

## SHIFT OF CHEMICAL DISSOCIATION EQUILIBRIUM IN NONISOTHERMAL DISCHARGE

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The problem of the equilibrium constant of dissociation and its influence on the concentration of starting substances under nonisothermal conditions was treated theoretically. A nonisothermal discharge enables to perform, in addition to decomposition processes, synthesis in certain cases with "superequilibrium" concentrations.

In solving chemical problems, a question often arises whether the studied system is capable of reacting in a sufficiently short time. If not, a catalyst must be used or the temperature must be raised to obtain a plasma. Although many plasma reactions have been studied, this method has found relatively little application owing to a high consumption of energy and to the fact that under usual conditions the products are mostly fragments of molecules. Plasma, however, offers new possibilities if its nonisothermal form is concerned, *i.e.* the state where the temperature of electrons is higher than the one of translative motion of molecules, radicals and ions.

It is known that under these conditions certain compounds ( $\text{NO}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ) are formed<sup>1-3</sup> in higher concentrations than would correspond to chemical thermodynamics, in "superequilibrium" concentrations; in compounds capable of polymerization, products of high molecular mass are found in larger quantities.

Calculating the concentrations of components of a mixture is based, as a rule, on the equilibrium constant. The problem in what form the generalized "equilibrium constant" can be expressed under nonisothermal conditions (in a system with more than one temperature), and what is its meaning in the case of more complex reactions, is dealt with in the present work.

The "superequilibrium" concentrations can occur even in the "frozen" state, *i.e.* under nonequilibrium conditions, *e.g.* so that the dissociated particles are suddenly cooled; the low temperature causes recombination, exchange reactions are slow and the equilibrium state is practically not reached. We shall not deal with these problems.

## THEORETICAL

*Properties of Nonisothermal Plasma*

The nonisothermal plasma is characterized by different temperatures of the translative motion of heavy particles,  $T_h$ , and free electrons,  $T_e$ . Under conditions of glow discharge, normally  $T_h < 500$  K and  $T_e \approx 10^4$  K. Then it is suitable to use formally the Boltzmann distribution law and to ascribe to the remaining degrees of freedom other temperatures<sup>4</sup>. Such temperatures should be understood as auxiliary quantities equal to the temperatures of isothermal systems with the same effect. (In our case we shall introduce only dissociation temperature  $T_D$  defined by Eq. (5).) Another difference against normal conditions consists in that the discharges contain molecules and electrons in different concentrations. For example,  $10^{16}$  molecules and  $10^9$  electrons are present in  $1 \text{ cm}^3$  in a glow discharge at a current density of  $10 \text{ mA/cm}^2$  and a pressure of 1 Torr.

*Equilibrium Dissociation Constant*

It is known that up to 50% dissociation, *e.g.* of hydrogen, can be attained in low-pressure discharges (1 Torr). Such a degree of dissociation corresponds under isothermal conditions to a temperature of 2500 K. However, solely in view of the fact that the discharge takes place in a glass tube, the temperature of the translative motion of molecules is much lower. We shall attempt to find out what factors determine the effective temperature of dissociation. For a reaction of the type  $A_2 \rightleftharpoons 2 A$ , the isothermal equilibrium constant is given by<sup>5</sup>

$$K = [A]^2/[A_2] = [(Q_r^A)^2/Q_r^{A_2} Q_t^A Q_v^A] \exp(-D/RT), \quad (1)$$

where  $Q$  with subscripts  $r$ ,  $t$ ,  $v$  denotes partition functions of rotation, translation and vibration, and  $D$  dissociation energy of the electron ground state. Eq. (1) holds with the assumption that heavy particles excite gradually their vibration levels and disintegration to atoms takes place on the highest vibration level. In a nonisothermal plasma, free electrons can participate on the mentioned process by exciting bound electrons to repulsive levels. Since excitation by heavy particles to repulsive levels and mostly dissociation by a free electron through vibration levels is negligible<sup>6</sup>, we shall not consider these processes. According to phenomenological kinetics, the change of the number of dissociated particles with time for the considered reaction can be expressed as

$$d[A]/dt = \bar{k}[A_2] - \bar{k}[A]^2. \quad (2)$$

According to statistical physics, the forward rate constant,  $\bar{k}$ , is equal to  $\sum Z_y \bar{P}_y \exp(-D/RT_y)$ , where  $y = h, e$ ;  $Z$  means frequency factor (number of colli-

sions per unit volume and unit time). The probability factor  $\vec{P}$  expresses the probability of the event that the kinetic energy of an interacting particle is higher than its dissociation energy and the deviation from Maxwell distribution. It is equal to the product of the partition function  $\vec{Q}$  and quantum mechanical probability  $P^*$ . In the case of an equilibrium it follows from the mentioned equations that

$$K = [Z_h \vec{P}_h \exp(-D/RT_h) + Z_e \vec{P}_e \exp(-D^*/RT_e)] / \bar{k}, \quad (3)$$

where  $D^*$  means dissociation energy with respect to repulsive electron states and  $\bar{k}$  recombination rate constant<sup>5</sup> which can be formally expressed as  $\sum Z_y \vec{P}_y = \sum Z_y \vec{Q} \vec{P}_y^*$ . If  $y = h$  and  $Z_e = 0$ , Eq. (3) takes the form of (1) since  $\vec{P}_h^* = \vec{P}_h$ . In a glow discharge, usually  $T_h \ll T_e$  and  $Z_e \vec{P}_e \ll Z_h \vec{P}_h$ . Then the terms  $Z_h \vec{P}_h \exp(-D/RT_h)$  and  $Z_e \vec{P}_e$  can be neglected and

$$K = \alpha (\vec{Q}/\bar{Q}) \exp(-D^*/RT_e), \quad (4)$$

where  $\alpha = Z_e P_e / Z_h P_h$ . As a first approximation, we set  $\vec{Q}/\bar{Q}$  equal to the partition term in (1). The value of  $\vec{Q}/\bar{Q}$  has been derived exactly<sup>7</sup>. We now introduce the dissociation temperature  $T_D$ :

$$\exp(-D^*/RT_D) = \alpha \exp(-D^*/RT_e). \quad (5)$$

In the derivation of the equilibrium constant (4), only volume recombination was assumed. (If the wall of the discharge tube has a catalytic character, the gas can recombine on it; the recombination on the surface can be more rapid than in the

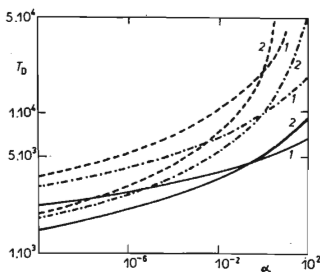


FIG. 1

Calculated Dissociation Temperature  $T_D$ (K) in Dependence on  $\alpha = Z_e P_e / Z_h P_h$

Temperature of electrons: ——— 5.10<sup>3</sup>, - - - - - 1.10<sup>4</sup>, - · - · - 2.10<sup>4</sup> K; dissociation energy  $D$ : 1 100 and 2 200 kcal/mol.

volume. This case will not be considered here.) The values of  $T_D$  calculated from Eq. (5) as function of  $\alpha$  for various dissociation energies and temperatures of the electrons are plotted in Fig. 1. The coefficient  $\alpha$  was estimated from ref.<sup>8,9</sup>; its value is of the order of  $10^{-5}$  at a pressure of 1 Torr and current density of 100 mA/cm<sup>2</sup>. If we assume, as usual<sup>8,10</sup>,  $T_e = 10^4$  K, we obtain from Fig. 1 for the dissociation mechanism of hydrogen the dissociation temperature of 3000 K in an approximate accord with experimental data.

It follows from Eq. (5) or Fig. 1 that with increasing  $D^*$ ,  $T_D$  increases for  $\alpha < 1$  but decreases for  $\alpha > 1$ . Then for  $\alpha < 1$  a higher effective temperature of repulsive electron states against vibration states can be assumed together with their dominant role in the dissociation mechanism. Further, it is apparent that the effective temperature is determined not only by the temperature of electrons but also by the parameter  $\alpha$ . Since the latter is directly proportional to the current density,  $j$ , hence to the number of electrons in a unit volume, and inversely proportional to the pressure,  $p$ , i.e. to the density of molecules, the dissociation temperature should be directly proportional to the current density and inversely proportional to the pressure. Eq. (4), however, enables in the general case to determine only the character of the influence of various factors since neither the temperature of the electrons (more exactly, their distribution function), nor the parameter  $\alpha$  can be presently determined with a sufficient accuracy.

### Complicated Mechanisms

We concluded in the preceding paragraph that in a nonisothermal discharge, a different dissociation temperature must be ascribed to every particular dissociation. Then, similarly as in chemical thermodynamics, we can obtain the equilibrium constant of the whole reaction by a suitable combination of the equilibrium constants of the particular dissociations; the difference is that a different temperature is ascribed to every dissociation. However, it is more instructive to use equations of the type (4) and to calculate the dissociation temperature of the whole mechanism. We shall deal first with a reaction where the change of the number of mols during the reaction is negligible, such as  $N_2 + O_2 \rightleftharpoons 2 NO$ ; the partial reaction steps are  $N_2 \rightleftharpoons 2 N$ ,  $O_2 \rightleftharpoons 2 O$  and  $NO \rightleftharpoons N + O$  with equilibrium constants  $K_N$ ,  $K_O$  and  $K_{NO}$ ; then

$$[NO] = (K_N K_O [O_2] [N_2])^{1/2} / K_{NO} \quad (6)$$

This equation can be rearranged with the use of (4) to give

$$[NO] = (P'_{NO} / \alpha_{NO}) (\alpha_N \alpha_O / P'_N P'_O)^{1/2} ([O_2] [N_2])^{1/2} \exp(-\Delta E / RT_e), \quad (7)$$

where  $\Delta E$  denotes difference between dissociation energies of final and starting compounds (we assume positive value) and  $P'$  partition term  $\bar{Q}/\bar{Q}$ . We shall estimate the influence of the individual terms assuming that  $\alpha_N \approx \alpha_O \approx \alpha_{NO}$  as a first approxima-

tion. The temperature of the whole reaction is determined by that of the electrons. Its increase causes the nitrogen oxide concentration to increase as long as the dissociation of  $N_2$ ,  $O_2$  or  $NO$  is not appreciable; then it decreases. Under isothermal conditions, the temperature corresponding to oxygen dissociation would be given by that of the electrons, and in our case also by the parameter  $\alpha$  as follows from Eq. (4). Then, for a sufficiently small value of  $\alpha$ ,  $[NO]$  can increase with  $T_e$  above the value predicted by thermodynamics of isothermal processes. It follows that "superequilibrium" concentrations can be established under nonisothermal conditions. It can not yet be stated whether the mentioned mechanism is decisive in all nonisothermal discharges and whether the system can still be optimized, since the properties and possibilities offered by the nonisothermal plasma are not well known.

As an example of a reaction in which the number of mol changes, we choose  $O_3 \rightleftharpoons O_2 + O$  (formally analogous to the preparation of  $H_2O_2$ ). On setting  $K_O = [O]^2/[O_2]$  and  $K_{O_3} = [O][O_2]/[O_3]$ , we obtain

$$[O_3] = (\alpha_O/P_O)^{1/2} (P_{O_3}'/\alpha_{O_3}) [O_2]^{3/2} \exp(-\Delta E/RT_e). \quad (8)$$

If  $\alpha_O \approx \alpha_{O_3}$ , the effective temperature of the reaction mechanism is determined by the term  $\alpha^{-1/2} \exp(-\Delta E/RT_e)$ . Then the concentration of ozone will increase with increasing pressure and decreasing current density. Indeed, higher pressures at low current densities are used in the manufacture of ozone. The dissociation of oxygen exerts the same effect as in the preceding case. In contrast to the synthesis of ozone, for a model reaction  $A_2 + 3 B_2 \rightleftharpoons 2 AB_3$  we have

$$[AB_3] \sim \alpha [A_2]^{1/2} [B_2]^{3/2} \exp(-\Delta E/RT_e) \quad (9)$$

and the coefficient  $\alpha$  has an inverse influence.

## CONCLUSIONS

Under nonisothermal conditions, different dissociation temperatures must be ascribed to every particular dissociation reaction. This temperature is, as a rule, the higher the higher is the dissociation energy and is determined mainly by the current density and pressure of the reaction mixture and also by the temperature of electrons. With more complex mechanisms, the resulting concentration of the studied compound depends mainly on the effective temperature of the whole reaction mechanism. If the number of mols is constant during the reaction, the temperature is determined by that of the electrons, in the opposite case also by the current density and pressure. Another factor is the degree of dissociation. In contrast to the isothermal state, the dissociation temperature of the individual reaction step can differ from the temperature of the overall reaction. Then at a low temperature of dissociation and

high temperature of the overall reaction there is a possibility of the formation of "superequilibrium" concentrations. Our knowledge of discharges is not sufficient to enable exact calculations and to optimize the reaction conditions.

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