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THERMODYNAMIC EQUILIBRIUM IN STRONG ELECTRIC FIELDS AND FIELD CHEMISTRY CONSEQUENCES (*)

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On his 90th birthday

(Reçu le 27 janvier 1977, révisé le 26 avril 1977, accepté le 21 juin 1977)

Résumé. — Des champs électriques de l'ordre de 10^8 à 10^9 V/cm appliqués à un système de réactions chimiques sont capables de déplacer l'équilibre thermodynamique de manière remarquable. Parfois les concentrations dans les conditions d'équilibre normales sont inversées par le champ électrique.

Aussi la cinétique des réactions peut être influencée par des champs de cet ordre non seulement par la variation de l'écart à l'équilibre du système ou par les polarités des liaisons chimiques qui sont engagées dans la réaction mais aussi de façon remarquable à cause de la diminution de l'énergie d'activation. Cette dernière entraîne l'accélération des réactions chimiques. Par des calculs théoriques classiques, non seulement le déplacement des équilibres mais encore les accélérations des vitesses de réaction sont déterminés en fonction du champ électrique. Les résultats théoriques sont comparés avec les observations expérimentales. Des corrélations valables sont trouvées.

Abstract. — Strong enough electric fields — especially of the order of 10^8 to 10^9 V/cm — when applied to a chemically reactive system may shift the thermodynamic equilibria in a remarkable way. Even inversion of the normal equilibrium situations can occasionally occur.

Reaction kinetics may also be influenced by fields of this order, not only on account of the systems altered equilibrium distance, or through bond polarities of those bonds which participate in the reaction, but also by a remarkable decrease of the activation energy. This latter is chemical acceleration. By an almost classical calculation, the equilibrium variation and the acceleration of the reaction rates can be determined as a function of the electric field strength. The theoretical results have been compared with experiment and reasonably good correlation was found.

1. Introduction. — Matter under the influence of strong electric fields generally shows a polarization of its molecules. The creation of induced dipoles affords a means of storing additional energy in the system. Besides this, the electric field orientates those molecules which already have permanent dipoles along the field lines.

Both effects — the creation of induced dipoles, and the orientation of permanent dipoles — lead to a variation of the thermodynamic state of the system. In the case of a chemically reactive system, this leads to a shift of the thermodynamic equilibrium. The shift

of equilibrium can occur in either direction of a chemical reaction and will depend on the polarizabilities and the strength of the permanent dipoles of the reacting substances.

Furthermore these field induced dipoles — and also of course the oriented dipoles — of the reacting compounds should interact so as to lead to a decrease of the transition state energy, and in this way cause a special type of chemical catalysis. Since it had been shown [1, 2, 3, 4] that chemical catalysis is primarily an electrical interaction between the transition state and the catalyst, it is not surprising to find a catalytic effect of strong enough electric fields.

Such electric fields are not only effective in normal chemical catalysis. There are similar actions also in radio or reactor chemistry. The field carrying species here are the charged corpuscles, protons, α - and

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β -particles and also some others. A comparable situation exists in a plasma. It seems to be only a question of the point of view, whether one regards the quasi catalytical effects under these conditions as an interaction between induced or orientated dipoles influenced by the charge carrying particles, or as a chemical reaction between molecules in a lesser or higher state of electronic excitation

In the last few years much research has been done [5, 6, 7] in the theoretical development of this *hot atom* chemistry, which corresponds in a formal way to the better known photo chemistry. In this paper the author tries to come to a quantitative understanding of *field chemistry* and/or *field catalysis* by assuming that the molecules — the reacting ones especially — will be polarized and orientated in sufficiently strong electric fields. The mathematical and physical procedures are almost completely classical. The basic work has already been published recently [8] but we show here, in more detail, the agreement between theoretical and experimental results for some typical field chemical reactions.

2. The behaviour of matter in electric fields. — For the study of chemical reactions under influence of electric fields, there exist two main items of important practical interest — the chemical equilibrium and chemical reaction kinetics. Whilst in the case of equilibrium the thermodynamic state is completely determined by the polarizabilities and permanent dipoles of all present molecules, the calculation of kinetic data also needs knowledge of how the polarities of the reacting bonds are directed. Table I [9] shows the polarities for some frequently used chemical bonds.

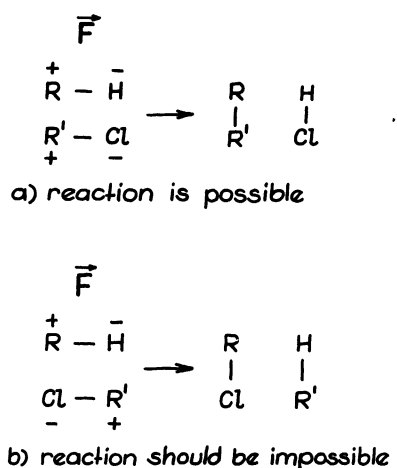


FIG. 1. — Influence of bond polarity on field chemical reaction.

In methane e.g. and its homologs as well as in the mono alkyl halides, hydrogen is the negative partner [10, 11]. The knowledge of bond polarity is of importance since it determines with respect to orientation in the electric field whether a reaction between two molecules — their corresponding bonds respectively — is possible or not. Figure 1 demonstrates this situation. Production of hydrogen chloride should be expected and was indeed experimentally observed. But not so the exchange of chlorine between the two organic radicals.

3. The chemical equilibrium. — The equilibrium constant K_p of any chemical reaction is determined by several thermodynamic parameters, the absolute temperature T , enthalpy H and entropy S :

$$- RT \cdot \ln K_p = H_0 - T \cdot S_0 . \quad (1)$$

The index « 0 » relates to the normal thermodynamic condition, and the absence of an electric field. A similar relation will apply in the presence of an electric field

$$- RT \cdot \ln K_p(F) = H(F) - T \cdot S(F) . \quad (2)$$

In this relation F refers to the field strength, which is assumed for the calculations to be homogeneous.

Enthalpy and entropy under the field influence are given by

$$\begin{aligned} H(F) &= H_0 + \Delta H(F) \\ S(F) &= S_0 + \Delta S(F) \end{aligned} \quad (3)$$

since both thermodynamic properties are additive. As shown in an earlier paper [8] the variation of enthalpy with field strength is given by

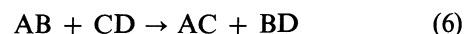
$$\Delta H = \frac{1}{2} \cdot F^2 \cdot \sum_1^n v_i \cdot \alpha_i . \quad (4)$$

In this relation α_i means the polarizabilities and v_i the stoichiometric factors of the participants in the chemical reaction.

The change in entropy caused by the presence of the field can be expressed as [8]

$$\Delta S = k \cdot \sum_1^n v_i \cdot \ln \left(\frac{1}{2\pi} \cdot \sqrt{\frac{k \cdot T}{2 \cdot \mu_{0i} \cdot F}} \right) \quad (5)$$

where k is the Boltzmann constant and μ_{0i} the permanent dipoles of the reaction participants. n is the maximal number of molecules which belong to a chemical reaction. For the very general reaction



n equals 4.

TABLE I

Bond polarities. Group moments in Debye units [9]

$\begin{array}{c} + & - \\ \text{C} & - & \text{H} \\ & & 0.4 \end{array}$	$\begin{array}{c} + & - \\ \text{H} & - & \text{O} \\ & & 1.6 \end{array}$	$\begin{array}{c} + & - \\ \text{C} & = & \text{O} \\ & & 2.3 \end{array}$	$\begin{array}{c} + & - \\ \text{C} & - & \text{O} \\ & & 0.7 \end{array}$	$\begin{array}{c} + & - \\ \text{C} & - & \text{Cl} \\ & & 1.5 \end{array}$	$\begin{array}{c} + & - \\ \text{C} & - & \text{OH} \\ & & 1.6 \end{array}$	$\begin{array}{c} + & - \\ \text{C} & - & \text{COOH} \\ & & 1.0 \end{array}$	$\begin{array}{c} + & - \\ \text{C} & - & \text{NO}_2 \\ & & 3.7 \end{array}$
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Relation (5) was derived on the basis of statistical thermodynamics. A permanent dipole in an electric field will oscillate and rotate around the field lines by the random thermal movement of the molecules. Figure 2 shows this situation.

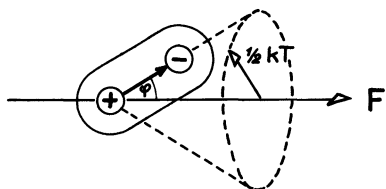


FIG. 2. — Random thermal movement (rotation and oscillation) of permanent dipoles around the field lines.

Using (5), (4), (3) and (2), the equilibrium constant $K_p(F)$ under the action of an electric field is easily calculated as will be shown later for several chemical reactions.

4. **The chemical reaction kinetics.** — The reaction rate (6) is normally given by

$$\frac{d\vec{n}}{dt} = \vec{K}_c \cdot [AB] \cdot [CD] \quad (7)$$

and the rate of the opposite reaction is — normally again — defined as

$$\frac{d\vec{n}}{dt} = \vec{K}_c \cdot [AC] \cdot [BD] \quad (8)$$

With the equilibrium condition

$$\frac{d\vec{n}}{dt} = \frac{d\vec{n}}{dt} \quad (9)$$

the well known Guldberg-Waage rule follows

$$\frac{[AC] \cdot [BD]}{[AB] \cdot [CD]} = \frac{\vec{K}_c}{\vec{K}_c} = K_c = K_p = K_x \quad (10)$$

The equality of the equilibrium constants K_c , K_p and K_x — x meaning the molar fraction — is valid only if the number of particles is unaltered during reaction !

In the case of

$$\frac{d\vec{n}}{dt} \geq \frac{d\vec{n}}{dt} \quad (11)$$

we will obtain

$$\begin{aligned} \frac{dn}{dt} &= \frac{d\vec{n}}{dt} = \frac{d\vec{n}}{dt} \\ &= \vec{K}_c \cdot [AB] \cdot [CD] - \vec{K}_c \cdot [AC] \cdot [BD] \geq 0 \quad (12) \end{aligned}$$

or, using (10),

$$\frac{dn}{dt} = \vec{K}_c \cdot \left\{ [AB] \cdot [CD] - \frac{[AC] \cdot [BD]}{K_c} \right\} \quad (13)$$

The difference on the right hand side of relation (13) represents the *equilibrium distance* of the reacting system. In this respect the over all reaction rate is a function of the equilibrium state and must generally be taken into account.

The reaction rate also depends on the rate coefficient \vec{K}_c which is defined by the well-known relation

$$\vec{K}_c = z \cdot \sigma \cdot e^{-E_A/RT} \quad (14)$$

where z is the number of random impacts per second, σ is the steric factor and E_A means the activation energy of the chemical reaction. The steric factor controls the spatial or geometric orientation during the reaction.

There is certainly no serious variation in z when an electric field is applied to a chemical system. If molecules with permanent dipole moment participate in the reaction, a variation of the steric factor by the effect of field orientation should be possible. But this effect is expected to be relatively small in comparison to the effect of the field on the activation energy. In the following therefore this effect will be neglected.

As already mentioned in the introduction, the field-induced or oriented dipoles should interact with each other as is schematically shown in figure 3. The interaction energy of two equal dipoles of dipole length l has been calculated [8] as

$$\overline{\Delta E} \cong \left\{ \frac{2}{r} - \left[2 + \frac{3}{2} \cdot \left(\frac{r \cdot l}{r^2 + l^2} \right)^2 \right] \cdot \frac{1}{\sqrt{r^2 + l^2}} \right\} \cdot e^2 \quad (15)$$

or with the simplifying substitution $r/l = x$

$$\overline{\Delta E} \cong \left\{ \frac{2}{x} - \left[2 + 1.5 \cdot \left(\frac{x}{x^2 + 1} \right)^2 \right] \cdot \frac{1}{\sqrt{x^2 + 1}} \right\} \times \frac{e^2}{l} \quad (16)$$

This function (Fig. 4) shows a characteristic minimum at

$$\begin{aligned} r_{\min} &= 2.6 \cdot l \\ \overline{\Delta E}_{\min} &= -0.0090 \cdot \frac{e^2}{l} \quad (17) \end{aligned}$$

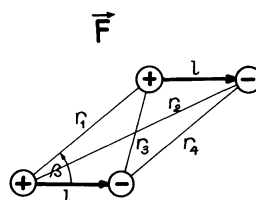


FIG. 3. — Interaction of induced or oriented dipoles.

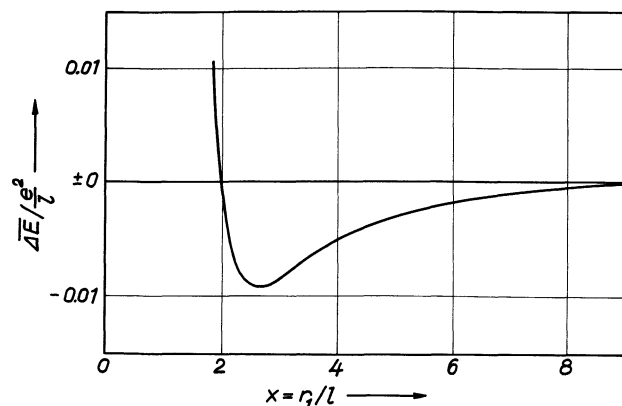


FIG. 4. — Interaction potential of two equal dipoles.

With the definition of the electric field strength as the force acting on unit electric charge through a distance l

$$F = \frac{e}{l^2} \quad (18)$$

we get instantly

$$\frac{e^2}{l} = e \cdot l \cdot F. \quad (19)$$

And with the well known relations for the dipole moment

$$\mu = e \cdot l = \alpha \cdot F \quad (20)$$

we finally obtain

$$\frac{e^2}{l} = \alpha \cdot F^2. \quad (21)$$

Since a decrease of the transition state energy is equivalent to a decrease of the activation threshold (Fig. 5), the last result gives

$$\Delta E_A = -0.0090 \cdot \alpha \cdot F^2. \quad (22)$$

Here one must bear in mind that for the derivation of (22) a constant value for α was assumed — i.e. the same value for both reacting compounds. In practical cases of chemical reactions, the participants will certainly have different α values. But for approximation purposes it should be possible to use a constant average $\bar{\alpha}$ for α .

In summarizing the theoretical results up to this point we may state :

1) Application of electric fields on chemical reactions results in an increase of the system energy or enthalpy, and also in a variation of the entropy by orientation of the permanent dipoles. By this means, the thermodynamic equilibrium is shifted. This equilibrium shifting can possibly occur in either direction of a chemical reaction.

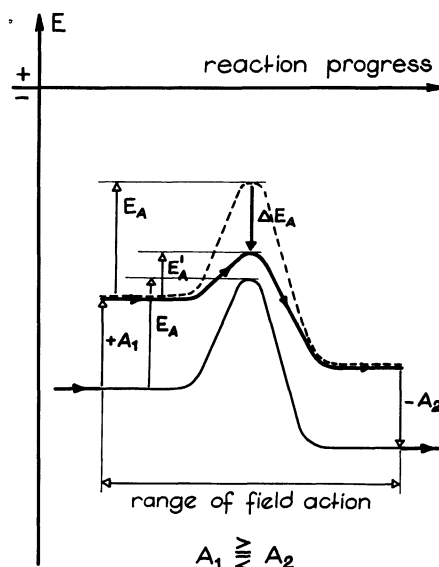


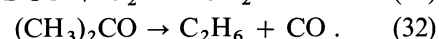
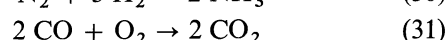
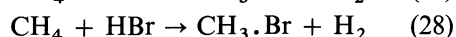
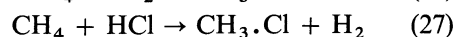
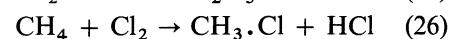
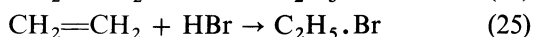
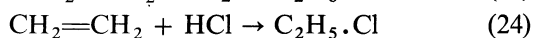
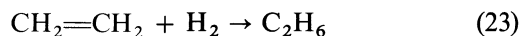
FIG. 5. — The field-effect — alteration of thermodynamics and reaction kinetics — upon chemical reactions. $A_1 \neq A_2$ means variation of the equilibrium.

2) The overall reaction rate depends — apart from the bond polarities of the reacting chemical bonds — in a very definite manner on the equilibrium distance of a reacting system. It also depends importantly on the decrease in activation energy as effected by the electric field.

5. Comparison with experimental experience. —

Of most important practical interest should be the question of the necessary strength of the electric field to obtain a noticeable acceleration of the reaction or equilibrium shift.

For this purpose theoretical results have been calculated and compared with experimental observations of the following chemical reactions



These reactions were selected because of their easy experimental and analytical handling, as well for the fact that all necessary parameters (reaction enthalpy, normal entropy, polarizabilities and permanent dipoles) were known [12, 13, 14]. Many other reactions (more than 100) have also been studied experi-

mentally but with a lack in the parameter knowledge, it was impossible to compare with theoretical results.

First of all the normal — i.e. in absence of electric field — thermodynamic equilibria were calculated, which was done in the well-known first-order approximation [13]. The necessary thermodynamic data were taken from the usual source books [12, 13, 14]. Then by the theoretical relations developed (4) and (5), the variations of enthalpy and entropy under influence of electric field were determined. And lastly using (3) and (2) the equilibrium constants in the presence of the field were calculated. Table II shows a summary of these theoretical results. Practically all these equilibrium constants have extremely high or low values. This means that all equilibria are lying nearly completely at one side of the reaction. In the field free situation for the reactions (23), (24), (25), (26), (29), (30), (31) and (32) the reaction products of the right hand sides of the chemical equations are preferred while in the reactions (27) and (28) the compounds at the left hand sides are the thermodynamically stable ones.

Even field strengths as high as 10^8 V/cm cause only small variations of the equilibrium constants for nearly all of the studied reactions. But a further increase in field strength up to only 10^9 V/cm causes remarkable shifts in the equilibrium situation. Some of the reactions are shifted further in their original directions as e.g. the hydrogenation of ethylene or the addition of HBr to ethylene.

Quite another situation exists for the synthesis of ammonia. Under normal conditions and also field free, a stoichiometric mixture of nitrogen and hydrogen shows an ammonia content of 96.75 mole %. The reaction then nearly goes completely to the ammonia production. Under a field strength of 10^9 V/cm the equilibrium situation has abruptly changed — only small traces of ammonia now exist. The situations for the reaction between hydrogen and chlorine or the oxidation of carbon monoxide are similar. In these

three cases an inversion of the original reaction direction must be expected by field action.

Since all the studied reactions have their equilibrium states nearly completely at one side of the reaction equation we get a very precise interpretation of reaction rates by the Boltzmannian *Acceleration factor*

$$e^{-\Delta E_A/RT} = \exp\left(\frac{0.009 \ 0. \bar{\alpha} \cdot F^2}{RT}\right). \quad (33)$$

Table III shows the calculated results again for the two field strengths of 10^8 and 10^9 V/cm. First of all it is remarkable that the variation of the Boltzmann factors by a field strength of 10^8 V/cm is very small — mostly only up to 10 % or still less. But the application of 10^9 V/cm yields a tremendous acceleration. There are also big differences between the single reactions. In the cases of equilibrium inversion by field effect, the acceleration factors were calculated for the inverted reactions. This is designated by an arrow on the top of the figures in the table. A still better demonstration of the field influence is shown in figure 6 for the production of ethylbromide in reaction (25). All other chemical reactions behave in the same way.

The experiments were performed with an apparatus which is shown in a somewhat simplified form in figure 7. 220 V a.c. was transformed with a high voltage-high frequency pulse generator into pulsating (sometimes up to 10 000 pulses per second) high-frequency sequencies (up to about 10 MHz) of very high voltage. These high-frequency pulses were transmitted to a parallel plate chemical reactor whose plates had a very small separation (about 10^{-2} cm), and whose outside surfaces were covered with metallic foils, in this way serving as an electric capacitor. The voltage of this capacitor was indicated by means of an oscilloscope. In the same way the number of pulses per second was determined, with their high frequency

TABLE II

The thermodynamic equilibrium under the influence of strong electric fields

$p = 1$ (atm)	$T = 25$ (°C)	K_p (0) (*)	K_p (10^8) (*)	K_p (10^9) (*)
$\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	(23)	$10^{17.65}$	$10^{18.3}$	$10^{79.7}$
$\text{CH}_2=\text{CH}_2 + \text{HCl} \rightarrow \text{C}_2\text{H}_5 \cdot \text{Cl}$	(24)	$10^{4.58}$	$10^{5.12}$	$10^{71.6}$
$\text{CH}_2=\text{CH}_2 + \text{HBr} \rightarrow \text{C}_2\text{H}_5 \cdot \text{Br}$	(25)	$10^{7.35}$	$10^{8.18}$	$10^{113.7}$
$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3 \cdot \text{Cl} + \text{HCl}$	(26)	$10^{18.33}$	$10^{15.75}$	$10^{52.3}$
$\text{CH}_4 + \text{HCl} \rightarrow \text{CH}_3 \cdot \text{Cl} + \text{H}_2$	(27)	$10^{-14.84}$	$10^{-15.3}$	$10^{-51.3}$
$\text{CH}_4 + \text{HBr} \rightarrow \text{CH}_3 \cdot \text{Br} + \text{H}_2$	(28)	$10^{-13.65}$	$10^{-14.4}$	$10^{-70.0}$
$\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$	(29)	$10^{33.4}$	$10^{29.05}$	$10^{-75.2}$
$\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$	(30)	$10^{5.73}$	$10^{2.02}$	$10^{-71.2}$
$2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$	(31)	$10^{90.1}$	$10^{89.2}$	$10^{-14.1}$
$(\text{CH}_3)_2\text{CO} \rightarrow \text{C}_2\text{H}_6 + \text{CO}$	(32)	$10^{2.58}$	$10^{4.52}$	$10^{35.7}$

(*) In brackets the electric field strength in (V/cm).

TABLE III

Reaction kinetics under the influence of strong electric fields.
Experimental field strength of about 10^8 to 10^9 V/cm

$p = 1$ (atm)	$T = 25$ (°C)	$\exp\left(-\frac{\Delta E_A(10^8)}{RT}\right)^{(1)}$	$\exp\left(-\frac{\Delta E_A(10^9)}{RT}\right)^{(1)}$	% conversion (obs.)	
$\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	(23)	1.082 3	2 700	(²)	up to 60
$\text{CH}_2=\text{CH}_2 + \text{HCl} \rightarrow \text{C}_2\text{H}_5\cdot\text{Cl}$	(24)	1.111 2	38 000	~ 10	
$\text{CH}_2=\text{CH}_2 + \text{HBr} \rightarrow \text{C}_2\text{H}_5\cdot\text{Br}$	(25)	1.126 3	147 300	50-61	up to 100
$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\cdot\text{Cl} + \text{HCl}$	(26)	1.117 2	55 000	98-99	up to 100
$\text{CH}_4 + \text{HCl} \rightarrow \text{CH}_3\cdot\text{Cl} + \text{H}_2$	(27)	1.079 9	2 160	1.3-2.8	
$\text{CH}_4 + \text{HBr} \rightarrow \text{CH}_3\cdot\text{Br} + \text{H}_2$	(28)	1.086	3 800	~ 0.5	
$\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$	(29)	1.078 5	1 910	2-3	
$\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$	(30)	1.060 4	348	~ 2	up to 80
$2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$	(31)	1.142	20 000	~ 2	up to 35
$(\text{CH}_3)_2\text{CO} \rightarrow \text{C}_2\text{H}_6 + \text{CO}$	(32)	1.082 8	2 850	7.0	

(¹) In brackets the electric field strength in (V/cm).

(²) Under comparable conditions.

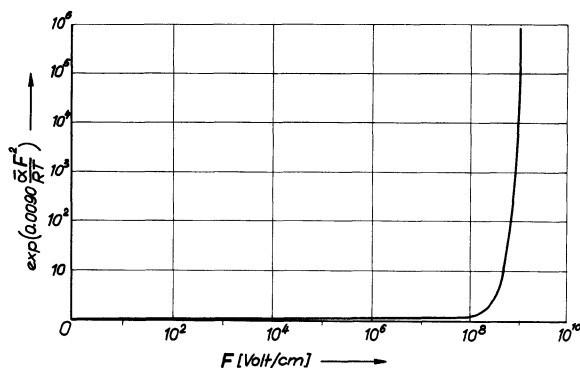


FIG. 6. — The Boltzmannian acceleration factor as a function of electric field strengths in the production of ethylbromide.

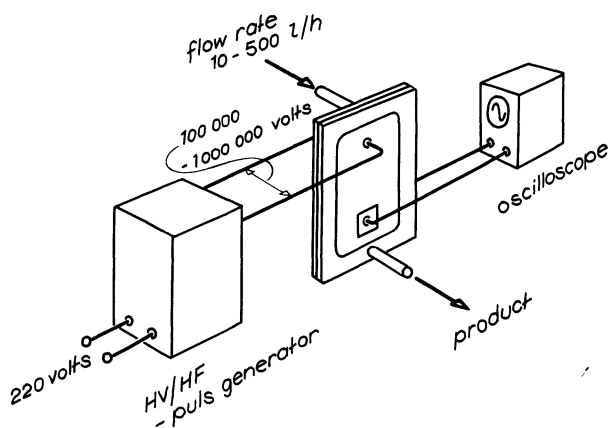


FIG. 7. — Apparatus for field chemical experiments.

fine structure. Maximal indication reached the order of several million volts.

With respect to the plate distances in the reactor and the measured potentials between the condenser plates, we could easily reach field strengths up to

10^8 V/cm and still a little more. Under these conditions (small plate distances and high frequencies) we had no trouble with electric break through.

The consumption of electric energy e.g. per kilogram was in some cases extraordinarily low. For the production of ethylbromide we needed about 250 W/1 kg ethylbromide per hour. This energy loss was the total loss — that means losses by dielectric heating of the reactor material (mostly glass) and additional losses in the transformers, etc. A separate determination of the hitherto inevitable losses by dielectric heating of the reactor showed e.g. only 35 W/1 kg n-propylbromide per hour! This seems to be an encouraging result for technical development.

The different materials passed the reactor in stationary streams ranging from 10 to several hundred liters per hour. As a rule all components were added in stoichiometric ratios. All observations which are reported here were made under normal pressure and temperatures of about 300 K.

The two last columns in table III show the experimental conversion data — i.e. what percentage (%) of the starting material was converted — for the studied reactions. The data of the first of these columns were obtained under constant working conditions, whilst the last ones correspond to different (optimal!) experimental conditions.

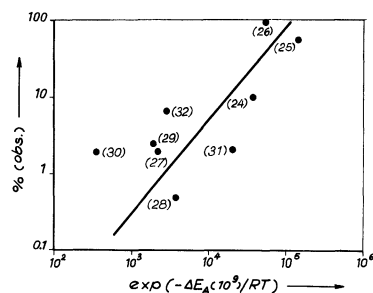


FIG. 8. — Correlation plot between theoretical acceleration factors and experimental conversions of several chemical reactions.

Figure 8 shows a correlation graph for the experimentally comparable data and the theoretical acceleration factors. One should expect here a certain correlation because all of these reactions have their equilibrium extensively at one side. The correlation is not very close but there obviously exists a trend that higher conversions corresponds to larger acceleration factors. Besides the observational errors, these smaller or larger deviations from the average correlation function probably have their main origin in the differences between the original activation energies.

6. Discussion. — Much experience with a lot of different chemical reactions has led us to a classification of the experimental results into four main groups :

- 1) no reaction at all,
- 2) only traces of conversion ($< 1\%$),
- 3) medial conversions (1-10%),
- 4) nearly complete conversion.

It was the intention of the developed theory to understand these quite different behaviours. We have achieved this, particularly concerning the effect of electric fields — i.e. strong electric fields — upon chemical reactions.

But there are still further difficulties and problems. Higher electric field strengths are needed to bring the group 1) to 3) reactions to better conversions. Unfortunately we are then again faced with the possibility of electrical break through. And finally, in our experiments we had hitherto a broad spectrum of field strengths, this probably prevents reaction selectivity in many cases. We do feel that there should be a similar resonance type relation between the transition state and electric field energy as we found [1, 2, 3, 4] for normal chemical catalysis. But this is a question for further experimental development and particularly theoretical research also.

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