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Abstract

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THE INFLUENCE OF AN EXTERNAL ELECTRIC FIELD ON A CHEMICAL REACTION IN A GAS

(Presented by Academician A. N. Frumkin, 15 IX 1956)

In a previous paper (^{1}), when considering the influence of ions on a chemical reaction in a gas, it was pointed out that in the case when the reaction products and the initial substances interact differently with ions, the electric field of the ions affects the equilibrium composition of the reaction. It is therefore natural to consider the question of the influence of an external electric field on the equilibrium composition of a reaction in which the initial substances are nonpolar molecules and the reaction products are polar molecules.

For definiteness, let us consider the reaction of ammonia synthesis $3H_2 + N_2 = 2NH_3$, which satisfies this condition.

The equilibrium composition of the reaction must be determined from the condition that, in the state of equilibrium, the system has minimal energy if the entropy and temperature remain constant. In the presence of an external electric field, a decrease in the total energy of the system must occur through an increase in the number of NH_3 molecules in the gas, since these molecules interact with the external electric field more strongly than the molecules N_2 and H_2, and the energy of this interaction is negative. Therefore, in the presence of an external electric field, the equilibrium composition of the reaction must shift toward an increase in the amount of ammonia.

Indeed, the condition of chemical equilibrium is the equality

$$\sum \mu_i \nu_i = 0. \tag{1}$$

For the reaction under consideration it is written as:

$$3\mu_3 + \mu_2 = 2\mu_1, \tag{2}$$

where μ_3, μ_2, and μ_1 are, respectively, the chemical potentials of the molecules of hydrogen, nitrogen, and ammonia.

In the case where an external electric field of intensity E is applied, the chemical potentials can evidently be written as:

$$\begin{aligned}
\mu_1 &= \mu_{1\,\mathrm{id}} - E\left(d\overline{\cos\vartheta} + \beta_1 E\right), \\
\mu_2 &= \mu_{2\,\mathrm{id}} - E^2\beta_2, \\
\mu_3 &= \mu_{3\,\mathrm{id}} - E^2\beta_1.
\end{aligned}$$

Here $\mu_{1\,\mathrm{id}}$, $\mu_{2\,\mathrm{id}}$, and $\mu_{3\,\mathrm{id}}$ are, respectively, the chemical potentials of ideal gases consisting of NH_3, N_2, and H_2 without a field; β_1, β_2, and β_3 are their polarizabilities, d is the dipole moment of the NH_3 molecules; $\overline{\cos\vartheta}$ is the known Langevin function.

$$\overline{\cos\vartheta} = -\frac{1}{a} - \frac{e^a + e^{-a}}{e^a - e^{-a}}, \tag{4}$$

where

$$a = \frac{Ed}{kT}.$$

The chemical potentials $\mu_{i\,\mathrm{id}}$, as is known, are equal to

$$\mu_{i\,\mathrm{id}} = kT \ln P_i + \chi_i(T), \tag{5}$$

where P_i is the partial pressure of particles of the i-th kind in the mixture, and $\chi_i(T)$ is a certain function of temperature

$$\chi_i(T) = -kT \ln\left\{\left(\frac{m_i kT}{2\pi\hbar^2}\right)^{3/2} \sum_{k_i} \exp\left(-\frac{\varepsilon^1_{k_i}}{kT}\right)\right\} - kT\ln kT. \tag{6}$$

Here $\varepsilon^1_{k_i}$ are the energy levels of a molecule of the i-th kind (not including the energy of translational motion), and m_i is the mass of a molecule of the i-th kind.

The sum appearing in expression (6) cannot be calculated in general form without some assumptions about the properties of the molecules. To take into account the influence of the external field there is no need for this.

Substituting expressions (5) and (3) into (2), replacing the partial pressures P_i by the concentrations C_i, and carrying out the corresponding transformations, we obtain

$$\frac{C_2 C_3^3}{C_1^2} = P^{-2} K_p(T) \exp\left\{-\frac{2dE\,\overline{\cos\vartheta} + 2\beta_1 E^2 - 3\beta_3 E^2 - \beta_2 E^2}{kT}\right\}, \tag{7}$$

where:

$$K_p(T) = \exp\left\{-\frac{\sum_i \nu_i \chi_i(T)}{kT}\right\}$$

is the equilibrium constant of the ammonia synthesis reaction in the absence of a field; C_1, C_2, and C_3 are, respectively, the concentrations in the gas of ammonia, nitrogen, and hydrogen molecules.

In practice one can almost always choose the field strength and temperature so that the following inequality is satisfied:

$$2dE\,\overline{\cos\vartheta} + 2\beta_1 E^2 > (3\beta_3 + \beta_2)E^2. \tag{8}$$

In the case of weak fields, when one may set

$$\overline{\cos\vartheta} = \frac{Ed}{3kT}, \tag{9}$$

inequality (8) is rewritten as

$$\frac{2d^2}{3kT} + 2\beta_1 > 3\beta_3 + \beta_2.$$

In this case, an estimate of the last inequality shows that at $T = 10^{3\circ}$ the left-hand side of the inequality is greater than the right-hand side by almost a factor of 10. This inequality will also be satisfied at large field strengths, when $\overline{\cos\vartheta}$ is expressed not by equation (9), but by the more exact equation (4).

Thus, under these conditions, as is seen from equation (7), the electric field shifts the equilibrium composition of the reaction toward an increase in the concentration of ammonia molecules, and the more so, the greater the strength of the electric field.

Analogous considerations are applicable to any reaction in which the initial substances are nonpolar molecules and the reaction products are dipole molecules.

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CITED LITERATURE

1. B. L. Timan, ZhETF, **27**, 5 (11) (1954).
2. L. Landau, E. Lifshitz, *Statistical Physics*, 1951.

Note: Figure translations are in progress. See original paper for figures.