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TEMPERATURE DEPENDENCE OF THE KNIGHT SHIFT OF THE Na^{23} - $N^{14}H_3$ SYSTEM

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Temperature Dependence of the Knight Shift of the $Na^{23} + N^{14}H_3$ System

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ABSTRACT

The Knight Shift of Na^{23} and N^{14} in sodium-ammonia solution was measured over the temperature interval -33 to +22°C and in the concentration range corresponding to mole ratio 5.7 to 700 (NH_3 per Na). The results in the dilute region, R ≥ 300, were interpreted in terms of the equilibrium constants K_1 and K_2 for the reactions

$$Na(am) = Na^+(am) + e^-(am) \text{ and } Na(am) = 1/2\ Na_2(am).$$

The effective Knight Shifts, k_0 for Na^{23} in Na(am) and k_1' for N^{14} in e^-(am) were found to be

$$k_0 = (0.034 \pm .001)\ T^{-1} \text{ and } k_1' = (13.5 \pm 1)\ T^{-1}.$$

The measured standard enthalpy and entropy of reaction for the dissociation and the dimerization equilibria are respectively, $\Delta H_1^o(298^o) \cong -6.6$ and $\Delta H_2^o = -7.3 \pm 1$ kcal/mole and $\Delta S_1^o(298^o) \cong -34$ and $\Delta S_2^o = -24.1 \pm 3$ cal/deg mole. The change in enthalpy for the dissociation equilibrium was temperature dependent and indicated that a large negative change in heat capacity accompanied the reaction. The electron densities at the Na^{23} nucleus were $\rho_1(Na^{23}) = .071\ a_0^{-3}$ for the concentrated (R ≃ 5.7) and dilute solutions (R ≥ 300), respectively.

The study of the electromagnetic properties of the alkali and alkaline earths in liquid ammonia has supplied a great deal of information about the chemical nature of these solutions. As a result of conductivity measurements, Kraus[1] has proposed that there exist, present in solution, solvated atoms,

(1) Kraus, C. A., J. Am. Chem. Soc. 43, 749 (1921); for review work also see Kraus, C. A., J. Chem. Education 30, 83 (1953).

positive ions and electrons. The presence of paramagnetic species was indeed verified by Huster[2] and Freed and Sugarman[3] from the static magnetic suscep-

(2) Huster, E., Ann. Physik. 33, 477 (1938).

(3) Freed, S. and N. Sugarman, J. Chem. Phys. 11, 354 (1943).

tibility, χ, and by Hutchison and Pastor[4] from the paramagnetic absorption by

(4) Hutchison, C. A., Jr. and R. C. Pastor, J. Chem. Phys. 21, 1959 (1953).

means of ESR. The main conclusions to be drawn from these measurements are: a) the magnetic susceptibility of the metal in ammonia solution lies always below the expected Curie value which is approached asymtotically only as the dilution increases to infinity and b) the 1/T temperature dependence of χ is not obeyed. Becker, Lindquist and Alder[5] explained these results by assuming

(5) Becker, E., R. H. Lindquist and B. J. Alder, J. Chem. Phys. 25, 971 (1956).

the existence of four different species, solvated metal dimers, atoms and positive ions and electrons in the dilute solutions, and then proceeded to evaluate the chemical equilibrium constants for the dissociation and dimerization of the

solvated metals atoms or monomers from the ESR data.[4] These reactions may be written

$$Na(am) = Na^{+}(am) + e^{-}(am) \quad (1)$$

$$Na(am) = \frac{1}{2} Na_2(am) \quad (2)$$

with the combined reaction

$$\frac{1}{2} Na_2(am) = Na^{+}(am) + e^{-}(am) \quad (3)$$

where the respective equilibrium constants are K_1, K_2 and K_3. The Knight Shift (KS) data of McConnell and Holm[6] for the Na^{23}-$N^{14}H_3$ solutions at room temperature

(6) McConnell and C. H. Holm, J. Chem. Soc. 26, 1517 (1957).

in the concentration range R = 5-500 supported these views. Pitzer[7] and Blum-

(7) Pitzer, K. S., J. Chem. Phys. 29, 453 (1958).

berg and Das[8] were able to explain some of the features of the KS data[6] by

(8) Blumberg, W. D. and T. P. Das, J. Chem. Phys. 30, 251 (1959).

calculating the distribution of electron densities in the solvated paramagnetic species. Moreover, both Dye, Smith and Sankauer[9] and Evers and Frank[10] derived

(9) Dye, J. L., R. F. Sankauer and G. E. Smith, J. Am. Chem. Soc. 83, 4797, 4803, (1960).

(10) Evers, E. C. and P. W. Frank, J. Chem. Phys. 30, 61 (1959).

sets of equilibrium constants from conductance measurements of Kraus[1] at t = -33°C together with transference number data. Their respective results are in fair agreement.

The vapor pressure studies of Dewald[11] and the calorimetric results of

(11) Dewald, J. F., Ph.D. Thesis, California Institute of Technology (1948).

Gunn and Green[12] also support the proposed equilibria of BLA.[5] However, the

(12) Gunn, R. S. and L. R. Green, J. Chem. Phys. 36, 363, 368 (1962).

equilibrium constants K_1 and K_2 as obtained from ESR[5] are larger, by a factor of three than those computed from the conductance experiments.[9,10] However, K_3 has substantially the same value from either source. In this work, the KS of Na^{23} and N^{14} in the $Na-NH_3$ solutions has been determined in the temperature interval -40° to 22°C. In the concentration range where the chemical equilibria, given in Eqs. 1 and 2, are valid the constants K_1 and K_2 are evaluated from the KS data together with the activity coefficient of the charged species, obtained from the Debye-Huckel theory. Although the relative accuracy of the measurements is very low at -33°C, fair agreement is obtained with the values obtained from the conductance measurements, (1), (9), (10).

Experimental Results

The KS's of the $Na-NH_3$ solutions with respect to a standard of .5 molal NaCl in NH_3, were measured with a Varian -4200 Wide Line NMR spectrometer operating at 2.77 and 10.0 Mc/sec. for Na^{23} and N^{14} resonance respectively in a constant magnetic field of 8881 oe.

The stability of the magnetic field and of the rf frequency were the determining factors in the experimental accuracy. The rf frequency was determined with a Hewlett-Packard counter No. 5248 to ± 2 cps while the field, stable to ± 5ppm, was swept with a linear potentiometer. The spectra were recorded by

means of the sideband technique[13] with a modulation frequency ω_M = 412 cps.

(13) Acrivos, J. V., J. Chem. Phys. 36, (in press).

The separation between the sidebands of 824 cps was then used to calibrate the potentiometer reading.

The temperature of the samples was measured to ± .5°C, by means of a copper-constantan thermocouple in contact with the sample tube. The sample tubes were immersed in a freezing mixture and contained in a Dewar flask which allowed the rf to penetrate. The constant temperatures were obtained as follows, 0°C with an ice-water mixture, -15.3°C with a solid-liquid mixture of benzyl alcohol, -30.6°C with a solid-liquid mixture of Br-benzene, and below -33°C with acetone-dry ice mixtures. The samples were then allowed to attain the equilibrium temperature inside the closed dewar. The Dewar flask is shown in Fig. 1. The tip which contained the samples was not silvered but was covered with a thin layer of Pt (Hanovia) in which a cross and lengthwise grill was cut at every 2 mm. intervals in such a manner that the inner and outer surfaces would be concentric so as to allow perfect rf penetration.

The Na-NH_3 samples were prepared in vacuum by first distilling a known weight of Na into the side arm of a sample tube and then distilling the required volume of NH_3 from a Na-NH_3 solution. The sample tubes were first aged in dilute HCl then passed through hot cleaning solution and finally steamed and dried in the absence of dust. No decomposition was noticed when warming the samples to room temperature for long periods, as shown by the reproducibility of the NMR measurements within the expected accuracy. The samples were stored in liquid nitrogen when not in use. The concentration of the Na-NH_3 solution is reported in terms of the mole ratio, R or the sodium molality, m.

$$R = \frac{[NH_3]}{[Na]} = \frac{58.7}{m} = 1.35 \quad \frac{V_{NH_3} \cdot \rho_{NH_3}}{w_{Na}}$$

where V is the volume of ammonia determined before the solution was made, ρ its density at that temperature, see for instance Yost and Russell[14],

(14) Yost, D. M. and H. Russell, Jr., "Systematic Inorganic Chemistry", Prentice-Hall, 1948.

p. 138, and w is the weight of sodium. For the more dilute samples, a chemical analysis for total sodium was carried out after the measurements were finished. For R = 730 the nuclear resonance signal to noise ratio at room temperature for Na^{23} was barely unity but rose to 10 at -33°. The KS data are given in Table 1, with the temperature and concentration dependence shown in Figs. 2 and 3. The values at room temperature are in agreement, within the experimental accuracy, with the results of McConnell and Holm,[6] when a correction is made for the chemical shift of Na^+(am) with respect to Na^+(aq) of 17 ppm.

KNIGHT SHIFT

The value of the effective field at the nucleus under observation, $\underset{\sim}{H}_e$ is in general different from that of the externally applied one, H_o. Thus,

$$\underset{\sim}{H}_e = \underset{\sim}{H}_o + \underset{\sim}{H}_s + \underset{\sim}{H}_d + \underset{\sim}{H}_e \quad c \qquad (4)$$

where $\underset{\sim}{H}_s$ is the contribution due to the magnetization, $\underset{\sim}{M}$:[15,16]

(15) Bloembergen, N. and Dickinson, W. C., Phys. Rev. 79, 179 (1950).
(16) Dickinson, W. C., Phys. Rev. 81, 717 (1951).

$$\underset{\sim}{H}_s = \left(\frac{4}{3}\pi - \alpha\right) \underset{\sim}{M} + q \underset{\sim}{M}$$

Table 1 - Knight Shift of Na^{23} and N^{14} in Na-NH_3 Solutions with Respect to 0.5 Molal NaCl in NH_3.[a]

Sample Number	R	m	t(°C)	k(Na)x10^4 ± .10	k(N)x10^4 ± .10	Rk(N) x10^4
1	5.7	10	9.5	1.40	a	a
			0	1.25		
20	12.2	4.8	22	1.45	-	-
			0	1.06	5.58	68.07
			-27	1.00	-	-
			-46	.94	-	-
18	25	2.4	22	.87	3.62	91
			0	.68	3.46	87
			-27	.63	2.78	70
			-30	{.35[b] .78	-	-
			-31	-	2.82	71
			-60		.26[d]	7.[d]
10	46	1.3	22.5	.61	a	a
			0	.56		-
15	49	1.2	0	.51	a	a
25	52	1.1	26.3	.68	-	-
			22	-	2.55	133
			14	.48	-	-
			5	-	2.23	116
			0	.29	2.05	107
			-15	.16	1.61	84
			-31.2	.06	-	-
			-47	-	.28	15

Table 1 - continued

Sample Number	R	m	t(°C)	k(Na)x10^4 ± .10	k(N)x10^4 ± .10	Rk(N) x10^4
9	60	.98	0	.34	1.54	80
			-19.5	-	1.40	84
			-24	.27	-	-
			-65	-	.40	24
			0	-	{1.20[c] 1.73	72 104
12	78	.75	22	.52	a	a
			- 7	.31	-	-
26	90	.66	25.1	.55	-	-
			23	-	1.87	168
			15.5	.50	-	-
			4	-	1.14	103
			0	.27	1.06	95
			-12	-	.82	74
			-22	.13	.47	42
			-39	.07	--	-
			-56	.03	.20	18
11	110	.53	22	.56	a	a
17	111	.53	22	.51	1.66	184
			- 7	.26	-	-
			- 19.5	-	.89	99
			-24	.21	-	-
7	118	.50	22	.46	a	a
			10	.37	-	-
			0	.29	-	-
			- 46	.03	-	-
13	210	.28	- 7	.28	-	-

Table 1 - Continued

Sample Number	R	m	t(°C)	k(Na)x10^4 ± .10	k(N)x10^4 ± .10	Rk(N) x10^4
31	323	.18	22.8	.64	-	-
			21	-	1.11	358
			13.5	-	1.14	368
			9	.42	-	-
			4.5	-	.90	291
			0	.35	.81	262
			- 9	-	.46	149
			-22	.15	-	-
			-27.5	-	.44	142
			-31	-	.37	120
			-52	-	.29	94
14	450	.13	22	.53	.83	374
			0	.31	.78	351
			- 7	.30	-	-
			-17	-	.48	216
			-24	.20	-	-
					-	-
			-29	-	.55	247
			-44	.07	-	-
			-46	.07	-	-
			-63	-	.10	45
37	730	.080	18.5	.62	.53	387
			11.5	.53	.60	438
			4.2	.49	.57	416
			0	.42	-	-
			-20	.18	-	-
			-22	-	.43	314
			-285	.18	-	-
			- 30.5	-	.30	219
			- 34	-	.13	95
			-43	-	.02	15
			- 51	.02	-	-

Table 1. Continued

(a) Poor annealing of the glass led to cracks at liquid nitrogen temperature and not all the runs could be completed.

(b) Here the Na^{23} resonance shows two absorption lines. Although the temperature is above the critical value, the cause may be a different phase adsorbed on the surface of the sample tube. The N^{14} absorption gave a single line at this temperature.

(c) Here the N^{14} resonance shows two absorption lines. Shaking the sample produced no effect, however upon refreezing and warming up to 0°C only one absorption was observed. The Na^{23} absorption was a single line at this temperature.

(d) Measured for the dilute phases in the two phase region.

Here the Lorentz cavity field, $\frac{4}{3}\pi \underset{\sim}{M}$ arises from the induced dipoles on the surface of a microscopic hypothetical sphere which contains the nucleus, α is the bulk diamagnetic correction factor, $\alpha = \frac{4}{3}\pi$ or 2π respectively for a sample shaped as a sphere or an infinite cylinder. For $\chi \approx 10^{-7}$,[4] and infinite cylinder sample shape, the first term is of the order of .2 ppm. q is a steric factor which depends on the anisotropy of the electronic g factor of any paramagnetic species present in solution.

$$q = \frac{16\pi}{45} \left(\frac{b}{a}\right)^3 \frac{g_{\perp}^2 - g_{\parallel}^2}{g^2},$$

where b is the radius of the paramagnetic species and a is its distance from the nucleus under observation, $g_{\parallel}$ and $g_{\perp}$ are respectively the g-factors in the directions parallel and perpendicular to the applied field. The g-factor for the $Na\text{-}NH_3$ solutions is $g = 2.0012$ which is lower than the free electron value of 2.0025. Since $g^2 = \frac{1}{3}(2g_{\perp}^2 + g_{\parallel}^2)$, in solution, if one assumes $g_{\parallel} = 2.0025$, the anisotropy in the g factor gives a negligible contribution, $q\,\underset{\sim}{M} \sim .003$ ppm. $\underset{\sim}{H}_d$ is the field due to the orbital motion of the electrons in the individual species. For Na^+(am) it may be assumed that $\underset{\sim}{H}_d$ is constant and independent of the anion as is the case for aqueous solutions of different sodium salts.[17,18]

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(17) Wertz, J. E. and O. Jardetzky, J. Chem. Phys. 25, 357 (1956).

However the diamagnetic correction for Na_2(am) and Na(am) is likely to be different from that for Na^+(am) and the estimate of this value is probably the largest source of error. The diamagnetic contribution from the electrons in expanded orbitals in the Na(am) and Na_2(am) species is thus, (see for instance

Pople, Bernstein and Schneider[18] p. 175).

(18) Pople, J. A., W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, 1959.

$$-\frac{H_d}{H_0} = \frac{e^2}{3mc^2}\int\frac{\rho_1}{\epsilon r}\,d\tau$$

where ρ_1 is the electron density and ϵ the dielectric constant, which is larger than unity but smaller than the value for the bulk material. If $\langle\frac{1}{\epsilon r}\rangle \sim .1\ a_0^{-1}$, the diamagnetic shift at the central atom is of the order 2 ppm for each electron, and zero at the coordinated NH_3 molecules. $\underset{\sim}{H}_c$ is the field at the nucleus due to the Fermi contact term[19] in the paramagnetic species. Thus

(19) Fermi, E., Z. Physik. 60, 320 (1930).

$$\underset{\sim}{H}_c = \frac{8\pi}{3}\,g\beta\,\rho_1(\underset{\sim}{r}_n)\langle\underset{\sim}{S}^z\rangle, \quad \left\{\rho_1(\underset{\sim}{r}_n) = \langle|\psi_e(\underset{\sim}{r}_n)|^2\rangle\right\}$$

where

$$\langle S^z\rangle = \frac{1}{2}\left[\exp\left(\frac{g\beta H_0 S^z}{kT}\right) - \exp-\left(\frac{g\beta H_0 S^z}{kT}\right)\right]$$

$$= \chi^{mol}\ \frac{H_0}{N_0(g\beta)}$$

ψ_e is the unpaired electron wave function and N_0 is Avogadro's number. This term is now assumed to give the leading contribution to $\underset{\sim}{H}_e$ in addition to $\underset{\sim}{H}_0$. Thus, the field shift with respect to NaCl in NH_3,

$$k = \frac{H_e - H_0}{H_0} \simeq \frac{H_c}{H_0} = \frac{8\pi}{3}\,\frac{\chi^{mol}}{N_0}\,\rho_1(\underset{\sim}{r}_n) \qquad (5)$$

is the KS[20] and in the case where the chemical species containing the nucleus,

(20) Townes, C. H., C. Herring and W. D. Knight, Phys. Rev. 72, 852 (1950).

n, under observation undergoes fast chemical exchange it can be shown[21] that:

(21) Gutowsky, H. S., D. W. McCall and C. P. Slichter, J. Chem. Phys. 21, 279 (1953)

$$k(n) = \sum k_i x_i \qquad (6)$$

where k_i and x_i are the mole fraction and KS of the corresponding species.

CHEMICAL EQUILIBRIA

In the concentration range where the chemical equilibria 1 and 2 are valid, $R \geq 150$, the observed KS obey the following relationships:

$$k(Na^{23}) = x_0 k_0$$

$$R \cdot k(N^{14}) = (x_0 k_0' + x_1 k_1')$$

$$= k_1' \left(\frac{k_0'}{k_1'} x_0 + x_1 \right) \qquad (7)$$

where k_1, k_0' and k_1' are respectively the KS for Na^{23} and N^{14} in the individual species Na_{am} and e^-_{am}, present in the amount of mole fractions x_0 and x_1. The volumetric and optical spectral properties of Na(am) and of $Na^+(am) + e^-(am)$ are practically identical. Jolly, Gold, and Pitzer[22] concluded these facts that

(22) Jolly, W. L., M. Gold and K. S. Pitzer, submitted to publication.

Na(am) probably consisted of ion pairs of solvated sodium ions and electrons. From this model one would expect the KS for N^{14} to be substantially unchanged by this ion pair association and we shall hereafter assume $k'_0 = k'_1$.

The room temperature value of k'_1 is obtained by extrapolating $[R \cdot x(N)]$ to infinite dilution, see Fig. 4.

$$k_1' = \lim [R \cdot k(R)] \quad \text{as } R \longrightarrow \infty$$

$$= 500 \times 10^{-4}$$

or

$$k_1' = \frac{14.6}{T} \tag{8}$$

when the Curie temperature dependence of the susceptibility is introduced. In order to determine k_0, the functional dependence of $k(Ma)$ with respect to m must be known. Thus, if the solutions obey the equilibrium relationships:

$$K_1' = \frac{K_1}{\gamma_{\pm}^2} = \frac{m\, x_1^2}{x_0}$$

$$K_2^2 = \frac{x_2}{m x_0^2}$$

$$x_0 + x_1 + 2x_2 = 1 \tag{9}$$

it follows that

$$\left(\frac{\partial \ln x_0}{\partial \ln m}\right)_{\gamma_{\pm}, T} = \frac{x_1 - 4x_2}{1 + x_0 + 6x_2}$$

$$\left(\frac{\partial \ln (x_1 + x_0)}{\partial \ln m}\right)_{\gamma_{\pm}, T} = -x_2 \frac{\left(4 + \frac{2x_1}{x_1 + x_0}\right)}{1 + x_0 + 6x_2} \tag{10}$$

where x_2 is the mole fraction of the species $Ma_2(am)$ and $\gamma_{\pm}$ the activity coefficient for the charged species. Hence, if one assumes that the value of the activity coefficient will not vary appreciably with concentration, the value of k_0 may be determined when $k(Ma)$ attains a maximum value. Thus, from Eq. 9 and 10,

$$k_0 = \frac{[k(Na)]_{max}}{3[R \cdot k(N)]_{max} - 2k_1'}$$

$$\left.\frac{\partial \ \ln [R \cdot k(N)]}{\partial \ \ln m}\right|_{\gamma_\pm, T, k(Na)_{max}} = -2 x_2 \left(1 + \frac{2x_2}{1-2x_2}\right) \qquad (11)$$

At room temperature, $\frac{dk(Na)}{dn} = 0$ for $R \cong 700$, see Fig. 3. Thus, according to Eq. 11:

$$k_0 = 1.2 \times 10^{-4} = \frac{0.0348}{T} \qquad (12)$$

and

$$\left.\frac{\partial \ \ln [R \cdot k(N)]}{\partial \ \ln m}\right|_{\gamma_\pm, T, k(Na)max} = -.19$$

is to be compared with the mean slope

$$\frac{\Delta \ \ln [R \cdot k(N)]}{\Delta \ \ln m} = -.16, \text{ between } R = 450 \text{ and } 730.$$

In addition, the values of k_0 and k_1' were determined by comparison of the KS data interpolated or extrapolated to -33°C, with the average values of the equilibrium constants at this temperature,[9,10]

$$K_1 = .013 \text{ (moles/kg)}$$

$$K_2 = 19.0 \text{ (moles/kg)}^{-1/2}$$

Thus, at t = -33°C

$$k_0 = 1.4 \times 10^{-4}$$

$$k_1' = 508 \times 10^{-4}$$

or

$$k_0 = \frac{.0336}{T}$$

$$k_1' = \frac{12.3}{T} \qquad (13)$$

Here the activity coefficients were evaluated from the Debye-Huckel theory, making use of the dielectric constant[23] and the density of pure ammonia[14]

(23) Table of Dielectric Constants of Pure Liquids, NBS, Circular 514, (1951).

together with the distance of nearest approach of 5.5 A, as chosen by Dye et al.[9] Hence, the agreement of the room temperature and -33°C values of k_0 and k_1', justifies the assumption that $k_0' = k_1'$. The equilibrium constants for Eq. 1 and 2 in the temperature interval 22° to -33°C, are now obtained from the KS data together with the average values,

$$k_1' = \frac{13.5 \pm 1}{T}$$

$$k_0 = \frac{.034 \pm .001}{T} \qquad (14)$$

They are given in Table 2. Figure 5 shows the temperature dependence of the equilibrium constants.

The chemical equilibria 1, 2 and 3 are not satisfied for $R \lesssim 111$, however, in this concentration range higher order sodium polymers, leading to a minimum in the KS, start to appear. As the concentration increases, $R \lesssim 90$, the appearance of a metallic state is evidenced by an increase in the KS, which for Na^{23} tends to the limiting value of $k = 1.5 \times 10^{-4}$ for the saturated solution at room temperature.

Table 2. Equilibrium constants for the dissociation and dimerization of Na(am) in Na-NH_3.

T	K_1(moles/kg)	K_2(moles/kg)$^{-1/2}$	$K_3 \times 10^3$(moles/kg)$^{3/2}$
295	.0027 ± .001	1.6 ± .2	1.7
290	.0035	1.6	2.2
277	.0049	3.4	1.4
273	.0070 ± .0005	4.2	1.7
252	.010	12.2 ± .5	0.84
244	.011	15.8	0.67
240[a]	.013 (.045)[b]	19 (67)[b]	0.69 (.65)[b]

(a) The values of the equilibrium constants at this temperature are taken from the analysis of the conductance data of Kraus,[1] by Dye, Smith and Sankauer,[9] and Evers and Frank.[10]

(b) The equilibrium constants obtained from the ESR data[4] by Becker, Lindquist and Alder[5] are given for comparison.

Energy Calculations

The standard heats of reaction for the chemical equilibria 1, 2 and 3 are obtained from the temperature dependence of the respective equilibrium constant, thus from Fig. 5:

$$\Delta H_1^o\ (298) \cong -6.6 \text{ kcal/mole}$$
$$\Delta H_2^o \quad = -7.3 \pm 1 \text{ kcal/mole}$$
$$\Delta H_3^o\ (298) = \Delta H_1(298) - \Delta H_2 \cong 0.7 \text{ kcal/mole} \qquad (15)$$

Here ΔH_2^o is found to be constant throughout the temperature interval, whereas ΔH_1^o and consequently ΔH_3^o are not. The value of ΔH_3^o at room temperature is in agreement with the heat of dilution determined by Gunn and Green[12], $\Delta H_3 = 1.2$ kcal/mole. Also, the temperature dependence of ΔH_1^o indicates that a large negative change of heat capacity ΔC_p^o, of the order of -100 cal/mole deg., accompanies the dissociation reaction.[24,25]

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(24) Pitzer, K. S., J. Am. Chem. Soc. 59, 2365 (1937).

(25) Harned, H. S. and N. D. Embree, J. Am. Chem. Soc. 56, 1042, 1050 (1934)

The change in entropy for the dissociation and dimerization reactions are found to be

$$\Delta S_1^o \cong -34 \text{ cal/deg mole at } T = 298^oK$$
$$\Delta S_2^o = -24.1 \pm 3 \text{ cal/deg mole}$$

Electron Densities

The parameters k_0 and k_1' in Eq. 7 are respectively measures of the KS for Na^{23} and N^{14} in the single species Na(am) and e^-(am). Thus, the electron densities at the respective nuclei may be evaluted according to Eq. 5 if one

assumes χ^{mol} to be the theoretical susceptibility for $S = 1/2$. In the concentrated region, the density at the sodium nucleus was obtained from the KS making use of the combined Pauli spin susceptibility for a free electron gas with the Fermi energy evaluated from the metal electronic heat capacity.[26]

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(26) Knight, W. D., "Solid State Physics", Vol. 2, p. 93, Academic Press Inc., New York (1956).

The measured electron densities are given in Table 3 together with the values for the sodium free atom[27] and the metal.[26]

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(27) Kusch, P. and H. Taub, Phys. Rev. 75, 1477 (1949).

Table 3. Electron Densities in the $Na-NH_3$ Solutions

	$\rho_1(Na^{23})$ a_0^{-3}					$\langle\rho_1(N^{14})\rangle$ a_0^{-3}
	$Na-NH_3(R=5.7)$	$Na-NH_3(R\gtrsim300)$	Na (atom)	Na (metal)	Na^+ (F-center)	$Na-NH_3(R\gtrsim300)$
Experimental Value	0.071	0.00098	0.7525	0.54[d]	0.014 to 0.009[e]	0.39
Theoretical Value		0.066[a] 0.014[a] 0.016[b]				2.1[a] 1.0[a] 0.02[f]

(a) From two different solutions of the wave equation for the free electron in $Na \cdot 6NH_3$ [Blumberg and Das[8]].

(b) From the solution of the wave equation for $e^-(am) + Na^+(am)$ [Jortner[30]] where the distance between the ions is 7.2 a_0.

(c) From atomic beam measurements. [Kusch and Taub[27]].

(d) From KS measurements [Knight[26]].

(e) From the observed line widths in Na F and NaCl, F-centers [Lord[28]].

(f) From the solution of the wave equation for the electron in $e^- \cdot NH_3$ [Pitzer[6]].

In conclusion, the variation of the electron density at the Na^{23} nucleus, from 13% of the value for the metal in the concentrated region, $R = 5.7$, to .13% of the value for the free atom in the dilute region, $R \geq 300$, indicates in the same manner as the conductance measurements of Kraus,[1] the existence of two different types of $Na-NH_3$ solutions. The concentrated solutions possess properties characteristic of a metal, but in the dilute solutions, the unpaired electrons are not closely associated with the sodium nuclei and therefore must occupy expanded orbitals in the dielectric medium. This is also evidenced by the high electron density observed for $N^{14}H_3$ in the dilute solutions. Here $\langle \rho_1(N^{14}) \rangle$ is the sum of the densities at the nitrogen nuclei of each of the ammonia molecules coordinated to the paramagnetic species, and since the unpaired electron moves in an expanded orbital, it will contribute to the density at several layers of coordination shells in the same manner that the electron in an F-center contributes to the density at nuclei removed several lattice distances from the vacancy.[28,29] The electron densities cannot be explained

(28) Eandy, N. W., Phys. Rev. 105, 756 (1957).

(29) Feher, G., Phys. Rev. 103, 834 (1956); 105, 1122 (1957).

On the basis of the $Na \cdot 6NH_3$ species, assumed by Blumberg and Das,[7] since the value of $\rho_1(Na^{23})$ obtained from this model are larger than the observed ones by more than an order of magnitude, see Table 3. On the other hand, although the models proposed by Pitzer,[6] and Jortner[30] and Jolly et al[22] are more plausible,

(30) Jortner, J., J. Chem. Phys. 30, 839 (1959); 34, 678 (1961).

the solution of the wave equation for the unpaired electron has to be refined

to determine the extension of the expanded orbitals in the dielectric medium, in order to obtain more accurate values of the electron density.

Acknowledgments

This work was performed under the auspices of the United States Atomic Energy Commission.

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5. Inverse temperature dependence of the dissociation and dimerization equilibrium constants of Na(am) in the Na-NH_3 solutions.

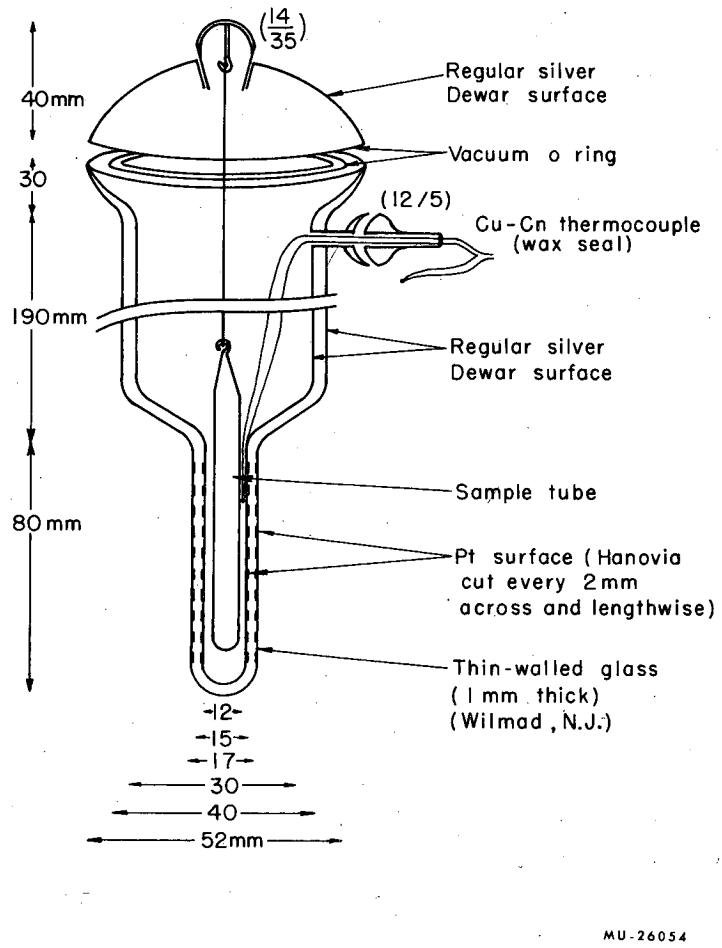
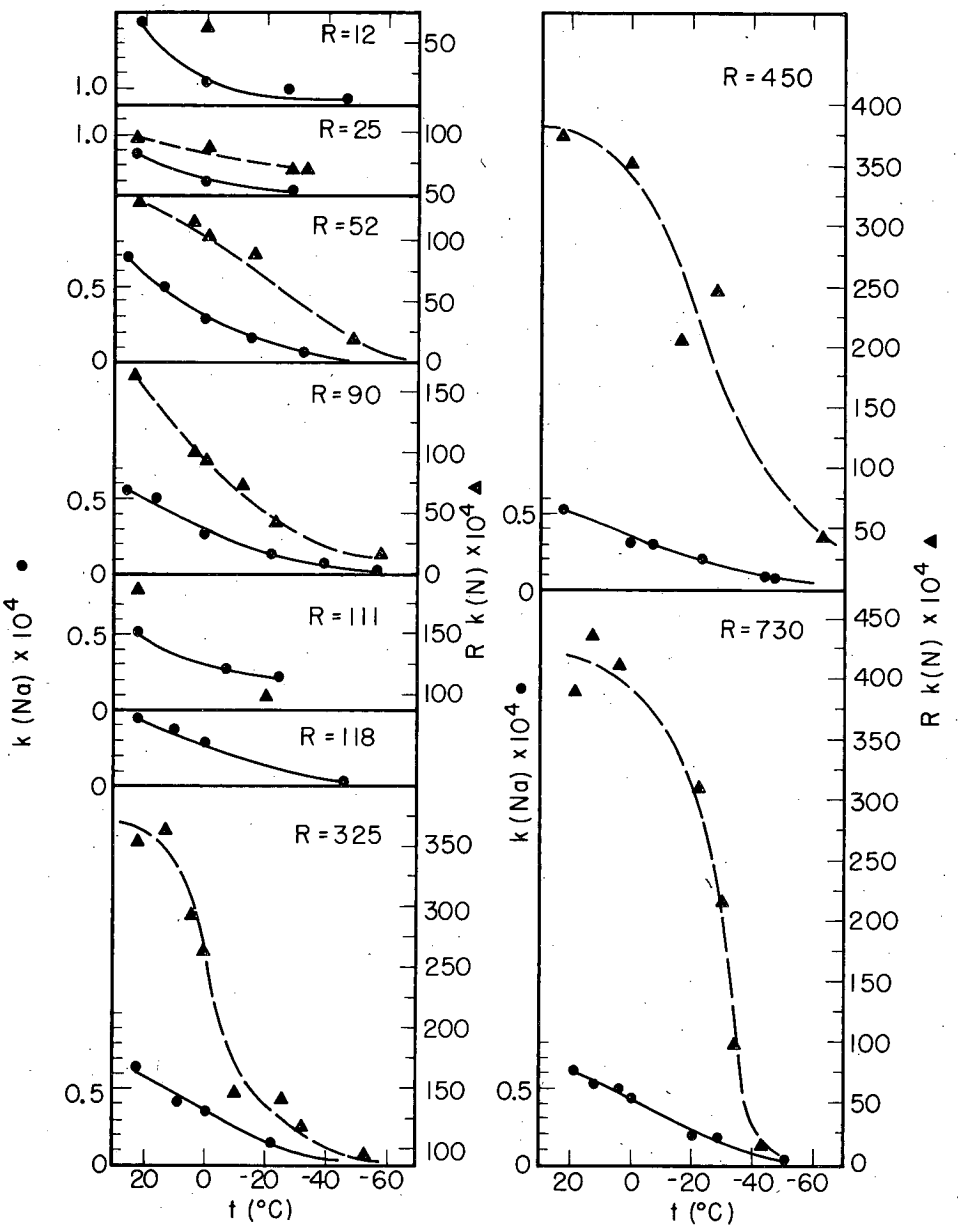

(14/35)
40mm
30
190mm
80 mm
Regular silver
Dewar surface
Vacuum o ring
(12/5)
Cu-Cn thermocouple
(wax seal)
Regular silver
Dewar surface
Sample tube
Pt surface (Hanovia
cut every 2mm
across and lengthwise)
Thin-walled glass
(1 mm thick)
(Wilmad, N.J.)
12
15
17
30
40
52mm
MU-26054

Fig. 1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R=25
R=52
R=90
R=111
R=118
R=325
R=450
R=730
k (Na) x 10^4 ●
R k(N) x 10^4 ▲
t (°C)
MUB-952

Fig. 2

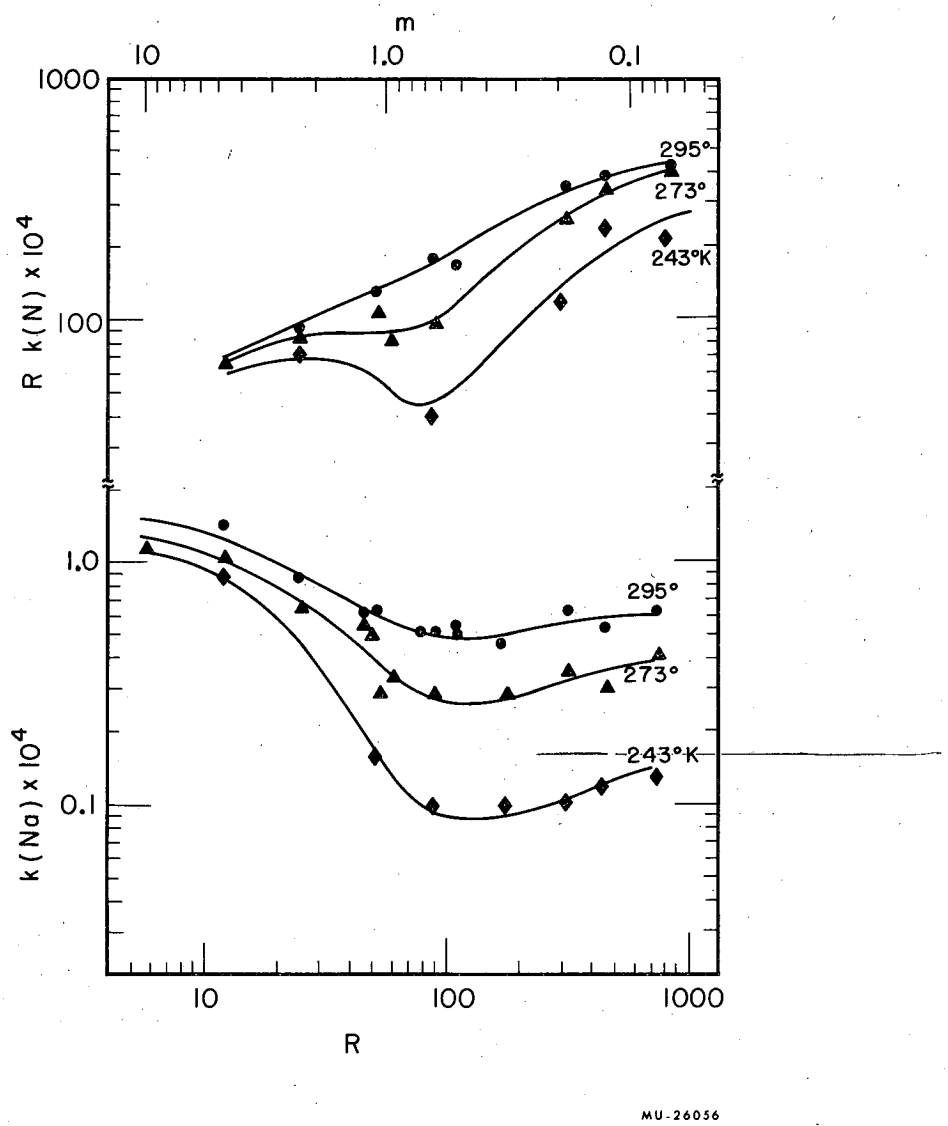
m
10
1.0
0.1
1000
100
1.0
0.1
R k(N) x 10^4
k(Na) x 10^4
295°
273°
243°K
295°
273°
243°K
10
100
1000
R
MU-26056

Fig. 3

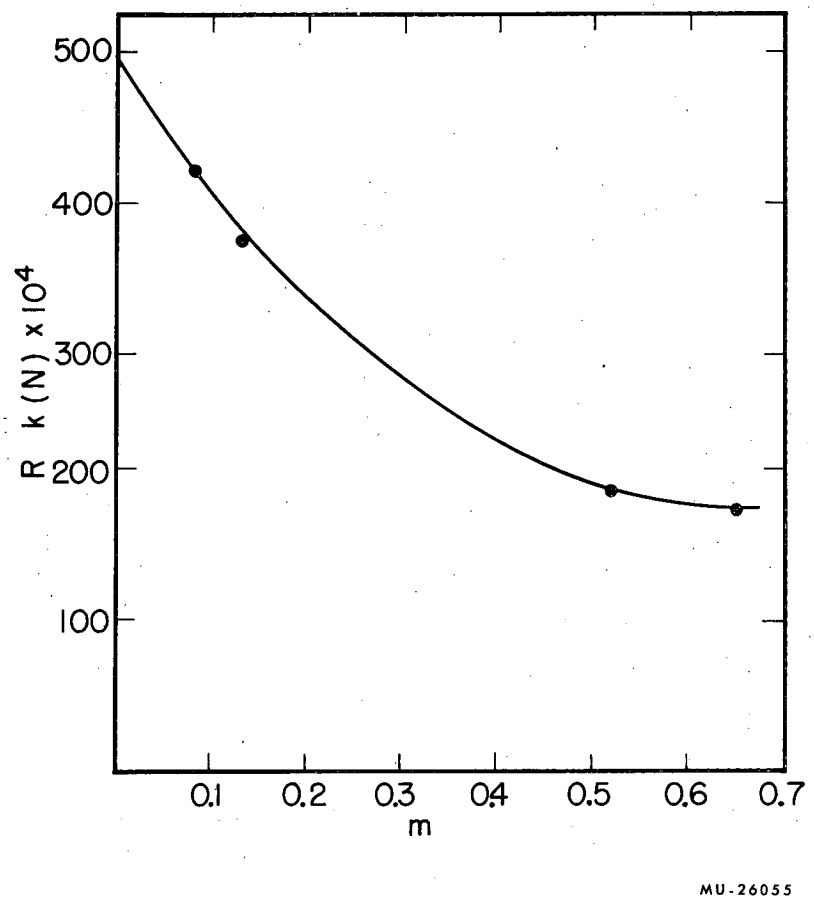

Fig. 4

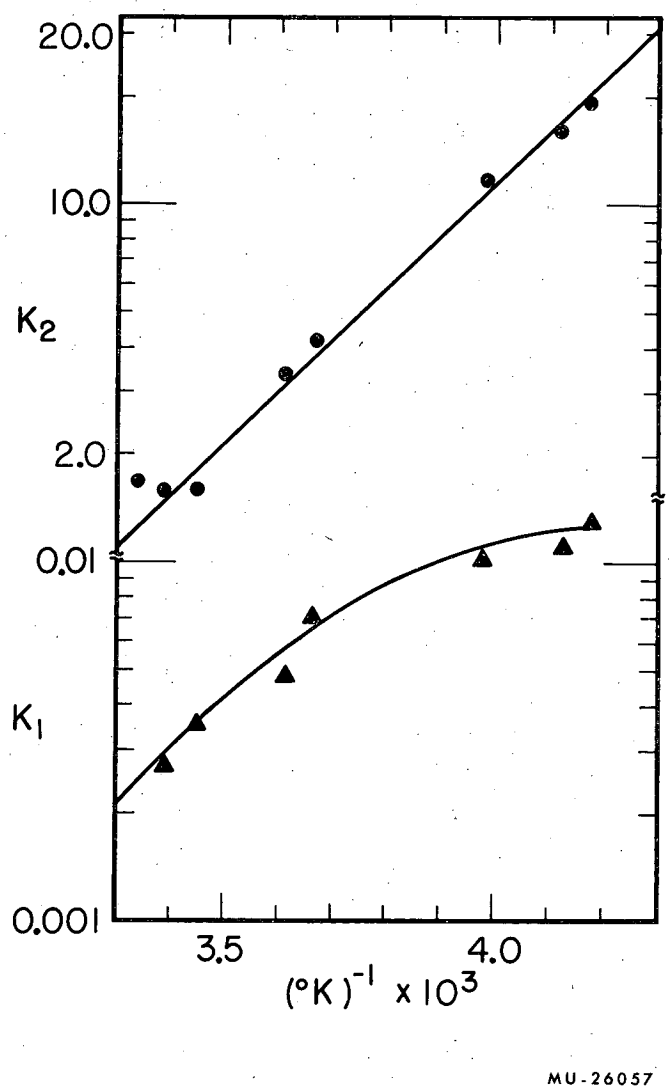

Fig. 5