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Abstract

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SPECTROSCOPIC STUDY OF THE EQUILIBRIUM OF THE REACTION $NaCl \rightleftarrows Na + Cl$ IN AN H_2+Cl_2 FLAME AND THE DISSOCIATION ENERGY OF $NaCl$

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In works ($^{1-3}$), for determining the dissociation energies of MgO, CaO, SrO, BaO, and AlO, a method was used based on determining the partial pressure of the corresponding metal introduced into a flame from the absolute intensity of the lines of metal atoms in the flame spectrum. In studies in oxygen and air flames (C_2H_2+ air, $C_2H_2 + O_2$, $H_2 + O_2$, etc.), this method, as a rule, makes it possible to determine only the dissociation energies of metal oxides, since in such flames most metals are present mainly in the form of oxygen compounds. Only in those cases when the metal does not form stable oxides can the dissociation energies of metal compounds with other combustion products (in particular with hydroxyl) also be determined as a result of studies in oxygen flames. It may be expected that, for the spectroscopic study of the dissociation energies of halide compounds of metals, a more favorable radiation source will be a flame in which the oxidizer is a halide. To clarify the possibility of determining the dissociation energies of metal chlorides in a hydrogen chloride flame, in the present work the dissociation energy of NaCl was investigated, the magnitude of which is known with sufficient accuracy (^{4}). The arrangement for obtaining the $H_2 + Cl_2$ flame is analogous to that described in work (^{1}). The difference consists only in the fact that the solution of the Na salt was introduced into the flame not with the oxidizer, but with a stream of hydrogen. Since chlorine reacts vigorously with mercury, a double differential manometer with a buffer layer of concentrated sulfuric acid was used to determine the chlorine flow rates.

The study was carried out in a flame fed by a combustible mixture $1.00\,H_2 + 0.80\,Cl_2 + 0.016\,H_2O$ (liq.). The temperature of this flame, calculated theoretically (^{5}) without allowance for heat losses and assuming that thermodynamic equilibrium is attained in the flame gases and that the combustion products contain only Cl, Cl_2, HCl, H_2, H, OH, and H_2O, is equal to 2450°K. The partial pressure of atomic chlorine under these conditions is $3.37 \cdot 10^{-2}$ atm. In the literature there is no information on experimental studies of the temperature of an $H_2 + Cl_2$ flame. The performed study of the flame temperature by reversal of the Na D lines at a distance of 3–6 mm above the reaction zone showed that it lies in the range 2350–2550°K. Because the chlorides of most metals have relatively high dissociation energies, it is difficult in a hydrogen chloride flame to create a high concentration of metal atoms, and a more accurate determination of its temperature by the reversal method is difficult (see (^{6})).

To study the equilibrium of the reaction NaCl $\rightleftarrows$ Na + Cl, dilute solutions of two different sodium salts were introduced into the flame ($1.02 \cdot 10^{-3}\,N$ solution of NaCl and $1.19 \cdot 10^{-3}\,N$ solution of Na_2CO_3). The partial pressure of Na in the flame was determined from the absolute intensity of the resonance lines 5890 and 5896 Å in the flame spectrum at a distance of several millimeters above the reaction zone. The method of measurements and of processing the experimental data is set forth in work (^{1}). It was assumed that the absolute probability

transition for both lines is $6.25 \cdot 10^7$ s^{-1} (7), and the effective width of the flame, determined from the transverse spectrogram, is 0.35 cm. The values of P_{Na} found as a result of studies upon introducing sodium salts into the flame are given in Table 1. Also given there are the values of $P_{\Sigma\mathrm{Na}}$, the sum of the partial pressures of Na and its compounds in the flame gases. The values of $P_{\Sigma\mathrm{Na}}$ are calculated on the basis of data on the concentration of the sodium salt introduced into the flame, the composition of the combustible mixture feeding the flame, and the composition of the flame gases.

Using the values of P_{Na} and the partial pressures of the gas components of the combustion products of the hydrogen chloride flame, it can be shown that under equilibrium conditions in this flame Na is present practically only in the form of NaCl, Na^+, and Na, while the partial pressures of NaH, NaOH, and Na_2Cl_2 are negligibly small. The values of P_{Na^+} were calculated from the relation

$$P_{\mathrm{Na}^+} = \sqrt{K_1 \left(1 + \frac{P_{\mathrm{Cl}}}{K_2}\right) P_{\mathrm{Na}}},$$

obtained from the system of equations:

$$\frac{P_{\mathrm{Na}^+} \cdot P_e}{P_{\mathrm{Na}}} = K_1, \qquad \frac{P_{\mathrm{Cl}} \cdot P_e}{P_{\mathrm{Cl}^-}} = K_2$$

and $P_{\mathrm{Na}^+} = P_{\mathrm{Cl}^-} + P_e$. The values $K_1 = 2.63 \cdot 10^{-9}$ and $K_2 = 1.377 \cdot 10^{-5}$ were calculated from Saha' s equation. The values of P_{Na^+} calculated in this way are given in Table 1; the values of $P_{\mathrm{NaCl}} = P_{\Sigma\mathrm{Na}} - P_{\mathrm{Na}^+} - P_{\mathrm{Na}}$, the equilibrium constant of the reaction NaCl $\rightleftarrows$ Na + Cl at the flame temperature, and

$$D_0(\mathrm{NaCl}) = T\left(\Phi^*_{\mathrm{Na}} + \Phi^*_{\mathrm{Cl}} - \Phi^*_{\mathrm{NaCl}} - R \ln K_p\right).$$

Table 1

Values of P_{Na}, $P_{\Sigma Na}$, P_{Na^+}, P_{NaCl} (in atm) in the $H_2 + Cl_2$ flame and $D_0(NaCl)$ (in kcal/mol)

Salt solution	$P_{\Sigma Na} \cdot 10^7$	$P_{Na} \cdot 10^{10}$*	$P_{Na^+} \cdot 10^8$**	$P_{NaCl} \cdot 10^7$**	$K_p \cdot 10^4$**	D_0**
NaCl $1.02 \cdot 10^{-3} N$	1.58	4.72 ± 0.93	5.50 ± 0.55	1.03 ± 0.06	1.54 ± 0.40	98.6 ± 1.2
Na_2CO_3 $1.19 \cdot 10^{-3} N$	1.85	6.87 ± 1.04	6.65 ± 0.50	1.18 ± 0.05	1.96 ± 0.40	97.5 ± 1.1

* Arithmetic means from the results of 20 measurements of the intensity of two Na lines.
** The errors given take into account only the scatter of individual measurements of the intensity of the sodium lines.

The Φ^*-potentials of Na, Cl, and NaCl required for calculating this value were computed by methods of statistical thermodynamics.

Taking into account possible systematic errors of the method (see (1)), $D_0(NaCl) = 98.0 \pm 3.00$ kcal/mol, i.e., it agrees excellently with the value recommended by Gaydon (4) (97.6 ± 1.3 kcal/mol) on the basis of data obtained by the method of atomic fluorescence and measurements of the heat of sublimation. The agreement of the measurement results obtained when working with solutions of two different salts with each other and with data obtained by other methods makes it possible to suppose that conditions close to equilibrium must be attained in the outer cone of the flame, and shows that the dissociation energies of metal chlorides can be investigated in a hydrogen chloride flame.

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