | 0.005001 | 510 | 710 | 870 | 960 | 990 | 987 | 968 | 940 | 886 | 836 | | | | |
| | 0.01000 | 410 | 565 | 755 | 855 | 905 | 920 | 918 | 888 | 851 | 804 | | | | |
| | 0.05000 | 265 | 400 | 505 | 630 | 705 | 745 | 760 | 760 | 751 | 732 | | | | |
| | 0.1000 | 250 | 365 | 460 | 585 | 665 | 701 | 722 | 728 | 726 | 718 | | | | |
| 600 | 0.00000 | 1340 | 1370 | 1360 | 1280 | 1210 | 1160 | 1095 | 1040 | 970 | 917 | | | | |
| | 0.0009996 | 660 | 895 | 1025 | 1130 | 1150 | 1140 | 1080 | 1020 | 964 | 8 | | | | |
| | 0.005001 | 450 | 655 | 825 | 930 | 970 | 972 | 955 | 938 | 880 | 824 | | | | |
| | 0.01000 | 350 | 520 | 705 | 830 | 885 | 908 | 903 | 878 | 844 | 790 | | | | |
| | 0.05000 | 220 | 355 | 465 | 605 | 680 | 720 | 735 | 743 | 735 | 721 | | | | |
| | 0.1000 | 205 | 315 | 425 | 555 | 640 | 675 | 700 | 710 | 710 | 707 | | | | |
| 650 | 0.00000 | 1330 | 1390 | 1340 | 1270 | 1210 | 1170 | 1090 | 1020 | 960 | | | | | |
| | 0.0009996 | 610 | 855 | 1000 | 1105 | 1135 | 1130 | 1071 | 1008 | 956 | | | | | |
| | 0.005001 | 405 | 610 | 780 | 900 | 950 | 955 | 935 | 912 | 870 | | | | | |
| | 0.01000 | 310 | 480 | 665 | 795 | 865 | 890 | 885 | 862 | 834 | | | | | |
| | 0.05000 | 190 | 315 | 435 | 570 | 650 | 692 | 710 | 722 | 717 | | | | | |
| | 0.1000 | 175 | 280 | 395 | 520 | 605 | 640 | 672 | 688 | 693 | | | | | |
| 700 | 0.00000 | 1390 | 1420 | 1360 | 1250 | 1200 | 1160 | 1080 | 1010 | 955 | | | | | |
| | 0.0009996 | 570 | 825 | 980 | 1075 | 1115 | 1120 | 1061 | 992 | 944 | | | | | |
| | 0.005001 | 370 | 575 | 740 | 860 | 920 | 935 | 915 | 892 | 858 | | | | | |
| | 0.01000 | 285 | 445 | 630 | 760 | 835 | 870 | 865 | 843 | 824 | | | | | |
| | 0.05000 | 165 | 280 | 400 | 535 | 610 | 665 | 688 | 700 | 698 | | | | | |
| | 0.10000 | 150 | 250 | 360 | 485 | 570 | 612 | 638 | 663 | 674 | | | | | |
| 750 | 0.00000 | 1200 | 1460 | 1360 | 1240 | 1190 | 1160 | 1070 | | | | | | | |
| | 0.0009996 | 535 | 775 | 950 | 1045 | 1090 | 1110 | 1048 | | | | | | | |
| | 0.005001 | 340 | 545 | 705 | 820 | 885 | 915 | 897 | | | | | | | |
| | 0.01000 | 245 | 415 | 595 | 720 | 800 | 848 | 845 | | | | | | | |
| | 0.05000 | 140 | 250 | 370 | 490 | 570 | 632 | 653 | | | | | | | |
| | 0.1000 | 125 | 220 | 330 | 445 | 525 | 577 | 612 | | | | | | | |
| 800 | 0.00000 | 1310 | 1550 | 1370 | 1240 | 1190 | 1160 | 1060 | | | | | | | |
| | 0.0009996 | 505 | 750 | 935 | 1010 | 1060 | 1095 | 1032 | | | | | | | |
| | 0.005001 | 310 | 520 | 670 | 775 | 850 | 892 | 875 | | | | | | | |
| | 0.01000 | 220 | 390 | 560 | 680 | 765 | 825 | 820 | | | | | | | |
| | 0.05000 | 122 | 225 | 345 | 445 | 525 | 595 | 620 | | | | | | | |
| | 0.1000 | 110 | 195 | 305 | 400 | 480 | 540 | 578 | | | | | | | |

The significance of this similarity in behavior of 1–1 electrolytes has already been discussed.[4–6]

*Calculation of the Complete Ionization Constant of NaI.* The ionization of NaI in aqueous solutions can be represented by the equations[7,8]

$$\mathrm{NaI(H_2O)}_j + k\mathrm{H_2O} \overset{K^0}{\rightleftharpoons} \mathrm{Na(H_2O)}_m^+ + \mathrm{I(H_2O)}_n^- \quad (6)$$

$$K^0 = a_{\mathrm{Na(H_2O)}_m^+}a_{\mathrm{I(H_2O)}_n^-}/a_{\mathrm{NaI(H_2O)}_j}a_{\mathrm{H_2O}}{}^k \quad (7a)$$

$$= K/a_{\mathrm{H_2O}}{}^k \quad (7b)$$

$$\log K = \log K^0 + k \log a_{\mathrm{H_2O}} \quad (8)$$

where $K^0$ is the complete ionization constant including the hydration reaction and $K$ is the conventional constant. The integers $j$, $m$, and $n$ represent hydration

**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

| | Density, g $cm^{-3}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$, °C | 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 $\Lambda_0$(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 p$K$ unit, with the greatest uncertainties occurring at the highest densities at all temperatures.

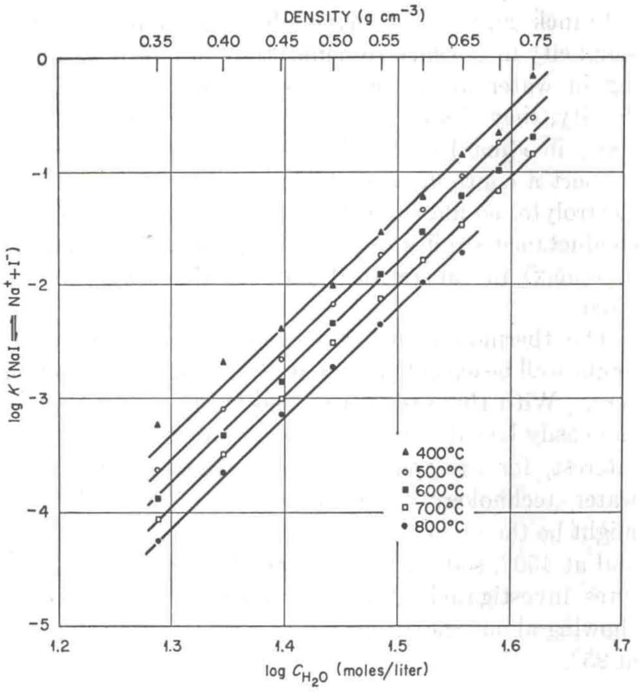

Figure 5. Log $K$(molar units) for the equilibrium NaI ⇌ $Na^+ + I^-$ as a function of the logarithm of the molar concentration of water at temperatures from 400 to 800°.

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

**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

| | NaCl | | NaBr | | NaI | |
|---|---|---|---|---|---|---|
| $T$, °C | 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 |

*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

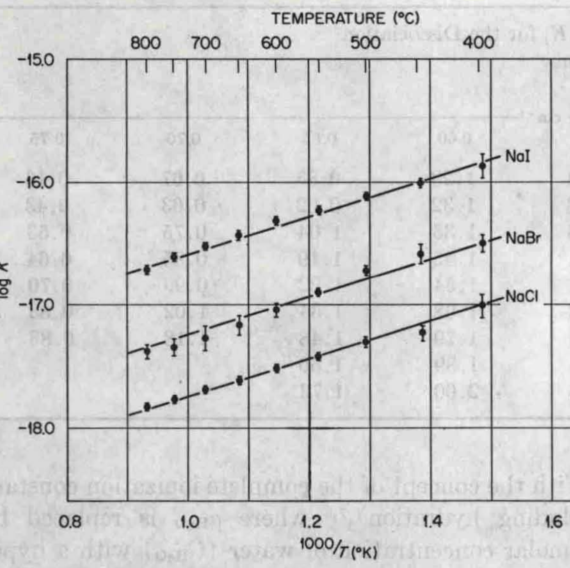

Figure 6. Log $K^0$ (molar units) for the equilibrium $NaX(H_2O)_j + kH_2O \rightleftharpoons Na(H_2O)_m^+ + X(H_2O)_n^-$ as a function of $T^{-1}$(°K) for NaCl, NaBr, and NaI.

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

**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 |

*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 $\Lambda_0$ *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 $\nu$(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 $\nu$(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°.

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