The Dissocationi Energy and Heat of Formation of the Molecule NaCu

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The reaction NaCu(g) = Na(g) + Cu(g) has been investigated by means of high-temperature mass-spectrometry, using a double oven technique. From the measured reaction enthalpy the dissociation energy D_0^0 (NaCu) = 41.2 ± 4.0 kcal mol^{-1} or 172.4 ± 16.7 kJ mol^{-1} and the standard heat of formation, $\Delta H_{f,298}^0$ [NaCu(g)] = 64.3 ± 4.4 kcal mol^{-1} or 269.0 ± 18.4 kJ mol^{-1} have been obtained. The experimental dissociation energy of NaCu(g) is markedly lower than the value of 54 kcal mol^{-1} calculated after the Pauling model of a polar single bond.

In a previous investigation of the molecule NaAg[1] we have obtained the unexpected result that the dissociation energy D_0^0 (NaAg) is only slighter larger than the average of the dissociation energies of Na_2 and Ag_2. The PAULING model of a polar bond[2] that has been found applicable to many intermetallic diatomic molecules[3] would have predicted a considerably higher value. To test further whether this irregularity holds also for the dissociation energies of other diatomic molecules of alkaligroup IB intermetallic compounds we have investigated the molecule NaCu and report here its dissociation energy and heat of formation.

The instrument and the experimental approach used for the Knudsen cell mass spectrometric investigation were the same as reported previously[1] except that the Knudsen cell (upper oven) contained copper instead of silver. Only a limited set of data could be obtained for the molecule NaCu, because of the temperature limitations of the experimental apparatus used. The pertinent ions Na^+, Cu^+, and $NaCu^+$ were identified as originating from the corresponding neutral species in the usual way. The appearance potential of $NaCu^+$ was measured as 7.3 ± 0.7 e.V., with reference to that of Hg^+ = 10.43 as a standard[4]. No evidence of a significant fragmentation of NaCu could be detected.

The ion currents were measured with 45 e.V. electrons. In order to correlate these ion currents with the corresponding partial pressures, a weighed amount of zinc was evaporated immediately following the investigation of the NaCu molecule, to determine the instrument constant ($k_{Zn} = 2.8_7 \times 10^{-9}$ atm A^{-1}K^{-1}). For this purpose, the capillary between the two ovens[1] was closed. The partial pressures, P_i, listed in Table 1 were then obtained using the relation: $P_i = k_i \, I_i^+ \, T$, where $k_i = k_{Zn} \, \sigma_{Zn} \, \gamma_{Zn} / (\sigma_i \, \gamma_i \, n_i)$, being the fractional abundance of the measured ion. The relative cross sections for maximum ionization, σ_i, were taken from MANN[5] for Zn (4.65), Na (4.02), and Cu (3.80). That for NaCu was estimated as 0.75 (4.02 + 3.80) = 5.87. The relative multiplier gains, γ_i/γ_{Zn} were taken from POTTIE *et al.*[6] as 1.67 (Na) and 1.76 (Cu). The corresponding value for NaCu was estimated as (1.67 + 1.76)/2 = 1.72).

The enthalpy, ΔH_{298}^0, of the reaction

$$\mathrm{NaCu(g)} = \mathrm{Na(g)} + \mathrm{Cu(g)} \qquad (1)$$

was evaluated by the third-law method using the relation $\Delta H_{298}^0/T = -R \ln K_p - \Delta[(G_T^0 - H_{298}^0)/T]$. The necessary values for the free energy functions, $(G_T^0 - H_{298}^0)/T$, were taken from literature for Na and Cu[7]. Those for NaCu(g) were calculated in an analogous manner as those for NaAg(g)[1] from estimated molecular parameters ($r_e = 2.45$ Å, $\omega_e = 290$ cm^{-1}, and a $^1\Sigma$ ground state) yielding $-(G_T^0 - H_0^0)/T$ values of 62.53, 63.09 and 63.62 cal mol^{-1}K^{-1} for T = 1500, 1600 and 1700 K, respectively. With $(H_{298}^0 - H_0^0) = 2.345$ kcal mol^{-1} the respective values for $-(G_T^0 - H_{298}^0)/T$ of 64.10, 64.56 and 65.00 cal mol^{-1}K^{-1} are obtained. Table 1 includes the logarithms of the equilibrium constants, the free energy function changes, and the enthalpy changes for Reaction (1). The error term in the average value given for the reaction enthalpy, ΔH_{298}^0 = 41.8 ± 0.3 kcal represents the standard deviation. The corresponding ΔH_0^0 value of 41.2 ± 0.3 kcal is obtained using the enthalpy increments, $H_{298}^0 - H_0^0$, from literature for Na and Cu[7] and the calculated value for NaCu. From the experimental reaction enthalpy the dissociation energy, D_{298}^0 (NaCu) = 41.8 ± 4.0 kcal mol^{-1} or 174.9 ± 16.7 kJ mol^{-1}, or D_0^0 (NaCu) = 41.2 ± 4.0 kcal mol^{-1} or 172.4 ± 16.7 kJ mol^{-1} is obtained. Here the error term takes also the uncertainties in the temperature measurement, the calibration constant, the free energy functions and in the relative ionization

Tab. 1. Third-Law Enthalpies for the Reaction NaCu(g) = Na(g) + Cu(g)[a].

T(°K)	P_{Na^+} atm	P_{Cu^+} atm	P_{NaCu^+} atm	$-\log K_p$	$-\Delta[(G_T^0 - H_{298}^0)/T]$ cal K^{-1}	ΔH_{298}^0 kcal
1640	6.53×10^{-5}	6.64×10^{-5}	4.70×10^{-8}	1.03_5	20.5_3	41.4
1675	7.00×10^{-5}	1.07×10^{-4}	7.04×10^{-8}	0.97_5	20.5_5	41.9
1680	1.14×10^{-4}	1.07×10^{-4}	1.16×10^{-7}	0.97_5	20.5_5	42.0

[a] ΔH_{298}^0 = 41.8 ± 0.3 kcal; ΔH_0^0 = 41.2 ± 0.3 kcal.

cross-sections and multiplier gains into account as well as the fact that only a limited amount of data could be obtained. Combining D^0_{298} (NaCu) with the standard heats of vaporization[7], $\Delta H_{v,298}$ of sodium (25.6 ± 0.1 kcal mol^{-1}) and copper (80.5 ± 0.3 kcal mol^{-1}) the standard heat of formation, $\Delta H^0_{f,298}$ [NaCu(g)] = 64.3 ± 4.4 kcal mol^{-1} or 269.0 ± 18.4 kJ mol^{-1} results.

The value, D^0_0 (NaCu) = 41.2 kcal mol^{-1} is by 10 kcal mol^{-1} larger than the average of D^0_0 (Na_2) = 17.3 kcal mol^{-1} and D^0_0 (Cu_2) = 45.0 kcal mol^{-1} (see[3]). The bond energy, D(NaCu) calculated after the Pauling model of polar bond[2] is 54 kcal mol^{-1}, that is by 13 kcal mol^{-1} larger than the experimental value. As in the case of NaAg the model does not predict correctly the actual dissocation energy and overemphasizes apparently the ionic contribution to the bond energy. But unlike as for NaAg a noticable ionic contribution to the bonding is observed for NaCu. More experimental determinations of dissociation energies of similar gaseous intermetallic compounds are indicated before a deeper insight into the particular bonding behavior can be gained.

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