ACTA BOLYAI

CONTRIBUTIONS FROM THE FACULTY OF SCIENCE OF THE BOLYAI UNIVERSITY,
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MATEMATIKAI ÉS TERMÉSZETTUDOMÁNYI KARÁNAK KIADVÁNYAI,
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Über einen Integraphen ebener Vektoren

von
S. Borbély
(Aus dem Institut für angewandte Mathematik)

In einer vorigen Arbeit[1] habe ich für die graphische Integration ebener Vektoren einer skalaren Veränderlichen von der Form $S_r^{\varphi}(\alpha)e^{i\alpha}d\alpha = R(\varphi)e^{i\vartheta(\varphi)}$ eine Konstruktion angegeben. Sie ist eine Näherung vierter Ordnung, da die differentiellen Bedingungen denen die vektorische Integralkurve unterworfen ist keine, mit der Rungeschen reellen Integralkonstruktion vergleichbare exacte graphische Auswertung zulässt.

Demgegenüber ist es leicht ein mechanisches System anzugeben, welches diese Bedingungen (abgesehen von den technischen Mängel der Ausführung) prinzipiell erfüllt, und somit die Grundlage zur Konstruktion eines Vektorintegraphen liefert.

In der Abb. 1 sind zwei zugehörige Vektoren des Integranden (*i*) und des Integrals (*I*) dargestellt. Es gilt: $\varkappa + \vartheta = \varphi$ und $\rho = r$ wobei ρ den Krümmungsradius der Integralkurve, und $\varkappa$ den Tangentenwinkel gegenüber dem Radiusvektor R bedeutet. D. h. die Evolute (*E*) der Integralkurve ist dadurch gekennzeichnet, dass sich ihre Bogenlänge als Differenz der entsprechenden Absolutbeträge des Integranden darstellen lässt, wobei alle ihre Tangenten auf die entsprechenden Radiusvektoren des Integranden senkrecht stehn. Falls wir diese letzte Bedingung dahin abändern, dass die Tangenten der Evolute dauernd zu den entsprechenden Radiusvektoren des Integranden parallel sein sollen, die erste Bedingung dagegen aufrecht erhalten, erscheint die Integralkurve um einen rechten Winkel in sich gedreht.

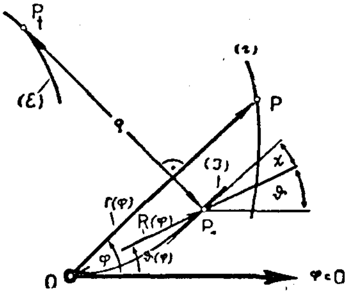

Abb. 1.

Diese beiden Bedingungen sind nun aber durch einen passend geführten Evolutenwagen und durch eine, die Integralkurve (oder eine

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[1] Zeitschrift für angewandte Mathematik und Mechanik, Bd. 22 (1942) S. 273.

ihrer Parallelkurven beschreibende) Evolventenführung auch hinsichtlich der technischen Ausführung leicht erfüllbar.

Der Fahrarm $m\,m$ gehe durch den Koordinatenanfangspunkt 0 (Abb. 2) und sei dort drehbar und verschiebbar gelagert. Mit dem Abtastpunkt P befahren wir die Kurve des Integranden. Durch die beiden Parallelführungen F und F' wird der Fahrarm $M\ M$, durch den die um $-\frac{\pi}{2}$ gedrehte Integralkurve erzeugt wird, parallel zu $m\ m$ geführt. Der Arm M trägt, gegenüber achsialen Vorschiebungen gesichert, ein schweres scharfkantiges Evolventenrad R_t, dessen Rollenebene senkrecht zu M steht. Die scharfe Kante und das Eigengewicht lassen für den Auflagepunkt P_t nur Verschiebungen in der Spurgeraden s der Rad- und Auflageebene zu.

Den zweiten Auflagepunkt des Armes M liefert der Evolutenwagen E, der auf M in Richtung des Armes verschiebbar angeordnet ist. Der Evolutenwagen rollt auf zwei scharfkantigen Rädern R_u auf der Auflageebene, deren gemeinsame Achse senkrecht zu M steht, so dass die Projektion des Achsenmittelpunktes P_u in die Spur von M und der Auflageebene fällt, wobei die Spuren der Radebenen mit der Auflageebene parallel zu M liegen. Dieser Wagen bewirkt also, dass bei einer Bewegung des Armes M der Punkt P_u (falls E auf M festgehalten wird) nur Verschiebungen parallel zu M ausführen kann, welche aber gerade durch R_t verhindert werden. In diesem Falle kann also ein jeder Punkt von M nur Kreise um P_u beschreiben. Wird bei der Bewegung von M der Evolutenwagen auf M selbst verschoben, so beschreibt $\genfrac{}{}{0pt}{}{P_u}{P_t}$ eine Kurve, deren $\genfrac{}{}{0pt}{}{\text{Tangentenrichtung}}{\text{Normalrichtung}}$ daurend in Richtung von M fällt, wobei der Krümmungsradius der Kurve P_t durch die Strecke $|\overline{P_uP_t}|$ dargestellt wird, und die Differenz der Bogenlänge $(s_u)_2 - (s_u)_1$ auf der E Kurve gleich der Differenz von $|\overline{P_uP_t}|_2 - |\overline{P_uP_t}|_1$ ist.

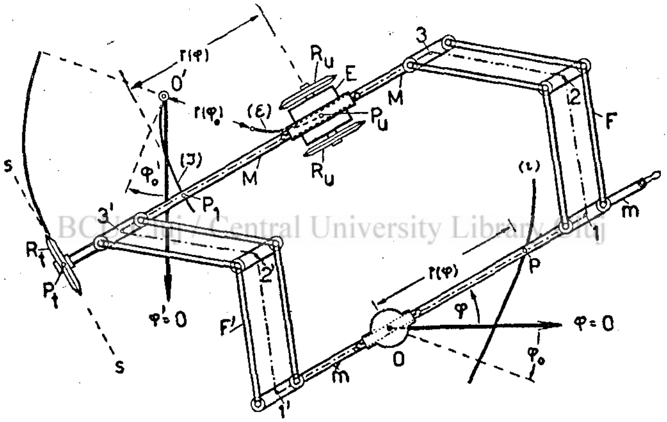

Abb. 2.

Wird E auf M so geführt, dass dauernd $|\overline{P_u P_1}| = r(\varphi)$ sei, so beschreibt der Fahrstift in P_1 die zur Evolvente P_t parallele Integralkurve I, und P_u deren Evolute. Dabei muss selbstverständlich in der Ausgangslage (Anfangswinkel φ_0) der Fahrstift P_1 so eingestellt werden, dass $|\overline{P_u P_1}|_0 = r(\varphi_0)$ sei. Der Anfangspunkt $0'$ des Koordinatensystems der Integralkurve fällt mit $(P_1)_0$ zusammen und die Nullrichtung ist um $-\frac{\pi}{2}$ gegenüber der Richtung $\varphi = 0$ gedreht.

Die Verschiebung des Evolutenwagens kann theoretisch durch zwei undehnbare Fäden bewirkt werden, deren Enden an dem festen Lager in 0, und beiderseits auch am Wagen E befestigt, über die Zapfenpunkte 1, 2, 3, 1′, 2′, 3′ der Parallelführung straff gespannt geführt werden. Die Gesamtlänge des Fadens ist bei jeder Lage des Systems theoretisch konstant, eine Radialverschiebung des Armes m bewirkt also eine gleich grosse Verschiebung von E auf M.

Bei einer praktisch verwertbaren konstruktiven Ausführung des Integraphen sind zwei Schwierigkeiten zu überwinden. Erstens, dass die beiden Fahrarme und die entsprechenden Stangen der Parallelführung stabil gelagert und geführt werden müssen. Weiterhin, da Kreuzungslagen im Allgemeinen vorkommen, müssen die entsprechenden konstruktiven Einheiten in verschiedenen Höhenebenen liegen. Zweitens, dass die Fäden praktisch nicht über die angegebenen Zapfen*punkte*, sondern nur über Rollen geführt werden können, wobei die Gesamtfadenlänge in verschiedenen Lagen des Systems nicht mehr als konstant betrachtet werden kann. Diese Schwierigkeit wird aber durch Einschaltung eines Übertragungsaggregates, dessen Prinzip aus Abb. 3 ersichtlich ist, leicht behoben.

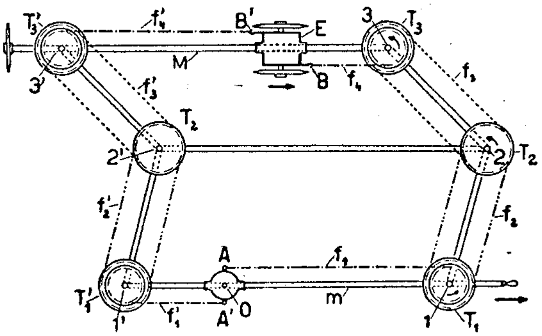

Abb. 3.

Auf den vertikalen Zapfen (Achsen) 1, 1′, 2, ... der Parallelführung, sind die Trommeln T_1, T_1', $T_2, \ldots$ drehbar gelagert. Die an dem festen Lager 0, in den Punkten A, A' befestigte Fäden f_1, f_1' liegen auf T_1, T_1' mit einigen Windungen straff gespannt auf. Die Trommeln $\genfrac{}{}{0pt}{}{T_1}{T_2}$ sind mit $\genfrac{}{}{0pt}{}{T_2}{T_3}$ durch die Fäden $\genfrac{}{}{0pt}{}{f_2}{f_3}$ gekoppelt. Die Trommeln T_3, T_3' arbeiten durch f_4, f_4' auf die Befestigungspunkte B, B' von E entsprechend wie A, A' durch f_1, f_1'

auf T_1, T'_1. Falls also der Abtastarm in radialer Richtung unverrückt bleibt, sich aber um 0 dreht, sind die Trommeln T_1, T'_1 fixiert, T_2, T_3 drehen sich zwar bezüglich den Stangen $\overline{1\,2}$, $\overline{2\,3}, \ldots$ bleiben aber, da sie ja im Prinzip wiederum je ein Gelenkvierek representieren bezüglich den Richtungen $\overline{1\,1'}$, $\overline{2\,2'}$, $\overline{3\,3'}$ in Ruhe, E erleidet keine Verrückung. Bei einer radialen Verschiebung von m wickeln sich die Fäden $\begin{matrix} f_1 \text{ von der} \\ f'_1 \text{ auf die} \end{matrix}$ Trommel $\begin{matrix} T_1 \text{ ab} \\ T'_1 \text{ auf} \end{matrix}$, diese Abwickelung wird auf T_3, T'_3 übertragen, womit E dieselbe radiale Verschiebung erleidet, wie m.

Egy vektorintegráfról

Borbély Samu

(A Matematikai Intézet közleménye)

Összefoglalás

Egy kényszerkapcsolásos éles kerekeken gördülő mechanikai rendszer leírása, mely valós-egyváltozós, sík vektorok integrálgörbéjét (elméletileg exacte) szolgáltatja.

A Deduction of Schrödinger's Equation

by

I. Fényes

(Contribution from the Institute of Theoretical Physics)

In the following paper a method is given by which SCHRÖDINGER's equation can easily be deducted. A basis of our deduction is the HEISENBERG's uncertainty relation. According to the uncertainty principle h (PLANCK's constant) represents an absolute limit to the simultaneous measurement of co-ordinate (q_i) and momentum (p_i). We have the relation

$$\Delta q_i \, \Delta p_i \geqslant \frac{h}{4\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if Δq_i and Δp_i are defined as root-mean squares. In consequence of this it is not possible to characterize the state of a system with the co-ordinates q_i and with the conjugated momenta p_i. Instead of this we will characterize the stationary states with a *probability distribution:* $\rho(q_i)$ in the configurational space. For the sake of simplicity let us confine ourselves to the problem of a single-body. Our consideration, however, will be valid to the problem of n-bodies aswell. In order to determine $\rho(q_i)$ let us investigate the behavior of a *great number* of the systems in question. Let us prepare a statistical survey of the position of the particles in a common space. (For instance in the case of H-atoms we determine the position of each electron in relation to the nucleus.) This statistical ensemble can be taken as a *fictive ideal gas* in which, however, the particles do not come into collision with each other. In a common ideal gas, as a consequence of the collisions, there also exists an uncertainty relation similar to (1):

$$\Delta q_i \, \Delta p_i \geqslant mD \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where D is the diffusional coefficient and m the mass of a particle. The lacking collisions in our fictive case are substituted by the HEISENBERG's uncertainty relation. Thus the complete stream vector, written as complex quantity, is

$$\vec{I} = n\,\vec{v} + iD \operatorname{grad} n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n represents the density of our fictive gas.

Taking into consideration that by the *law of great numbers* the density of our fictive gas, mentioned above, is proportional to the probability distribution of a particle. And so we get instead of (3) by comparing (1) and (2) for the *„stream vector“* of this probability distribution

$$\vec{j} = \rho\vec{v} + \frac{ih}{4\pi m}\,\mathrm{grad}\,\rho \tag{4}$$

Hence the *„density“* of the particle's energy is

$$U = \frac{m|\vec{j}|^2}{2\rho} + V\rho \tag{5}$$

where V is the potential.

We can substitute ρ and $\vec{v}$ by a *single* variable. Let be

$$\vec{v} = \frac{1}{m}\,\mathrm{grad}\,s$$

and

$$\varphi_1 = e^{-\frac{2\pi i}{h}s}$$

Thus

$$\vec{v} = -\frac{h}{2\pi i m}\,\varphi_1^*\,\mathrm{grad}\,\varphi_1$$

where

$$\varphi_1^* = \frac{1}{\varphi_1}$$

Let furtheron be

$$\rho = \varphi_2^2$$

According to these substitutions we get

$$\vec{j} = -\frac{h}{2\pi i m}\left(\varphi_2^2\,\varphi_1^*\,\mathrm{grad}\,\varphi_1 + \varphi_1^*\,\varphi_1\,\varphi_2\,\mathrm{grad}\,\varphi_2\right) \tag{6}$$

where we multiply the second term by $\varphi_1^*\varphi_1 = 1$. From (6) by the substitution

$$\varphi_1\varphi_2 = \psi,\ (\varphi_1^*\varphi_2 = \psi^*,\ \psi^*\psi = \rho) \tag{7}$$

we get

$$\vec{j} = -\frac{h}{2\pi i m}\,\psi^*\,\mathrm{grad}\,\psi \tag{8}$$

and so the *„density“* of a particles energy

$$U = \frac{h^2}{8\pi^2 m}|\nabla\psi|^2 + V|\psi|^2 \tag{9}$$

The total energy has a minimum in a stationary state and so

$$\delta \int U \, d\tau = 0 \quad \ldots \ldots \ldots \ldots \quad (10)$$

where $d\tau$ is the volumen element. In consequence of the meaning of ρ

$$\int \rho \, d\tau = 1 \quad \ldots \ldots \ldots \ldots \quad (11)$$

From (10) and (11) ultimately follows

$$\Delta \psi + \frac{h^2}{8\pi^2 m} (E - V) \psi = 0$$

being SCHRÖDINGER's equation.

A Schrödinger egyenlet levezetése

Fényes Imre

(Az Elméleti Fizikai Intézet közleménye)

Összefoglalás

A kvantummechánikai bizonytalansági reláció (1) és a klasszikus statisztika analóg relációja (2) alapján egy rendszer „valószínűségi eloszlása“ egy ideális gáz sűrűségével azonosítható. Ebből a tényből igen egyszerűen következik a Schrödinger egyenlet. A Born-féle hipotézis szintén következményként szerepel.

Beiträge zum Mechanismus des Kristallwachstums

von

Z. Gyulai

(Institut für Experimental-Physik)

§. 1. Der Mechanismus des Kristallwachstums wird theoretisch von Kossel und Stransky auf Grund molekularer, von Volmer auf Grund thermodymamischer Betrachtungen behandelt. Experimentell kann man noch nicht zwischen den beiden Theorien entscheiden. Gyulai[1] fand, durch einige experimentelle Beobachtungen die Kosselschen Überlegungen unterstützen zu können, aber die Übereinstimmung ist nur rein qualitativ. Kossel rechnet in seinen Betrachtungen mit dem Anlagern von einzelnen Ionen und Ionenschichten an den Kristallkörper, wogegen man in der Wirklichkeit Anlagerungsschichten von ungefähr 10.000 Ionen beobachtet. Diese Ionenschicht überragt diese Dicke, die zu der Theorie als Grundlage dient, viel zu stark. Kossel selbst meint, dass es notwendig sein wird, seine Betrachtungen auf Ionenpaare und auf das mehrfache von Ionenpaaren auszudehnen und dass bei dem Kristallwachstum aus der Lösung auch die Hydratation der Kristalloberflächen in Rechnung zu ziehen ist. Die Beobachtung findet doch zwischen der Wachstumsart und der Theorie gewisse formelle Übereinstimmung und diese Tatsache lässt auf tiefere Zusammenhänge schliessen.

§. 2. Im folgenden wollen wir die theoretischen Überlegungen im Sinne von Kossel ergänzen und die Resultate mit einigen neueren Beobachtungen vergleichen. Diese Ergänzung wollen wir zunächst in bezug auf die Kosselschen Bauelemente durchführen. Kossel rechnet nur mit Ionen, wogegen in der Wirklichkeit diese Bauelemente wenigstens teilweise Ionenpaare sind. Wenn diese Kristallisation aus der Lösung stattfindet, sind die Bauelemente möglicherweise schon Ionenpaare. Das Kristallwachstum fängt erst an, wenn die Lösung schon gestättigt ist. Bei gesättigten Lösungen sind aber die Ionen teilweise nicht dissoziert. Man kann also daran denken, dass in gesättigten Lösungen die nicht dissozierten Ionen — Ionenpaare — diejenigen Elemente sind, welche am Kristallwachstum am ehesten teilnehmen. Wenn sich das Kristallwachstum aus Dampf

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[1] Z. Gyulai: Zeitschr. f. Kristallographie 1935.

vollzieht, dann sind die Bauelemente Ionenpaare — wahrscheinlich auch vielfache von Ionenpaaren — weil nach der allgemeinen Auffassung die Dämpfe von Ionenkristallen keine Elektrizitätsleiter d. h. nicht ionisiert sind. Die Kosselsche Betrachtungsweise erleidet dadurch keine Veränderung; es wird nur die Energie des wiederholbaren Schrittes geändert. Diese Energie ist aber leicht zu berechnen dadurch, dass man die Kosselsche Energiegewinne für zwei Ionen nimmt, welche bei zwei nacheinander folgenden Ioneneinlagerungen gewonnen werden, und davon wird die Vereinigungsenergie von zwei Ionenpaaren abgezogen, weil die Vereinigung von zwei Ionenpaaren schon vorher geschehen war. Durch dieses Vorgehen kann man die Kosselsche Rechnungstechnik auf auch die neue Betrachtungsweise übertragen.

§. 3. Bei den bisherigen Beobachtungen ist der Kosselsche Grundsatz, nämlich, dass das neue Anwachsen vom Schichten seinen Anfang an Ecken und Kanten nimmt, immer in Gültigkeit; in den physikalischen Umständen aber besteht doch ein gewisser Unterschied.

In der Lösung ist die Oberfläche des Kristalls immer hydratisiert. Die Oberfläche, auf welcher eine Ionenschicht gerade fertig geworden ist, wird gleichzeitig auch mit Wassermolekülen überzogen, weil die Kristallfläche mit Wasser umgeben ist. Diese Hydratschicht besteht vielleicht nicht bloss aus Wassermolekülen, sondern möglicherweise aus einem mehr oder weniger geordneten System von Wassermolekülen und Ionen oder Ionenpaaren. Dieses System bildet an der Oberfläche eine ziemlich stabile Schicht. Beim Kristallisieren aus Dampf dürfte diese Oberflächenschicht viel weniger bedeutungsvoll sein. In diesem Falle dürfte nur eine Oxygenschicht im Betracht kommen. Über diese Oxygenschicht bei 800 C^0 Grad Temperatur lässt sich nichts aussagen, höchstens etwa soviel, dass wegen der hohen Temperatur diese Oxigenschicht dem Kristallwachstum gegenüber weniger behinderlich sein dürfte, als eine Hydratschicht. Die Kosselschen Überlegungen gelten für Systeme von dem Typ Kristall-Vakuum. Für diesen Fall gibt es meines Wissens bis jetzt keine experimentellen Beobachtungen.

§. 4. Kossel behandelt das Kristallwachstum als einen sehr langsamen Vorgang. Die beobachteten langsamsten Fälle [1] sind noch immer zu rasch, und die von Gyulai beobachteten Fälle beziehen sich absichtlich auf rasches Wachstum. Gyulai macht schon in seiner ersten Publikation darauf aufmerksam, es sei nicht unmöglich, dass das ausscheidende Material schon unmittelbar vor der Ausscheidung in halbgeordnetem Zustand vorhanden sein sollte. Es ist nämlich für den anschaulich denkenden Beobachter sehr schwer sich vorzustellen, dass die geordnete Ausscheidung so rasch vor sich gehen könnte, wie es beobachtet wird. Es ist also nötig, die Möglichkeit einer solchen vorhergehenden Ordnung zu überlegen. Diese Überlegung ist auch deshalb notwendig, weil in der Literatur Bemerkungen geäussert wurden,[2] welche die Richtigkeit der Kosselschen molekularkinetischen Betrachtungsweise überhaupt in Frage stellten. Wir wollen

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[1] Spangenberg und Neuhaus.

[2] W. Kleber; Kolloidzeitschrift. 94.1941-39. und ebenda D. Balarew: 96.1941.—23.

also hier den von Kossel aufgestellten idealisierten Fall und die experimentellen realen Verhältnisse mit der Hilfe einiger eigenen Betrachtungen zu überbrücken trachten.

Wir wollen also den einfachsten beobachteten Fall hier nochmals in Betracht ziehen. Nehmen wir an, ein Tropfen von NaCl-Lösung befinde sich im Verdampfen, und im Tropfen sei ein Kristall im Wachsen begriffen. An der Oberfläche entweichen Wassermoleküle und die freiwerdenden Ionen verteilen sich im Inneren der Lösung durch Diffusion gleichmässig. Es sei dieser Vorgang stationär. Weil die Lösung übersättigt ist, ist es nicht ausgeschlossen, dass einige Ionen sich paarweise zu neutralen Molekülen vereinigen.

Die Beobachtung[1] zeigt, dass sich auf einmal auch eine Schicht von 0,001 $^m/_m$ Dicke bilden kann. Man kann gewöhnlich nur einen kleinen Ausschnitt aus der Oberfläche des Kristalls beobachten, wobei die Ausscheidung nach Kossels[2] Voraussage pulsierend geschieht. Die ausgeschiedene NaCl-Masse — 0 001 $^m/_m$ dick — würde in der Lösung bei gleichmässiger Verteilung eine 7-mal dickere Schicht ausfüllen. Wenn man aber bedenkt, dass nur diejenigen Ionen ausscheiden können, welche über die Sättigungsgrenze die Übersättigung verursachen, so füllen die ausgeschiedenen Ionen in der Lösung eine viel dickere Schicht. Man kann sich sehr schwer vorstellen, dass die ausscheidenden Ionen durch Diffusion im Augenblick der Ausscheidung bis zur Kristalloberfläche plötzlich einen so langen Weg zurücklegen könnten.

Diese Überlegung war es, welche schon in der ersten Publikation auf einen vorher vorhandenen halborientierten Zustand schliessen liess. In den folgenden Zeilen wollen wir die Wahrscheinlichkeit dieses Gedankens mit Hilfe noch weiterer Annahmen bekräftigen.

Die Ionen des Kristalls bringen über die Oberflächenschicht hinaus ein elektrisches Feld zustande, wie das Hirschel[3] nach der Methode von Madelung ausgerechnet hat. Nach dieser Rechnung lässt sich die elektrische Feldstärke als Funktion des Abstandes von der Kristalloberfläche mit Hilfe folgender Formel ausdrücken:

$$E \cong \frac{e}{a^2} z\pi \cdot 16 \cdot e^{-2\pi\sqrt{2}\cdot\frac{z}{a}} \, ,$$

wo e das elektrische Elementarquantum, a die Gitterkonstante, z den Abstand von der Oberfläche bedeutet. Diese Feldstärke reicht also über die Oberfläche hinaus, und sie nimmt mit zunehmendem Abstand sehr stark ab, kann aber in unmittelbarer Nähe bedeutend werden. Die Feldstärke wird infolge der hohen Dielektrizitätskonstante des Wassers bedeutend erhöht.

Wir wollen uns nun überlegen, was für Wirkungen diese elektrische Feldstärke in der Nähe der Oberfläche zustande bringen kann. In der Lösung sollen auch Moleküle vorhanden sein, weil die Lösung gesättigt

[1] Gyulai: Zeitschr. für Kristallographie 1935.
[2] Kossel: Leipziger Vorträge. 1928.
[3] Hirschel: Phys. Zs. 1921.

ist. In der Nähe der Kristalloberfläche trachten sich diese NaCl-Moleküle, d. h. NaCl-Dipole, unter der Wirkung der elektrischen Feldstärke senkrecht auf die Kristalloberfläche zu stellen. Es ist möglich, dass diese Dipole infolge ihrer Dipolkräfte so aufeinander wirken, dass eine geregelte Ordnung umso leichter zu Stande kommt. Die elektrische Feldstärke, welche nach aussen fällt, übt auf die Dipole eine Anziehungskraft aus. Infolgedessen werden die Moleküle in der Oberflächennähe verdichtet. Die Moleküle wandern also von den entfernteren Teilen der Lösung gegen die Oberfläche. Es entsteht also in der unmittelbaren Nähe der Kristalloberfläche eine gewisse Ordnung der NaCl-Ionenpaare. Die Dichte der NaCl-Moleküle wird also in dieser Schicht grösser als sonst in der Lösung. In dieser Oberflächenschicht werden auch Wassermoleküle vorhanden sein, aber Wassermoleküle sind auch Dipole und infolgedessen kann man annehmen, dass möglicherweise auch diese Wasserdipole an der Ordnung dieser hypotetischen Oberflächenschicht teilnehmen. Diese Ordnung wird durch die Wärmebewegung der Moleküle gestört. Diese störende Wirkung der Wärmebewegung gegen die ordnende Kraft dürfte als Ausgangspunkt für eine matematische Behandlung des Problems dienen. Die Ausbildung dieser Schicht braucht eine gewisse Zeit, und hängt von der Temperatur und von dem Grad der Übersättigung ab.

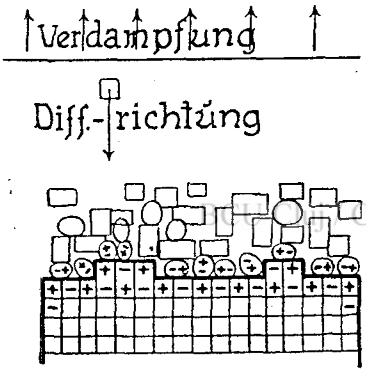

Fig. 1. Schematisches Bild des halbgeordneten Zustandes an der Kristalloberfläche.

Nach diesen Überlegungen können wir wirklich an der unmittelbaren Nähe der Krisstallfläche eine Lösungsschicht annehmen, in welcher die NaCl-Moleküle gewissermassen geordnet und dichter vorhanden sind. Siehe Fig. 1. Die experimentelle Prüfung dieser halbwegs geordneten Lösungsschicht wäre erwünscht und dürfte auch nicht so schwer sein.

§. 5. Wir wollen nun weiter gehen. Die Verteilung der elektrischen Feldstärke um den Kristall ist so, dass diese um die Kanten und Ecken noch grösser ist als über die Flächen. Infolgedessen wird die Anziehungskraft auf die NaCl-Moleküle und infolgedessen auch die Ordnung um die Kanten und Ecken der NaCl-Dipole grösser. Diese geordneten Dipole — welche Ordnung teilweise der Kristallordnung ähnlich sein wird, — werden nach der Formel von Madelung ihrerseits wieder zu der elektrischen Feldstärke beitragen und infolgedessen werden die NaCl-Moleküle in der Nähe von Kanten und Ecken noch dichter gelagert sein. Man kann also erwarten, dass, wo die Dichte der NaCl-Moleküle die grösste und der vorhandene halbgeregelte Zustand der beste ist, — also an den Ecken und Kanten — die NaCl-Moleküle die an der Oberläche sitzenden Wassermoleküle am leichtesten verdrängen können. Wenn einmal in einem Punkt der vorhandenen halbgeordneten Schicht die NaCl-Moleküle ihre stabile Lage an der Kristalloberfläche erhalten, geht dieser Vorgang in der

Schicht von Punkt zu Punkt weiter. Kommt in der Schicht irgendeine Art Hindernis vor, wodurch dieser Vorgang gestört wird, hört das weitere Anlagern der NaCl-Moleküle auf, bis eine neue Gelegenheit zum weiteren Anlagern kommt. Wenn diese nicht kommt, kann ein neuer Kern entstehen, wie man es immer beobachtet, dass in der Nähe eines Kristalls sehr leicht neue Kerne entstehen.[1] Man kann sogar die schon lang beobachtete Tatsache, dass Kerne überhaupt an kleinen Fremdkörpern (Staubkörner, u. s. w.) leicht entstehen, in dem Sinne erklären, dass in der Nähe eines Staubkornes eine Art Anziehungs- und ordnende Kräfte auf die NaCl-Moleküle wirksam sind.

Wenn also der Vorgang einmal in einem Punkt seinen Anfang genommen hat, spielt er sich mit grosser Schnelligkeit ab, der ganze Vorrat an NaCl-Molekülen setzt sich also an den Kristall als eine neue angewachsene Schicht. Diese Schichten sind es, welche man im Mikroskop beobachten kann. Die Oberfläche wird natürlich wieder mit Wassermolekülen überzogen und der Vorgang fängt von neuem an. Aus den Beobachtungen wissen wir, dass die Wachstumsgeschwindigkeit nicht gleichmässig ist, einzelne Individuen wachsen in einer Richtung sehr langsam oder sehr schnell: manchmal wachsen einzelne Säulen in der Längsrichtung sehr schnell. Es wirken hier gewiss noch sekundäre Umstände mit. Wie man sieht, geschieht das Wachstum des Kristalls — nach Kossels Ausdruckweise — pulsierend, aber es setzt sich auf einmal nicht eine einzige Ionenschicht auf den Mutterkristall, sondern eine dickere Schicht. Der Grund des pulsationsartigen Wachsens ist urprünglich der Kosselsche Gedanke, nur modifiziert in seiner Auswirkung. Kossels Grundgedanke war, dass an den Ecken der Energiegewinn am grössten ist. In unserer Betrachtung ist die Austrahlang der elektrischen Feldstärke an den Ecken am grössten und infolgedessen die Moleküldichte und die Dicke der halbwegs geordneten Schicht auch, und der Vorgang des Anwachsens nimmt hier seinen Aufgang. Der Kosselsche idealisierte Fall ist also hier der Wirklichkeit angepasst, also die Kluft zwischen dem Ideallfall und Wirklichkeit überbrückt so, dass das von Kossel vorhergesagte pulsationsartige Wachsen auch in der der Wirklichkeit angepassten Überlegung begründet bleibt.

Die Diffasionsmöglichkeiten haben wir hier weiter nicht berücksichtigt, aber zu den Ecken geht die Diffusion aus einem grösseren Raum vor, infolgedessen kann sich dort diese halbgeordnete Schicht früher ausbilden. Auf diese Möglichkeit weist auch diese Tatsache hin, dass in der Nähe der Ecken auch neue Kerne leichter gebildet werden. Diese Tatsache beobachtet auch Lengyel,[2] bei seinen Spherokristallen. Er hat durch ausserordentlich rasches Verdampfen aus Lösungen Kristalle wachsen lassen. Diese Kristalle nehmen alle ihren Anfang aus einem Punkt. Wenn sich also in einem Punkt schon ein Kristallkern gebildet hat, bilden sich dort sehr rasch viele neue Kerne.

§. 6 Der Vorgang des Kristallwachstums spielt sich im Dampf auch ungefähr in der vorher geschilderten Weise ab. Die Oberfläche ist wahr-

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[1] l. c. Z. Gyulai 1935.

[2] Lengyel: Spherokristalle, Zeitschr. f. Kristallographie. 1937.

scheinlich viel weniger mit einer fremden Schicht überzogen. Die Temperatur ist doch 800 C°. Im Dampfraum treten sehr intensive Luftströmungen auf, aber in der unmittelbaren Nähe ($10^{-3}\ {}^{m}/_{m}$) der Oberfläche sind diese Strömungen schon wegen der Reibung schwach, so dass man wenigsten an gewissen Stellen von diesen absehen kann. Im Dampfraum ist es also auch möglich, dass eine Schicht ausgebildet wird, weil die Kräfte hier auch vorhanden sind. Diese halbgeordnete NaCl-Molekülschicht wächst dann in einem Akt zu dem Kristall an. Dass dieser Vorgang auch im Dampfraum zu verwirklichen ist, zeigt die geschichtete Struktur der in Dampf gebildeten Kristalle. Ich muss hier auf meine Kristallisationsarbeit von 1944[1] verweisen, wo reiches Bildmaterial vorhanden ist. Dass die Ecken auch bei den aus Dampf gebildeten Kristallen eine Sonderrolle spielen, sieht man aus meiner Kristallisationsarbeit aus dem Jahre 1935. Die Beweglichkeit der Ionen oder Molekülen wird durch die hohe Temperatur möglich gemacht.

Bei Kristallwachstum aus Lösungen wird die Beweglichkeit der Ionen durch die Lösung ermöglicht. In der hypotetischen halbgeordneten Schicht, welche schon nicht als übersättigte Lösung, sondern als eine Art neue Phase gelten kann, sind auch Wassermolekel vorhanden, welche die Struktur genügend auflockern. Die letzte Phase der Kristallisation besteht also eben darin, dass die Ionen die fremden Wassermolekel aus den Zwischenräumen herausdrücken, und sie ihre endgültige regelmässige Gitterlage aufnehmen.

§. 7. Das theoretische Ergebnis, dass eine reguläre Ionen-Kristallfläche um sich ein elektrisches Feld erzeugt, wird auf die von Kossel entwickelten Gedanken des Kristalwachstums angewendet. Es werden qualitativ folgende Resultate abgeleitet:

1. In der Nähe einer Kristalloberfläche bilden Ionen und NaCl-Moleküle eine halbwegs geordnete Struktur. Die Wirkung an Ecken und Kanten ist grösser, so dass das Anlagern an den Mutterkristall an den Ecken und Kanten ihren Anfang nimmt.
2. Die halbwegs geordnete Dipolschicht selbst trägt zu der ordnenden Feldstärke bei.
3. Für die Dicke dieser kritischen Schicht ist die Feldstärke, die Temperaturbewegung der Moleküle und die Verdampfungeschwindigkeit der Lösung massgebend.
4. Diese Überlegung kann man auch auf den Fall des Kristallwachstums aus dem Dampf anwenden.

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[1] Z. Gyulai: Pohlscher Festband 1944.

Adalékok a kristálynövekedés mechanizmusához

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Összefoglalás

A Kossel-féle molekuláris szemlélődés igen áttekinthető képet ad a kristálynövekedés egyes pontjairól. Az elmélet azonban több ellenzőre is talált. Igy Balarew azt állítja, hogy semmi igaz sincs benne. Ezzel szemben egyes megfigyelhető jelenségek formailag igazolták Kosselt,[1] bár a Kossel-féle elméleti ideális eset — egyes ionok — és a megfigyelhető rétegvastagság — 10.000 ion között tényleg tág tér van. Szerző itt felhasználja Hirschelnek a Madelung módszere szerint levezetett formuláját, amely szerint a kristály maga körül elektromos teret hoz létre. Az elektromos tér:

$$E \backsimeq \frac{e}{a^2} z\pi \cdot 16 \cdot e^{-z\pi\sqrt{z}\cdot\frac{x}{a}}$$

Ennek az elektromos térnek a felhasználásával el lehet képzelni azt, hogy a kristályfelület közvetlen közelében NaCl-molekulák félig elrendezett állapotban, egyes vizmolekulákkal együtt, mintegy folytatását képezik a kristályrácsnak. Ez az elrendezettség nagyobb az éleken és legnagyobb a csucsokon. Igy a teljes szabályos elrendeződés a csucsokon indul meg. Ebben a félig elrendezett rétegben a NaCl-molekulák sűrűsége nagyobb mint az oldatban és így a diffuzió lassuságából következő nehézségek is meg vannak oldva.

Ezzel az elgondolással a Kossel-féle ideális eset és a valóságos lefolyása a kristályosodás jelenségének olyan áthidalást nyert, amelyben a Kossel-féle fontos következtetések formailag megmaradnak.

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[1] Gyulai: Zeitschr. f. Kristallographie. 1935.

On the Asymmetry of Electrodes of the Second Class

by

L. Imre and F. Sarusi

(Contribution from the Institute of General and Physical Chemistry)

INTRODUCTION

In order to understand the thermodynamic properties of chemical systems composed of more than one pure substances, one may have a peculier interest in studying the solutions of extreme dilution, especially in view of the very simple behaviour of such solutions as ideal mixtures. On the other hand, such systems often seem, for the moment, rather „abnormal", because of the non-validity of the laws applied for solutions of common concentrations. So it could be shown by the senior author[1] that the electrochemical potential values on the boundary of very diluted ion solutions and polar crystall lattices do not always hold for Nernst's general formula concerning the electrode potential values. This statement could be made by studying, in general, the connexion between the adsorption phenomena and the electrode function on the surface of such crystalls.

The surface phenomena of the mentioned kind are characterised by the fact that the affinities to the surface, of the cations and anions, are in general not equivalent with oneanother, i. e. the adsorption isotherms of the two sorts of ions have a certain asymmetry, concerning both their form and arrangement, with respect to the saturated solution of the adsorbent crystall as starting solution. The asymmetry appears also in the so called self-adsorption-systems (made up of a crystall and a solution of one sort of its ions), both in the true adsorption and the exchange adsorption (this latter being easily detected by the method of the radioactive indicators), to an equal measure. The asymmetry in the adsorption of the two kinds of ions results in a specific electrical surface charge, characteristic of the crystall, and so it may be expected that the same asymmetry manifests itself also in the electrochemical potential values of the crystall as electrode of second kind, being immersed once into the

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[1] L. Imre: Múzeumi Füzetek, Kolozsvár (Cluj) 1943., I, No. 5.

solution of the one sort of its constituent ions, and then into the solution (with the same concentration) of the other sort of its ions.

The author in his cited work has investigated this question only with respect to the silver chloride electrode, immersed into Ag^+ and Cl^--ion solutions, having demonstrated that a causal connexion exists between the adsorption and the electrode function, wich can be expressed also in a strict mathematical manner. In the mean time further experiments have been carried out, in the course of which the connexion of the two phenomena (adsorption and electrode function) could be disclosed more precisely, and now it seems possible, based upon our theoretical and experimental investigations, to discuss in more details the necessity of confining within limits the validity of the NERNST formula dealing with electrode potential values.

A.) EXPERIMENTAL PROOF OF THE CAUSAL CONNECTION BETWEEN ION ADSORPTION AND ELECTRODE FUNCTION

In the preliminary investigations, mentioned above, a fused silver chloride wedge played the role of the electrode. But, apart from the fact that fusing may somewhat change the surface of the electrode substance, this method could not taken into account with respect to materials of very high melting point, such as e. g. the very little soluble salts of the alcali earth metals. On the other hand, these salts nearly suggest themselves for studying the problem, as far as the adsorption on the surface of their microcristalline modifications can easily be measured. Fortunately, some of these substances occur also in natural minerals, and in such a pure state, too, that they can be used for electrode materials. Finally, most of the electrodes, to be accounted for below, have been produced also by electrolysis, e. g. the silver iodide in such a way that a potassium iodide solution has been electrolysed with a silver-plated platinum anode. No material differences could be detected in the behaviour of electrodes of the same substances, produced in different ways.

The electrode potentials have troughout been measured with the aid of a quadrant electrometer (in view of the very high resistance, e. g., of the natural crystall electrodes), in such a way that the solution in pure distilled water of the respective electrode material has been taken for ground solution. Therefore, the figures communicated in the Tables 1.—6. below (the values of $\varepsilon - \varepsilon_0$) denote the electromotive forces of such concentration cells, in which one of the electrolyte concentrations corresponds to the pure watery solution of the electrode substances. The diffusion potentials have been eliminated in the usual way, by inserting a potassium nitrate solution between the two component solutions of the concentration element.

The adsorption measurements have been carried out with the aid of microanalytical methods or with the method of the electrical conductometry, yet when it was possible, also with the method of the radioactive indicators. These procedures having been described in previous works of one of the authors (L. I.), may not taken a detailled notice of here.

TABLE 1.

The electrode potential of the silver crystall electrode, relative to solutions of its constituent ions of various concentrations. Temp.: 20 C°.

Electrolyte-solvent	Concentration of Ag^+-ion	$\varepsilon - \varepsilon_0$ in milli-volts	Electrolyte-solvent	Concentration of Cl^--ion	$\varepsilon - \varepsilon_0$ in milli-volts
pure wat. sol.	1·06. 10^{-5} norm.	0·00	pure wat. sol.	1·06. 10^{-5} norm.	0·00
0·85. 10^{-6}n. $AgNO_3$	1·092 „ „	+ 1·19	—	—	—
1·0 „ „	1·10 „ „	+ 4·74	1. 10^{-6}n. HCl	1·10. 10^{-5} norm.	— 2·96
2·0 „ „	1·153 „ „	+ 5·62	2. „ „	1·153 „ „	— 3.8
3 0 „ „	1·21 „ „	+ 6·5	3. „ „	1·21 „ „	— 5·9
5·0 „ „	1·32 „ „	+ 9·4	5. „ „	1·32 „ „	— 7·9
8·0 „ „	1 52 „ „	+ 12·3	8. „ „	1·52 „ „	— 10·7
1·0 10^{-5}n. „	1·66 „ „	+ 15·8	1. 10^{-5}n. „	1·66 „ „	— 13·4
2·0 „ „	2·44 „ „	+ 22·9	2. „ „	2·44 „ „	— 21·0
4·0 „ „	4·27 „ „	+ 35·6	4. „ „	4·27 „ „	— 33·6
8 0 „ „	8·10 „ „	+ 50·4	8. „ „	8·10 „ „	— 47·4
1·0. 10^{-4}n. „	10·02 „ „	+ 55·4	1·0. 10^{-4}n. „	10·02 „ „	— 53·4
5·0 „ „	50·01 „ „	+ 93·8	5. „ „	50·01 „ „	— 91·3
1·0. 10^{-3}n. „	100·0 „ „	+ 110·6	1·0. 10^{-3}n. „	100·0 „ „	— 107·8

TABLE 2.

The potential of the silver bromide, relative to the solutions of its ions, at 20 C°.

Electrolite-solvent	Concentration of Ag^+-ion	$\varepsilon - \varepsilon_0$ in milli-volts	Electrolyte-solvent	Concentration of Cl^--ion;	$\varepsilon - \varepsilon_0$ in milli-volts
pure wat. sol.	0·47. 10^{-6} norm.	0·00	pure wat. sol.	9·47. 16^{-6} norm.	0·00
1. 10^{-7}n. $AgNO_3$	5·0 „ „	+ 5·3	1. 10^{-7}n. KBr	5·0 „ „	— 2·7
3. „ „	6·21 „ „	+ 13·0	3. „ „	6.21 „ „	— 7·6
5. „ „	7·62 „ „	+ 18·4	5. „ „	7.62 „ „	— 13·6
7. „ „	9·18 „ „	+ 22·9	7. „ „	9.18 „ „	— 17·2
1. 10^{-6}n. „	11·71 „ „	+ 30·3	1. 10^{-6}n. „	11.71 „ „	— 24·3
2. „ „	20·95 „ „	+ 44·5	2. „ „	20.95 „ „	— 38·6
4. „ „	40·49 „ „	+ 60·9	4. „ „	40.99 „ „	— 55·4
1. 10^{-5}n. „	100·0 „ „	+ 84·6	1. 10^{-5}n. „	100.0 „ „	— 78·4

TABLE 3.

The potential of the silver iodide crystall electrode, relative to solutions of its constituent ions of various concentrations. Temperatur: 20 C°.

Electrolyte-solvent	Concentration of Ag$^+$-ion	$\epsilon - \epsilon_0$ in milli-volts	Electrolyte-solvent	Concentration of J$^-$-ion	$(\epsilon - \epsilon_0)$ in milli-volts
pure wat. sol.	0.85. 10^{-8} norm	0.00	pure wat. sol.	0·85. 10^{-8} norm.	0·00
4. 10^{-9}n. AgNO$_3$	1.80 „ „	$\overset{ca}{+}$ 12·5	4. 10^{-9}n. KJ	1·80 „ „	— 3·3
7. „ „	1.97 „ „	$\overset{ca}{+}$ 15·5	7. „ „	1·97 „ „	— 5·8
1. 10^{-8}n. „	2.16 „ „	+ 18·4	1. 10^{-8}n. „	2·16 „ „	— 7·9
3. „ „	3.68 „ „	+ 31·8	3. „ „	3·68 „ „	— 21·6
5. „ „	5.46 „ „	+ 42·7	5. „ „	5·46 „ „	— 31·5
7. „ „	7.34 „ „	+ 49·6	7. „ „	7·34 „ „	— 38·2
1. 10^{-7}n. „	10.1 „ „	+ 60·4	1. 10^{-7}n. „	10·1 „ „	— 46·5
5. „ „	50 „ „	+ 100·8	5. „ „	50 „ „	— 87·7
5. 10^{-6}n. „	500 „ „	+ 160	5. 10^{-6}n. „	500 „ „	— 145·0

TABLE 4.

The potential of lead chromate crystall electrode, relative to solutions of its constituent ions of various concentrations. Temperatur: 20 C°.

Electrolyte-solvent	Concentration of Pb^{++}-ion	$\epsilon - \epsilon_0$ (milli-volts)	Electrolyte-solvent	Concentration of CrO$_4^{--}$-ion	$\epsilon - \epsilon_0$ (milli-volts)
pure wat. sol.	2·27. 10^{-7} norm.	0·00	pure wat. sol.	2·72. 10^{-7} norm.	0·00
2. 10^{-7}n. Pb(NO$_3$)$_2$	3·88 „ „	+ 6·9	2, 10^{-7}n. K$_2$CrO$_4$	3·88 „ „	— 4·4
4. „ „	5·36 „ „	+ 13·1	4. „ „	5·36 „ „	— 8·1
6. „ „	7·04 „ „	+ 17·5	6. „ „	7·04 „ „	— 12·5
8. „ „	8·82 „ „	+ 20·0	8. „ „	8·82 „ „	— 14·1
2. 10^{-6}n. „	20·35 „ „	+ 32·5	2. 10^{-6}n. „	20·35 „ „	— 25·6
3. „ „	30·24 „ „	+ 40·0	3. „ „	30·24 „ „	— 32·5
6·6. „ „	66·1 „ „	+ 47·5	6·6. „ „	66·1 „ „	— 39·4

TABLE 5.

The potential of the bariumsulphate crystall electrode, relative to solutions of its constituent ions of various concentrations. Temperatur: 20 C°.

Electrolyte-solvent	Concentration of Ba++-ion	$\epsilon-\epsilon_0$ (milli-volts)	Electrolyte-solvent	Concentration of SO_4-- -ion	$\epsilon-\epsilon_0$ (milli-volts)
pure wat. sol.	2·23. 10^{-5} norm.	0·00	pure wat. sol.	2·23. 10^{-5} norm.	0·00
0·5. 10^{-5}n. $BaCl_2$	2·26 „ „	+ 1·6	—	—	—
0·7 „ „	2·40 „ „	+ 2·5	0·7. 10^{-5}n. H_2SO_4	2·40. 10^{-5} norm.	— 2·3
1·0. 10^{-5}n. „	2·56 „ „	+ 3·0	1·0 „ „	2·56 „ „	— 2·7
3·0 „ „	4·0 „ „	+ 9·1	3·0 „ „	4·0 „ „	— 8·7
5·0 „ „	5·7 „ „	+ 13·3	5·0 „ „	5·7 „ „	— 12·6
7·0 „ „	7·57 „ „	+ 17·4	7·0 „ „	7·57 „ „	— 16·6
1·0. 10^{-4}n. „	10·4 „ „	+ 21·2	1·0. 10^{-4}n. „	10·4 „ „	— 20·3

TABLE 6.

The potential of the lead sulphate chrystall electrode, relative to solutions of its constituent ions of various concentrations. Temperatur: 0 C°.

Electrolyte-solvent	Concentration of Pb++-ion	$\epsilon-\epsilon_0$ (milli-volts)	Electrolyte-solvent	Concentration of SO_4-- -ion	$\epsilon-\epsilon_0$ (milli-volts)
pure wat. sol.	2·0. 10^{-4} norm.	0·00	pure wat. sol.	2·0. 10^{-4} norm.	0·00
1. 10^{-5}n. $Pb(NO_2)_3$	2·05 „ „	+ 0·3	—	—	—
4 „ „	2·21 „ „	+ 1·6	4. 10^{-5}n. K_2SO_4	2·21. 10^{-4} norm.	— 1·3
8 „ „	2·44 „ „	+ 2·6	8 „ „	2·44 „ „	— 2·5
1. 10^{-4}n. „	2·56 „ „	+ 3·1	1. 10^{-4}n. „	2·56 „ „	— 3·0
2 „ „	3·24 „ „	+ 6·5	—	—	—
4 „ „	4·83 „ „	+ 10·7	4. 10^{-4}n. K_2SO_4	4·83. 10^{-4} norm.	— 10·7
6 „ „	6·61 „ „	+ 14·8	6 „ „	6·61 „ „	— 14·7
1. 10^{-3}n. „	10·39 „ „	+ 20·0	1. 10^{-3}n. „	10·39 „ „	— 20·0

The experimental results collected in the following tables admit at once to find out that the electrodes, talked about, show up potential values, relative to the solutions of their constituent ions, the absolute values of wich often considerably differ from oneanother, the same ion concentrations being compared. This asymmetry is relatively important in the case of silver halides, in the sens that it increases from the silver chloride through the silver bromide towards the silver iodide. According to the above cited preliminary investigations of the senior author, this fact is a necessary consequence of the former statement[1] that the adsorption power of the silver halides, too, increases in the same succession, in the way that the measure of the adsorption of the halide ion, relative to that of the silver ion is greatest on the silver iodide surface. Also the lead chromate shows a greater adsorption power against the negative ion[2] (CrO_4^{--}), and this corresponds to our finding that the $PbCrO_4$ electrode, dipping into a Pb^{++}-ion solution, appears more positive (compared with the pure watery saturated solution of lead chromate) than shows itself negative, when immersed in a CrO_4^{--}-ion solution of the same concentration. Considerabily less is the asymmetry on the bariumsulphate electrode (TABLE 5), corresponding to the fact that the adsorbent power, too, of the bariumsulphate against Ba^{++}- and SO_4^{--}-ions is almost the same (TABLE 8). Finally, on the lead sulphate electrode we could not at all establish any asymmetry (TABLE 6), in full accord with previous experiments[3] giving evidence for the equality of the adsorbent power of lead sulphate against the Pb^{++}- and the SO_4^{--}- ions.

TABLE 7.

The adsorption of Ag^+- and of Cl^--ion on silver chloride surface, at 20 C°.

Adsorbent: 20·16 gr AgCl   Adsorbent: 10·08 gr AgCl

c_0	a	c	c_0	a	c
1. 10^{-5}n. AgNO$_3$	1·332. 10^{-7}gr moles	0·778. 10^{-5}n	1. 10^{-5}n. KCl	0·80. 10^{-7}gr moles	0·867. 10^{-5}norm
2·5 „ „	2·02 „ „	2·13 „ „	2·5 „ „	1·445 „ „	2·225 „ „
3·5 „ „	2·40 „ „	3·10 „ „	—	—	—
5·0 „ „	2·88 „ „	2·25 „ „	5·0 10^{-5}n. KCl	3·01· 10^{-7}gr moles	4·50. 10^{-5}norm.

Designations: c_0 = concentration of the adsorptiv before adsorption
c = „ „ „ „ after „
a = adsorbed quantity. Volume: throughout 60 ccm.

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[1] A. Lottermoser and A. Rothe: ZS. phys. Chem. 62. (1908). 364.
[2] L. Imre: Koll.-ZS. 99 (1942). 147.
[3] L. Imre: Koll. ZS. 91. (1940). 32.

TABLE 8.

The adsorption of Ba++- and of SO_4^{--}-ions on bariumsulphate surface, at 20 C°. Volume: 50 ccm. The other designations: like in Table 7. Adsorbent: 10 gr. $BaSO_4$

c_0	a	c	c_0	a	c
1.10^{-5}n. $BaCl_2$	0·52.10^{-7}gr moles	0·792.10^{-5} n.	1.10^{-5}n. H_2SO_4	0·53.10^{-7}gr moles	0·758.10^{-5}norm
2 " "	0·73 " "	1·708 " "	2 " "	0·84 " "	1·664 " "
3 " "	0·78 " "	2·688 " "	3 " "	0·98 " "	2·607 " "
—	—	—	4 " "	1·04 " "	3·584 " "
5.10^{-5}n. $BaCl_2$	0·89.10^{-7}gr moles	4·645.10^{-7} n.	5 " "	1·08 " "	4·570 " "
7 " "	0·92 " "	6·63 " "	7 " "	1·14 " "	6·545 " "
1.10^{-4}n. "	0·95 " "	9·62 " "	1.10^{-4}n "	9·44 " "	9·54 " "

In the data of the above tables not only the qualitative proof of an equal character of adsorption and electrode function is comprised, but also a more quantitative information about the reciprocity of the two phenomena. According to the above cited investigations of the senior author, the values of the electrode potential, relative to the pure watery solution of the electrode (i. e. the values of $\varepsilon - \varepsilon_0$) can be expressed as follows:

$$\varepsilon - \varepsilon_0 = \frac{RT}{\nu F} \cdot \ln \frac{C_+}{(C_+)_0} - \frac{1}{2} \cdot \frac{RT}{\nu F} \cdot \left[\ln \frac{X_-}{X_+} - \ln \left(\frac{X_-}{X_+} \right)_0 \right] \quad \ldots \ldots \; 1.),$$

the following symbols being used:

X = number of the active spots on the surface of the electrode, provided for the negative resp. positive ions, in the presence of the pure watery solutions $[(X^-)_0, (X_+)_0]$ resp. of any other solutions (X_-, X_+); $(C_+)_0$, C_+ = concentration of the positive ion of the electrode substance in the pure watery solution resp. in any other solution; ν = valency of the ion; F = Faraday number. (The equation in this form applies only for binaer electrolytes). Sufficiently precise adsorption data, which may admit a rather exact evaluation of Equ. 1, are available, for the present, only with reference to the following electrodes: silver chloride, silver iodide, lead chromate and bariumsulphate.

From the adsorption isotherms, constructed on the basis of the data of TABLE 7., we derived (with the aid of a graphical analysis) the value 1·28 for (X_-),$/(X_+)_0$, referred to silver chloride. On the other hand, with increasing ion concentration the two values of the active spots become more and more equal: $X_+ \rightarrow X_- = (X_-)_0$. (We have always observed this equisation, in all adsorption systems, examined thoroughly enough so far; the phenomenon shall exactly be motivated in a later publication). Thus, the silver chloride electrode appears (at 20 C° temperature), when immersed into somewhat more concentrated Ag_+-ion solution, by ca.

$$0{\cdot}029 \,.\, \log \,.\, 1{\cdot}28 \approx \text{millivolts}$$

more positive (relative to the pure watery silver chloride solution), than when dipped into Cl^--ion solutions of the same resp. concentrations. This theoretical conclusion is in rather good agreement with the experimental result (see: TABLE 1). According to the analogous calculation, the silver iodide electrode, immersed into Ag^+-ion solutions, becomes at best by about 16—17 millivolts more positive, than when immersed into J^--ion solutions of the same resp. concentrations. This theoretical result, too, is in good accord with the experimental data, see TABLE 3.

The surface of lead chromate, in contact with its pure watery saturated solution, possesses about 3-times as much active spots for $CrO_4^=$-ions as for Pb^{++}-ions,[1] i. e.

$$(X_-/X_+)_0 \approx 3$$

[X_- being, here too, throughout equal to $(X_-)_0$]. Thus, one derives from Equ. 1, putting $X_-/X_+ = 1$, at 20 C° temperatur:

$$[(\varepsilon-\varepsilon_0)_+ - (\varepsilon-\varepsilon_0)_-]_{\max} = \Delta(\varepsilon-\varepsilon_0)_{\max} \approx \frac{1}{2}\cdot\frac{0{\cdot}058}{2}\cdot\log 3 \approx 8 \text{ millivolts};$$

this, too, agrees rather well with the experimental results (see: TABLE 4).

Adsorption experiments made with bariumsulphate (TABLE 8) yielded the value

$$(X_-/X_+)_0 \approx 1{\cdot}25.$$

Thus, it can computed that at 20 C° temperatur

$$\Delta(\varepsilon-\varepsilon_0)_{\max} \approx \frac{1}{2}\cdot\frac{0{\cdot}058}{2}\cdot\log 1{\cdot}25 \approx \text{ millivolts};$$

essentially the same result have been found by the experiments (TABLE 5.)

Now, there is still the question to be cleared up, if the Equ. 1, holds only for the maximum of the electrode asymmetry (i. e. for somewhat greater ion concentrations), or if it is in conformity to all experiments made with any ion concentrations. When there are adsorption measurments available, then this question may be studied very simply in that way that one compares the tangents of the adsorption isotherms (constructed in the sens of Langmuir's formula) with the values of the electrode potential. It is namely, according to Langmuir:

$$\frac{\partial}{\partial c}\left(\frac{c}{a}\right) = \frac{1}{X}.$$

Now, we have made experiments on the exchange adsorption of lead chromate (measured with the aid of radioactive *ThB*-indicator), the results of which, represented according the formula:[2]

$$\frac{\text{quantity of } ThB\text{, remained in the solution}}{\text{adsorbed quantity of } ThB} = \frac{C_+}{X_+}\cdot\text{const.} \quad . \; 2.),$$

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[1] L. Imre: Koll.-ZS. 99. (1942). 156.

[2] L. Imre: Koll.-ZS. 99. (1941). 152. Equ. 18.,

yielded the following values for the number of the active spots:

at $C_+ = 3.17^{-7}$ gr moles/litre concentration: $X_+/X_+ = 2{\cdot}2$;
„ „ $= 1{\cdot}10^{-6}$ „ „ „ : „ $= 3{\cdot}5$;
„ „ $= 3{\cdot}3.10^{-6}$ „ „ „ : „ $= 4{\cdot}34$.

These figures admit (on the basis of Equ. 1.) the following values of the electrode asymmetry [$= \Delta(\varepsilon - \varepsilon_0)$] on the lead chromate surface (putting within brackets the corresponding experimental data from TABLE 4.):

5 mV (5·9); 7 mV (6·9); 9 mV (8·1) respectively.

The agreement is sufficiently good. But the real importance of the probleme is not so much implied by the question: how depends the electrode potential on the relative numbers of the active spots, but rather by this one: how varies the electrode potential with varying ion concentrations. The quantitative details of this question shall be discussed in one of our later publications, but we make already here the attempt of outlining the ground ideas, in the limits of which our further investigations are made.

B.) THE ELECTRODE ASYMMETRY AS THEORETICAL FUNCTION OF THE ELECTROLYTE CONCENTRATION

Electrodes of the second class may often be very useful for purposes of potentiometric analysis, especially in systems, which are agressive chemical agents against the resp. metal electrodes. Already this practical point of view alone, apart from other, meanwhile only more theoretical problems, justifies enough our attempting to discover the real laws, according which the potential values of electrodes of this kind depend on the existing ion concentrations. A single look cast at the above tables will be enough, to make one convinced of the fact that NERNST's electrode potential formula becomes uncertain in the region of very small ion concentrations. Still more curious appers the question of the validity of NERNST's formula by our observing the circumstance that not every sort of ion gives rise to deviations from Nernst's theory. The lead sulphate electrode, for example, in contact both with Pb^{++}- and SO_4^{--}-ion solutions, throughout behaves so as is prescribed by Nernst's formula. The silver halide electrodes, too, obey the prescription of Nernst's formula, downwards to the slightest ion concentrations available, *when* immersed into the corresponding halide ion solutions, whereas the concentrations of Ag^+-ion solutions are not yet indicated by these electrodes in the same way as it is expected on ground of Nernst's theory. Similarly, the asymmetrical behaviour of the lead chromate electrode, too, consists mainly in the indicating the Pb^{++}-ions in a manner inconsistent with Nernst's formula, whilst, on the other hand, in contact with CrO_4^{--}-ion solutions it strictly corresponds to the requirements of this formula, over the whole region of concentration. Also the bariumsulphate electrode is „regular“ against the SO_4^{--}-ions, but in Ba^{++}-ion solutions it already shows up well observable deviations from the classical theories etc. etc.

It is clear, therefore, that the „abnormities" of the electrodes of second type, being observed in the slight-concentrated solutions, are not due to the mere presence of any slight concentration, but one has to take into consideration some individual effects of ions, especially with respect to the surface, in order to understand the deeper character of the phenomenon.

The most important common feature of these specific ion properties will at once be discerned, if one bears in mind the new definition of the active spots (centres of adsorption) of the phase surface, given in the above cited works of the senior author. The variation of the free energy of the surface layer, which has most interest for our purpose, may be illustrated by the following exemple, relied on experiments with silver iodide.

The silver iodide adsorbes the J^--ions to a higher amount than the Ag^+-ions; the reason of this lies in the energy of hydration of the Ag^+-ions being greater than that of the J^--ions. As a consequence of the differences in the energies of hydration, the J^--ions stay, in the average, during a longer time on the surface of silver iodide than do the Ag^+-ions, i. e. the J^--ions will be solved back from the surface of silver iodide with a smaller speed than do the Ag^+-ions. Now, the speed of dissolution of molecules of the solid surface wall at all is determined, according to general kinetic principles, by that component of the molecules, which has the smallest speed of dissolution: consequently, the solution tension of the solid crystall at all depends, in this case, on the solution tension o the J^--ions. Thus, the solution tension of the solid lattice wall is determined by the free energy of the J^--ions, wich, for its part, can be expressed by the logarithme of the product

$$\frac{1}{(\delta v)_0} \cdot e^{E_0/RT},$$

$(\delta v)_0$ being the phase volume of the adsorbed J^--ions, E_0 their adsorption energy. On the other hand, one gets the number of the active spots for wichever adsorptiv ion by summing all the products[1]

$$\frac{1}{\delta v} \cdot e^{E_0/RT},$$

referred to the surfaces elements, and dividing this into the above product

$$\frac{1}{(\delta v)_0} \cdot e^{E_0/RT}.$$

If, therefore, the sum

$$\sum \frac{1}{\delta v} \cdot e^{E/RT},$$

referred to anyone sort of adsorptiv ion may vary in a different way than do the fundamental product

$$\frac{1}{(\delta v)_0} \cdot e^{E_0/RT},$$

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[1] L. Imre: Koll.-ZS. 91. (1940), 32.

then the number, (X) of the active sports for the resp. ion will be changed. It is evident that, as a matter of course, also the number (X_+) of the active spots for Ag^+-ions on silver iodide surfaces will be changed, if the solution tension of the adsorbed negative ions (J^--ions) varies in an other rate than does the solution tension of the Ag^+-ions.

Now, inquiring for reasons that make one understand possible changes (with varying ion concentrations) of the solution tension, one may at first consider the Debye—Hückel effect existing in the electrolyte solutions. In the theory of this effect the „a"-parameter, i. e. the smallest possible distance between the ions (in the liquid phase), plays an important part. Many experiments admit to believe that the values of this parameter is, in the case of well soluble electrolytes, often of the same order of magnitude as the corresponding lattice constants[1], whereas the „a"-parameter of the slightly soluble electrolytes is, as a rule, much smaller, and even, especially in the application of the original theory, sometimes it must be supposed negative.[2]

At any case, one has to bear in mind a relatively rapid decrease of the coefficient of ion activity, when the J^--ions are together with Ag^+-ions present in the solution. And since this decrease of the coefficient of ion activity indicates, at the same time, the change of the free energy of the whole solid surface (see above), so by increasing $AgNO_3$ concentration also the fundamental product

$$\frac{1}{(\delta v)_0} \cdot e^{E_0/RT}$$

will be decreased. At the same time, however, the activity coefficient of the Ag^+-ions decreases but a little, since the Ag^+-ions mainly collide with NO_3^--ions, and the „a"-parameter of these collisions are relatively large.

It follows from all this that in the presence of excessive J^--ions (e. g. KJ) the relative number of the active spots throughout remains equal to the starting value:

$$X_-/X_+ = (X_-/X_+)_0\,,$$

that is, the electrode potential obeys, according to Equ. 1., with full exactness the formula of Nernst:

$$\varepsilon - \varepsilon_0 = \frac{RT}{\nu F} \cdot \ln \frac{C_+}{(C_+)_0} \quad \dots\dots\dots\dots\dots \quad 3.$$

In contrast with this, the presence of excessive Ag^+-ions may considerably diminish the value of X_-/X_+. At the same time, one sees quite clearly that, when there is the negative ion that lattice-constituent, which has the smaller solution tension, then one has throughout the whole region of ion concentrations:

$$X_- = (X_-)_0\,,$$

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[1] P. Debye and E. Hückel: Phys. ZS. 24. (1923), 185; T. H. Gronwell, V. K. La Mer and K. Sandved: Phys. ZS. 29. (1928), 358; V. K. La Mer, T. H. Gronwall and L. J. Greiff. J. phys. Chem. 35, (1931), 2245.

[2] O. Schärer: Phys. ZS. 25. (1924), 145.

conseqently, one may write the Equ. 1. also in the form:

$$\varepsilon - \varepsilon_0 = \frac{RT}{\nu F} \cdot \ln \frac{C_+}{(C_+)_0} + \frac{1}{2} \cdot \frac{RT}{\nu F} \cdot \ln \frac{X_+}{(X_+)_0} \quad \ldots\ldots\ldots \quad 4.$$

Unfortunately, there are just the substances of extremely slight solubility and, accordingly, of the highest adsorbent power, on the „a"-parameter of which, as yet, no reliable data are available. On roughly estimating the Debye—Hückel effect, on ground of any reasonable numerical values of the „a"-parameter, one gets the belief that the above considerations can hold up only if, computing the free energy of the surface layer, one takes into account not only the actual lattice constituent ions (J^--ions in the above example), but also the strange ions being present (NO_3^--ions, when the excessive Ag^+-ions be added in form of $AgNO_3$), as adsorptiv ions. Little as the exchange adsorption of these latter (NO_3^--ions) may be, it is to be considered, for this extremely slight NO_3^--ion content of the solid surface wall, too, raises in relatively very high degree the average solution tension of the negative crystall constituent ions (being in the upper layer of the solid), i. e. it diminishes the value of the fundamental product

$$\frac{1}{(\delta v)_0} \cdot e^{E_0/RT}$$

and thereby raises the value of the number of the active spots for the positive lattice constituent ion (Ag^+-ion). In our next publication on this subject some further experimental data shall be treated in all quantitative details, from the standpoint of both the Debye-Hückel effect and the effect of the exchange adsorption, altering the surface layer, of the strange ions.

Másodfajú elektródok aszimmetriájáról

Imre Lajos és Sarusi Ferenc

(Az Általános és Fizikai Kémiai Intézet közleménye)

Összefoglalás

Egyik réggebbi doglozatában (Muzeumi Füzetek, 1943. évf. I. kötet) a szerzők egyike (I. L.) arra az elméleti következtetésre jutott, hogy a másodfajú elektródok potenciálja az igen kis koncentrációjú elektrolit-oldatokkal szemben a Nernst-féle formulától eltérő értékeket vehet fel. Ha az elektródpotenciált az elektród anyagának tiszta vizes telített oldatára vonatkoztatjuk, vagyis ha olyan koncentrációs galvánelemet készitünk, melyben a $(C_+)_0$ koncentrációjú, telített tiszta vizes oldat áll szem-

ben a tetszésszerinti más, C_+ koncentrációjú oldattal (C_+ = az elektród pozitiv ion-alkatrészének koncentrációja ez utóbbi oldatban), akkor ennek a galvánelemnek az elektromótoros ereje a szerző elméleti vizsgálatai szerint:

$$\varepsilon - \varepsilon_0 = \frac{RT}{\nu F} \cdot \ln \frac{C_+}{(C_+)_0} - \frac{1}{2} \cdot \frac{RT}{\nu F} \cdot \left[\ln \frac{X_-}{X_+} - \ln \left(\frac{X_-}{X_+} \right)_0 \right] \quad \ldots\ldots \quad 1.$$

(X_-, X_+ = az anión ill. katión aktívhelyeinek a száma a tetszésszerinti C_+ koncentráció esetén, (X_-), $(X_+)_0$ = ugyanaz a $(C_+)_0$ katión-koncentráció esetén, valamennyi az elektród egyazon felületrészletére számitva, ν = iónvegyérték, F = Faraday-féle szám.) A jelen dolgozatban ennek az elektródpotenciál-formulának a kisérleti vizsgálatáról és az elmélet továbbépítéséről van szó.

Az 1. egyenletet úgy ellenőrizték a szerzők, hogy különböző, természetes és mesterséges kristályok elektródpotenciál-értékeit (melyeket quadránselektrométerrel végzett mérések útján nyertek) összehasonlították ugyanezen kristályok anyagából készült, nagyfelületű poroknak a katión- és anion-alkatrészeikkel szemben tanusított adszorpcióképességével. Ez utóbbi (adszorpciós) méréseknek a Langmuir-féle izoterma-egyenlet szerint való ábrázolása révén, grafikusan levezetett X értékeket az 1. egyenletbe helyettesítvén, olyan számadatokat nyertek, melyek általában jól egyeztek a közvetlen potenciálmérési adatokkal.

Az elmélet tovább-építése azt célozza, hogy az elektródpotenciál számértékeit adszorpciómérések *nélkül* is megadhassuk, mint az elektrolit-koncentráció függvényét. Ez a feladat szintén megoldhatónak látszik a szerző által definiált aktívhely-fogalom (Koll.-ZS. 91., 1940., 32.) segítségével. Az erre vonatkozó *részletes* számításokat a szerző egy következő dolgozatában fogja közzétenni, a jelen közleményben körvonalazott gondolatok alapján, melyek a határfelületi kristályréteg szabadenergiájának a Debye—Hückel-féle effektus és az idegen iónok kicserélődési adszorpciója következtében beálló változását tartják szem előtt.

Investigations on Furan Compounds
I. Communication: Conversion of 2-Aceto-furan into Hexen-2-dion-4, 5-acetal-1 and Pyrocatechol

by

L. Vargha, J. Ramonczai and P. Bite

(Contribution from the Institute of Organic Chemistry)

Several investigators have already tried the synthesis of the 2-amino-furan. R. Leimbach has attempted to reach this aim through the hydrolysis of furan-2-ethylurethan[1], while H. M. Singleton and W. R. Edwards[2] through the hydrolysis of the 2-benzoyl and 2-propionylamino-furan, respectively. But all these experiments remained unsuccessfull, only tar-like products and ammoniac has been produced thereby; the formation of 2-amino-furan could not, even in traces, be demonstrated. These circumstances showed us clearly, that the 2-amino-furan must be an extremely sensitive substance, and that its production is to be expected only under the mildest experimental conditions. We, therefore, thought of the application of a process, discovered by P. W. Neber, wich proceeds really under the mildest conditions. For Neber and v. Friedolfsheim[3] have found that the p-toluenesulphonyl esters of certain aromatic ketoximes transform into amines in alcoholic medium even at room-temperature. Thus, for example, p-toluenesulphonyl benzyl-methyl-ketoxime and p-toluenesulphonyl acetophenon-oxime gave rise to the p-toluenesulphonic acidic salts of benzylamine[3] and aniline[4], respectively, in good yields, when the esters were shaken in ethyl alcohol. As an interpretation of this remarcable change the outhers suppose[3] that the mentioned esters (A) undergo first the Beckmann's transformation, then the thus formed products (B) suffer hydrolytical decomposition under the influence of water traces (C, D):

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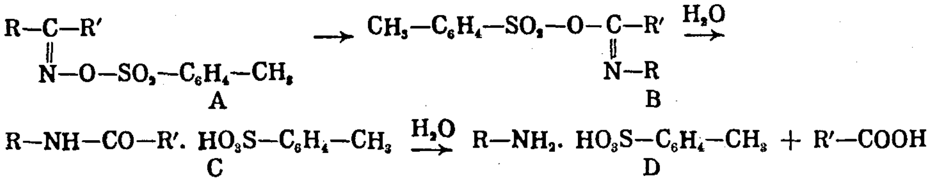
[1] Leimbach, R., Journ. f. pr. Chem. (2) 65, 20 (1902).

[2] Singleton, H. M and Edwards, W. R., Journ. Amer. chem. Soc. 60, 540 (1938).

[3] Neber, P. W., Ann. 449, 109 (1926).

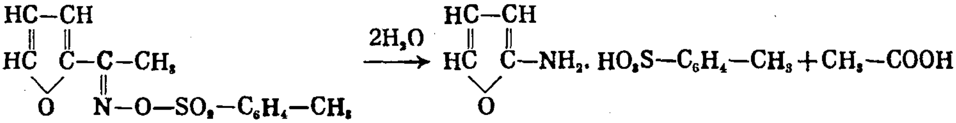
[4] Neber, P. W. and Huh, G., Ann. 515, 292 (1935).



$$\underset{A}{R-\underset{\substack{\| \\ N-O-SO_2-C_6H_4-CH_3}}{C}-R'} \longrightarrow \underset{B}{CH_3-C_6H_4-SO_2-O-\underset{\substack{\| \\ N-R}}{C}-R'} \xrightarrow{H_2O}$$

$$\underset{C}{R-NH-CO-R'.\ HO_3S-C_6H_4-CH_3} \xrightarrow{H_2O} \underset{D}{R-NH_2.\ HO_3S-C_6H_4-CH_3} + R'-COOH$$

It could, therefore, be hoped that the p-toluenesulphonic acidic salt of the 2-amino-furan (II) would be formed from the p-toluenesulphonyl ester of the 2-aceto-furan-oxime (I) according to the analogy of Neber's reaction:



I II .

The experiments, however, which we carried out with ethanol exactly according to Neber's prescription, did not justify our supposition. For, instead of the expected 2-amino-furan salt, a nitrogenless yellowish green liquid and the ammonium salt of the p-toluenesulphonic acid could be isolated from the reaction product in very good yield. The liquid can be distilled in vacuo at constant temperature without becoming decomposed, it showes a strong reducing power even in the cold and is very sensitive toward heat. These remarcable properties of the new compound have drawn our interestedness and now we set forth the problem to clear up its constitution and the mechanism of its formation.

At the beginning of these examinations we have started from the consideration that the substance is formed as a result either of a further transformation of the primer product expectable according to Neber's formulas (A, B, C, D) or of a process quite of an other nature. As Neber's mechanism could not give a reliable basis relating to the structure, we had to start from the very beginning.

First of all, from the analysis and the result of the determination of the molecular weight, ensued the elementary formula $C_{10}H_{16}O_4$ (III), on the basis of which it could be set up the elementary equation of the reaction-process as well:

$$C_6H_6O-N-O-SO_2-C_6H_4-CH_3 + H_2O + 2\,C_2H_5OH = C_{10}H_{16}O_4 + CH_3-C_6H_4-SO_3NH_4$$

The alcohol is involved in the building of III, for the reaction with methanol instead of ethanol gives rise to the same ammonium salt and to a substance, different from III but in its properties very similar to them, which, according to our analysis, has the elementary formula $C_8H_{12}O_4$ (IV) and is formed according to the following equation:

$$C_6H_6O-N-O-SO_2-C_6H_4-CH_3 + H_2O + 2\,CH_3OH = C_8H_{12}O_4 + CH_3-C_6H_4-SO_3NH_4$$

It is difficult to reconcile these formulas with the presence of the original furan structure. Also the observation that from III no adduct with maleic anhydride originates[5], is inconsistent with the furan structure. III and IV take up, at the catalytical hydrogenation, only one mol. of hydrogen easily in the presence of palladium catalist giving rise to two liquids of the elementary formulas $C_{10}H_{18}O_4$ (V) and $C_8H_{14}O_4$ (VI), respectively, while a furan compound would require 2 mol. of hydrogen at least.

These experiments showed, consequently, that the furan ring opens during the reaction with alcohol and the substances (III, IV), formed thereby, are to be regarded as unsaturated aliphatic compounds.

In spite of the strong reducing power of the substances III—VI the presence of free aldehyde groops could not be supposed in them, because they redden the fuchsin sulphurosic acid solution only after hydrolysis. It was, however, presumable, that the entered 2 alcohol groups are linked like acetals. There were in favour of this the results of the hydrolysis of III—VI, at which, in the presence of deluted acids, from III and IV even at standing in cold aqueous solution, the formation of ethanol and methanol, respectively, can be established. It is surprising that from the unsaturated compounds III and IV acetic acid is also formed during the hydrolysis. The acetal character of 2 oxygen atoms in III and IV could be proved, finally, by the reaction with aqueous hydroxylammonium chloride, whereby, at room-temperature, the same oxime of the formula $C_6H_6O_2{=}NOH$ (VII) was formed with splitting off of 2 mol. alcohol, The fact that VII is a true aldoxime or ketoxime, was proved by benzoylation, at which the expected benzoyl ester $C_6H_6O_2{=}N{-}O{-}CO{-}C_6H_5$ (VIII) was produced. The oxime VII is formed, therefore, according to the following equation:

$$C_6H_6O_2(OR)_2 + H_2NOH = C_6H_6O_2{=}NOH + 2\,ROH$$

From the remaining both oxygen atoms of III and IV was to be presumed that they are present as carbonyl groups, for no activ hydrogen could be demonstrated in equivalent quantity according to ZEREWITINOW's method. One of these carbonyls could be experimentally demonstrated by phenylhydrazine. It was formed, namely, from III and IV the same bisphenylhydrazone of the formula $C_6H_6O({=}N{-}HN{-}C_6H_5)_2$ (IX) at room-temperature splitting off 2 mol. of alcohol. The second carbonyl group showes a reduced reactivity, its presence, however, could not be demonstrated, owing to the fact, too, that the substance suffers thorough decomposition heating it with the usual carbonyl reagents on the water-bath.

According to the experiments, detailled above, it seemed probable that in III and IV one acetal group, one acetyl group and one carbon double bond occur and the character of 3 oxygen atoms could be determined. The forth oxygen atom might, eventually, be also in ether linkage, which, however, could hardly brought into accordance with the supposed open chain.

The oxydative degradations have given us a further evidence of the structure. Treating IV by ozone glyoxal is produced, which was iso-

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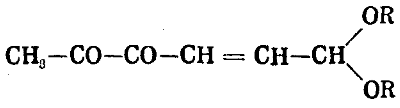
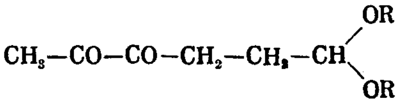
[5] Alder, K. and Schmidt, C. H., Ber. 76, 18 (1943).

lated in form of its phenylosazone. The oxydation by potassium permanganate leads to the formation of acetic acid and oxalic acid. The formation of glyoxal at the oxydation by ozone on one hand proves the position 1 of the acetal group and thus its aldehyd character, just as the position 2, 3 of the double bond. The formation of acetic acid, during the oxydation by potassium permanganate, is in accordance with the result of the hydrolytical cleavage; the presence of an acetyl group may, therefore, be taken as proved.

Having these experimental proofs the elementary formulas of III—VI can be dissolved into the following structure formulas:



$$CH_3-CO-CO-CH=CH-CH\begin{matrix}OR\\OR\end{matrix}$$



$$CH_3-CO-CO-CH_2-CH_2-CH\begin{matrix}OR\\OR\end{matrix}$$

III, $R = -C_2H_5$. IV, $R = -CH_3$. V, $R = -C_2H_5$. VI, $R = -CH_3$.

III and IV are, therefore, to be designated as hexen-2-dion-4, 5-diethyl-acetal-1 (dimethylacetal-1, respectively) V and VI as hexan-dion-4, 5-diethylacetal-1 (dimethylacetal-1, respectively).

The correctness of these structure formulas could be confirmed also by other degrading reactions. A. F. Hollemann[6] and J. Böeseken[7] have shown that the oxydation of the 1,2-diketones by hydrogen peroxyde results in the corresponding carbonic acids according to the following scheme:

$$R-CO-CO-R' + H_2O_2 \longrightarrow R-COOH + R'-COOH.$$

Having carried out the oxydation of IV in glacial acetic acid solution, we obtained maleic acid, in consequence of the simoultaneous hydrolysis of the acetal linkage and further oxydation of the so formed aldehyde to acid:

$$CH_3\text{-}CO\text{-}CO\text{-}CH{=}CH\text{-}CH(OCH_3)_2 \rightarrow CH_3\text{-}COOH + HOOC\text{-}CH{=}CH\text{-}CHO + 2CH_3OH \rightarrow HOOC-CH=CH-COOH$$

The formation of the second excepted reaction product, the acetic acid, evidently, could not be demonstrated under the applied conditions. This result confirmes not only the correctness of the structure formulas, established by us, but it proves also the cis configuration of IV, which could exist in 2 geometrical isomer modifications.

The oxydation of VI by silver oxyde in aqueous solution resulted in succinic acid, in good accordance with the result of the previous experiment. With the position 1,4 of the acetal and of one carbonyl group is as well in accordance the formation of a substance from VI with

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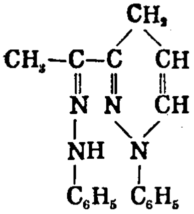
[6] Hollemann, A. F.: Recueil Trav. Chim. Pays-Bas, 23, 169 (1904).

[7] Böeseken, J.: Recueil Trav. Chim. Pays-Bas, 30, 142 (1911).

penylhydrazine, which is, according to the analysis, to be regarded as the penylhydrazone of the 1-penyl-3-aceto-dihydropyridazin (X). Accordingly, VI reacts with penylhydrazine like certain other 1,4-dicarbonyl compounds forming pyridazine derivatives, as known from the literature.[8]

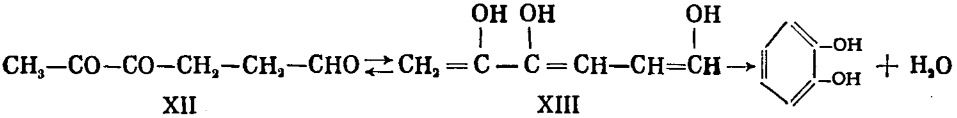


X

In the course of our further work we have intended to study the free aldehydes, corresponding to the acetals III—VI, for it might be expected that these compound-types, less known in the literature, would show an enhanced reactivity.

As already mentioned, the unsaturated diketoaldehyde (hexen-2-dion-4, 5-al-1, $CH_3—CO—CO—CH=CH—CHO$, XI), correspondent to the acetals III and IV, could not be produced by hydrolysis, because its carbon chain suffers a hydrolytic cleavage between the adjacent carbonyl groups 4 and 5 even upon the action of cold water. Unfortunately, we did not succeed to isolate any other scission product besides acetid acid and alcohol, though, the formation of maleic dialdehyde might be expected. Certainly, this easy cleavage of the carbon linkage between the neighbouring carbonyls is to be attributed to the loosening effect of the double bond beeing in position 2, 3.

The hydrolysis of the saturated acetals V and VI also lead to a surprizing result, because instead of the expected diketoaldehyde (hexan-dion-4, 5-al-1, XII) a crystalline substance could be isolated, which, according to its properties, melting point and the analysis, proved to be pyrocatechol. The formation of the pyrocatechol, however, can easily be explained through the enol form XIII of XII according to the following scheme:



$$\underset{\text{XII}}{CH_3-CO-CO-CH_2-CH_2-CHO} \rightleftarrows \underset{\text{XIII}}{CH_2=\overset{OH}{C}-\overset{OH}{C}=CH-CH=\overset{OH}{CH}} \rightarrow \ldots + H_2O$$

It could doubtlessly be demonstrated by estimation of the active hydrogen according to Zerewitinow that even VI is present partially in the eno form.

Since the pyrocatechol derivatives are very common in nature, even the pyrocatechol itself occurs in certain plants, it is perhaps of interest to show a possible way, by which these aromatic compounds can eventually be formed from the carbohydrates through furan derivatives. The formation of pyrocatechol from VI, at the same time, can be regarded as a firm support of the structure formulas established by us.

At present no definitive interpretation can be given of the mechanism of the conversion of I into III and IV. The reaction can hardly go according to Neber's formulas (A, B, C, D) through 2-amino-furan, because the formation of a six-membered carbon chain can not be explained thereby. It is probable that here a reaction of an entirely other nature

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[8] Smith, A.: Ann. 289, 310 (1896); Ber. 35, 2169 (1902).

proceeds, which perhaps is in connection with the specific properties of the furan ring. It is known that the furan ring often opens even to quite mild influences. For example, from the 2-methyl-furan, in methyl-alcoholic hydrogen chloride solution, levulinaldehyde-dimethylacetal forms.[9]

EXPERIMENTAL

2-Aceto-furan-oxime.

A solution of 2-aceto-furan[10] (40 g.), hydroxylammonium chloride (30 g.) and anhydrous sodium acetate[11] (40 g.) in ethyl-alcohol (200 c.c.) was boiled for 5 hours under reflux on the steam-bath. Then the hot solution was filtered from the precipitated sodium chloride, the filtration concentrated in vacuo and to the residue ice water was poured. The substance, separating oily at first, became crys alline at friction very soon. It was filtered off, washed with a little water and recrystallised from methanol. Yield, 90%. M. p.: 104^0.

p-Toluenesulphonyl 2-aceto-furan-oxime, I.

50 g. of fine-powdered p-toluenesulphonyl chloride was added gradually to a solution of 2-aceto-furan-oxime (30 g.) in anhydrous pyridin (140 c. c.) at -10^0 with stirring. The reaction mixture, after standing for 2 hours at 0^0, then for 30 minutes at room-temperature, was poured into ice water. The crystallised ester was filtered off, washed with water, dried in vacuo and recristallised from benzene by addition of petroleum ether. Colourless needles were obtained, which melts at 80^0 with decomposition. Yield: almost quantitative. The pure ester is long lasting, the impure one decomposes rapidly. It is easily soluble in ether, benzene and acetone, sparingly soluble in alcohol, practical insoluble in water and petroleum ether.

Found: C 55·95%, H 4·61%. Calc. for $C_{13}H_{13}O_4NS$ (279·3): C 55·90%, H 4·69%.

Hexen-2-dion-4,5-diethylacetal-1, III.

50 g. of the p-toluenesulphonyl ester (I) was shaken at room-temperature in 250 c. c. of 95% ethyl-alcohol 5 days by the machine. Then the separated p-toluenesulphonic acidic ammonium was filtered, the filtration was concentrated in vacuo at $30-35^0$ bath-temperature to a small volume and to the residue 250 c. c. of ether was poured. After filtration of a small quantity of precipitated ammonium salt, the ether solution was agitated with a little water, dried with anhydrous sodium sulphate and the solvent distilled off at first under atmospheric pressure, finaly in vacuo. The remaining liquid distilles at $75-90^0$ under 3 mm. The bath temperature, however, may not rise above 130^0, because the

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[9] Harries, C.; Ber 31, 37 (1898).

[10] Sandolin, S. S.; Ber. 33. 492, 1176 (1900). Torrey, H. A.; and Zanetti, I. E.; C. 1911, 1. 81.

[11] Sandolin applied sodium carbonate instead of sodium acetate and the yield was only 50%.

resineous residue decomposes at overheating with explosion-like violence. At the rectification the substance distilled mostly at 65—68^0 under 1 m. m. Yield: 80% of the theoretical. The obtained acetal is a yellowish green liquid easily soluble in water and in the usual organic solvents. It reduces the Fehling solution and the ammoniacal silver solution even in the cold. Its freshly prepared aqueous solution does not redden the fuchsine sulphurosic acid, reacts to litmus neutral, after staying, however, it becomes sour in consequence of the formation of acetic acid.

Found: C 59·64%, H 8·25%. Calc. for $C_{10}H_{16}O_4$ (200·2): C 59·96%, H 8·06 %. Mol. weight found, by determination of the freesing point depression in benzene,: 198.

Hexen-2-dion-4,5-dimethylacetal-1, IV.

The preparation of the dimethylacetal was carried out like that of the diethylacetal (III), but methanol was applied instead of ethanol. The obtained yellowish green liquid showes the same properties as III. B. p.: 80·5—81·5^0 under 3 m. m. Yield: 80—90 % of the theoretical.

Found: C 55·93%, H 7·11%. Calc. for $C_8H_{12}O_4$ (172·2): C 55·78%, H 7·03%. Mol. weight found, estimated as above,: 171·6.

Attempt to produce an adduct from III with maleic anhydride.

An ether solution of the equivalent quantities of III and maleic anhydride was left to stay for 2 days in ice-safe. After distillation of the solvent the starting material was recovered unchanged almost quantitatively. The formation of an adduct could not be demonstrated.

Hexan-dion-4,5-diethylacetal-1, V.

20·2 g. of hexen-2-dion-4, 5-diethylacetal (III), in 100 c. c. of ethylalcohol, was hydrogenated in the presence of 3 g. of palladised charcoal (10% Pd) at room-temperature under atmospheric pressure. The substance took up 1 mol. hydrogen during a few hours, then the reaction velocity decreased. At this time the hydrogenation was interrupted, the filtered solution evaporated in vacuo and the remaining liquid destilled. B. p.: 73—75^0 under 3 m. m. An almost colourless liquid was obtained, which reduces the ammoniacal silver solution even in the cold. It is easily soluble in water and in the usual organic solvents. Yield: 80% of the theoretical. According to Zerewitinow's method the substance contains ca. 0·3 atom active hydrogen.

Found: C 59·45%, H 9·19%. Calc. for $C_{10}H_{18}O_4$ (202·2): C 59·41%, H 8·91%. Mol. weight found, determinated as above,: 200·5.

Hexan-dion-4,5-dimethylacetal-1, VI.

This substance was prepared from the dimethylacetal IV like V from III. The properties of both saturated acetals (V and VI) are very similar to one another. B. p.: 79—82^0 under 2 m. m. According to Zerewitinow's method the substance contains 0·2 atom active hydrogen.

Found: C 54·64%, H 8·21%. Calc. for $C_8H_{14}O_4$ (174·2): C 55·14%, H 8·10%.

Hydrolysis of the hexen-2-dion-4,5-dimethylacetal-1.

A solution of the acetal IV (5 g.) in 2% sulphuric acid (50 c. c.) was boiled 30 minutes under reflux. The solution gets at first yellow then brown and at last some resinous product precipitates. Then the filtered solution was evaporated in vacuo, the distillate neutralised exactly with 0·1 n-sodium hydroxyde and then ca. $^2/_3$ of its volume distilled again. In this distillate the presence of methyl-alcohol could be demonstrated by Denigès's reaction. The residue was evaporated to dryness on the steam-bath and mixed with a saturated silver nitrate solution. The formed crystalline precipitate was filtered off, washed with a little cold water and dried in vacuo. It was proved to be silver acetate.

Found: Ag 64·18$_2$%. Calc. for $C_2H_3O_2Ag$: Ag 64·64%.

Hexen-2-dion-4,5-aldoxime-1, VII.

To the solution of one of the both unsaturated acetal (0·5 g. of III or IV) in water (10 c. c.) was added a concentrated aqeous solution of hydroxylammonium chloride (0·5 g.). The formed oxime very soon precipitated crystalline. It was filtered and recrystallised from hot water. Colourless light-sensitive needles were obtained. M. P.: 236° with decomposition. The oxime is easily soluble in alkalies, sparingly soluble in water and alcohol and almost insoluble in the other usual solvents. Its aqueous solution showes a red colouration with ferric chloride.

Found: C 51·26%, H 5·18%, N 9·99%. Calc for $C_6H_7O_3N$ (141·1): C 51·03%, H 4·96%, N 9·92%.

Benzoyl hexen-2-dion-4,5-aldoxime-1, VIII.

0·1 g. of the oxime VII, dissolved in 15 c. c. of 2n sodium hydroxyde, was shaken with 0·5 g. of benzoyl chloride 15 minutes. The formed ester was filtered, washed with water and recrystallised from alcohol. Colourless needles, m. p.: 168°.

Found: N 5·77%. Calc. for $C_{13}H_{11}O_4N$ (246·4): N 5·71%.

Bisphenylhydrazone of the hexen-2-dion-4,5-al-1, IX.

1 g. of the acetal III or IV, dissolved in 30 c. c. of water, was mixed with a solution of 3 g. of hydrochloric phenylhydrazine in 15 c. c. of water. The bisphenylhydrazone, precipitated at first oily, became soon crystalline. It was then filtered, washed with water and recrystallised from alcohol with charcoal. Orange-red needles, m. p.: 209° with decomposition.

Found: C 70·48%, H 5·94%, N 18·19%. Calc. for $C_{18}H_{18}ON_4$ (306·4): C 70·55%, H 5·92%, N 18·29%.

Oxydation of the hexen-2-dion-4,5-dimethylacetal-1 by ozone.

Into a solution of the acetal IV (6 g.) in anhydrous chloroform (30 c. c.) 1·1 mol. of ozone was introduced. Then the solvent was distilled off in vacuo and the oily residue was boiled with water (60 c. c.) for 2 hours under reflux. Beeing the substance completly dissolved, an acetic acidic solutiun of phenylhydrazine was added. The thus obtained precipitate was recrystallised from alcohol. It proved to be glyoxal-bisphenylhydrazone, according its m. p. alone and in admixture with an authentic specimen (169°).

Oxydation of hexen-2-dion-4,5-dimethylacetal-1 with potassium permanganate.

To the acetal IV (6·8 g.) dissolved in water (50 c. c.), which was made slightly alkaline by adding a few drops of potassium hydroxyde, a solution of potassium permanganate (28 g.) in water (500 c. c.) was dropped at 5—10° during 12 hours with stirring. After finished oxydation, the solution, filtered from the precipitated manganese dioxyde, was concentrated in vacuo to 100 c. c., then acidified with deluted sulphuric acid to congo and ca. 70 c. c. of them distilled. The acid distillate was exactly neutralised with 0·1 n sodium hydroxyde and evaporated to dryness on the steam-bath. To decompose the formed formic acid, the dry residue was treated with conc. sulphuric acid, then deluted with water and distilled again. From this distillate the acetic acid, produced by the oxydation, could be isolated in form of its silver salt.

Found: Ag 64·12%. Calc. for $C_2H_3O_2Ag$ (166·9): Ag 64·64%.

From the residue of the first distillation, by adding an acetic acidic solution of phenylhydrazine, a colourless substance crystallised in plates, which was recognised as the phenylhydrazine salt of the oxalic acid. M. p.: 182°, in admixture with an authentic specimen there was no depression.

Oxydation of IV with hydrogen peroxyde.

1 g. of the acetal IV, dissolved in 10 c. c. of glacial acetic acid, was refluxed with a solution of 10 c. c. of 15% hydrogen peroxyde for 4 hours. The colourless substance, obtained after evaporation of the solution in vacuo and recrystallisation of the solide residue from water, was recognised as maleic acid. M. p. alone and in admixture with an other specimen of maleic acid: 132°.

Oxydation of hexan-dion-4,5-dimethylacetal-1 with silver oxyde.

4 g. of the acetal VI, dissolved in 100 c. c. of wather, was boiled with 4 g. of freshly prepared silver oxyde for 1 hour under reflux. Then the hot filtered solution was saturated with hydrogen sulphide, filtered from precipitated silver sulphide and evaporated to dryness on the steam-bath. The solide residue was recrystallised from abs. alcohol. A colourless substance was obtained, which proved to be succinic acid. M. p. alone and in admixture with an authentic specimen: 183°.

1-Phenyl-3-aceto-dihydropyridazin-phenylhydrazon, X.

The acetal V or VI (0·5 g.) was heated with phenylhydrazine (1 g.) in glacial acetic acid (5 c. c.) for 10 minutes on the steam-bath. The precipitated substance was filtered and washed with water and alcohol. It is a pale yellow crystall-powder, practical insoluble in water.and the other usual solvents. It does not smelt up to 280^0.

Found: C 74·51%, H 6·44%, N 19·12%. Calc. for $C_{18}H_{18}N_4$ (290·3): C 74·41%, H 6·24%, N 19·34%.

Hydrolysis of hexan-dion-4,5-dimethylacetal-1. The formation of pyrocatechol.

A solution of the acetal VI (2·5 g) in 2% sulphuric acid (60 c. c.) was boiled for 1 hour under reflux. After cooling the solution, turned faintly brown, was saturated with sodium bicarbonate and extracted with ether. Then the ether extract was, after drying with anhydrous sodium sulphate, evaporated and the residue distilled in vacuo. B. p.: 111—112^0 under 3 m. m. The distillate crystallised from ligroine in colourless plates. The substance showes all the characteristic properties of the pyrocatechol, its aqueos solution gives with ferric chloride an emerald green colouration, and smelts alone or in admixture with an authentic specimen of pyrocatechol at 104^0.

Found: C 65·78%, H 5·59%. Calc. for $C_6H_6O_2$ (110·05): C 65·45%, H 5·45%.

Vizsgálatok a furan-vegyületek köréből I. közlemény: hexen-2-dion-4, 5-acetal-1 és pyrocatechin képződése 2-aceto-furanból

Vargha László, Ramonczai Jenő és Bite Pál

(A Szerves Kémiai Intézet közleménye)

Összefoglalás

A 2-amino-furan előállítására irányuló kisérleteink közben azt találtuk, hogy ha p-toluolsulfo-2-aceto-furan-oximot (I)* aethylalkohollal reakcióba hozunk, p-toluolsulfonsavas ammonium és egy sárgás-zöld nitrogénmentes folyadék keletkezik igen jó hozammal, amely feltűnő kémiai sajátságokat mutat. Az új anyag ugyanis erősen redukál, igen érzékeny hő és kémiai behatások iránt, mindazonáltal vákuumban bomlás nélkül desztillálható. Megállapítottuk, hogy az anyag elemi összetétele a $C_{10}H_{16}O_4$ (III) tapasztalati képlettel fejezhető ki. Amikor a reakciót aethanol helyett methanollal hajtottuk végre, p-toluolsulfonsavas ammoniumon kívül egy III-hoz igen

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* A képleteket és irodalmi idézeteket l. az angol szövegben.

hasonló, de vele nem azonos folyadék keletkezett, melynek tapasztalati képlete az analizisek alapján $C_8H_{12}O_4$ (IV).

III és IV szerkezetét, valamint configuratióját sikerült felderíteni alkalmas módszerek segélyével. Vizsgálataink eredményeképpen bebizonyítottuk, hogy III szerkezete a $CH_3—CO—CO—CH = CH—CH(OC_2H_5)_2$ strukturképlettel fejezhető ki és racionális neve, tekintetbe véve a configuratiot is, cis-hexen-2-dion-4, 5-diaethylacetal-1, IV pedig a megfelelő dimethylacetal (cis-hexen-2-dion-4, 5-dimethylacetal). Ez anyagok képződésének mechanizmusára vonatkozólag még nem tudunk határozott képet nyujtani.

E telítetlen acetaloknak megfelelő telítetlen aldehydet (cis-hexen-2-dion-4, 5-al-1, XI) nem sikerült III vagy IV hydrolyzise utján előállítani, mert az már hideg vizes oldatban is elbomlik. A várható bomlástermékek közül ecetsavat sikerült izolálni, melynek képződése jelzi, hogy a szénlánc a 4-es és 5-ös carbonyl-csoportok között hydrolytikus bomlást szenved. Föltételezhető, hogy a szénlánc kettészakadása, mely ilyen feltünően enyhe hatásra is bekövetkezik, a 2, 3-helyzetű kettős kötés lazitó hatásának a következménye.

A telített aldehyd (hexan-dion-4, 5-al-1, XII) sem bizonyult stabil vegyületnek. Ugyanis amikor a megfelelő telített acetalokat, melyeket III és IV katalytikus hydrogénezése utján állítottunk elő (V és VI), hydrolyzisnek vetettük alá, a várt telített aldehyd (XII) helyett meglepő módon pyrocatechin képződött. A pyrocatechin képződése azonban könnyen érthetővé válik, ha közbeeső termékként XII trienol alakját (XIII) tételezzük fel.

Ez utóbbi tény alapot szolgáltat ahhoz a feltevéshez, hogy talán a természetben nagy számban előforduló pyrocatechin-származékok a szénhydrátokból furan-vegyületeken keresztül hasonló folyamatok következtében keletkezhetnek.

Investigations on Sugar Alcohols
IV. Communication: 2,5-Anhydro-l-idit

by

L. Vargha, T. Puskás and E. Nagy

(*Contribution from the Institute of Organic Chemistry*)

In the III. communication[1] of this series it has been reported on researches, resulted in clearing up the constitution and configuration of a monotoluenesulphonyl anhydro-hexit[2]. It has been demonstrated doubtlessly, that this compound is to be regarded as 1-p-toluenesulphonyl 2, 5-anhydro-l-idit (I). Our experiments, however, failed to prepare the 2, 5-anhydro-l-idit itself from this l-idit derivative by hydrolysis or from the 1, 6-dijodo derivative[1] in the usual way. It has not been possible to isolate any well defined substance, since the reactions did not go on uniformly. In the meantime Prof. K. FREUDENBERG has kindly called our attention to one of his earlier experiments, by which he has succeeded to produce diacetone glucose from the 3-p-toluenesulphonyl diacetone glucose reducing it by sodium amalgame[3]. As we have, in general, been interested in the elimination of the p-toluenesulphonyl groups from its ester derivatives, we tried to apply this reducing method not only to our l-idit derivative, but also to p-toluenesulphonyl esters of other polyalcohols.

Treating the 1-p-toluenesulphonyl 2, 5-anhydro-l-idit (I) in diluted alcohol by sodium amalgame we obtained, besides the sodium salt of the p-toluenesulphinic acid, a sirupy product, which in its acetate form can be separated into two fractions by distillation under strongly diminished pressure. Having saponified the fraction of higher boiling point, we could obtain a uniformly crystallised substance which proved to be the expected 2, 5-anhydro-l-idit (II). The fraction of lower boiling point however could not be brought into crystalline state even after saponifying it. We suppose, according to our analysis, that this substance is a dianhydro-hexit, the constitution of which, however, has not been examined thoroughly.

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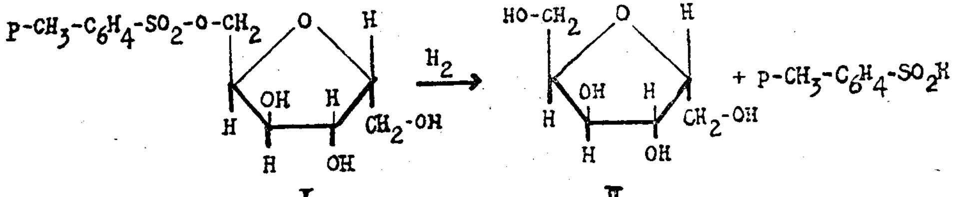
[1] Vargha, L. and Puská , T.; Ber. 76,859 (1943).

[2] Vargha, L.; Ber. 68,1377 (1935).

[3] Freudenberg, K. and Brauns, F.; Ber. 55,3238 (1922). We wish to thank to Prof. K. Freudenberg for his kind information.



I II

We tested, in a similar way, also the reduction of the 6-p-toluenesulphonyl[4] and of the 5,6-di-p-toluenesulphonyl 1, 2-acetone-glucofuranose[5]. We have obtained, thereby, 1, 2-acetone-glucofuranose (ca. 40% yield) and a sirupy substance from the 6-p-toluenesulphonyl 1, 2-acetone-glucofuranose and 5-p-toluenesulphonyl 3, 6-anhydro-1, 2-acetone-glucofuranose[6] besides a small quantity of a undefined product from the 3, 6-di-p-toluenesulphonyl compound.

These examinations showed us the fact that though the reductive cleavage of the p-toluenesulphonyl esters, into alcohols and p-toluenesulphinic acid, can often be carried out, but simultaneously, as a undesirable by-product, anhydro compounds can be also formed during splitting off of p-toluenesulphonic acid, probably an influence of the alcaline medium. To hinder the formation of such anhydro compounds, we carried out the reduction in an approximately neutral medium also by introducing in it carbon dioxide. These experiments did not give the desired result neither, since from the 6-p-toluenesulphonyl 1, 2-acetone-glucofuranose, in surprising good yield, the 5, 6-anhydro-1, 2-acetone-glucofuranose[7] has been formed, while the 5,6-di-p-toluenesulphonyl 1, 2-acetone-glucofuranose remained unchanged.

EXPERIMENTAL

Reduction of the 1-p-toluenesulphonyl 2,5-anhydro-l-idit by sodium amalgame. Tetraaeetyl 2,5-anhydro-l-idit and diacetyl dianhydro-hexit

10 g. of 1-p-toluenesulphonyl 2, 5-anhydro-l-idit (I) in 160 c. c. of 80% alcohol was stirred 3 days at 15° with 200 g. of 2% sodium amalgame. Then the solution was poured off from the mercury, neutralised by carbonic acid and filtered from the precipitated sodium bicarbonate. Having repeated the described procedure, the alcoholic solution was evaporated and the residue extracted by 30 c. c. of pyridin. The part insoluble in pyridin was dissolved in a little water, the solution strongly acidified by sulphuric acid and the thereby crystalline precipitated substance was filtered off, washed with a little cold water and dried. The substance proved to be p-toluene sulphinic acid according to its melting point alone (88°), or in admixture with an authentic specimen. Having evaporated the pyridinic solution in vacuo, we obtained a thick sirup

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[4] Ohle, H. and Spencker, K.; Ber. 59,1836 (1926).
[5] Ohle, H. and Dickhäuser, E.; Ber. 58,2593 (1925).
[6] Ohle, H., Vargha, L. and Erlbach, H. Ber. 61,1211 (1928).
[7] Ohle, H. and Vargha, L.; Ber. 62,2435 (1929).

(4·6 g.), which could not be crystallised. To be acetylated, therefore, it was left during the night in 30 c. c. pyridin with 20 c. c. of acetic anhydride at room temperature, Then we distilled the pyridin off in vacuo, dissolved the residue by water and chloroform and after drying and evaporating the chloroform solution, the obtained sirup was distilled under 0·003 mm. pressure. Two fractions were taken, the first one distilled at 108—124° bath temperature, the second one at 124—140°. Yields: 1·8 g. and 3·3 g., respectively. The first fraction represents, according to the analysis, an diacetyl dianhydro-hexit. It is a clear sirup, easily soluble in alcohol, ether, chloroform and benzene, almost insoluble in water and petroleum ether.

$[\alpha]_D^{20} = + 5{\cdot}15°$ (chloroform, c = 2·329).
Found: C 52·14%, H 6·25%, Calc. for $C_{10}H_{14}O_6$ (230·2): C 52·17%, H 6·13%

The second fraction showes similar solubility and is, according to our analysis, tetraacetyl 2, 5-anhydro-l-idit. Not one of the both sunstances could be obtained in crystalline form.

$[\alpha]_D^{20} = - 13.19°$ (chloroform, c = 1·9556).
Found: C 50·97%, H 6·52%. Calc. for $C_{14}H_{20}O_9$ (332·3): C 50·60%, H 6·06%.

2, 5-Anhydro-l-idit, II.

Adding 11 g. of barium hydroxide dissolved in 130 c. c. of water to the solution of 3·3 g. of tetraacetyl 2, 5-anhydro-l-idit (second fraction) in 20 c. c. of alcohol, the mixture was shaken 24 hours by the machine. Then the excessive barium hydroxide was saturated with carbonic acid, the barium carbonate filtered off and the soluted barium precipitated by the equivalent sulphuric acid. After filtration the solution was evaporated in vacuo, the remaining sirup dissolved in a little abs. alcohol and the solution mixed with abs. ether until it begins to trouble. Standing in ice-safe, the substance was crystallised in colourless prismes, easily soluble in water and alcohol. M. p.: 111—113°. Yield: 1.1 g.

$[\alpha]_D^{20} = + 12{\cdot}6°$ (water, c = 2·525).
Found: C 43·94%, H 7·55%, Calc. for $C_6H_{12}O_5$ (164·16): C 43·90%, H 7·37%.

Dianhydro-hexit.

The solution of 1·8 g. diacetyl dianhydro-hexit (first fraction) in 12 c. c. of alcohol was shaken 20 hours with 7 g. of barium hydroxide in 80 c. c. of water. After removing the barium, as described above, and evaporating the solution in vacuo, we obtained a sirup, easily soluble in water and alcohol, which could not be brought into crystalline form.

$[\alpha]_D^{20} = + 12{\cdot}3°$ (water, c = 3·079).
Found: C 49·63%, H 7·02%. Calc. for $C_6H_{10}O_4$ (146·14): C 49·31%, H 6·80%.

Reduction of the 6-p-toluenesulphonyl 1, 2-acetone-glucofuranose by sodium amalgame.

2 g. of the substance was stirred 24 hours in 30 c. c. of $80^{0}/_{0}$ alcohol with 25 g. of $2^{0}/_{0}$ sodium amalgame at 15°. After neutralising it by carbonic acid and removing the barium, as described above, the solution was evaporated in vacuo and the residue extracted by ethyl acetate. The part remained unsoluble proved to be the sodium salt of the p-toluenesulphinic acid; from its solution in little water the p-toluenesulphinic acid (m. p. 88°) could be isolated. From the concentrated ethyl acetate solution the 1, 2-acetone-glucofuranose (m. p. 158°) crystallised out. Yield: 0·5 g. After evaporation of the mother liquid an oily resideu (0·6 g.) remained, that could not be get crystalline.

The reduction was carried out also introducing carbon dioxide simoultaneously. In this case a colourless substance could be isolated, which showed, after recrystallisation from benzene, all the properties of the 5, 6-anhydro-1, 2-acetone-glucofuranose. Yield: $70^{0}/_{0}$. M. p.: 132°.

$$\left[\alpha\right]_{D}^{20} = -26{\cdot}4^{0} \text{ (water, } c = 3{\cdot}025).$$

The reduction of the 5, 6-di-p-toluenesulphonyl 1, 2-acetone-glucofuranose by sodium amalgame.

The reduction was carried out as described above. From the concentrated ethyl acetate extract a colourless substance was obtained, which proved to be identical with the 5-p-toluenesulphonyl 3, 6-anhydro-1, 2-acetone-glucofuranose. M. p. alone and also in admixture with an authentic specimen 133°. The ethyl acetate mother liquid still contained, in small quantity, an oily product.

At the reduction, introducing carbon dioxide simoultaneously, the starting material was recovered almost quantitatively.

Vizsgálatok a cukoralkoholok köréből
IV. közlemény: 2, 5-anhydro-1-idit

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Összefoglalás*

Megelőző közleményünkben[1] beszámoltunk azokról a vizsgálatokról, melyek során bebizonyitottuk, hogy az 1-p-toluolsulfo-2, 4-benzal-5, 6-anhydro-d-sorbit-ból előállítható monotoluolsulfo-anhydro-hexit[2] szerkezete és konfiguratioja I. formulával ábrázolható, tehát az anyag 1-p-toluolsulfo-2, 5-anhydro-1-idit. Nem sikerült azonban magát az alapanyagot, a

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* Képleteket és irodalmi idézeteket l. az angol nyelvű szövegben.

2, 5-anhydro-l-iditet (II) sem I hydrolyzise utján, sem pedig az 1, 6-dijodszármazékon[1] keresztül egységes állapotban előállítani. Közben Prof. K. **Freudenberg** levélben felhivta figyelmünket egy régebben publikált munkájára, melynek során neki sikerült 3-p-toluolsulfo-diaceton-glykose-ból nátriumamalgammal való reduktio útján diaceton-glykoset jó termeléssel előállítani, tehát az említett vegyületből a toluolsulfo-csoportot p-toluolsulfinsav alakjában mellékreakciók nélkül eltávolítani[3]. Mivel minket a toluolsulfo-csoport eltávolitása polyalkoholokkal alkotott estereiből általánosan érdekelt, megvizsgáltuk e reduktív módszernek az említett célra való alkalmazhatóságát. Kisérleteink eredményét az alábbiakban foglaljuk össze.

1. I nátriumamalgámmal való redukciója nem vezet egységes termékhez, mert a várt 2, 5-anhydro-l-iditen (II) és p-toluolsulfinsavon kivül p-toluolsulfonsav lehasadása következtében egy dianhydro-hexit is képződik egyidejüleg. A két terméket azonban acetatjaikon keresztül sikerült elkülöníteni és így II-t egységes, kristályos állapotban előállítani. A dianhydro-hexit szirupszerű anyag, szerkezetét még nem vizsgáltuk meg behatóbban.

2. A 6-p-toluolsulfo-1, 2-aceton-glykofuranose[4] és az 5, 6-di-p-toluolsulfo-1, 2-aceton-glykofuranose[5] redukciója sem vezet egységes termékhez. Az előbbiből a várt 1, 2-aceton-glykofuranosen (hozam 40%) kivül még egy szirupszerű anyag is, az utóbbiból pedig főleg, 3, 6-ahydro-1, 2-aceton-glykofuranose[6] keletkezik, tehát ez utóbbi esetben a reakció csaknem kizárólag p-toluolsulfonsav lehasadása közben megy végbe.

3. Mivel fel lehetett tételezni, hogy a p-toluolsulfonsav lehasadása, tehát anhydro-vegyületek képződése a lúgos kémhatás következménye, a redukciót megközelítőleg neutrális közegben, széndioxid bevezetése közben is végrehajtottuk. Ezek a kisérletek még kevésbbé vezettek a kivánt eredményre. Ugyanis ebben az esetben a 6-p-toluolsulfo-1, 2-aceton-glykofuranoseból 5, 6-anhydro-1, 2-aceton-glykofuranose[7] keletkezett igen jó hozammal, mig az 5, 6-di-p-toluolsulfo-1, 2-aceton-glykofuranose változatlan maradt.

Kisérleteink tehát azt mutatják, hogy bár a p-toluolsulfonsav több értékü alkoholokkal képezett esterei reduktív uton gyakran a megfelelő alkoholokká és p-toluolsulfinsavvá bonthatók, azonban p-toluolsulfonsav lehasadása következtében egyidejüleg anhydro-vegyületek is képződhetnek.

The Influence of the β-Indole-acetic Acid on the Growth and Multiplication of the Algae

by

I. Péterfi

(Contribution from the Institute of Plant Physiology)

The physiological roll of the heteroauxin on the growth and multiplication of the algae is studied relativly very little. The results obtained generally are contradictorials, and the experiences repeated by different authors, upon the same species of algae, have given unconcludent or contrary results.

Consulting the literature published in this matter, we see that Weij (1933) is announcing the presence of growth substance in the marine algae. Later on Granick and Dunham (1936) are studiing the action of the β-indole-propionic acid upon the *Chlorella pyrenoidosa* and *Cystococcus cohaerens* in pure cultures, without finding any difference of growth among the cultures treated with the β-indole-propionic acid and the controled ones. In 1937 more studies are made concerning the importance and physiological roll of the heteroauxin in the physiology of the growth of the algae. According to Albaum, Kaiser and Nestler (1937) the penetration of the β-indole-acetic acid in the cells of the *Nitella* is in relation with the hydrogen-ion concentration. The penetration of the growth substance in the cells is more rapid at pH 3·98 then at pH 6·80. Brannon (1937) in a preliminary note brings in evidence the effect of the growth substance upon the *Chlorella vulgaris, Chlorella pyrenoidosa* and *Oocystis sp.* Leonian and Lilly (1937) are asking if heteroauxin is a growth substance ? The authors based upon the cultures made with heteroauxin on synthetic nutrient mediums (one part per million and one part in one hundred thousand) are getting to the conclusion that the heteroauxin does not activate, but inhibits the growth of the unicellular algae *Chlorella pyrenoides, Chlorella viscosa, Oocystis Naegelii* and *Cystococcus cohaerens.* In the *Fucus,* according to Olson and Du Buy (1937) the β-indole-acetic acid determines the polarity of the egg; the rhizoides are formed on that part of the egg, which is placed in contact with the solution of heteroauxin. According to the researches made by Yin (1937) the β-indole-acetic acid is not producing the activation of cell multiplication of the *Chlorella vulgaris,* but the growth (with 30% against the normal cells) of the diameter respective of the cell's volume. Contrary to the results obtained by Yin, Pratt (1938) states that the β-indole-acetic acid does not provoke the growth of the volume of the cells at the *Chlorella vulgaris,* but is activating the cellular division (there are 300 times more cells formed in the culture with heteroauxin, than in the control cultures). The researches made by Brannon and Bartsch (1939) show the influence of the growth substance upon the growth and cell division of the green algae: *Chlorella vulgaris, Coccomyxa simplex* and *Mesotaenium caldariorum.* In certain concentrations the β-indole-acetic acid stimulates the multiplication of the algae *Chlorella vulgaris* and *Coccomyxa simplex,* but it has not a stimulent effect upon the multiplication of the *Mesothaenium caldariorum.* At *Chlorella vulgaris* and *Coccomyxa simplex* the heteroauxin does not activate the growth of the size of the cells. But, at *Mesotaenium* was remarked an enlargement of the cell's size. According to the results obtained by Rădulescu (1939) the effect of the heteroauxin upon the development of the *Stichococcus bacillaris* and *Scenedesmus quadricauda* is limited upon the division of the cells.

For making a study of the physiologic roll of the β-indole-acetic acid in the multiplication phenomen and the growth of the algae I have made experiences with green algae cultivated in pure cultures, unialgale and without strange organisme (Bacteria, Fungi etc.).

The species of algae used for the experiences were the following ones:

1. *Stichococcus exiguus* Gerneck, (Grintzesco—Péterfi 1933).
2. *Stichococcus mirabilis* Lagerheim, 3585, origin: Roumania, Lacul Ghilcoş—Gyilkostó 20. IX. 1942.
3. *Stigeoclonium variabile* Naegeli, 3277, origin: Roumania, Cluj—Kolozsvár, Someş—Szamos, 1. VI. 1940.
4. *Stigeoclonium nudiusculum* Kützing, 3620, origin: Roumania, Cluj—Kolozsvár, Fânaţe—Szénafű 8. VI. 1939.
5. *Microthamnion Kützingianum* Naegeli (Péterfi 1937).
6. *Pseudendoclonium basiliense* Vischer, 3564, origin: Roumania, Cluj—Kolozsvár, Valea Pleşca—Plecska völgy 26 IV. 1942.
7. *Pseudopleurococcus Printzii* Vischer, 3548, origin: Roumania, Bicaz—Békás, Părăul Şugăului—Sugópatak. 18. IX. 1942.

In all my experiences I used flasks (Erlenmayer flasks, balloons, eprouvettes, etc.) made of Schott-Jena glass, washed them before using with an oxidant mixture of sulfuric acid and potassium bichromate, then with water, distillated water and then bidistillated water. The water used for preparing the nutrient solution was a bidistillated water, second time distillated in a distillating apparatus, constructed of Schott-Jena glass.

The used chemicals were „pro analysi" or „purissimum" substances from Merck-Darmstadt.

The used nutrient solution is a variety of the Benecke solution with the following composure: H_2O bidestill. . . . 1000 cm³, $Ca(NO_3)_2$ . . . 0·12 g., $MgSO_4$ . . . 0·02 g., KH_2PO_4 . . . 0·05 g., $FeCl_3$ . . . 0·001 g. The nutritive solution was divided in certain quantities in glass balloons and then sterilised in autoclav at a temperature of 105° C for 30 minutes. At one of the sterilised Benecke solution I added the β-indole-acetic acid (neoauxin Scheering) in a quantity of 1·75 mg. Out of this solution of neoauxin, by succesiv diluation with correspondent quantities of Benecke solution, I realised 10 types of concentrations given in the following table:

The concentration of the β-indole-acetic acid (neoauxin-Scheering) at 100 cm^3 Benecke solution.

1. 1x10^{-4} Mol . . . = 1·75 mg. % = 1750 γ %
2. 1x10^{-5} " . . . = 0·175 mg. % = 175 γ %
3. 1x10^{-6} " . . . = 0·0175 mg. % = 17·5 γ %
4. 1x10^{-7} " . . . = 0·00175 mg. % = 1·75 γ %
5. 1x10^{-8} " . . . = 0·000175 mg. % = 0.175 γ %
6. 1x10^{-9} " . . . = 0·0000175 mg. % = 0·0175 γ %
7. 1x10^{-10} " . . . = 0·00000175 mg. % = 0·00175 γ %
8. 1x10^{-11} " . . . = 0·000000175 mg. % = 0·000175 γ %
9. 1x10^{-12} " . . . = 0·0000000175 mg. % = 0·0000175 γ %
10. Benecke solution, control.

Inoculation have been made out of the culture made in Benecke solution and homogenised by the agitation of the eprouvette, with the help of graded pipette 120 mm^3 were inoculated in each flask of culture. For each series of culture the initial density of the algae in the culture liquid was determinated. Out of each experience I have made three parallel series. The cultures were placed and kept for 30—40 days at the room's temperature (20—24° C) and at northern light. I also determined the initial pH of the liquids of the culture. At the end of the experience I determinated the number and the size of the cells or of the thalli, as well as the final pH of the nutrient solution.

The quantitative determination of the growth has been made by centrifugal method (with special tubes with 2 mm^3 divisions) or by haematometric method (with the aid of Tuerck haemocytometer). The determination of the dimensions of the cells and thalli was made at the microscope with the aid of the Reichert-mikrometer okular. The pH was determined with the aid of Hiltner colorimeter, using as indicators: Bromcresolpurple-Merck, Bromthymolblue-Merck, Bromphenolblue-Schuchardt, Methylred-Riedel-Haën and Phenolred-Schuchardt.

1. THE INFLUENCE OF THE β-INDOLE-ACETIC ACID ON THE GROWTH AND DIVISION OF DIFFERENT ALGAE

Experiences with the Stichococcus species

I have studied the action of the neoauxin upon the *Stichococcus exiguus* Gerneck and *Stichococcus mirabilis* Lagerheim. On the liquid nutrient mediums, Benecke solutions with addition of neoauxin in the concentration given in Table I and II, certain quantities of the both *Sticho-*

coccus species were inoculated, determinating the number of the inoculated cells in the culture medium and the initial pH of the nutrient solution. After 28 (at *Stichococcus exiguus*) respectivly 37 days (at *Stichococcus mirabilis*) the cultures were examined at the microscope, determinating the number of the cells with Tuerk haematocytometer per mm^3 of nutrient solution, mesuring the dimension of the cells (diameter and the lenght) as well as the final pH of the culture media. The results of the experiences with the *Stichococcus* species are given in Table I and II, Fig. 1, 2 and 8.

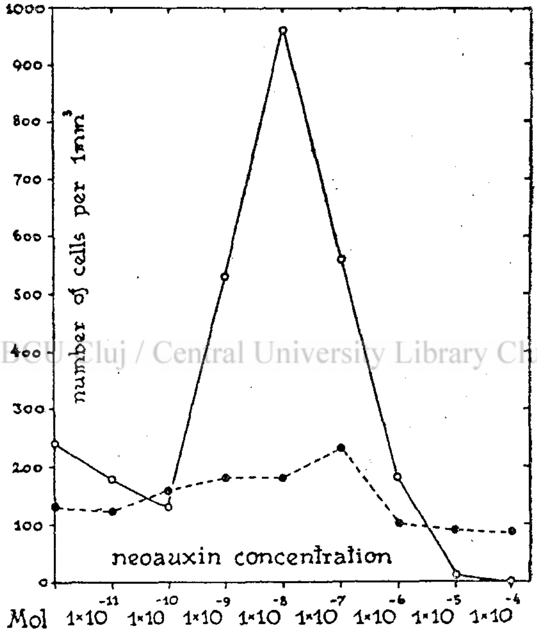

Fig. 1. Multiplication of *Stichococcus exiguus* ———— and *Stichococcus mirabilis* - - - - - - - - - in several concentrations of β-indole-acetic acid.

From the results of these experiences can be established that the *Stichococcus* species behave differently towards the β-indole-acetic acid. From the two *Stichococcus* species, *Stichococcus exiguus* is much more sensibil toward this substance than the *Stichococcus mirabilis*. Such concentration as 0·175 mg per centum of neoauxin is inhibiting the multiplication of the cells of the *Stichococcus exiguus*, while a concentration of 1·75 mg per centum of neoauxin is toxic for the *Stichococcus exiguus* stoping completely the development. The *Stichococcus mirabilis* Lagerheim tolerates a higher concentration of β-indole-acetic acid, although the cell's multiplication is more reduced than in the control cultures.

The optimal concentration for the activation of the cell's division of *Stichococcus exiguus* is 0·175 γ % of neoauxin. In this concentration with

TABLE I. Effect of β-indole acetic acid upon growth and cell division in *Stichococcus exiguus* Gerneck.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Number of cells per 1 mm³ nutrient solution		Dimension of cells μ	
	initial 27. VIII. 1943	final 24. IX. 1943	initial number 27. VIII. 1943	final number 23. IX. 1943	diameter	lenght
1×10^{-4} Mol	3·7	3·7	1·5	—	—	—
1×10^{-5} Mol	3·9	4·4	1·5	9·25	3·1	5—7·5
1×10^{-6} Mol	4·0	4·7	1·5	117·5	3·7	5—7·5
1×10^{-7} Mol	4·0	6·8	1·5	560·0	2·5—3·1	6—8·5
1×10^{-8} Mol	4·0	6·8	1·5	967·5	2·5—3·1	10—15
1×10^{-9} Mol	4·0	6·9	1·5	530·0	2·5—3·1	7·5—40
1×10^{-10} Mol	4·0	6·5	1·5	127·5	2·5—3·1	5—12·5
1×10^{-11} Mol	4·0	6·6	1·5	177·5	2·5—3·1	5—11
Control	4·0	6·5	1·5	247·5	2·5—3·7	6—10

TABLE. II. Effect of β-indole acetic acid upon growth and cell division in *Stichococcus mirabilis* Lagerheim.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Number of cells per 1 mm³ nutrient solution		Dimension of cells μ	
	initial 16. XII. 1943	final 20. I. 1944	initial number 15. XII. 1943	final number 17. I. 1944	diameter	lenght
1×10^{-4} Mol	4·0	4·9	25·6	9·0	3·7	3·7—6·2
1×10^{-5} Mol	4·2	6·1	25·6	97·5	1·8—3·1	7·5—21·0
1×10^{-6} Mol	4·2	6·3	25·6	107·5	2·5—3·1	6·25—12·5
1×10^{-7} Mol	4·3	6·3	25·6	235·0	2·5—3·1	6·5—12·5
1×10^{-8} Mol	4·2	6·4	25·6	185·0	1·8—2·5	7·5—12·5
1×10^{-9} Mol	4·3	6·3	25·6	180·0	2·5—3·7	10·6—16·5
1×10^{-10} Mol	4·3	6·3	25·6	162·0	2·5—3·7	10·0—16·5
1×10^{-11} Mol	4·2	6·3	25·6	125·0	2·5—3·1	6·2—18·7
Control	4·3	6·2	25·6	137·5	2·5—3·1	10·0—21·0

290·9 % were produced more cells than in the control culture. The growth in lenght of the cells of the *Stichococcus exiguus* is activated by the neoauxin. The optimal concentration for the growth in lenght of the cells is 0·0175 γ % of β-indole-acetic acid. The growth in lenght of the cells in this concentration is with 193·75 % greater than at the cells developed in the control medium.

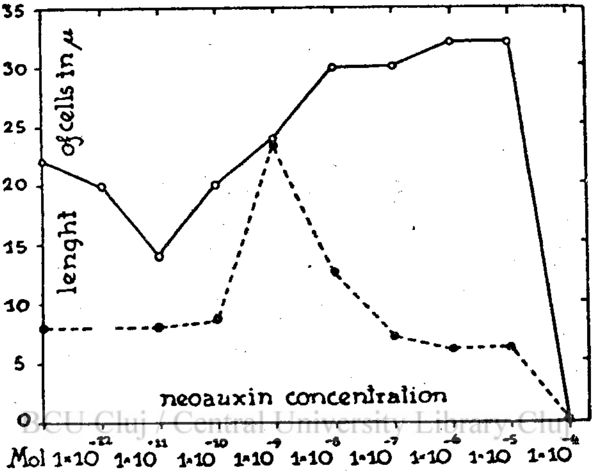

Fig. 2. Cells lenght of *Stichococcus exiguus* ——— and *Pseudopleurococcus Printzii* - - - - - - in several concentrations of β-indole-acetic acid, in acid medium.

The stimulatory effect of the β-indole-acetic acid upon the rate of multiplication of the *Stichococcus mirabilis* is more reduced. The optimal favourising concentration is 1·75 γ % of neoauxin, at which might be observed a cell division with 70·90 % bigger than in the control cultures. In Table II could be seen that the dimensions of the cells grown in a medium with β-indole-acetic acid does not vary in comparison with the dimensions of the cells formed in the nutrient solution of control.

Experiences with the Stigeoclonium species.

For studying the effect of the β-indole-acetic acid upon the development of the *Stichococcus* I have made pure cultures of the species *Stigeoclonium variabile* Naegeli and *Stigeoclonium nudiusculum* Kützing on solutions made of Benecke solutions adding neoauxin in different small concentrations given in Table III and IV. In each culture flask I inoculated in aseptic way, a certain number of thalli. The cultures were exposed to northerly light at the room's temperature. I also determined the initial pH of the nutrient solution.

At the experiences with the *Stigeoclonium variabile* the results were taken and studied after a month from the date of inoculation. Then I determined the terminal pH of the culture media too. The determination of the quantity of the thalli developed on different media with different concentrations of growth substance was made by centrifugal method. The cultures were examined at microscope, measuring the thalli's lenght, the cell's diameter and the lenght of the terminal and subterminal cells of the thalli.

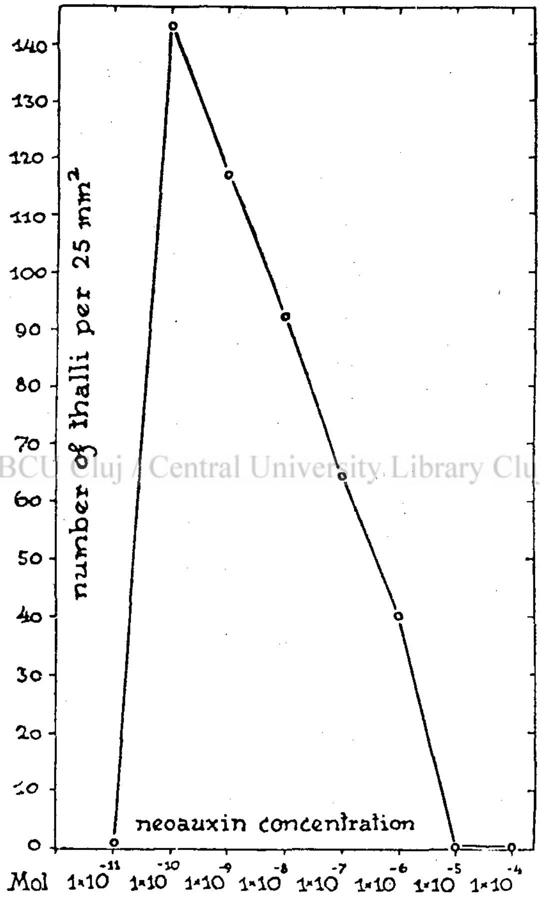

Fig. 3. Multiplication of *Stigeoclonium nudiusculum* in several concentrations of β-indole-acetic acid.

In the case of the experiences with *Stigeoclonium nudiusculum* being that this species is developing slowly, the results were taken only after 5 months. At this date I determined the final pH, the dimensions of the thalli and of the cells.

The results of these two experiences are given in Table III and IV. Fig. 3, 4 and 5.

We can see that the multiplication of the *Stigeoclonium* variabile is very much activated by this auxin. The quantity of 1·75 mg of β-indole-acetic acid added to 100 cm^3 of Benecke solution stopes complecteley the development. The optimal concentration of heteroauxin for the activation of the multiplication of this species is 0·0175γ—0·00175γ per centum. In this concentration zone with 200 % more thalli were produced in comparison with the quantity of the thalli formed in the control culture. At this optimal concentration the thalli's growth in lenght is at the maximum too. The increase of the thalli's growth at this optimal concentration is of 60·7 $^0/_0$ reported to the control culture. Examining the cell's dimension we do not find in plus any growth in lenght, in comparison with the cells developed in solution without auxin. Therefor the neoauxin at the *Stigeoclonium variabile* activates the multiplication and the division of the cells.

Examining Table IV and Fig. 3 and 4 we can see that the *Stigeoclonium nudiusculum* is very sensitive under the action of this growth substance. The action of the neoauxin in this case is more evident due to the fact that the *Stigeoclonium nudiusculum* develops very slowly in a mineral solution. It is verified that after five months there could be found only those two thalli, in the Benecke solution, which were inoculated at the beginning of the experience. In a concentration of 0·0000175γ $^0/_0$ the neoauxin activates all ready the reproduction through the zoogonidium of the *Stigeoclonium nudiusculum*, so that thalli are formed out of the germination of the zoogonidium fixed on the walls of the culture flasks. On a 34·6 mm^2 surface there could be found one thallus. In higher concentration (0·175—1·75 mg $^0/_0$) the *Stigeoclonium nudiusculum* suffers, the reproduction is withhold. Starting from this maximal extrem concentration to higher diluation of neoauxin, the reproduction of the algae is more and more accentuated, till the optimal concentration (0·00175γ $^0/_0$) at which the reproduction and the development is maximum (there are 143·6 thalli fixed on a 25 mm^2 surface). At the same time is verified an activation of the thalli's growth too. But, having in consideration that an activation of the growth in the cell's growth is not manifested in an accentuated way, the difference in the dimension of the thalli is due to the number of the cells. So being, the neoauxin exercises an evident acceleration of the reproduction through the zoogonidium and through the division of the cells of the *Stigeoclonium nudiusculum*.

The experience with Pseudendoclonium basiliense Vischer.

For the experience made with *Pseudendoclonium* I used a Benecke nutrient solution with total concentration as in the previous experiences. With this solution I prepared the whole series of solutions of the different neoauxin concentration, beginning with the $1x10^{-4}$ Mol concentration and till $1x10^{-11}$ Mol. In each culture flask there was inoculated 120 mm^3 homogenised suspension of thalli. I determined the initial pH of the solutions. The cultures were placed at northerly light and at the room's temperature. The results of the experiences were taken after a

TABLE III. Effect of β-indole acetic acid upon multiplication and growth in alga *Stigeoclonium variabile* Naeg.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Initial number of thalli 1. XII. 1943.	Terminal quantity of thalli in mm³ per 15 cm³ nutrient solution 5. I. 1944	Lenght of thalli μ	Diameter of cells μ	Lenght of cells μ	
	initial 1. XII. 1943	final 7. I. 1944					terminale cells	subterminale cells
1×10^{-4} Mol	4·1	5·0	20	—	—	—	—	—
1×10^{-5} Mol	4·2	6·0	20	6·0	900—1400	3·1—8·75	13—29	16—46
1×10^{-6} Mol	4·3	6·1	20	3·0	700—900	3·7—5	20—30	25—38
1×10^{-7} Mol	4·2	5·9	20	6·0	800—1100	3·1—4·3	25—30	16—30
1×10^{-8} Mol	4·3	6·0	20	7·5	560—700	3·7—5	20—25	15—26
1×10^{-9} Mol	4·2	5·6	20	9·0	700—840	3·7—4·3	15—20	12—26
1×10^{-10} Mol..	4.2	6·0	20	9·0	1800—2700	3·7—5	15—20	12—20
1×10^{-11} Mol..	4·2	5·9	20	6·0	1800—2400	3·7—5	20—25	16—18
Control	4·2	6·0	20	3·0	1000—1800	3·1—5	20—25	12·5—21

TABLE IV. Effect of β-indole acetic acid upon multiplication and growth in alga *Stigeoclonium nudiusculum* Kütz.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Number of thalli		Lenght of thalli μ	Dimension of cells	
	initial 18. X. 1943	final 23. III. 1944	initial number of thalli per 15 cm³ nutrient solution 16. X. 1943.	terminal number of thalli per 25 mm² 22. III. 1944		diameter μ	lenght μ
1×10^{-4} Mol	4·0	5·8	2	—	—	—	—
1×10^{-5} Mol	4·2	6·8	2	—	—	—	—
1×10^{-6} Mol	4·2	7·8	2	40	420—700	21—112	27—84
1×10^{-7} Mol	4·2	7·8	2	64·3	420—840	14—98	14—84
1×10^{-8} Mol	4·2	7·5	2	92·3	560—800	14—70	35—56
1×10^{-9} Mol	4·2	6·1	2	117	800—835	51—84	21—84
1×10^{-10} Mol	4·2	7·8	2	143·6	210—980	21—112	21—98
1×10^{-11} Mol	4·2	7·8	2	0·75	182—230	42—63	28—70
Control	4·2	7·0	2	—	—	—	—

TABLE V. Effect of β-indole acetic acid upon multiplication and growth in alga *Pseudendoclonium basiliense* Vischer.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Initial number of thalli per 15 cm³ nutrient solution 15. XII. 1943	Terminal quantity of thalli (in mm³) 19. I. 1944
	initial 16. XII. 1943	final 20. I. 1944		
1×10^{-4} Mol	4·0	5·5	1200	0·74
1×10^{-5} Mol	4·2	4·8	1200	3·0
1×10^{-6} Mol	4·2	4·7	1200	6·0
1×10^{-7} Mol	4·3	4·6	1200	4·40
1×10^{-8} Mol	4·2	4·9	1200	7·50
1×10^{-9} Mol	4·3	4·8	1200	6·0
1×10^{-10} Mol	4·3	5·7	1200	9·0
1×10^{-11} Mol	4·2	5·9	1200	9·0
Control	4·3	4·9	1200	3·0

month; the final pH, the centrifugal determination of the thalli and the microscopical examination.

As it could be seen in Table V. and Fig. 5. the *Pseudendoclonium basiliense* tolerates in greater concentration too the neoauxin. The maximum of the development might be observed in the $1x10^{-10}$—$1x10^{-11}$. Mol concentrations. The β-indole-acetic acid activates the multiplication of the *Pseudendoclonium.* An activation of the cell's growth could not be observed.

2. THE INFLUENCE OF THE β-INDOLE-ACETIC ACID IN RELATION WITH THE pH OF THE NUTRIENT MEDIUM.

Experiences with Microthamnion Kützingianum Naegli and Pseudopleurococcus Printzii Vischer.

For seeng the physiological relation between the effect of the β-indole-acetic acid and the hydrogen-ion concentration I used the *Microthamnion Kützingianum* and *Pseudopleurococcus Printzii.* We know that the

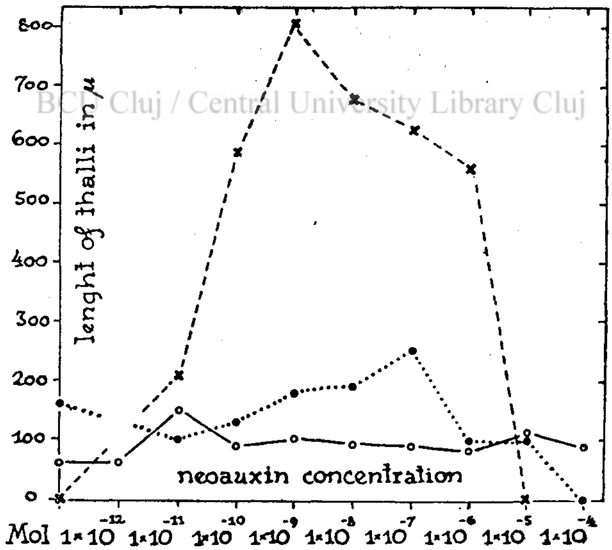

Fig. 4. Lenght of thalli in several concentrations of β-indole-acetic acid. *Stigeoclonium nudiusculum* -------------, *Microthamnion Kützingianum* ...., in acid medium and *Microthamnion Kützingianum* ———— in alkaline medium.

Microthamnion Kützingianum is a euryionical species, which grows on acid, neutral and alkaline media, having an optimal development at pH 5·5—6 (Péterfi 1937). The *Pseudopleurococcus Printzii* is a calcophil species, which developes, however on acid or neutral nutrient media too.

I have realized two series of nutrient media. The fundamental nutrient solution was a Benecke solution to which I added by succesive dilutions neoauxin in different concentration. One of the series was prepared with KH_2PO_4 0·136 g $^0/_{00}$ producing the acid reaction of the Benecke solution, while the other was prepared with K_3PO_4 0.28 g $^0/_{00}$, giving to the nutrient solution a basic reaction. On the both series of nutrient solution I inoculated 120 mm^3 of homogenised suspension of thalli of the *Microthamnion* respectivly of the *Pseudopleurococcus*. The cultures were placed at the room's temperature to northerly light. After inoculation I determined the initial pH of the nutrient solution and I determined the number of the inoculated thalli. At the end of the experiences I measured the final pH of the nutrient liquide, as well as the dimensions of the cells and thalli. The quantitative dose of the formed thalli was made by centrifugal method. The results of the experiences are given in Table VI—IX, Fig. 2, 4—8.

It is established that the neoauxin activates the reproduction through the zoogonidium at the *Microthamnion Kützingianum*, more in an acid medium and less in basic medium. This fact is corresponding with the dataes known from the physiology of the reproduction of the *Microthamnion* (Péterfi 1937), namely that the acid reaction of medium accelerates the reproduction through gamets and zoogonidia. In alkalin medium the gametangium is formed more slowly.

Comparing the results obtained for the *Microthamnion* on acid and basic media, we can see from the Table VI, VII and Fig. 5 that in the acid medium the neoauxin activates more the multiplication of the thalli, and less in basic medium. In acid medium the $1x10^{-4}$ Mol concentration of neoauxin is toxic, restrains completely the development of the thalli. In basic medium the toxicity decreases, the development of the thalli in solution with $1x10^{-4}$ Mol concentration of β-indole-acetic acid is made with the same intensity as in the control medium. In acid medium the optimal concentration of neoauxin is $1x10^{-7}$ Mol, in basic medium the optimal concentration rises to $1x10^{-7}$—$1x10^{-5}$ Mol. The result is that the toxicity of the β-indole-acetic acid is increasing through the alkalinity of the nutrient medium. This result is in concordance with the researches made by Albaum, Kaiser and Nestler (1937), according to which the hydrogen-ion concentration regulates the penetration of the β-indole-acetic acid in the cells. In acid medium at the optimal concentration of neoauxin the growth of the thalli is with 89·47% bigger than in mineral medium of control. In the basic media the quantity of the developed thalli at the optimal concentration of neoauxin is only with 20 % greater than the one from the control solution.

Examining Table VIII, IX of the experiences with *Pseudopleurococcus Printzii* we can see that in this case too could be observed the same relations. In acid medium the neoauxin in concentration of $1x10^{-4}$ Mol is toxic, stopes completely the development of the thalli. In basic medium the toxicity is put aside and at this greater concentration the algae developes as vigorously as in the control solution. At *Pseudopleurococcus* the optimal concentration varies too after the pH of the medium,

TABLE VI. Effect of β-indole acetic acid upon multiplication and growth in alga *Microthamnion Kützingianum* Naeg., acid medium.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Initial number of thalli 27. VIII. 1943	Terminal quantity of thalli in mm³ per 15 cm³ nutrient solution 23. IX. 1943	Lenght of thalli μ	Diameter of cells μ	Lenght of cells μ	
	initial 27. VIII. 1943	final 24. IX. 1943					terminale cells	subterminale cells
1×10^{-4} Mol ..	4·1	4·4	27	—	—	—	—	—
1×10^{-5} Mol ..	4·5	6·6	27	6	84—130	3·1—4·3	10 —13·3	13·7—17·5
1×10^{-6} Mol ..	4·5	6·5	27	9	84—126	3·1	22·5—23	15 —20
1×10^{-7} Mol ..	4·5	6·4	27	36	224—280	3·1—4·3	30 —52	25 —43
1×10^{-8} Mol ..	4·5	6·4	27	15	168—210	3·1—4·3	37.5—50	25 —26
1×10^{-9} Mol ..	4·5	6·5	27	15	140—224	3·1—4·3	30 —46	18 —22
1×10^{-10} Mol ..	4·5	6·6	27	6	98—168	3·1—3·7	22·5—27	22 —25
1×10^{-11} Mol ..	4·6	6·5	27	6	140—170	3·1—3·7	16 —18	15 —18
Control	4·6	6·1	27	19	112—210	3·1—4·3	18 —40	14 —32·5

TABLE VII. Effect of β-indole acetic acid upon multiplication and growth in alga *Microthamnion Kützingianum* Naeg., alkaline medium.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Initial number o thalli 31. I. 1944	Terminal quantity of thalli in n m³ per 15 cm³ nutrient solution 3. III. 1944	Lenght of thalli μ	Diameter of thalli μ	Lenght of cells μ	
	initial 1. II. 1944	final 7. III. 1944					terminale cells	subterminale cells
1×10^{-4} Mol ..	7·5	8·3	27	12	75—110	2·5—5	15—25	12·5—17·5
1×10^{-5} Mol ..	7·5	8·3	27	15	100—140	3·1—3·7	12·5—14	10—20
1×10^{-6} Mol ..	7·5	8·3	27	3	75—100	2·5—3·7	10—15	11—18
1×10^{-7} Mol ..	7·5	8·3	27	15	80—100	2·5—3·1	12·5—17·5	9—20
1×10^{-8} Mol ..	7·5	8·3	27	12	60—100	3·1—3·7	14—20	14—18
1×10^{-9} Mol ..	7·5	8·3	27	12	75—125	2·5—3·75	21—45	16—37·5
1×10^{-10} Mol ..	7·5	8·3	27	12	85—100	3·1—4·3	32—45	23—25
1×10^{-11} Mol ..	7·5	8·3	27	13	125—190	3·1—4·3	27—41	25—37·5
1×10^{-12} Mol ..	7·5	8·4	27	12	130	3·1—3·7	18—25	10—25
Control	7·6	8·4	27	12·5	50—80	3·1—3 7	12·5—28·5	15—18·5

probably in relation with the toxic concentration. Comparing the maximum growth obtained at the optimal concentration of the neoauxin from the media of different reactions, we can see, that in the acid medium in a relativ way there are formed more thalli than in the basic medium.

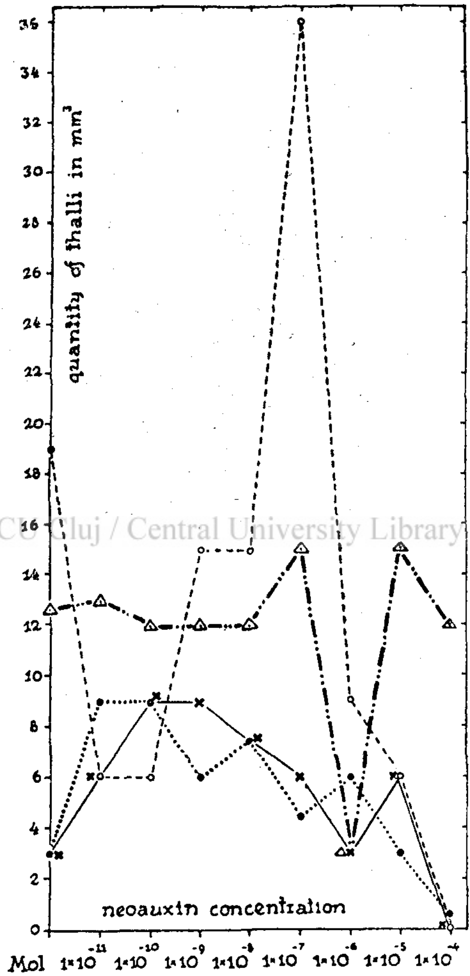

Fig. 5. Multiplication of algae in several concentrations of β-indole-acetic acid.
.... = *Pseudendoclonium basiliense,*
———————— = *Stigeoclonium variabile,*
—··—··—··—·· = *Microthamnion Kützingianum,* in alkaline medium and
············· = *Microthamnion Kützingianum* in acid medium.

In acid medium at the optimal concentration of the neoauxin ($1x10^{-11}$ Mol), there is formed a growth of thalli with 1275 % greater than in the mineral control medium. In alkaline medium at the optimal concentration of neoauxin ($1x10^{-9}$ Mol) the quantity of the thalli is only with 67·44 % greater than the thalli's quantity found in the Benecke solution.

Examining the lenght of the cells from *Microthamnion Kützingianum* which were formed on solutions with different concentration of neoauxin and of different chemical reactions (Table VI, VII, Fig. 4, 8) we establish that generally the lenght's growth of the cells is more accentuated in the acid media. In the acid solutions the optimal neoauxin concentration for the activation of the cell's growth is of $1x10^{-8}$—$1x10^{-7}$ Mol. In this concentration the growth of the cell's lenght is with 48·27 % greater in comparison with the control culture. In basic medium the growth in lenght of the cells is activated by neoauxin. The optimal concentration of neoauxin in basic medium for the lenght growth of the cells is $1x10^{-10}$—$1x10^{-11}$ Mol. In this concentration the growth in lenght of the cells might be with 90 % greater than of the cell's formed in the control solution. For the evaluation of these results we have to consider the results published by Migula, Péterfi, Vischer, according to which the acidity of the medium provokes a greater growth of the algae's cells, the ones prodused by a neutre or basic reaction (Péterfi 1937).

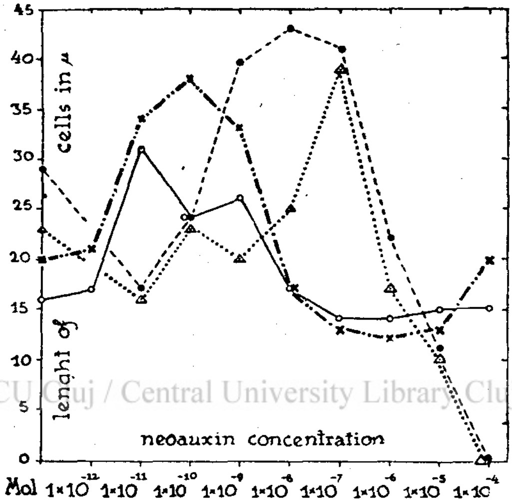

Fig. 6. Cells lenght of *Microthamnion Kützingianum* in sevaral concentrations of β-indole-acetic acid.

Lenght of terminale cells in acid medium --------------
and alkaline medium —..—..—..—.. .
Lenght of subterminale cells in acid solution ....
and in alkaline solution ————————— .

At the *Pseudopleurococcus Printzii* the growth in lenght of the cells is more accentuated in acid medium and much more redused in basic medium. In acid solutions the optimal β-indole-acetic acid concentration for the growth in lenght of the cells is of 1x10^{-5}—1x10^{-6} Mol. In the optimal concentration the growth of the cells in lenght is with 45·45% greater than in the control medium. The optimal concentration in basic medium is between 1x10^{-9} Mol and 1x10^{-5} Mol, at which the growth is with 50% greater than in the control solution.

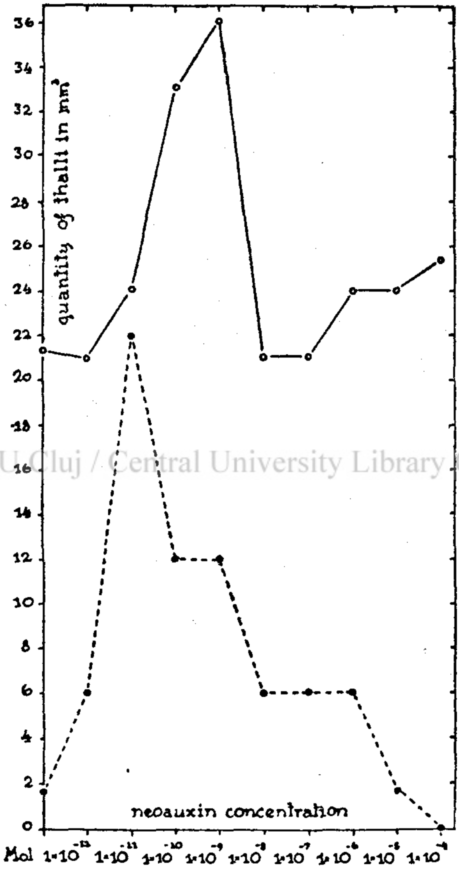

Fig. 7. Multiplication of *Pseudopleurococcus Printzii* in several concentrations of β-indole-acetic acid.

- - - - - - - - - - in acid medium (pH 4·5—4·6) and

———————— alkaline medium (pH 8·3—8·4).

The neoauxin is not presenting any activating effect on the diametrical growth of the cells of the *Microthamnion* and *Pseudopleurococcus.*

The lenght of the thalli depends of the number and of the lenght of the cells. The number of the cells for the pluricellular thallus represents the grade or the speed of the cellular division. The neoauxin in-

TABLE VIII. Effect of β-indole acetic acid upon multiplication and growth in alga *Pseudopleurococcus Printzii* Vischer, acid medium.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Initial number of thalli 7. II. 1944	Terminal quantity of thalli in mm³ per 15 cm³ nutrient solution 10. III. 1944	Dimension of cells μ		Lenght of thalli μ
	initial 8. II. 1944	final 14. III. 1944			diameter	lenght	
1×10^{-4} Mol	4·1	4·3	2400	—	—	—	—
1×10^{-5} Mol	4·5	4·5	2400	0·8	3·7—11·25	13—52·5	120—180
1×10^{-6} Mol	4·5	4·5	2400	3	3·7—7·5	10—55	75—180
1×10^{-7} Mol	4·5	4·5	2400	3	3·1—7·5	10—50	60—120
1×10^{-8} Mol	4·5	4·6	2400	3	3·1—6·25	10—50	60—120
1×10^{-9} Mol	4·5	4·5	2400	6	3·1—7·5	8·75—44	75—120
1×10^{-10} Mol	4·5	4·6	2400	6	2·5—5	6·25—35	50—60
1×10^{-11} Mol	4·6	4·6	2400	11	3·1—5	8·7—21	60—75
1×10^{-12} Mol	4·4	4·5	2400	3	3·1—5	6·7—35	60—70
Control	4·6	4·6	2400	0·8	3·1—10·5	5—40	60—70

TABLE IX. Effect of β-indole acetic acid upon multiplication and growth in alga *Pseudopleurococcus Printzii* Vischer, alkaline medium.

Concentration of β-indole acetic acid (neoauxin) per 100 cm³ Benecke solution	pH of nutrient solution		Initial number of thalli 31. I. 1944	Terminal quantity of thalli in mm³ per 15 cm³ nutrient solution 2. III. 1944	Dimension of cells μ		Lenght of thalli μ
	initial 1. II. 1944	final 7. III. 1944			diameter	lenght	
1×10⁻⁴ Mol	7·5	8·3	2400	25·50	3·75—7·5	5 —8·75	75—85
1×10⁻⁵ Mol	7·5	8·3	2400	24	3·1—7·5	3·7—10	100—110
1×10⁻⁶ Mol	7·5	8·4	2400	24	4·3—6·25	3·7—10	85—100
1×10⁻⁷ Mol	7·5	8·3	2400	21	4·3—7·5	4·3—7·5	100
1×10⁻⁸ Mol	7·5	8·3	2400	21	3·7—7·5	3·7—10	100—110
1×10⁻⁹ Mol	7·5	8·3	2400	36	3·1—6·25	3·75—11·25	100—110
1×10⁻¹⁰ Mol	7·5	8·3	2400	33	3·7—7·5	3·7—7·5	110—120
1×10⁻¹¹ Mol	7·5	8·3	2400	24	5 —7·5	5—10	50—90
1×10⁻¹² Mol	7·5	8·3	2400	21	4·3—6·25	3·75—8·75	140—170
Control	7·6	8·4	2400	21·5	3·7—7·5	3·7—7·5	80—120

fluences the lenght of the thalli too. Examining the dataes shown in Table VI and VIII, concerning the dimension of the thallus of *Microthamnion*, we can see, that the optimal concentration for the lenght of the thallus (1x10^{-7}—1x10^{-8} Mol) in acid medium, coincides, more or less,

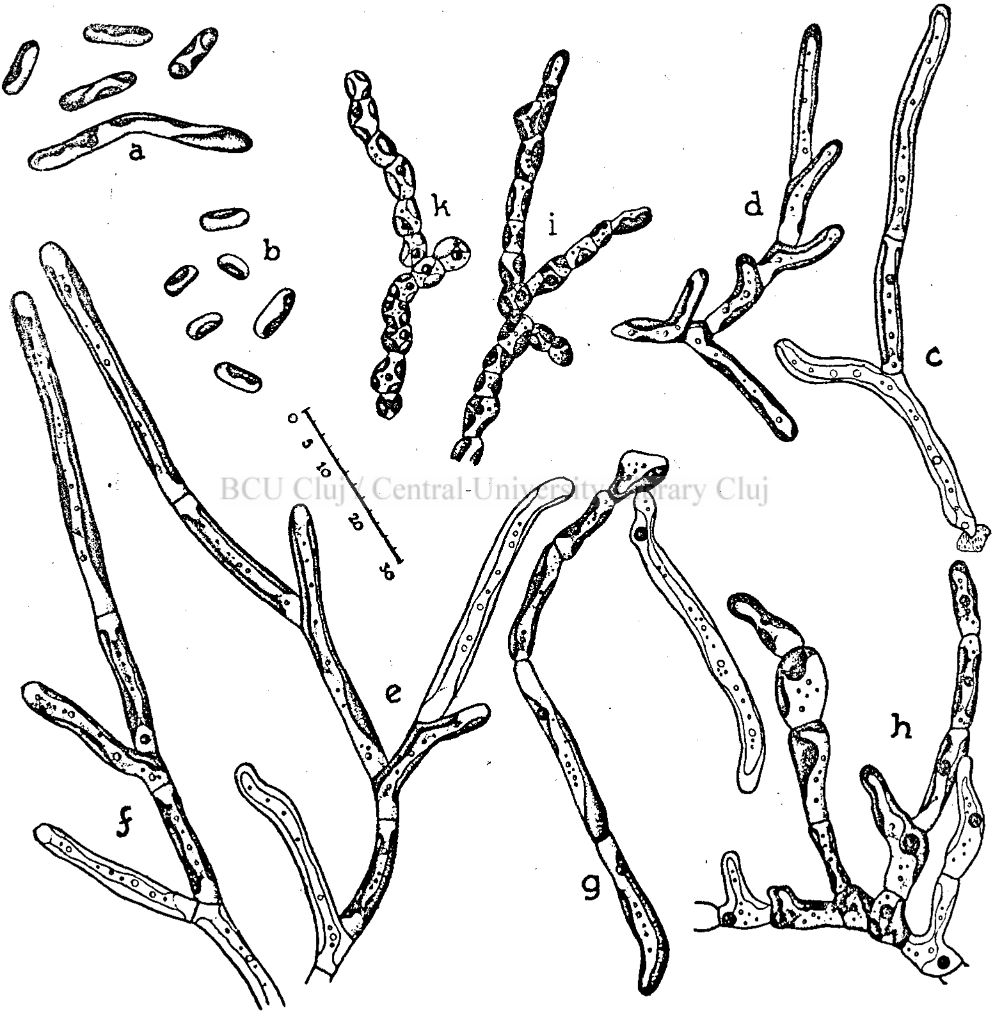

Fig. 8. Effect of β-indole acetic acid upon growth of algae: a) *Stichococcus exiguus*, neoauxin conc. 1×10^{-9}, pH 6·9. — b) *Stichococcus exiguus*, control, pH 6·5. — c) *Microthamnion*, neoauxin conc. 1×10^{-10}, pH 8·3. — d) *Microthamnion*, control, pH 8·4. — e) *Microthamnion*, neoauxin conc. 1×10^{-7}, pH 6·4. — f) *Microthamnion*, control, pH 6·1. — g) *Pseudopleurococcus*, neoauxin conc. 1×10^{-6}, pH 4·5. — h) *Pseudopleurococcus*, control, pH 4·6. — i) *Pseudopleurococcus*, neoauxin conc. 1×10^{-9}, pH 8·3. — k) *Pseudopleurococcus*, control, pH 8·4. (Mikrometer in μ).

with the optimal concentration for the growth in lenght of the cells. At the optimal concentration the lenght of the thallus with 55·55 % is greater than in the control medium. Taking the difference between the percentage of the lenght of the thallus at its optimum and the percentage of the cell's growth in lenght one finde that the cellular division of the thallus of *Microthamnion* is with 7·28 % more active than of the thalli from the control solution. In the basic medium the optimal concentration for the lenght of the thallus of *Microthamnion* ($1\text{x}10^{-11}$ Mol) corresponds with the optimal concentration for the lenght of the cells. The percentage increase of the lenght of the thalli at the optimal concentration is 141·53 %, while the difference with the percentage of growth in the cell's lenght is 51·53 %, representing by percentage the activity of the neoauxin upon the process of cellular division.

The lenght of the thallus of the *Pseudopleurococcus* presents variations in report to the neoauxin concentration. In acid medium the optimal concentration for the growth of the thallus is $1\text{x}10^{-5}$ Mol, at which there are formed with 130·76 % longer thalli than in the Benecke solution without neoauxin. Cellular divisions at this optimal concentration are very rare, fact that can be established at the microscopic examination too (Fig. 8.) In alkaline media I have found the longest thalli at $1\text{x}10^{-12}$ Mol of neoauxin, at which there were formed with 50 % longer thalli than in the control medium. The lenght of the thallus compared to the cell's growth in lenght is showing that in the optimal neoauxin concentration the cellular division is less active, with 5 % greater than in control medium.

Conclusions

After the researches made for the action of the β-indole-acetic acid upon the development of the studied algae I could verify that in certain concentrations the neoauxin presents a toxic effect upon the development of the algae, inhibiting completely their development. The toxic concentration of neoauxin varies with the species of the algae. The hydrogen-ion concentration influencing the penetration of the growth substance in the cells, is regulating its toxicity. In acid medium the neoauxin activates more toxic, in alkaline medium its toxicity is more reduced. In a bigger diluation the neoauxin stimulates the development of the studied algae. The optimal concentration of neoauxin is different, it varies after the algae species and with the pH of the solution. The favorable action of the neoauxin upon the algae's development is manifested in the stimulation of cellular division [vegetativ cellular division (*Stichococcus, Microthamnion, Stigeoclonium*) and the formation of special cells of reproduction: zoogonidium, gamet (*Microthamnion, Stigeoclonium*)] and in an activity effect of the cellular growth in lenght (*Stichococcus, Microthamnion, Pseudopleurococcus*).

The auxogenic effect of the neoauxin in alkaline medium is manifested more favorably at *Microthamnion* and *Pseudopleurococcus*. The percentage of the cellular division and of the cellular growth in lenght, resulted after the influence of the growth substance, is greater in alkaline medium. The cellular growth and division more accentuated in acid medium is apparent and is explaned through the insummation of the hydrogen-ion effect upon the acceleration of cellular division and growth and of the auxogenic influence of the neoauxin. Therefore, it is evident, that the neoauxin is not influencing by its hydrogen-ions or by its —COOH radical. Discarding the acidity from the culture medium we can see that in alkaline medium the neoauxin not anly remains active, but in reality is producing a greater effect.

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A β-indolecetsav hatása az algák növekedésére és szaporodására

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(A Növényfiziológiai Intézet közleménye)

Összefoglalás

A heteroauxim physiologiai hatásával foglalkozó irodalomból láthatjuk, hogy a különböző szerzők által, különböző vagy azonos algafajokon végzett tenyésztési-kisérletek eredményei eltérőek, sőt ellentétesek. A β-indolecetsav növekedés- és szaporodásphysiologiai hatását *Stichococcus, Stigeoclonium, Pseudendoclonium, Microthamnion* és *Pseudopleurococcus* fajokon tanulmányoztam, melyeket Bakteriumoktól és Gombáktól mentes tisztatenyészetekben neveltem. A 0·191 $^0/_{00}$-es totális koncentrációjú Benecke-féle tápoldathoz Scheering-féle neoauxint használtam 1×10^{-4}—1×10^{-12} Mol hígításban. A tápoldat kezdeti és vég-pH értékét kolometrikus módszerrel mértem. A képződött thallusok mennyiségi meghatározását fajok szerint haemocytométerrel illetőleg nitrocentifugálási módszerrel végeztem. Okuláris nikrométer segítségével mértem és mikronban fejeztem ki a sejtek és thallusok dimenzióit.

A kisérletek számeredényeit az angol szövegben található táblázatokban (I—IX) és ábrákban (1—8) foglaltam össze.

A *Stichococcus* fajokkal végzett kisérletek mutatják, hogy ezek a neoauxinnal szemben különböző módon viselkednek; fajok szerint változik a neoauxin toxikus és optimális koncentrációja. A *Stichococcus exiguus* nevű fajnál a neoauxin elősegiti a sejtosztódást és sejtmegnyúlást, ezzel szemben a *Stichococcus mirabilis*nél csak a sejtosztódás gyarapodását észleltem.

Stigeoclonium és *Pseudendoclonium*mal végzett kisérleteim csak thallus- és sejtgyarapodást mutattak, ezeknél a fajoknál tehát a neoauxin optimális töménységben a sejtek vegetatív osztódását és a zoogonidiémok képződését segíti elő.

A neoauxin serkentő hatása és a tápoldat hidrogénion koncentráció-növekedésphysiologiai hatása közötti összefüggést a *Microthamnion Kützingianum* és *Pseudopleurococcus Printzii* fajokon tanulmányoztam. Mindkét faj érzékeny, egyrészt a neoauxin, másrészt a hidrogénion koncentráció fejlődésbefolyásoló hatására. A neoauxin hatása ezeknél a fajoknál a zoogonidiumokkal illetőleg ganétákkal való szaporodás, a sejtek vegetatív osztódása és a sejtek megnyúlás által való növekedése stimulálásában nyilvánul meg. Az eredmények pontos leértékelhetése céljából, százalékosan számítottam ki, az ellenőrző kisérlethez arányitva, a neoauxin serkentő hatására előálló gyarapodást a thallus mennyisége, a sejtek megnyúlása és a sejtek osztódása esetében. Ezen összehasonlításból kitűnik, hogy a *Microthamnion* és a *Pseudopleurococcus* telepek szaporodását (zoogodinium és gameta képződést) a neoauxin erősebben aktiválja a a savanyú kémhatású, mint a bazikus reakciót mutató tápoldatokban, ezzel szemben viszont a sejtnövekedés és sejtosztódás neoauxin okozta százalékos gyarapodása a lúgos kémhatású tápoldatokban nagyobb.

A kisérletek eredményei azt mutatták, hogy a neoauxin nagyobb koncentrációkban (1×10^{-4}—1×10^{-5} Mol) toxikusan hat az algák fejlődésére, megakadályozva teljesen a fejlődést. A neoauxin mérgező hatású koncentrációja változik a tápoldat pH-értékével. Savanyú kémhatású oldatokban a neoauxin fejlődésgátló hatása nagyobb, míg az oldatok bazikus hatása csökkenti ezt a toxikus hatást. Nagyobb hígitásban (1×10^{-7}—1×10^{-11}) a β-indolecetsav stimulálja az algák fejlődését. Ez az optimális neoauxin koncentráció változik fajok és az oldat pH értéke szerint. A β-indolecetsav kedvező, auxogenikus hatása erősebben nyilvánul meg a bázikus kémhatású tápoldatokban fejlődő algák esetében. A savanyú tápoldatokban észlelhető, látszólagos nagyobb sejtosztódás és sejtnövekedés a hidrogénion koncentráció és a neoaxin hatásának összegeződésével magyarázható. A neoauxin növekedésserkentő hatása nem hidrogénionjainak illetőleg savgyökének tulajdonítható. Ha kiküszöböljük a tápoldatok aciditását, a neoauxin serkentő hatása nemcsak hogy megmarad, de nagyobb effecttussal érvényesül a bazikus oldatokban.

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TARTALOM

(Idegen nyelvű közlemények, magyar összefoglalásokkal)

Felelős kiadó: **Csik Lajos**
Minerva Rt. Cluj-Kolozsvár. No. 99. Fsoc. jud. Cluj. 10151. Felelős vezető: Kiss Márton igazgató

Despre un integraf de vectori plani

Samuil Borbély

(Comunicarea Institutului de Matematică Aplicată)

Rezumat

Descrierea unui dispozitiv mecanic rulând pe roţi ascuţite, care ne dă (teoretic exact) curba integrală a vectorilor plani de o variabilă reală.

O deducţie a ecuaţiei lui Schrödinger

I. Fényes

(Publicaţia Institutului de Fizică Teoretică)

Rezumat

Pe baza relaţiei de incertitudine a mecanicei cuantice (1) şi a relaţiei analoage a statisticei clasice (2), „distribuţia probabilităţii" unui sistem, poate fi identificată cu densitatea unui gaz ideal. Din acest fapt rezultă foarte simplu ecuaţia lui Schrödinger. Şi ipoteza lui Born urmează ca un rezultat al acestui fapt.

Contribuţiuni la mecanismul creşterei cristalelor

Zoltan Gyulai

(Publicaţia Institutului de Fizică Experimentală)

Rezumat

Teoria moleculară a lui Kossel ne dă o imagine clară în ce priveşte unele puncte relative la creşterea cristalelor. Însă teoria are şi mulţi adversari. Astfel Balarew îşi exprimă neîncrederea că ar putea să fie ceva adevărat în această teorie. Dar totuşi unele fenomene experimentale

justifică în mod formal pe Kossel, deşi între cazul ideal prevăzut de teoria lui Kossel (ioni singulari) şi între grosimea stratului pe care-l putem cbserva (10.000 de ioni) există o mare diferenţă. Autorul întrebuinţează aici formula lui Hirschel, dedusă după metoda lui Madelung, după care un cristal produce în jurul său un câmp electric. Intensitatea câmpului electric:

$$E \backsimeq \frac{e}{a^2} z\pi \cdot 16 \cdot e^{-2\pi\sqrt{2}\cdot\frac{z}{a}}$$

Admiţând acest câmp electric ne putem închipui că în imediata vecinătate a suprafeţei de cristal, molecule de NaCl împreună cu molecule de apă se găsesc într'o stare mai mult, sau mai puţin aranjată şi formează astfel continuarea reţelei de cristal. Aceasta aranjare e mai mare la muchii şi cea mai accentuată este la vârfuri. Astfel aranjarea complect regulată va porni dela vârfuri. În acest strat, mai mult sau mai puţin aranjat, densitatea moleculelor de NaCl e mai mare ca în soluţie şi astfel sunt înlăturate şi greutăţile rezultate din vitezele mici de difuziune.

In această concepţie cazul ideal a lui Kossel şi procesul adevărat al fenomenului de cristalizare sunt în aşa fel în legătură, încât deducţiunile importante ale teoriei lui Kossel rămân în mod formal valabile.

Despre asimetria electrozilor de ordinul al II-lea

Ludovic Imre şi Francisc Sarusi

(Contribuţiunea Institutului de Chimie Generală şi de Chimie Fizicală)

Rezumat

Într'o lucrare precedentă („Múzeumi Füzetek" anul 1943 vol. I.) unul dintre autori (L. I.) a ajuns la concluzia teoretică, că potenţialul electrozilor de ordinul al II-lea faţă de soluţiunile electrolitice de foarte mică concentraţie, poate avea valori diferite de valorile prescrise de formula lui Nernst.

Raportând potenţialul electrodic la soluţiunea saturată în apă pură a electrodului, adică dacă construim un element galvanic de concentraţie în care avem soluţiunea cu concentraţiunea arbitrară $(C_+)_0$, faţă de soluţiunea cu concentraţiunea arbitrară C_+ ($C_+ =$ concentraţiunea în această ultimă soluţiune a componentului de ion pozitiv al electrodului) atunci vom găsi conform cercetărilor teoretice ale autorului următoarea valoare pentru forţa electromotrice a elementului galvanic de concentraţiune:

$$\varepsilon - \varepsilon_0 = \frac{RT}{\nu F} \cdot \ln \frac{C_+}{(C_+)_0} - \frac{1}{2} \cdot \frac{RT}{\nu F} \cdot \left[\ln \frac{X_-}{X_+} - \ln \left(\frac{X_-}{X_+} \right)_0 \right] \quad . \ . \ . \ (1).$$

(X_-, X_+ = numărul locurilor active al anionului, respectiv al cationului, în cazul concentraţiunii arbitrare C_+.
X_-, X_+ = aceleaşi valori în cazul concentraţiunii $(C_+)_0$ a cationului; toate valorile fiind calculate în legătură cu aceaşi suprafaţă a electrodului,
ν = valenţa ionului, F = numărul lui Faraday.)

In lucrarea de faţă se tratează examinarea experimentală a acestei formule de potenţial electrodic precum şi desvoltarea mai departe a teoriei mai sus menţionate.

Controlul experimental al formulei Nr. (1) a fost făcut de autori în modul următor: Au comparat valorile potenţialului electrodic ale diferitelor cristale naturale şi artificiale (valorile au fost obţinute prin electrometru cu cadran) cu puterea de adsorpţie faţă de componentele de anioni şi cationi ale pulberilor fine cu mare suprafaţă de adsorpţie, făcute din aceleaşi cristale. Prin reprezentarea grafică a acestor măsurări de adsorpţie conform ecuaţiei-isoterme dată de LANGMUIR, s'au dedus valorile lui X, care fiind substituite în ecuaţia Nr. (1), au condus la rezultate numerice, care în general au fost în perfectă concordanţă cu datele obţinute de măsurările directe de potenţial.

Desvoltarea mai departe a teoriei de mai sus are de scop determinarea valorilor numerice ale potenţialului electrodic în funcţiune de concentraţia electrolitului, fără efectuarea măsurărilor de adsorpţie. Această problemă se prezintă deasemenea rezolvabilă cu ajutorul noţiunii de „loc-activ", a cărui definiţie a fost dată deasemenea de autor (Koll. Zs. 91, 1940., 32). Calculele amănunţite referitoare la această problemă vor fi publicate de autor într'o lucrare următoare, şi aceste calcule vor fi bazate pe ideile arătate în publicaţiunea de faţă. Aceste idei au ca punct de plecare variaţia energiei libere a stratului cristalin de pe suprafaţa de separaţie a fazelor în urma efectului DEBYE—HÜCKEL şi în urma adsorpţiei de substituţie a ionilor străini.

Cercetări în domeniul combinaţiunilor furanice. Comunicarea I.: Hexen-2-dion 4,5-acetal-1 şi formarea pirocatechinei din 2-acetil-furan

Ladislau Vargha, Eugen Ramonczay şi Paul Bite

(Comunicarea Institutului de Chimie Organică)

Rezumat

Cu ocazia încercărilor făcute pentru obţinerea 2-amino-furanului am găsit, că prin acţiunea alcoolului etilic asupra p-toluensulfo-2-acetil-furan-oximei (I)*, se formează p-toluensulfonat de amoniu şi, cu randament

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* Formulele şi citatele din literatură v. în textul englez.

bun, un lichid galben verzui fără azot, care prezintă proprietăţi chimice remarcabile. In adevăr noua substanţă reduce energic, este foarte sensibilă faţă de căldură şi agenţii chimici cu toate acestea poate fi distilată în vacuum fără descompunere. Am stabilit, că compoziţia elementară a substanţei poate fi exprimată prin formula moleculară $C_{10}H_{16}O_4$ (III). Când am făcut să acţioneze alcoolul metilic în locul alcoolului etilic, am obţinut pe lângă p-toluensulfonat de amoniu un lichid foarte asemănător cu III, dar totuşi nu identic cu el, care pe baza analizelor are formula moleculară $C_8H_{12}O_4$ (IV).

Cu ajutorul metodelor potrivite am reuşit să lămurim constituţia şi configuraţia substanţelor III şi IV. Ca rezultat al cercetărilor noastre am dovedit, că structura substanţei III poate fi exprimată cu formula de constituţie: $CH_3\text{-}CO\text{-}CO\text{-}CH = CH\text{-}CH(OC_2\text{-}H_5)_2$ şi luând în considerare şi configuraţia are numele raţional cis-hexen-2-dion-4,5-diethilacetal-1, iar substanţa IV este dimetilacetalul respectiv (cis-hexen-2-dion-4,5-dimetilacetal-1). Asupra mecanismului de formare al acestor substanţe încă nu putem da o schemă precisă.

Aldehida nesaturată (cis-hexen-2-dion-4,5-al-1, XI) corespunzătoare acestor acetali nesaturaţi nu a putut fi obţinută prin hidroliza acetalului III sau IV, căci aceasta se descompune deja la rece în soluţie apoasă. Dintre produşii de descompunere aşteptaţi am reuşit să izolăm acid acetic, a cărui formare arată, că lanţul de carbon se rupe hidrolitic între grupările-carbonilice-4 şi -5. Probabil, că ruperea catenei, care se produce deja printr'o acţiune atât de blândă, se datoreşte acţiunei labilizante a dublei legături din poziţia 2, 3.

Nici aldehida saturată (hexan-dion-4,5-al-1, XII) nu s'a dovedit a fi o combinaţie mai stabilă. In adevăr, când am supus hidrolizei acetalii saturaţi (V şi VI), obţinuţi prin hidrogenarea catalitică a acetalilor III şi IV, în locul aldehidei saturate (XII) aşteptate în mod surprinzător s'a format pirocatechina. Formarea pirocatechinei se poate înţelege uşor, dacă presupunem ca produs intermediar forma trienolică (XIII) a aldehidei XII.

Acest din urmă fapt serveşte de bază presupunerii, că derivaţii pirocatechinei atât de răspândiţi în natură, poate se formează din hidraţii de carbon prin intermediul combinaţiunilor furanice în urma unor procese asemănătoare.

Cercetări în domeniul alcoolilor zaharici.
Comunicarea IV: 2,5-anhidro-1-idita

Ladislau Vargha, Tiberiu Puskás şi Andrei Nagy

(Comunicarea Institutului de Chimie Organică)

Rezumat*

In comunicarea[1] anterioară am făcut o dare de seamă asupra cercetărilor în decursul cărora am dovedit, că structura şi configuraţia mono-

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* Formulele şi citatele din literatură v. în textul englez.

toluensulfo-anhidro-hexitei[2] obţinută din 1-p-toluensulfo-2,4-benzal-5,6-anhidro-d-sorbită se poate reprezentă prin formula I, deci substanţa este 1-p-toluensulfo-2,5-anhidro-1-idita. Nu am reuşit însă să obţinem în stare unitară substanţa de bază 2,5-anhidro-1-idita, nici prin hidroliza combinaţiei I, nici prin intermediul derivatului 1,6-diiodat.[1] Între timp prof. K. FREUDENBERG într'o scrisoare ne-a atras atenţia asupra unei lucrări publicate de el mai de mult, în care el a reuşit să obţină cu randament bun diaceton-glucoza prin reducerea 3-p-toluensulfo-diaceton-glucozei cu amalgam de sodiu, deci să îndepărteze din combinaţiunea amintită gruparea toluensulfonică sub formă de acid p-toluensulfinic fără reacţii secundare.[3] Fiindcă pe noi ne-a interesat în mod general îndepartarea grupei toluensulfonice din esterii formaţi cu polialcooli, am cercetat aplicabilitatea în scopul amintit al acestei metode reductive. Rezultatul cercetărilor îl rezumăm în cele de mai jos.

1. Reducerea substanţei I cu amalgam de sodiu nu conduce la un produs unitar, căci pe lângă 2,5-anhidro-idita (II) şi acidul p-toluensulfinic aşteptat, prin scindare de acid p-toluensulfonic se mai formează şi o dianhidro-hexită. Cei doi produşi pot fi separaţi prin intermediul acetaţilor lor aşa, că am reuşit să obţinem substanţa II în stare unitară, cristalizată. Dianhidro-hexita este o substanţă siropoasă, constituţia ei încă n'am studiat-o mai de aproape.

2. Nici reducerea a 6-p-toluensulfo-1,2-aceton-glucofuranozei[4] şi a 5,6-di-p-toluensulfo-1,2-aceton-glucofuranozei[5], nu conduce la un produs unitar. Din prima pe lângă 1,2-aceton-glucofuranoza (randament 40%) aşteptată se mai formează şi o substanţă siropoasă, din ultima în mare parte se obţine 3,6-anhidro-1,2-aceton-glucafuranoză[6], deci în acest ca din urmă reacţia merge aproape exclusiv în sensul scindării de acid p-toluensulfonic.

3. Fiindcă se putea presupune, că scindarea de acid p-toluensulfonic, deci formarea combinaţiunilor anhidro se datoreşte reacţiunii alcaline, am efectuat reducerea şi în mediu aproape neutru prin întroducere de bioxid de carbon. Aceste încercări au condus şi mai puţin la rezultatul dorit. In adevăr în acest caz din 6-p-toluensulfo-1,2-aceton-glucofuranoză s'a format cu randament bun 5,6-anhidro-1,2-aceton-glucofuranoză[7], iar 5,6-di-p-toluensulfo-1,2-aceton-glucofuranoză a rămas neschimbată.

Cercetările noastre arată deci, că cu toate, că în multe cazuri esterii acidului p-toluensulfonic cu polialcooli pot fi scindaţi prin reducere în alcoolii corespunzători şi acid p-toluensulfinic, totuşi din cauza scindării de acid p-toluensulfonic se pot forma concomitent şi derivaţi anhidro.

Influenţa acidului β-indol-acetic asupra creşterii şi multiplicaţiei algelor

I. Péterfi

(Publicaţiunea Institutului de Anatomie şi Fiziologie Vegetală)

Rezumat

Din literatura care se ocupă cu rolul fiziologic al heteroauxinei la alge reese, că rezultatele obţinute sunt în general contradictorii, experienţele repetate de diferiţi autori, chiar la aceeaş specie de algă, au dat rezultate neconcludente sau contrare.

Am studiat acţiunea acidului β-indolacetic asupra fiziologiei creşterii şi multiplicaţiei la speciile de *Stichococcus*, *Stigeoclonium*, *Pseudendoclonium*, *Microthamnion* şi *Pseudopleurococcus* cultivate în culturi pure fără Bacterii şi Ciuperci.

La soluţia nutritivă Benecke — de o concentraţie totală de 0,191‰ — am folosit neoauxina Scheering în concentraţie de 1×10^{-4}—1×10^{-12} Mol. Valoarea iniţială şi finală a pH-ului soluţiei nutritive am determinat-o cu metoda colorimetrică. Determinarea cantitativă a recoltei am făcut-o după specii, cu ajutorul haemocytometrului şi prin metoda de centrifugare. Dimensiunea celulelor şi a talurilor am măsurat-o cu ajutorul micrometrului ocular exprimând-o în microni.

Rezultatele numerice ale experienţelor le-am rezumat în Tabelele (I—IX) şi Figurile (1—8) ce se află în textul englez.

Experienţele cu speciile de *Stichococcus* arată că ele se comportă diferit faţă de acţiunea neoauxinei; concentraţia toxică şi optimă a neoauxinei variază după specie. La specia *Stichococcus exiguus* neoauxina stimulează diviziunea celulară şi creşterea în lungime, în schimb la *Stichococcus mirabilis* n'am observat decât stimularea diviziunii celulare.

Experienţele cu *Stigeoclonium* şi *Pseudendoclonium* arătau numai o creştere a talurilor şi a celulelor, deci la aceste specii neoauxina administrată în concentraţie optimă stimulează diviziunea celulară vegetativă şi formarea zoogonidiilor.

Raportul dintre efectul auxogenic şi concentraţia pH a soluţiei nutritive am studiat-o la speciile *Microthamnion Kützingianum* şi *Pseudopleurococcus Printzii.* Ambele specii sunt sensibile atât la acţiunea auxogenică a neoauxinei, cât şi la concentraţia ionilor de hidrogen. Acţiunea neoauxinei la aceste specii se manifestă prin: stimularea înmulţirii prin zoogonidii şi gameţi, stimularea diviziunii celulare vegetative şi al creşterii în lungime a celulelor. Pentru stabilirea exactă a rezultatelor am calculat procentual creşterea cantitativă a talului, lungirea celulelor şi sporirea diviziunii celulare sub influenţa stimulatoare a neoauxinei raportată la experienţa de control. Din această comparaţie rezultă că, înmulţirea talurilor (formarea zoogonidiilor şi gameţilor) la *Microthamnion* şi *Pseudopleurococcus* este activată mult mai intens de neoauxină în soluţiunile nutritive cu reacție acidă decât în cele cu reacție bazică. In schimb creșterea celulelor și diviziunea celulară exprimată procentual este cu mult mai mare în mediu bazic.

Rezultatele experiențelor au arătat că neoauxina în concentrațiuni mai mari (1×10^{-4}—1×5^{-5} Mol) are un efect toxic asupra desvoltării algelor, împiedecându-le complect desvoltarea. Concentrația toxică de neoauxină variază cu valoarea pH a mediului. In mediu acid neoauxina acționează mai toxic, pe când în mediu alcalin toxicitatea ei este mai scăzută. Intr'o dilufiune mai mare (1×10^{-7}—1×10^{-11}) acidul β-indolacetic stimulează desvoltarea algelor. Concentrația optimă de neoauxină variază după speciile de alge și cu pH soluției. Acțiunea favorizantă, auxogenică a acidului β-indolacetic se manifestă mai intens în cazul algelor cultivate în mediu bazic. Creșterea și diviziunea celulară mai accentuată în mediu acid este aparentă și se explică prin însumarea efectului ionilor de hidrogen și al influenței auxogenice al neoauxinei. Evident că neoauxina nu influențează prin ionii săi de hidrogen sau prin radicalul său acid. Inlăturând din mediul de cultură aciditatea vedem că în mediul alcalin neoauxina nu numai că rămâne activă, dar în realitate produce un efect mai mare.