On the Polarography of Formaldehyde *

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In the paper a mathematical treatment is given for the polarographic behaviour of formaldehyde in neutral and alkaline solutions. This treatment is co-ordinated with earlier, simplified solutions, which are valid at high rates of methylene glycol dehydration. The derivations are extended to give a method for determination of the equilibrium and dehydration rate constants when the limiting current is controlled both by catalysis and by diffusion. The effect of the hydroxyl ions produced at the electrode surface has been considered for the case of unbuffered or slightly buffered solutions. The theoretical conclusions are verified experimentally. The spectrophotometric equilibrium constant of methylene glycol—formaldehyde is checked experimentally and found to be in agreement with earlier published results.

Despite the fact that the polarographic determination of formaldehyde is a well-established analytical process, only simplified mathematical treatments are given for the formaldehyde polarographic current. The purpose of the following paper is to give a more rigorous treatment, in order to make it possible to find equilibrium and dehydration rate constants for the system formaldehyde—methylene glycol from experimental data. The rate of dehydration is of a considerable interest in discussions on the mechanism of several formaldehyde reactions, *e. g.* in the methylol urea synthesis.

WATER SOLUTIONS OF FORMALDEHYDE

According to *e. g.* Auerbach and Barschall¹, in concentrated water solutions formaldehyde is present as trioxymethylene glycol, $\text{HO} \cdot (\text{CH}_2\text{O})_3 \cdot \text{OH}$. When diluted, this compound depolymerises to methylene glycol, $\text{HO} \cdot \text{CH}_2 \cdot \text{OH}$. The rate of the depolymerisation,

has been studied by Wadano *et al.*², and it has been shown that it is dependent on pH, having a minimum at $\text{pH} \sim 3.5$.

In the electrolytic dissociation of methylene glycol the following reactions probably occur:

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Wadano ³ states that reaction (B) is of interest at $\text{pH} < 2.6$, (C) at $2.6 < \text{pH} < 4.6$ and (D) at $\text{pH} > 4.6$. The dissociation constant of reaction (D) has been determined by *e. g.* Euler and Lövgren ⁵ and Lévy ⁶. A large temperature effect has been observed, at 0°C $\text{pK} = 14.0$, at 20°C $\text{pK} = 13.4$ and at 50°C $\text{pK} = 12.5$.

A spectrophotometric study of the equilibrium between methylene glycol and formaldehyde

has been made by Schou ⁷ in a 13 M solution and by Bieber ⁸ in a 0.86 M solution. Schou estimates the equilibrium constant to be $< 1/1250$, and by means of extrapolation from measurements in a temperature range close to 60°C Bieber gets a probable constant value at 20°C of the order 10^{-4} .

THE POLAROGRAPHIC BEHAVIOUR OF FORMALDEHYDE

The polarographic reduction of formaldehyde at low temperatures (25°C) gives a limiting current which is less than that deduced from the concentration polarisation, *i. e.* from the Ilkovič ⁷ equation:

$$\bar{i}_d = 607 n C \sqrt{D} m^{2/3} t_1^{1/6} \quad (1)$$

where $\bar{i}_d$ = diffusion current in μA , n = number of Faradays of electricity required per mole of electrode reaction, C = concentration of the solution of the electroreducible substance in millimoles/l, D = diffusion constant of the same substance in cm^2/sec , m = weight of mercury flowing from the capillary in mg/sec and t_1 = drop time in seconds.

From comparisons between Mn^{2+} and formaldehyde at a high temperature (80°C), where the formaldehyde reduction also follows eq. (1), Jahoda ⁸ found the following electrode reaction:

i. e. $n = 2$. In the same paper Jahoda reports that the temperature coefficient of the limiting current at low temperatures is too large to be explained solely as a function of the change of the diffusion constant of formaldehyde. It was also assumed that the behaviour mentioned could be explained if the rate of the electrode reaction was controlled by the depolymerisation of formaldehyde polymers, *e. g.* in accordance with reaction (A). However, Jahoda's assumption is not in agreement with the findings of Auerbach and Barschall ¹ and Wadano *et al.* ² Later Winkel and Proske ⁹ introduced the idea that only the dehydrated formaldehyde was able to take part in the electrochemical reaction at the electrode surface, and that the equilibrium corresponding to reaction (E) controls the limiting current. This approach has subsequently been applied by Veselý and Brdička ¹⁰ and Bieber and Trümpler ¹¹. Their work has demonstrated that no real concentration polarisation occurs at the electrode surface; the limiting current is determined by the rate of dehydration of methylene glycol when the formaldehyde concentration at the electrode surface decreases in consequence of the electrode reaction. According to Bieber and Trümpler ¹¹, the limiting current is highly dependent on pH and temperature. In buffered solutions the relationship between limiting current and formaldehyde concentration was found to be linear; in unbuffered solutions this was not the

case. Veselý and Brdička¹⁰ found that reaction (E) is subject to acid — base catalysis as defined by Brönsted, *i. e.* the current is not only dependent on pH but also on the activities of the acids and bases present.

Briefly, we have the following picture of the electrode reaction: When the equilibrium between formaldehyde and methylene glycol is disturbed by the reduction at the electrode surface, the aldehyde deficiency is compensated by dehydration of the glycol. If the rate of dehydration is small in comparison with the diffusion of formaldehyde, the latter rate determines the limiting current. If the rate of dehydration is high, the current is still determined by a rate of diffusion, but in this case the diffusion is that of methylene glycol. However, if the rates of dehydration and diffusion are of the same order, both are of importance.

In a simplified mathematical treatment on the polarography of formaldehyde, Veselý and Brdička¹⁰ applied a method introduced by Wiesner¹² for similar electrode processes. This treatment is based on the statistical "half mean path" which can be traversed by a molecule between dehydration and hydration. In accordance with this, the limiting current can be expressed as follows:

$$\bar{i}_k = \frac{0.573 \sqrt{t_1 k_2 k_h}}{1 + 0.573 \sqrt{t_1 k_2 k_h}} \cdot \bar{i}_d^* \quad (2)$$

where $\bar{i}_k$ = limiting current, "catalytic current", t_1 = drop time, k_2 = the rate constant of the dehydration of the methylene glycol under the conditions occurring and k_h = the equilibrium constant of reaction (E). $\bar{i}_d^*$ is the theoretical diffusion current, calculated from eq. (1), assuming that concentration polarisation of the analytical amount of formaldehyde is the current-determining step.

When considering the decrease in methylene glycol concentration at high pH due to a dissociation reaction in accordance with (D), the following equation was given:

$$\bar{i}_k = \frac{b \sqrt{a_{H_2O^+}}}{a_{H_2O^+} + K_a + b \sqrt{a_{H_2O^+}} + b K_a / \sqrt{a_{H_2O^+}}} \cdot \bar{i}_d^* \quad (3)$$

where $b = 0.573 \sqrt{t_1 k_2 k_h}$, K_a = dissociation constant of reaction (D).

Veselý and Brdička used eq. (3) to calculate K_a from experimental data, and found a good agreement with earlier mentioned values.

However, the mathematical treatment reviewed above involves several approximations: a) The non-linearity of the concentration gradient and b) the change of this gradient due to the growth of the mercury drop are neglected. c) The assumption on "half the mean path" is not significant from the theoretical point of view.

In an investigation concerning the catalytic currents in the polarography of some organic acids, *e. g.* pyruvic acid, Koutecký and Brdička¹³ have given a mathematical treatment not involving the approximations a) and c). If we apply this method of treatment to the polarography of formaldehyde we get:

$$\bar{i}_k = \frac{0.81 \sqrt{t_1 k_2 k_h}}{1 + 0.81 \sqrt{t_1 k_2 k_h}} \bar{i}_d^* \quad (4)$$

This is valid if the electrode is regarded as a steady sphere with the same area as the mean area of the dropping electrode. The very small correction for the curved surface of the electrode is, as usual, neglected in this case as well. When the theories are tested on experimental data, eq. (2) and (4) are identical, as the difference in the constants 0.57 and 0.81 only changes the numerical value of the parameter $k_2 \cdot k_h$.

During 1953 rigorous mathematical solutions, valid for several kinds of catalytic currents were given by Koutecký¹⁴⁻¹⁷. A mathematical technique was used that originated from Mejman¹⁸. However, in the case of formaldehyde only a simplified solution was given (Koutecký¹⁷), valid under the same conditions as needed for eq. (2) and (4), i. e. when the gradient layer is very close to the electrode surface. The equation derived is

$$\bar{i}_k = \frac{0.87 \sqrt{t_1 k_2 k_h}}{1 + 0.87 \sqrt{t_1 k_2 k_h}} \bar{i}_d^* \quad (5)$$

In the following a rigorous treatment will be given, avoiding the approximations a), b) and c). The mathematical technique is based on the Mejman-Koutecký method.

THEORETICAL

When considering the influence of the growth of an electrode drop on the concentration gradient in the solution surrounding the drop, we get, in accordance with Ilkovič⁷, the following equation:

$$\left(\frac{\partial C_{\text{HCHO}}}{\partial t} \right)_{\text{diffusion}} = D \frac{\partial^2 C_{\text{HCHO}}}{\partial x^2} + \frac{2x}{3t} \frac{\partial C_{\text{HCHO}}}{\partial x} \quad (6a)$$

where x is the distance from the electrode surface.

Since

$$\left(\frac{\partial C_{\text{HCHO}}}{\partial t} \right)_{\text{catalysis}} = k_2 C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} - k_1 C_{\text{HCHO}} \quad (6b)$$

we obtain

$$\frac{\partial C_{\text{HCHO}}}{\partial t} = D \frac{\partial^2 C_{\text{HCHO}}}{\partial x^2} + \frac{2x}{3t} \frac{\partial C_{\text{HCHO}}}{\partial x} + k_2 C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} - k_1 C_{\text{HCHO}} \quad (7a)$$

and correspondingly:

$$\begin{aligned} \frac{\partial C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}}{\partial t} = D \frac{\partial^2 C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}}{\partial x^2} + \frac{2x}{3t} \frac{\partial C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}}{\partial x} - \\ - k_2 C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} + k_1 C_{\text{HCHO}} \end{aligned} \quad (7b)$$

where k_2 is the dehydration and k_1 the hydration rate constant of reaction (E) and $D \sim D_{\text{HCHO}} \sim D_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}$ (this will be discussed later).

Initial conditions: $t = 0, x > 0$: $C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} = C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}^*$, $C_{\text{HCHO}} = C_{\text{HCHO}}^*$.
Boundary conditions: $t > 0, x = 0$: $C_{\text{HCHO}} = 0$, $(\partial C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} / \partial x) = 0$. (No flux of $\text{HO} \cdot \text{CH}_2 \cdot \text{OH}$ at the electrode surface.)

Introducing:

$$\psi = \text{CHO} \cdot \text{CH}_2 \cdot \text{OH} + \text{CHCHO}, \varphi = \text{CHO} \cdot \text{CH}_2 \cdot \text{OH} - \sigma \cdot \text{CHCHO}, k_2 = \varrho, k_1/k_2 = 1/k_h = \sigma \quad (8)$$

and adding eq. (7a) and (7b), then multiplying eq. (7a) by σ and subtracting from eq. (7b) will give the respective equations:

$$\frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2} + \frac{2x}{3t} \frac{\partial \psi}{\partial x} \quad (9a)$$

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} + \frac{2x}{3t} \frac{\partial \varphi}{\partial x} - \varrho (1 + \sigma) \cdot \varphi \quad (9b)$$

$$\text{Substituting: } l = \varrho \cdot (1 + \sigma), s = x / \sqrt{\frac{12}{7} D t} \text{ and } \chi = l t \quad (10)$$

we have from eq. (9a) and (9b):

$$\frac{\partial^2 \psi}{\partial s^2} + 2s \frac{\partial \psi}{\partial s} - \frac{12}{7} \chi \frac{\partial \psi}{\partial \chi} = 0 \quad (11a)$$

$$\frac{\partial^2 \varphi}{\partial s^2} + 2s \frac{\partial \varphi}{\partial s} - \frac{12}{7} \chi \frac{\partial \varphi}{\partial \chi} = \frac{12}{7} \chi \varphi \quad (11b)$$

Initial conditions: $s \rightarrow \infty, \varphi = 0, \psi = \psi^* = \text{C}^* \text{HO} \cdot \text{CH}_2 \cdot \text{OH} + \text{C}^* \text{HCHO}$, i. e. the analytical formaldehyde concentration of the solution.

Boundary conditions: $s = 0, \varphi = \psi, (\partial \varphi / \partial s) = -\sigma (\partial \psi / \partial s)$;

Eq. (11b) can be transformed into an equation of the (11a) type by means of the substitution $\varphi = \Phi \cdot \exp(-\chi)$. It is assumed that the (11a) type has a solution in the form of a power series:

$$\psi = \sum_i \psi_i(s) \chi^i, \text{ and } \varphi = e^{-\chi} \sum_i \Phi_i(s) \chi^i \quad (12)$$

where ψ_i (and Φ_i) is determined by the equation:

$$\frac{d^2 \psi_i}{ds^2} + 2s \frac{d \psi_i}{ds} - 2\alpha_i \cdot \psi_i = 0 \quad (13)$$

If we assume that

$$K_\alpha = \sum_{j=0}^{\infty} \alpha_j^\alpha \cdot s_j, L_\alpha = \sum_{j=0}^{\infty} c_j^\alpha \cdot s_j + 1 \quad (14)$$

are linear, independent solutions of eq. (13), and $\alpha_0^\alpha = c_0^\alpha = 1$.

$\alpha_{j+2}^\alpha / \alpha_j^\alpha = 2(\alpha - j) / (j + 1)(j + 2), c_{j+2}^\alpha / c_j^\alpha = 2(\alpha - j - 1) / (j + 2)(j + 3)$, and from this: $\lim_{s \rightarrow 0} K_\alpha = 1, \lim_{s \rightarrow 0} L_\alpha = 0, \lim_{s \rightarrow 0} K'_\alpha = 0$ and $\lim_{s \rightarrow 0} L'_\alpha = 1$.

For this the following recurrence equation is obtained:

$$p_\alpha p_{\alpha+1} = 2(\alpha + 1); p_\alpha = \lim_{s \rightarrow \infty} K_\alpha(s) / L_\alpha(s) \quad (15)$$

(p_α can also be expressed as a Γ -function, e. g. for $\alpha = 6/7$ we have

$$p_{6/7} = 2 \Gamma(6 \cdot 1/14 + 1) / \Gamma(6 \cdot 1/14 + 1/2)).$$

From this, and with regard to the initial conditions, we get the solutions of eqs. (11a) and (11b):

$$\psi = \sum_{i=0}^{\infty} \alpha_i (K_{\alpha i} - p_{\alpha i} \cdot L_{\alpha i}) \cdot \chi^i + \psi^* p_\alpha L_\alpha \quad (16a)$$

$$\varphi = e^{-\chi} \sum_{i=0}^{\infty} b_i (K_{\alpha i} - p_{\alpha i} \cdot L_{\alpha i}) \cdot \chi^i \quad (16b)$$

(The initial conditions are fulfilled since $\lim_{s \rightarrow \infty} (K_{ai} - p_{ai} \cdot L_{ai}) = 0$ and $\lim_{s \rightarrow \infty} p_0 \cdot L_0 = 1$, as found when solving eq. (13) for L_0 .)

Remembering that $L_{ai}(0) = 0$ and $K_{ai}(0) = 1$, we get from the boundary conditions:

$$\varphi_{s=0} = e^{-\chi} \sum_{i=0}^{\infty} b_i \cdot \chi^i, \quad \psi_{s=0} = \sum_{i=0}^{\infty} a_i \cdot \chi^i \quad (17)$$

i. e. $\varphi = \psi$ when $s = 0$ gives:

$$\sum_{i=0}^{\infty} b_i \cdot \chi^i = e^{-\chi} \sum_{i=0}^{\infty} a_i \cdot \chi^i = \sum_{i=0}^{\infty} \sum_{j=0}^i \frac{a_j}{(i-j)!} \chi^i \quad (18)$$

The boundary condition $(\partial \varphi / \partial s) = -\sigma (\partial \psi / \partial s)$ when $s = 0$, and

$$\frac{\partial \varphi}{\partial s} = \sum_{i=0}^{\infty} a_i (K'_{ai} - p_{ai} L'_{ai}) \chi^i + \psi^* p_0 L'_0 \quad (19)$$

$$\frac{\partial \varphi}{\partial s} = e^{-\chi} \sum_{i=0}^{\infty} b_i (K'_{ai} - p_{ai} L'_{ai}) \chi^i$$

since $K'_{ai}(0) = 0$ and $L'_{ai}(0) = 1$:

$$\left(\frac{\partial \psi}{\partial s} \right)_{s=0} = - \sum_{i=0}^{\infty} a_i p_{ai} \chi^i + \psi^* p_0 \quad (20)$$

$$\left(\frac{\partial \varphi}{\partial s} \right)_{s=0} = - e^{-\chi} \sum_{i=0}^{\infty} b_i p_{ai} \chi^i$$

Then we have:

$$\frac{1}{\sigma} \sum_{i=0}^{\infty} b_i p_{ai} \chi^i = \psi^* p_0 \sum_{i=0}^{\infty} \frac{\chi^i}{i!} - \sum_{i=0}^{\infty} \sum_{j=0}^i \frac{a_j p_{aj}}{(i-j)!} \chi^i$$

and for the i :th term:

$$\frac{1}{\sigma} b_i p_{ai} = \psi^* \frac{p_0}{i!} - \sum_{j=0}^{i-1} \frac{a_j p_{aj}}{(i-j)!} - a_i p_{ai} \quad (21)$$

Similarly we have:

$$b_i = \sum_{j=0}^{i-1} \frac{a_j}{(i-j)!} + a_i \quad (22)$$

From eqs. (21) and (22) we have:

$$a_i p_{ai} = \frac{\psi^* p_0 \sigma}{(1+\sigma) i!} - \sum_{j=0}^{i-1} \frac{a_j p_{aj}}{(i-j)!} \left(1 + \frac{p_{ai} / p_{aj} - 1}{1+\sigma} \right) \quad (23)$$

Or, when $\sigma \gg 1$:

$$a_i p_{ai} = \frac{\psi^* p_0}{i!} - \sum_{j=0}^{i-1} \frac{a_j p_{aj}}{(i-j)!} \left(1 + \frac{p_{ai} / p_{aj} - 1}{\sigma} \right) \quad (24)$$

The equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \frac{2x}{3t} \frac{\partial c}{\partial x}$$

and the initial and boundary conditions $x > 0, t = 0: C = C^*, x = 0, t > 0: C = 0$ correspond to the conditions of concentration polarisation. As has been shown by Koutecký *et al.*¹⁹ we obtain from this:

$$i_d = -C^* p_0 n F q D \left(\frac{\partial s}{\partial x} \right)_{x=0}$$

(q = the average area of the mercury drop.) Since in accordance with Ilkovič⁷

$$\begin{aligned} i_k &= -n F q D \left(\frac{\partial \text{CHCHO}}{\partial x} \right)_{x=0} \quad \text{we have:} \\ i_k / i_d &= \Omega = (\partial \text{CHCHO} / \partial s)_{s=0} / p_0 \cdot C^* \end{aligned} \quad (25)$$

In accordance with earlier parts of the paper:

$$\psi = \text{CHO} \cdot \text{CH}_2 \cdot \text{OH} + \text{CHCHO}, \quad (\partial \text{CHO} \cdot \text{CH}_2 \cdot \text{OH} / \partial s)_{s=0} = 0$$

and we have: $\Omega = (\partial \psi / \partial s)_{s=0} / p_0 \cdot C^* \text{HCHO}$ (26)

Since $\psi^* = C^* \text{HO} \cdot \text{CH}_2 \cdot \text{OH} + C^* \text{HCHO}$ and $C^* \text{HO} \cdot \text{CH}_2 \cdot \text{OH} = \sigma \cdot C^* \text{HCHO}$

(chemical equilibrium) we obtain:

$$\Omega = 1 + \sigma - \sum_{i=0}^{\infty} \frac{a_i p_{ai}}{p_0 C^* \text{HCHO}} \chi_i \quad (27)$$

Or, on introducing the symbol

$$\varepsilon_i = a_i p_{ai} / p_0 C^* \text{HCHO} \quad (28)$$

$$\Omega = 1 + \sigma - \sum_{i=0}^{\infty} \varepsilon_i \chi_i \quad (29)$$

From this, by means of eq. (23):

$$\varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!} \left(1 + \frac{p_{ai} / p_{aj} - 1}{1 + \sigma} \right) \quad (30)$$

Or, when $\sigma \gg 1$:

$$\varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!} \left(1 + \frac{p_{ai} / p_{aj} - 1}{\sigma} \right) \quad (31)$$

(Since $\Omega = 1$ when $\chi = 0$ we find $\varepsilon_0 = \sigma$.)

However, if we start from the φ -function, we obtain:

$$\Omega = - (\partial \varphi / \partial s)_{s=0} / \sigma p_0 C^* \text{HCHO} \quad (32)$$

and if we write $v_i = b_i p_{ai} / p_0 C^* \text{HCHO}$ we obtain for $\sigma \gg 1$:

$$v_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!} (1 - p_{ai} / p_{aj}) \quad (33)$$

where ε_j is defined in accordance with eq. (31),

$$i. e. \quad \Omega = \frac{1}{\sigma} e^{-\chi} \sum_{i=0}^{\infty} \nu_i \chi^i \quad (34)$$

For small values of ϱ and large values of σ a solution can be obtained as follows: If these conditions are valid, $\text{CHO} \cdot \text{CH}_2 \cdot \text{OH}$ can be regarded as being constant, i. e. $\text{C}^*\text{HO} \cdot \text{CH}_2 \cdot \text{OH}$, and we get:

$$\frac{\partial \text{CHCHO}}{\partial t} = D \frac{\partial^2 \text{CHCHO}}{\partial x^2} + \frac{2x}{3t} \frac{\partial \text{CHCHO}}{\partial x} + \varrho \sigma \left(\frac{\text{C}^*\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}{\sigma} - \text{CHCHO} \right) \quad (35)$$

Initial and boundary conditions: $t = 0, x > 0$: $\text{CHCHO} = \text{C}^*\text{HCHO}$; $t > 0, x = 0$: $\text{CHCHO} = 0$.

Introducing $\text{C}^*\text{HO} \cdot \text{CH}_2 \cdot \text{OH} / \sigma - \text{CHCHO} = \tau$, $\varrho \sigma = l$, ($l = \varrho(1 + \sigma) \sim \varrho \sigma$, $\sigma \gg 1$.)

and $s = x / \sqrt{\frac{12}{7} D t}$, $\chi = l t$:

$$\frac{\partial^2 \tau}{\partial s^2} + 2s \frac{\partial \tau}{\partial s} - \frac{12}{7} \chi \frac{\partial \tau}{\partial \chi} = \frac{12}{7} \chi \tau \quad (36)$$

Initial and boundary conditions: $\chi = 0, s \rightarrow \infty$: $\tau = 0$; $\chi > 0, s = 0$, $\tau = \tau^* = \text{C}^*\text{HO} \cdot \text{CH}_2 \cdot \text{OH} / \sigma$.

In accordance with earlier parts of the paper:

$$\tau = e^{-\chi} \sum_{i=0}^{\infty} a_i (K_{ai} - p_{ai} L_{ai}) \chi^i \quad (37)$$

Here a_i has to be chosen so that the following boundary condition is satisfied:

$$\tau_{s=0} = e^{-\chi} \sum_{i=0}^{\infty} a_i \chi^i = \tau^*$$

Since $K_{ai}(0) = 1$, $L_{ai}(0) = 0$:

$$a_i \chi^i = e^{\chi} \tau^* = \tau^* \sum_{i=0}^{\infty} \frac{\chi^i}{i!}$$

and

$$a_i = \tau^* \frac{1}{i!} \quad (38)$$

$K'_{ai}(0) = 0$ and $L'_{ai}(0) = 1$ gives:

$$\left(\frac{\partial \tau}{\partial s} \right)_{s=0} = -\tau^* e^{-\chi} \sum_{i=0}^{\infty} p_{ai} \frac{\chi^i}{i!}$$

and

$$\Omega = e^{-\chi} \sum_{i=0}^{\infty} \frac{p_{ai}}{p_0} \frac{\chi^i}{i!} \quad (39)$$

Recapitulating, the results of the three different treatments given above are:

$$\text{I. } \Omega = 1 + \sigma - \sum_{i=0}^{\infty} \varepsilon_i \chi^i$$

$$\text{a) } \varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!} \left(1 + \frac{p_{ai}/p_{aj} - 1}{1 + \sigma} \right); \text{ general solution.}$$

$$\text{b) } \varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!} \left(1 + \frac{p_{ai}/p_{aj} - 1}{\sigma} \right); \sigma \gg 1.$$

$$\text{II. } \Omega = \frac{1}{\sigma} e^{-\chi} \sum_{i=0}^{\infty} \nu_i \chi^i$$

$$\nu_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!} (1 - p_{ai}/p_{aj}); \sigma \gg 1$$

$$\text{III. } \Omega = e^{-\chi} \sum_{i=0}^{\infty} \frac{p_{ai}}{p_0} \frac{\chi^i}{i!}; \text{ } \varrho \text{ comparatively small, } \sigma \gg 1.$$

For numerical calculations we need p_{ai} and p_{ai}/p_{aj} . If we compare eqs. (11a) and (13) we find $\alpha = 6/7$. By means of the earlier mentioned F -function and eq. (15) such calculations can be made. For $\varepsilon_i, \sigma \gg 1$, we obtain the following results: $\varepsilon_0 = \sigma$, $\varepsilon_1 = -0.500$, $\varepsilon_2 = 0.0585$, $\varepsilon_3 = -0.0112$, $\varepsilon_4 = 0.00320$, $\varepsilon_5 = -0.00101$, $\varepsilon_6 = 0.000226$ and $\varepsilon_7 = -0.0000491$. Since $\varepsilon_0 = \sigma$ and $\varepsilon_{i \neq 0} \ll \sigma$ we find that $\nu_i \sim \sigma p_{ai}/p_0 i!$; we here have the same factor as in solution III.

$p_{ai}/p_0 i!$ has, for other purposes, been calculated by Koutecký¹⁶. In that paper Koutecký has treated electrode reactions of the type $A \xrightleftharpoons{el} B$, i. e. the reduced compound B is reoxidized to A by an oxidizing agent, which is present in such an excess in the solution that its concentration can be regarded as constant even at the electrode surface. The solution obtained is the same as III, and it can easily be found that this problem and the reduction of formaldehyde under the conditions of III can be regarded as identical processes, even though Koutecký's mathematical treatment was somewhat different. When assuming $\sigma \gg 1$ ($\sigma \sim 10^4$, as will be discussed later), calculations on Ω as a function of χ from I—III give the same results for the χ -values in the range of practical interest; however, the slow convergence of the series makes them less suitable at high χ -values. Calculations under this condition will be discussed later.

Since the function i_k/i_d relates to the change in current during the life of the mercury drop, and in polarography the average current is measured, we have to find

$$\bar{\Omega} = \bar{i}_k / \bar{i}_d$$

where $\bar{i}_k$ and $\bar{i}_d$ are the average currents. The average current is defined by the equation

$$\bar{i} = \frac{1}{t_1} \int_0^{t_1} i \, dt$$

where t_1 is the drop time. (Ilkovič⁷). It is also found from Ilkovič that $i_d = \text{constant} \cdot t^{1/6}$, and then we have:

$$\bar{\Omega} = \frac{\bar{i}_k}{\bar{i}_d} = \frac{\int_0^{t_1} \frac{i_k}{i_d} t^{1/6} dt}{\int_0^{t_1} t^{1/6} dt} \quad (40)$$

and

$$\bar{\Omega} = \frac{\bar{i}_k}{\bar{i}_d} = \frac{7}{6} \chi_1^{-7/6} \int_0^{\chi_1} \Omega \chi^{1/6} d\chi \quad (41)$$

($\chi_1 = l \cdot t_1$)

The $\bar{\Omega}$ value related to III and the Ω function too, can be found in Koutecký¹⁶, where they were calculated for the electrode reaction mentioned previously. In the same paper it was also shown that when $\chi_1 > 10$ the following empirical equation approximates a solution of the $\bar{\Omega}$ function:

$$\bar{\Omega} = 0.812 \chi_1^{1/2} + 1.92 \chi_1^{-7/6} \quad (42)$$

Then, when $\chi_1 \gg 1$, we get the asymptotic solution:

$$\bar{\Omega} = 0.81 \sqrt{\chi_1} \quad (43)$$

For moderate and large χ_1 , three different equations have earlier been derived — (2), (4) and (5) — suitable for calculations. Eq. (5) is an approximation of the expression:

$$\bar{i}_k / \bar{i}_{d \text{ HO} \cdot \text{CH}_3 \cdot \text{OH}} = \sum_{i=0}^{\infty} \omega_i \eta^i, \quad \omega_i = \delta_i / (1 - 3i/7),$$

$$\eta = \sigma / \sqrt{\frac{12}{7} l t_1}, \quad \delta_0 = 1 \text{ and } \delta_{i+1} / \delta_i = -p_{-3} (i+1)/7.$$

or, for moderate values of $l t_1$:

$$\bar{i}_k / \bar{i}_{d \text{ HO} \cdot \text{CH}_3 \cdot \text{OH}} = \sum_{i=1}^{\infty} \beta_i \eta^{-i}, \quad \beta_i = \sqrt{\pi} \gamma_i / 2 (1 + 3i/7),$$

$$\gamma_1 = 1 \text{ and } \gamma_{i+1} / \gamma_i = -p_{3i/7} (\rho \sigma \gg 1, \sigma \gg 1. \text{ Koutecký}^{17})$$

From this we obtain $\beta_1 = 0.62$ and since $\eta^{-1} = \sqrt{\frac{12}{7} t_1 k_2 k_h} \cdot \frac{1}{\sigma}$:

$$\bar{i}_k / \bar{i}_{d \text{ HO} \cdot \text{CH}_3 \cdot \text{OH}} = 0.81 \sqrt{t_1 k_2 k_h} \quad (44)$$

for moderate values of $k_2 k_h$. The same result can be obtained from eq. (4) under the same conditions. Since $\chi_1 = k_2 t_1 / k_h$ and $k_h \bar{i}_{d \text{ HO} \cdot \text{CH}_3 \cdot \text{OH}} = \bar{i}_{d \text{ HCHO}}$ when $\sigma \gg 1$, eq. (43) can be written as eq. (44).

When dealing with formaldehyde we have, as will be shown later in this paper, $\sigma \gg 1$. That is, the functions deduced above, which are valid for small and moderate values of χ_1 , coincide asymptotically at $0.81 \sqrt{t_1 k_2 k_h}$ with the solutions for large values. From this we find that the two functions cover a large range of dehydration rates. For small and moderate values of $t_1 k_2 k_h$ eq. (44) is found to be a better approximation than the function $0.87 \sqrt{t_1 k_2 k_h}$, which is obtained from eq. (5), and when considering the whole range of validity, eq. (4) is probably better than eq. (5), as regards the accuracy. However, it has to be remembered that these equations involve the approximation $D_{\text{HCHO}} \sim D_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}}$; this is not the case with the functions for small values of χ_1 . (The diffusion of $\text{HO} \cdot \text{CH}_2 \cdot \text{OH}$ is negligible, as may be seen from comparisons between eqs. (6a), (6b) and (35) and the solutions corresponding to these equations.) Since the gradient layer at the electrode surface is thin (which can be found from the experimental results given later), the error introduced when neglecting the curvature of the electrode surface seems to be infinitesimal.

As was shown by *e. g.* Veselý and Brdička¹⁰, a pure catalytic current is independent of the height of the mercury column between the level of the mercury in the reservoir and the tip of the capillary. A diffusion current, however, is proportional to the square root of this height. This is the case since:

$$\bar{i}_d = \text{constant} \cdot m^{2/3} t_1^{1/6} \quad \text{and} \quad \bar{i}_k = \text{constant} \cdot m^{2/3} t_1^{2/3}$$

which easily can be derived from eq. (1) and (44).

An analysis of the dependence of the current upon the drop time can be used in order to investigate the electrode reaction; and in the case of formaldehyde we have:

- A. $\bar{i} \cong \bar{i}_d \text{HCHO}$ $\bar{i}$ dependent of the drop time.
- B. $\bar{i}_d \text{HCHO} \ll \bar{i} \ll \bar{i}_d \text{HO} \cdot \text{CH}_2 \cdot \text{OH}$ $\bar{i}$ independent of the drop time.
- C. $\bar{i} \cong \bar{i}_d \text{HO} \cdot \text{CH}_2 \cdot \text{OH}$ $\bar{i}$ dependent of the drop time.

In the case A the limiting current is a function of ρ , σ and t_1 as predicted by eqs. (39) and (41). Since

$$\lim_{\chi_1 \rightarrow 0} \bar{i}_k / \bar{i}_d \text{HCHO} = 1 \quad (45)$$

it is possible to determine σ from the effect of t_1 on the limiting current. For this purpose we can from experimental data plot the function:

$$\bar{i} / m^{2/3} t_1^{1/6} = f(t_1) \quad (46)$$

On extrapolating to $t_1 = 0$, *i. e.* $\chi_1 = 0$, we get, by means of eq. (1), $C_0 \text{HCHO}$, and when the analytical concentration of formaldehyde is known, σ can be calculated. A better accuracy than that of the extrapolation can be obtained by the following method:

Fig. 1. $\bar{i}/\bar{i}_d$ as a function of $f(t_1)/f(t_1/2)$.

We have:

$f(t_1)/f(t_1/2) = (\bar{i}_k/\bar{i}_d)_{t_1}/(\bar{i}_k/\bar{i}_d)_{t_1/2} = \bar{\Omega}(\chi_1)/\bar{\Omega}(\chi_1/2) = g(\chi_1)$
 $g(\chi_1)$ as being a function of χ_1 can be calculated from eqs. (39) and (41). Then $\bar{\Omega}(\chi_1) = (\bar{i}_k/\bar{i}_{d\text{HCHO}})_h$ is obtained from the equations mentioned above, i. e. a function $\bar{i}_k/\bar{i}_{d\text{HCHO}} = h(f(t_1)/f(t_1/2))$ can be deduced. This function is given in Fig. 1.

And from this $\bar{i}_{d\text{HCHO}}$, i. e. both ρ and σ can be found. In case B the limiting current follows eq. (43), in the case C eq. (4) or at very high pH values eq. (3)*. I. e. $\sigma = 1/k_h$ and $\rho = k_2$ can be calculated for the whole range A—C. From this discussion we find that both the equilibrium constant and the dehydration rate constants for the system methylene glycol-formaldehyde can be studied by means of polarography.

In accordance with reaction (F) hydroxyl ions are produced at the electrode surface during the polarographic reduction of formaldehyde. Since reaction (E) is acid-base catalysed, we can assume that in an unbuffered or slightly buffered solution no linear limiting current-formaldehyde concentration curve can be found. That this is the case in unbuffered solutions was shown by Bieber and Trümpler¹¹. Since the hydroxyl ions change the composition and the catalytic properties of the solution surrounding the electrode drop, the change of course depends on the degree of buffering, i. e. the more buffered the solution, the more linear the current-concentration curve. The mathematical analysis of a case involving a moderate degree of buffering seems to be very difficult; for unbuffered solutions a simple, approximate treatment can be given: From eqs. (1) and (43) we have:

$$\bar{i}/C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} m^{2/3} t_1^{1/6} = \text{constant} \cdot \sqrt{t_1 k_2 k_h} \quad (47)$$

* as found from the previous treatment $b = 0.81 \sqrt{t_1 k_2 k_h}$ is to be preferred.

The dehydration rate constant represents the sum of the products of the activity of the catalyst and the catalysing power constant:

$$k_2 = \sum_i k_1 a_i \quad (48)$$

(Vesely and Brdicka¹⁰). For unbuffered solutions we obtain a simplified solution to the problem if we only consider the OH^- concentration. And in such a case:

$$(\bar{i} / C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}} m^{2/3} t_1^{1/6})^2 = \text{constant} \cdot t_1 C_{\text{OH}^-} \quad (49)$$

If the reaction layer is supposed to be very thin, C_{OH^-} , the average concentration of hydroxyl ions in this layer, can be found from eq. (1), and

$$\bar{i} = \text{constant} \cdot (1 / m^{2/3} t_1^{7/6}) (\bar{i} / C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}})^2$$

or, when the capillary characteristics are constant:

$$\bar{i} = \text{constant} \cdot (\bar{i} / C_{\text{HO} \cdot \text{CH}_2 \cdot \text{OH}})^2 \quad (50)$$

This simplified solution is applicable in the range of validity of eq. (43) to solutions which are unbuffered or have a very low degree of buffering. (In the latter case, however, a slight contribution from the buffer substance catalysis can be expected.) As has been shown by Bieber and Trümpler¹¹ the half wave potential of formaldehyde increases with increasing pH. In the case mentioned above more or less skew polarograms can be expected, since the increase in current means an increase in pH.

EXPERIMENTAL

The investigations have been carried out in the following apparatus: In a large beaker, containing 0.1 *M* KCl, a "polarographic cell" is immersed. The solution to be investigated is brought into this cell in such a quantity that the level is above that of the KCl solution. This is done in order to prevent any back flow into the cell through the glass filter disc which separates the cell solution from that of the beaker. The capillary enters the cell by means of a cork stopper, and nitrogen can be bubbled through the solution in the cell, in order to remove dissolved oxygen. The gases can escape through a water trap; the use of this device prevents air from entering the cell. The flow of mercury at the electrode is determined by means of a funnel-fitted capillary, which enters the cell through the stopper. The funnel can be turned into the line of the dropping mercury, and after the required time has elapsed, the funnel is swung clear of the drops. The mercury in the funnel is then sucked up into a flask connected to the capillary outside the cell. The flask is then removed and the mercury washed with distilled water, after which it is dried and weighed. The mercury of the electrode is delivered from a reservoir, connected to the capillary by means of a thick-walled rubber tubing, which has been boiled in NaOH and rigorously rinsed and dried. The reference electrode is a saturated calomel electrode, immersed in the KCl solution. The electrode device is thermostated by means of an infrared lamp outside the beaker, and a contact thermometer and a relay give an on-off regulation of the lamp. The beaker solution is kept in motion by a stirrer. One of the advantages of this thermostating device is that the flow of heat is cut off practically at the same time as the current. By adjusting the distance between the lamp and the beaker the on-off periods can be given a suitable length. The temperature can easily be controlled within 0.03° C. Since the purity of the mercury used is of greatest importance, the mercury was distilled in a vacuum apparatus.

All chemicals in the investigation were of A. R. quality, except the formaldehyde, which was a Merck product of high purity, only containing traces of methanol and formic acid. ($<10^{-4}$ *M* in a solution containing ~380 g/l formaldehyde).

Table 1. Results of the polarographic measurements on formaldehyde.

Supporting electrolyte	$C(\text{HCHO})_a$ mmole/l	u cm	$\bar{i}$ μ A	t sec	m mg/ sec	$\bar{i}$	$\bar{i}$
						$\frac{2/3}{m} \frac{1/6}{t} \text{ C}$	$\frac{2/3}{m} \frac{2/3}{t} \text{ C}$
0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4 pH 6.86, 20° C pH 6.86	12.7	11.1					
		11.1					
		11.1					
		11.1	0.333	2.07	4.55	0.00846	0.00587
		11.0					
		10.9					
		11.0					
		11.0	0.330	3.00	3.05	0.0103	0.00594
	25.4	10.8					
		10.9					
		10.9					
		10.9					
		10.9	0.327	4.01	2.34	0.0116	0.00582
		10.8					
		10.7					
		10.8					
		10.8	0.324	4.93	1.89	0.0128	0.00577
	25.4	11.1					
		11.2					
		11.1					
		11.1	0.666	2.07	4.47	0.00852	0.00592
		11.0					
		11.1					
		11.0					
		11.0	0.660	3.04	3.09	0.0102	0.00585
	25.4	10.9					
		10.9					
		10.9					
		10.9	0.654	4.04	2.30	0.0117	0.00581
	25.4	10.8					
		10.8					
		10.7					
		10.8	0.648	5.02	1.86	0.0129	0.00575

Supporting electrolyte	$C(\text{HCHO})_0$ mmole/l	u cm	$\bar{i}$ μA	t sec	m mg/sec	$\bar{i}$	$\bar{i}$
						$\frac{2/3}{m} \frac{1/6}{t} \text{C}$	$\frac{2/3}{m} \frac{2/3}{t} \text{C}$
0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4 pH 6.86, 20° C	12.7	12.0 11.9 12.0	0.360	2.10	4.55	0.0099	0.00683
		12.0					
		11.8 11.7 11.8	0.354	2.94	3.06	0.0112	0.00656
		11.8					
		11.7 11.7 11.7	0.351	4.25	2.36	0.0136	0.00658
		11.7					
		11.6 11.6 11.5	0.354	5.88	1.74	0.0158	0.00652
		11.6					
	25.4	17.8 17.8 17.8	0.712	2.48	3.44	0.0106	0.00671
		17.8					
		17.7 17.7 17.7	0.710	2.82	3.07	0.0111	0.00662
		17.7					
		17.6 17.6 17.5	0.705	4.21	2.10	0.0135	0.00658
		17.6					
		17.4 17.4 17.4	0.695	5.82	1.45	0.0156	0.00646
		17.4					
pH 6.86							

Supporting electrolyte	C(HCHO) _a mmole/l	u cm	$\bar{i}$ μ A	t sec	m mg/ sec	$\bar{i}$	$\bar{i}$
						$m^{2/3} t^{1/6}$ C	$m^{2/3} t^{2/3}$ C
0.010 M Na ₂ CO ₃ pH 9.54, 20° C	6.35	12.2					
		12.2					
		12.2					
		12.2	0.448	2.75	2.82	0.0326	0.0197
		12.0					
		12.0					
		12.0					
		12.0	0.480	3.41	2.04	0.0382	0.0208
		11.9					
		11.9					
		11.9					
		11.9	0.437	4.80	1.45	0.0444	0.0202
	12.7	12.3					
		12.2					
		12.3	0.985	2.08	3.36	0.0305	0.0210
		12.1					
		12.1					
		12.0					
12.1		0.968	3.11	2.27	0.0366	0.0208	
11.9							
11.9							
11.9							
11.9	0.953	4.88	1.43	0.0455	0.0206		
0.010 M Na ₂ CO ₃ pH 10.44, 20° C	2.03	13.1					
		13.1					
		13.1					
		13.1	0.394	3.39	2.28	0.0920	0.0495
		13.0					
		13.1					
		13.1					
		13.1	0.394	3.82	2.04	0.0966	0.0494
		13.0					
		13.0					
		13.1					
		13.0	0.390	5.12	1.52	0.108	0.0490

Supporting electrolyte	$C(\text{HCHO})_a$ mmole/l	u cm	$\bar{i}$ $\mu\text{ A}$	t sec	m mg/ sec	$\bar{i}$	$\bar{i}$
						$m^{2/3} t^{1/6} \text{ C}$	$m^{2/3} t^{2/3} \text{ C}$
pH 10.46	4.07	19.7 19.6 19.7					
		19.7	0.789	2.78	2.82	0.0824	0.0494
		19.6 19.6 19.6					
		19.6	0.785	3.76	2.08	0.0945	0.0489
		19.6 19.5 19.5					
		19.5	0.780	5.11	1.52	0.109	0.0486
0.010 M Na_2CO_3 pH 10.83, 20° C	0.635	13.3 13.3 13.3					
		13.3	0.160	2.01	3.85	0.0915	0.0645
		13.4 13.4 13.4					
		13.4	0.161	4.10	1.95	0.129	0.0640
		13.3 13.4 13.3					
		13.3	0.160	5.26	1.48	0.147	0.0642
	1.27	10.7 10.6 10.7					
		10.7	0.321	2.06	3.87	0.0915	0.0648
		10.7 10.8 10.8					
		10.8	0.324	4.12	1.94	0.131	0.0645
		10.7 10.7 10.7					
		10.7	0.321	5.30	1.48	0.147	0.0642
pH 10.81	1.27	10.7 10.6 10.7					
		10.7	0.321	2.06	3.87	0.0915	0.0648
		10.7 10.8 10.8					
		10.8	0.324	4.12	1.94	0.131	0.0645
		10.7 10.7 10.7					
		10.7	0.321	5.30	1.48	0.147	0.0642

Supporting electrolyte	$C(\text{HCHO})_a$ mmole/l	u cm	$\bar{i}$ μA	t sec	m mg/sec	$\bar{i}$		$\bar{i}$	
						$m^{2/3}$	$t^{1/6}$	$m^{2/3}$	$t^{2/3}$
0.10 . M NaOH pH $\sim$ 12.7, 20° C	0.127	10.1	0.202	2.81	2.72	0.690	0.410		
		10.1							
		10.0							
		9.6	0.185	4.22	1.69	0.810	0.395		
		9.7							
		9.6							
		8.8	0.177	5.85	1.32	0.880	0.380		
		8.8							
		8.7							
		8.8	0.540	2.78	2.60	0.689	0.412		
		13.5							
		13.4							
		13.5	0.509	4.20	1.65	0.810	0.394		
		12.6							
		12.7							
		12.6	0.481	5.88	1.26	0.870	0.358		
		12.0							
		12.0							
		12.0							
pH $\sim$ 12.7	0.353	13.5							

The technique and chemicals described above were subsequently used in order to investigate the relationship between limiting current, flow of mercury and drop time at $20 \pm 0.03^\circ\text{C}$ for the solution compositions shown in Table 1. The formaldehyde concentration was determined on the stock solution by the method of Blank and Finkenheimer, and a result of $380 \pm 2\text{ g/l}$ was obtained. The buffer substances of the supporting electrolytes were dissolved in a measuring flask, the required amount of formaldehyde added, and the solution diluted to a volume close to the final. By means of HCl or NaOH pH was adjusted. For the pH determinations the glass electrode differential technique described in the Swedish Patent 129833 was applied, and an accuracy of $\pm 0.01\text{ pH}$ obtained. The solutions prepared were kept at 20°C for 24 hours, in order to prevent any influence from reaction (A). Then the pH was rechecked (no changes found), the solutions made up to the final volume with water and poured into the cell. Since the second wave of dissolved oxygen interferes with the formaldehyde wave at low concentrations of the aldehyde, a removal of dissolved oxygen is necessary, especially when a high degree of accuracy is needed. This was achieved by bubbling nitrogen slowly through the solution in the cell; this also provides valuable stirring during the period of temperature stabili-

Fig. 2. Polarogram of formaldehyde, $C(\text{HCHO})_a = 1.27 \times 10^{-3}$, 20°C , supporting electrolyte: $0.010 \text{ M Na}_2\text{CO}_3$, pH 10.81.

sation. Here, of course, we encounter the question of whether the formaldehyde concentration is disturbed during the process, *i. e.* whether any formaldehyde is removed by the nitrogen. However, it was found that during the time of bubbling used in this case, 30 minutes, no change could be found in any of the solutions investigated. It might be assumed that a rapid flow of nitrogen and very long bubbling times have to be avoided, especially at high pH values, since the rate of dehydration is then high. The capillary tubes were carefully cleaned, in order to make the drop cycle completely reproducible. A suitable method for cleaning is to suck concentrated nitric acid through the capillary tube for 10 minutes, then distilled water for 10 minutes, and finally methanol. The suction has to be maintained until the capillary is completely dry.

When evaluating the polarograms the method shown in Fig. 2 has been applied. With the small currents occurring in this case it is necessary to make a correction for the condenser current. The usual method for such a correction has been applied, *i. e.* the line A—A along the average current curve is drawn. The limiting current is then determined by the vertical distance u between the line A—A and the point of inflexion between formaldehyde and supporting electrolyte on the current-voltage curve. (This method has often been used, *e. g.* by Brdička²⁰.) The point of inflexion is found by drawing the mean current curve and the line B—B, and bisecting the part of the line that lies on the curve. The drop times and the flows of mercury were determined at the potential corresponding to the point of inflexion. The polarograms were recorded by means of a LKB type 3 266 polarograph and a Leeds & Northrup Speedomax G recorder. The rate of voltage increase was 0.1 V/min . As a secondary control a Radiometer type PO3g polarograph was used.

RESULTS

The results of the measurements are given in Table 1. The u values of three measurements for each composition of the solution are to be found in the table, the average of these values was used in the further treatments. The treatments involve the calculation of the numerical value of the function

$$\bar{i} / C(\text{HCHO})_a \cdot m^{2/3} t_1^{1/6} \quad (51)$$

i. e. the function (46), but including the analytical amount of formaldehyde ($\sigma \gg 1$). For each composition of the supporting electrolyte measurements

were made on two different aldehyde concentrations; this was done in order to find whether the earlier mentioned influence of the hydroxyl ions produced at the electrode surface is of importance. If this is the case, differences in the functions (51) should be found. Such differences did not occur, as can be seen from Table 1. The influence of the concentration of the buffer in the supporting electrolyte, *i. e.* the acid — base catalysis, is exemplified by the experiments at pH 6.86. In the diagrams 3—5 the expression (51) has been plotted against drop time, and from these curves functions in accordance with eq. (46) and the following discussion have been calculated. The results are given in Table 2,

Table 2. $f(t)/f(t/2)$ from experimental data.

Supporting electrolyte	pH	$C_{(\text{HCHO})_a} \times 10^3$	$f(5)/f(2.5)$
0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4	6.86	12.7 25.4	1.41
0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4	6.86	12.7 25.4	1.41
0.010 M Na_2CO_3	9.54	6.35 12.7	1.42
0.010 M Na_2CO_3	10.44 10.46	2.03 4.07	1.41
0.010 M Na_2CO_3	10.83 10.81	0.635 1.27	1.43
0.10 M NaOH	~12.7	0.127 0.353	1.30

and are in agreement with the postulates in Fig. 1: at pH 9.5, 10.4 and 10.8 the limit 1.4 is obtained. This is not the case at pH 12.7, as might be expected from eq. (3). The results at pH 6.86 are not obviously different from the values at pH 9.5—10.8, *i. e.* the equilibrium constant cannot be determined with a high degree of accuracy. In order to find whether the difference is statistically significant, the following expression has been included in the tables; since this is very suitable for tests on eq. (44):

$$\bar{i} / C_{(\text{HCHO})_a} \cdot m^{2/3} t_1^{2/3}$$

Regression analysis applied to the group pH 9.5, 10.4 and 10.8 and the group pH 6.86 reveals a significant difference. (I. Sandelius, private communication.)

From a diffusion constant of $16 \times 10^{-6} \text{ cm}^2/\text{sec}$ and the fact that $\bar{i}/i_d > 3.5$ (Fig. 1) it can be postulated that $k_h < 3 \times 10^{-4}$, and the value 10^{-4} seems to be very probable when regarding the significant difference mentioned above.

From measurements on the temperature dependence of the formaldehyde limiting current, Bieber and Trümpler¹¹ found an "activation energy" for this

Fig. 3. Relation between function (51) and drop time, 20° C, pH 6.86; $C_{(\text{HCHO})_a} = 12.7 \times 10^{-3}$ (●), 25.4×10^{-3} (○), supporting electrolyte: 0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4 ; $C_{(\text{HCHO})_a} = 12.7 \times 10^{-3}$ (+), 25.4×10^{-3} (x), supporting electrolyte: 0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4 .

Fig. 4. Relation between function (51) and drop time, 20° C, 0.010 M Na_2CO_3 ; $C_{(\text{HCHO})_a} = 6.35 \times 10^{-3}$ (●), 12.7×10^{-3} (x), pH 9.54; $C_{(\text{HCHO})_a} = 2.03 \times 10^{-3}$ (+), pH 10.44; $C_{(\text{HCHO})_a} = 4.07 \times 10^{-3}$ (○), pH 10.46; $C_{(\text{HCHO})_a} = 0.635 \times 10^{-3}$ (Δ), pH 10.83; $C_{(\text{HCHO})_a} = 1.27 \times 10^{-3}$ (▲), pH 10.81.

current of the order 14 kcal. From spectrophotometrical data Bieber⁶ deduced an activation energy of the dehydration of methylene glycol of 14.6 kcal. Since $k_1/k_2 = 1/k_h$ eq. (44) can be written:

$$\bar{i} / \bar{i}_d \text{HO} \cdot \text{CH}_2 \cdot \text{OH} = 0.81 k_h \sqrt{t_1 k_1} \quad (52)$$

From this we find that the hydration rate constant is only slightly dependent on the temperature. This means that measurements at other temperatures would not be more favourable when determining the equilibrium constant, since the change in this constant is chiefly dependent on the change in the dehydration rate. Measurements at 0° C and 50° C have confirmed this. Measurements at low pH values are also of no help, as can be found when examining the results from Bieber and Trümpler²¹; mixtures of methanol and water were also investigated in the present study, but no results of interest were obtained.

Fig. 5. Relation between function (51) and drop time, 20° C, 0.10 M NaOH, pH ~ 12.7; $C_{(\text{HCHO})_a} = 0.127 \times 10^{-3}$ (+), 0.353×10^{-3} (×).

In order to study the hydroxyl ion effect mentioned earlier, measurements were made on the following solutions at pH 9.20 and $20 \pm 0.03^\circ \text{C}$:

$C_{\text{borax}} \times 10^3$: 0.5, 1.0, 2.5, 5.0 and 15.0; $C_{(\text{HCHO})_a} \times 10^2$: 0.5, 1.0, 2.5, 3.5 and 5.0, and at $C_{\text{borax}} = 0$: $C_{(\text{HCHO})_a} \times 10^2$: 1.0, 1.25, 1.50 and 1.75 (29 different solutions). $\text{CHO} \cdot \text{CH}_2 \cdot \text{OH} = C_{(\text{HCHO})_a}$ since $\sigma \gg 1$.

The experimental results are given in Fig. 6, and in unbuffered or slightly buffered solutions the linear relationship required by eq. (50) is found. The

Fig. 6. Hydroxyl ion effect in unbuffered and slightly buffered solutions. $C_{\text{borax}} \times 10^3 = 0$ (×), 0.5 (+), 1.0 (●), 2.5 (Δ), 5.0 (○) and 15.0 (▲).

Fig. 7. Ultraviolet absorption curve of 4.75 M HCHO in 0.05 M KH_2PO_4 + KOH, pH 6.70, 50° C.

Fig. 8. An ultraviolet absorption curve of formic acid.

polarograms were also skew, in accordance with the earlier discussion. In the slightly buffered solutions the contribution of the buffer substance to the catalysis is shown by $(\bar{i} / C_{(\text{HCHO})_a})^2 \neq 0$ when $\bar{i} = 0$.

SPECTROPHOTOMETRICAL INVESTIGATIONS

Measurements in the ultraviolet range were made on formaldehyde in order to check Bieber's ⁶ result, and to find whether trioxymethylene glycol is of any importance at a temperature of 50° C. If such is the case, the extrapolation made by Bieber would be open to criticism.

The instrument used was a Hilger & Watt "Uvispec" spectrophotometer. The lid of the transmission cell housing was removed and replaced by another, with three holes. Through one of these connections hot air ($\sim 60^\circ \text{C}$) from a simple hair-drying device was blown into the housing, through another the air was allowed to escape through a long, curved rubber tubing, preventing any light leakage into the cell housing. Through the third hole a contact thermometer on-off regulates the air flow. The temperature of the cell solutions was measured by a thermo-couple, and the contact thermometer was adjusted so that the cell temperature was maintained at $50 \pm 0.5^\circ \text{C}$. The cells, protected by air-tight rubber caps, were kept in the housing during 20 minutes, which time was found to be enough to give a constant temperature in the cell solutions.

By means of this device the wavelength interval 2 000—3 200 Å was investigated; cell length 2 cm, temperature 50° C, $C_{(\text{HCHO})_a}$: 1.27, 3.18, 3.81, 5.08 and 6.35. The solvent was 0.05 M KH_2PO_4 + KOH, pH 6.70. Fig. 7 is an example of the absorption curves obtained. The curves have absorption bands at 2 300 and 2 800 Å. As postulated by *e. g.* Bieber ⁶ the latter is the

Fig. 9. Relation between maximum extinction and formaldehyde concentration, 0.05 M KH_2PO_4 + KOH, pH 6.70, 50° C.

formaldehyde band. The absorption in the 2 300 Å range is probably due to traces of formic acid present in the formaldehyde solution, the results of an investigation on a formic acid solution at the same pH and temperature makes this assumption very probable, as can be found from Fig. 8. Fig. 9 shows the relation between the maximum extinction in the 2 860 band and the formaldehyde concentration. If we use the extinction coefficient estimated by Bieber⁶ (13.5), and calculate the equilibrium constant at 50° C, we get the value 0.96×10^{-3} . This is in good agreement with the result obtained if Bieber's results are extrapolated to the same temperature: 1.15×10^{-3} . As a linear relationship is found for maximum extinction and formaldehyde concentration, the trioxymethylene glycol from reaction (A) seems to be of no importance. In accordance with Auerbach and Barschall¹, the trioxymethylene glycol fraction increases with increasing concentration, *i. e.* the methylene glycol fraction decreases. Of course, this may be compensated by a change in the extinction coefficient, since at high concentrations there is a solvent mixture of water, methylene glycol and trioxymethylene glycol. However, the probability of such compensation seems to be very low. At 20° C the case mentioned above can not be neglected, *i. e.* the influence of trioxymethylene glycol. From measurements at 20° C, $C_{(HCHO)_a} = 6.35$, and from the equilibrium constant 10^{-4} we find $C_{HO \cdot CH_2 \cdot OH} / \Sigma C_{HCHO} = 0.6$. This result is in agreement with the figure expected from Walker²². However, the result cannot be assigned too much value, in view of the influence of the solution composition on the extinction coefficient and the low accuracy at the low absorption in question. Finally, solutions with $C_{(HCHO)_a} = 6.35$ have been studied at 50° C and pH 4.6, 6.7, 9.2 and 10.8. No pH dependence could be detected.

Table 3. Dehydration rate constants of methylene glycol.

Electrolyte	k_2 20° C
0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4 pH 6.86	$\sim 1.9 \times 10^{-3}$
0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4 pH 6.86	$\sim 1.7 \times 10^{-3}$
0.010 M Na_2CO_3 pH 9.54 pH 10.44 pH 10.88	~ 0.3 ~ 1.8 ~ 2.8

From the above we see that nothing is in disagreement with Bieber's results. It has been shown that the extrapolation to 20° C is possible, since at 50° C no trioxymethylene glycol of practical importance seems to be present, even at high concentrations; Bieber's measurements have been made at a temperature above 50° C and a concentration below that used here. This means that the extrapolated values refer to dilute solutions. And we find that we have several reasons to accept Bieber's result:

$$k_h \cong 10^{-4}$$

A comparison with the polarographic result, $k_h < 3 \times 10^{-4}$, and the result of the spectrophotometrical measurement at 20° C, makes the value given above very probable.

THE RATE OF DEHYDRATION OF METHYLENE GLYCOL

Since $\bar{i} / \bar{i}_d > 3.5$ even at pH 6.9, eq. (44) can be applied to the pH range 7–11 without appreciable error, and the order of the rates of dehydration of methylene glycol can be calculated.

From eq. (44) and $k_h \sim 10^{-4}$ we get:

$$k_2 \text{ 20° C} = 0.7 \times 10^{-3} \cdot \bar{i}^2 / C_{(\text{HCHO})_a}^2 \cdot m^{4/3} t_1^{4/3} \quad (53)$$

The reaction rate constants calculated from eq. (53) and based on the measurements presented in Table 1, can be found in Table 3.

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