17 ## SÉANCE PUBLIQUE ANNUELLE DU 20 MAI 1905.

S. E. M. Julien Dunajewski, Vice-Protecteur de l'Académie, ouvre la séance au nom de Son Altesse Impériale et Royale, le Protecteur.

Le Président de l'Académie, S. E. M. le comte Stanislas Tarnowski, prononce l'allocution d'usage.

M. Boleslas Ulanowski, Secrétaire général, rend compte des travaux de l'Académie pendant l'année qui vient de s'écouler et annonce que dans la séance plénière du 19 mai. M. Guillaume Bruchnalski, professeur à l'université de Léopol, a été élu membre correspondant de la Classe de philologie.

Le Secrétaire général donne ensuite lecture des noms des savants étrangers, nommés en 1903 et 1904, membres de l'Académie, et dont l'élection a reçu la haute approbation de Sa Majesté l'Empereur et Roi.

Ce sont:

a) Dans la Classe des Sciences mathématiques et naturelles, membres titulaires:

MM. Pierre Duhem, professeur à l'université de Bordeaux,
François Kamieński, professeur à l'université d'Odessa,
Stanislas Kostanecki, professeur à l'université de Berne.

b) Dans la Classe de philologie, membres correspondants:

MM. Louis Fournier, rédacteur à la »Gazette des Beaux-Arts«, à Lyon,

Boleslas Erzepki, Secrétaire de la Société des amis des Sciences à Posen,

Stanislas Ptaszycki, agrégé à l'université de S. Pétersbourg.

c) Dans la Classe d'Histoire et de Philosophie, membres correspondants:

MM. Sigismond Celichowski, bibliothécaire à Kurnik,

Ladislas Smoleński, historien et homme de lettres à Varsovie,

l'abbé Stanislas Chodyński, prélat du chapitre à Wloclawek.

d) Dans la Classe des Sciences mathématiques et naturelles, membre correspondant:

M. Julien Talko-Hryncewicz, médecin à Troickojawsk en Sibérie.

M. Joseph Rostafiński fait ensuite une conférence sur le sujet suivant: *„La mémoire comme base générale du phénomène de la vie".*

Enfin, le Secrétaire général proclame les noms des lauréats de l'Académie.

Le Prix Barczewski d'une valeur de 2250 couronnes, destiné à récompenser l'ouvrage d'histoire le plus méritant est décerné à M. Joseph Tretiak pour sa monographie sur: *„Jules Slowacki".*

Le Prix Barczewski, de 2250 couronnes, pour le meilleur tableau est attribué à M. Casimir Pochwalski pour: *„Le Portrait de S. E. Zaleski".*

Le Prix du concours institué par l'abbé, Adam Jakubowski, d'une valeur de 1400 couronnes est décerné à M. Alexandre Brückner pour son livre: *„Nikolas Rej".*

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La veille de l'assemblée générale annuelle, c'est-à-dire le 10 mai, eût lieu la séance semestrielle administrative de l'Académie.

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Séance du mardi 9 Mai 1905.

Présidence de M. N. CYBULSKI.

18. M. M. H. GOLDMANN, J. HETPER et L. MARCHLEWSKI m. t. **Studya nad barwikiem krwi, IV.** *(Studies on the blood colouring matter, IV preliminary note).* *(Recherches sur la matière colorante du sang)*

It is well known that Nencki and Zaleski[1]) and Marchlewski and Nencki[2]) obtained by reduction of haematoporphyrin and phylloporphyrine respectively a substance of the formula $C_8 H_{13} N$, the so called haemopyrroline. According to the first two named authors haemopyrroline might be 3-methyl-4-propylpyrroline, a view which at first was shared by Küster[3]) and his coworkers, but lately[4]) called into question by him. Buraczewski and Marchlewski[5]) tried to further the problem by synthetical experiments. They reduced the synthetical methyl-propyl-maleinic imide, prepared according to Michael's and Tissot's[6]) method and obtained a minute quantity of a substance that possessed many properties of haemopyrroline; it gave for instance under the action of air a reddish brown colouring matter resembling urobilin, but these experiments were so far of purely qualitative nature and could not therefore decide the problem in question definitely.

For the pyrroline conception of haemopyrroline we have therefore so far only two, not quite binding, proofs: the empyrical formula and the fact that haemopyrroline colours firwood red. It occured to one of us (L. M.) that a strong support for the pyrroline conception of haemopyrroline might be obtained by studying its behaviour towards diazonium compounds. Pyrroline and some of its homoloques were investigated in this respect thoroughly by Fischer and Hepp[7]). These authors found that pyrroline reacts with diazonimucompounds yielding in acid solutions monoazocolouring matters, whereas in alkaline solutions in the presence of a sufficient

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[1]) This Bulletin **1901**, 217.
[2]) „ „ „ 277.
[3]) Ber. **35**, 2948 (1902).
[4]) „ **37**, 2470 (1904).
[5]) This Bull. **1904**, 397.
[6]) J. f. pract. Ch. [2] **46**, 300, 312.
[7]) Ber. **19**, 2251.

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quantity of the diazoniumcompound disazodyes are formed. It was also found that the diazonium radical may substitute as readily hydrogen atoms in the α as in the β position of the pyrroline nucleus, and it was therefore highly probable that haemopyrroline, should it really represent a homoloque of pyrroline, will also yield azodyes. These expectations were fully born out by experiments. We found that an ethereal solution of haemopyrroline shaken with a hydrochloric acid solution of a diazonium compound turns quickly reddish brown and on standing of the ethereal solution, which had been separated from the aequous solution, for some time reddish brown needles are formed which could represent a monoazo or a disazocompound of haemopyrroline. After this first experiment, carried out using only a comparatively small amount of haemopyrroline, we started experiments on a somewhat larger scale and found that the reaction between the product called haemopyrroline, and diazoniumcompounds is indeed far more complicated than was at first supposed and that there are formed at least three substances, of which up to now we succeeded in isolating in sufficient quantities only one.

Haemopyrroline and Benzenediazoniumchloride.

Haemopyrroline we obtained by reducing haemin with hydroiodic acid in the presence of phosphonium iodide. The haemin was prepared according to Nenckis and Zaleskis method, the quantity reduced for each experiment amounted to 5 g of haemin which were dissolved in a mixture of 100 g glacial acetic acid and 100 g of hydroiodic acid and heated on a waterbath. To this solution were added gradually 8 g of phosphonium iodide. As soon as the reduction was completed the excess of acetic acid was neutralised by adding caustic soda and distilled in a current of carbon dioxide. As soon as samples of the destilate showed no reaction with mercuric chloride we extracted the haemopyrroline with ether and treated the ethereal solution immediately with the diazoniumcompound obtained from 50 cm^3 $^1/_5$ n. aniline chloride solution, containing 2 mol. of free hydrochloric acid. The ethereal solution turned at once reddish brown and the colour gradually became dark violetish-brown. After separating the ethereal solution from the acid liquor the former yielded after a short time yellowish crystals which however after a days standing in the cold were replaced by brown

needles. These were filtered off washed with ether and then recrystallized in the following manner. They were dissolved in boiling alcohol and the solution obtained mixed with some ether saturated with hydrochloric acid and finally pure ether added. Under these conditions the crystallisation takes place rapidly and the product obtained shows a constant melting point of 233° and is, as analysis have shown, the hydrochloride of haemopyrroline-disazo-dibenzene.

Haemopyrroline-disazo-dibenzene hydrochloride crystallises in brown well developed pointed plates, resembling haemin; the crystals show faint metalic lustre, like nearly all azodyes. It dissolves in boiling alcohol comparatively easily with a violet-red colour, closely resembling the colour of permanganate solutions; in ether, benzene, chloroform it dissolves sparingly. Warm acetic acid dissolves it easily with a colour which appears more bluish than the alcoholic solution. The solution in conc. sulpuric acid appears at first bluish-violet but after some time it turns redder, and resembles at this stage alcoholic solutions.

We analyzed 6 different samples with the following results:

1) a, 0·1224 g. gave   0·0789 g. H_2O; 0·2908 g. CO_2
  b, 0·1475 „   „   0·0879 „   „   0·3508 „   „
2) a, 0·1065 „   „   0·0661 „   „   0·2566 „   „
  b, 0·1162 „   „   18·6 cm^3 N, $t=15$, $p=738$
3) a, 0·1181 „   „   19·35 „   N, $t=21$, $p=740$
4) a, 0·1417 „   „   0·0879 g. H_2O; 0·3414 g. CO_2
  b, 0·1300 „   „   21·1 cm^3 N, $t=13$, $p=746$
5) a, 0·1083 „   „   17·5 cm^3 N, $t=16$, $p=746$
  b, 0·1101 „   „   0·0723 g. H_2O; 0·2650 g. CO_2
6) a, 0·1925 „   „   0·0688 g. AgCl
  b, 0·1304 „   „   21·6 cm^3 N, $t=17$, $p=742$
  c, 0·1027 „   „   0·0659 g. H_2O; 0·2453 g. CO_2

	1		2		3	4		5		6		
	a	b	a	b	a	a	b	a	b	a	b	c
C	64·79	64·86	65·71			65·70			65·64			64·94
H	7·17	6·62	6·89			6·89			7·29			7·22
N				18·20	18·16		18·74	18·49			18·76	
Cl										8·83		

	Found (middle)	Calculated for $C_{20} H_{22} N_5 Cl$;	$C_{14} H_{18} N_3 Cl$
C	65·27%	65·25	63·75
H	7·01 „	6·03	6·83
N	18·47 „	19·08	15·94
Cl	8·83 „	9·64	13·48
	99·58 „	100·00	100·00

The results do not correspond exactly to the calculated values, but there cannot be any doubt, that if haemopyrroline possesses the formula $C_8 H_{13} N$, the azocompound is composed according to the formula $C_{20} H_{22} N_5 Cl$ and not the formula $C_{14} H_{18} N_3 Cl$, viz. it is a disazocompound of haemopyrroline.

An addition of caustic alkali to the alcoholic solution of the hydrochloride of haemopyrroline-disazo-dibenzene causes a considerable change in the coloration; the tint is now purer red, resembling the colour of oxyhaemoglobin. Water added to the alkaline solution precipitates the colouring matter in the form of a very fine precipitate and ether takes it up with a fine bright red colour. By evaporating the ethereal solution haemopyrroline-disazo-dibenzene is obtained in the form of a red lustrous amorphous body, easily soluble in alcohol, chloroform, benzene, petroleum ether and so forth. Its ethereal solution shaken up with diluted hydrochloric acid yields brownish needles of the hydrochloride compound described above. By dissolving the azodye in boiling alcohol and adding boiling water it may be obtained in the crystaline state but up to now we had not sufficient material to investigate it quantitatively.

As regards the constitution of haemopyrroline-disazo-dibenzene it might be expressed by the following formula:

$$CH_3 - C - C - C_3H_7$$
$$C_6H_5 - N_2 - C \quad C - N_2 - C_6H_5$$
$$NH$$
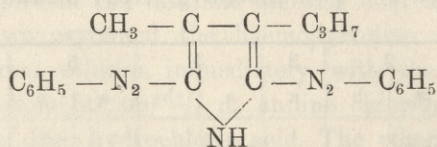
but we have so far no positive proofs that haemopyrroline is really methyl-propyl-pyrroline and not some other homoloque of pyrroline for instance diethyl-haemopyrroline or butylpyrroline; likewise there is no certainty that the alkylgroups occupy the β-positions.

It is however noteworthy that haemopyrroline forms so easily even in acid solutions diazocompounds and it is not improbable that this facility is in some manner connected with the constitution of the substance. An investigation of the behaviour of known bisubstituted homoloques of haemopyrroline towards diazoniumcompounds under similar conditions would prove highly interesting.

The optical properties of haemopyrroline - disazo - dibenzene are not particularly interesting. The solutions in neutral solvents cause in the spectrum two bands, corresponding to the following wave lengths:

Band 1, λ 551 — λ 532
Band 2. λ 517 — λ 495 .

The hydrochloride of haemopyrroline - disazo - dibenzene, dissolved in alcohol causes only one band which is not well defined and situated on the thallium line.

In the ultraviolet part of the spectrum no bands were found by applying the photographic method.

It is of some interest that haemopyrroline-disazo-dibenzene is able to form compounds with certain metals, for instance with zinc. Zincacetate, dissolved in alcohol of 50 % concentration, added to an alcoholic solution of the azocolour causes a change in the colouration; the previous bright red colour is surplanted by a violet blue, and the original spectrum also undergoes a characteristic change. There are now two bands, corresponding to the following wave lengths: 1. λ 607 — λ — 577; 2. λ 563 — λ 538.

Similar compounds are formed by haematoporphyrin, phylloporphyrin and mezoporphyrin; they have a different spectrum from that characterising the alkaline solution of the substances named and it is therefore quite justifiable to suppose that the constitutions of the two kinds of metalic salts are not alike, a view which is further supported by the fact that bimethylhaematoporphyrin, which does not contain any free hydroxylgroups is still able to form distinct compounds with zinc or copper salts. These compounds must therefore be caused by the presence of an imide group in the substance named, and the fact that haemopyrroline - disazo - dibenzene also forms similar metalic compounds supplies an additionary support for this view.

The crystals with the melting point 233⁰ are not the only pro-

duct which we succeeded in isolating from the ethereal solution containing the crude disazocompound; we mentioned already yellow crystals, the primary product of the reaction which up to now could not be isolated. But there is still a third substance formed in very minute quantities, the nature of which is not yet cleared up. It might be either an oxidationproduct of the disazocompound or its formation might indicate that haemopyrroline, obtained by destilation with steam is not a homogenous substance but a mixture of two substances of which each is able to combine with diazonium compounds. Judging from its properties and the mode of isolation the first mentioned view appears to be more probable. This substance can be isolated by working up the mother liquors of the chief product of the reaction (m. p. 233°). It crystallizes in beautiful copper-red crystals, possessing metalic lustre, dissolving in alcohol, chloroform and ether with difficulty, yielding blue solutions.

Haemopyrroline and Toluenediazoniumchloride.

Haemopyrroline-disazo-ditoluene may be obtained in exactly the same manner as the corresponding benzene derivative. Also in this case we noticed the primary yellow product, which is changed into brown crystals of the disazocompound and from the mother liquor we succeeded in isolating a very small quantity of copper-red crystals, possessing metalic lustre and dissolving in organic solvents with a blue colour.

The hydrochloride of haemopyrroline-disazo-ditoluene crystallizes exactly in the same manner as the hydrochloride of haemopyrroline-disazo-dibenzene and melts at 254. It dissolves in organic solvents with a reddish violet colour and yields with caustic soda the free azodye, easily soluble in ether, alcohol and so forth. The sulphuric acid solution is at first blue, but after some time the colour changes to reddish violet. The spectroskopic properties are very much like those of the benzene derivative. Analyses:

$$0.1125 \text{ g}, \quad v = 17.8, \quad t = 20, \quad p = 744$$

| Found	Calculated for $C_{22} H_{26} N_5 Cl$
N : 17.72%	17.69%

It may be mentioned that 15 g of haemin gave 0.3 g of pure haemopyrroline-disazo-ditoluene hydrochloride.

The discovery of the disazo compounds of haemopyrroline will facilitate considerably the identification of any products supposed to be identical with haemopyrroline. J. Buraczewski and one of us are engaged at present with the study of the reaction of the synthetical pyrroline derivative, obtained by the reduction of methylpropyl-maleinic imide, and diazoniumcompounds.

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19. M. ST. NIEMENTOWSKI m. c. **Kondensacya kwasu antranilowego z benzoyloctanem etylowym.** *(Über die Kondensation der Anthranilsäure mit Benzoylessigester). (Sur la condensation de l'acide anthranilique avec l'éther benzoylacétique).*

Die Kondensation der Anthranilsäure mit Benzoylessigester ist ein Spezialfall der allgemeinen, vom Verfasser vor 12 Jahren beschriebenen Reaktion, welche zwischen Verbindungen mit der Gruppierung $CH_2 . CO$ und zwischen aromatischen o - Amino - Karbonsäuren vor sich gehen kann.

Je nach den angewandten Mengeverhältnissen und dem Reinheitsgrade der Ausgangsmaterialien, der Einwirkungsdauer und der Temperaturgrenze der Reaktion können mehrere Körper entstehen. Als Hauptprodukt bildet sich in der Regel γ-Oxy-α-Phenyl-β-Chinolincarbonsäureester, gemäß der Gleichung

$$\text{(Strukturformel-Gleichung)}$$
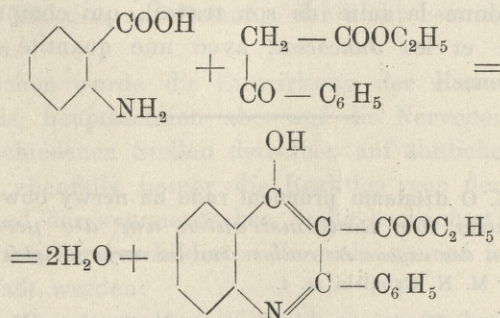
identisch mit dem von F. Just[1]) aus Anilbenzenylmalonsäureester durch innere Kondensation unter Alkoholabspaltung dargestelltem Körper vom Schmelzpunkt 262⁰. Daneben entstand ein bei 308⁰ schmelzender in sämtlichen, öfters gebrauchten Solventien schwer

[1]) F. Just Ber. d. chem. Ges. **18**. 2632 1885] und **19**. 1462 1886].

löslicher Körper, von der Zusammensetzung $C_{32} H_{20} O_5 N_2$, welcher den früher beschriebenen schwer löslichen Kondensationsprodukten des Acetessigester mit Anthranilsäure und m-Homoanthranilsäure an die Seite zu stellen ist.

Wenn der Kondensationsvorgang bei höherer Temperatur (bis 240⁰), oder entsprechend länger fortgesetzt wird, so entsteht das symmetrische Triphenylbenzol $C_6 H_3 (C_6 H_5)_3$, (Schmelzpunkt 171⁰) zweifellos durch Alkohol und Kohlensäureabspaltung aus Benzoylessigester:

$$3 C_6 H_5 . CO . CH_2 . COO C_2 H_5 = 3 CO_2 + 3 C_2 H_6 O + C_{24} H_{18}$$
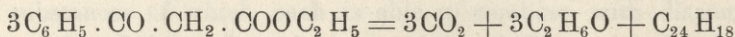
ein Vorgang, welcher möglicherweise durch Anwesenheit anderer Stoffe, besonders des Spaltungsproduktes der Anthranilsäure, des Anilins, katalytisch befördert wird.

Außer diesen Verbindungen wurden noch unter den Kondensationsprodukten gefunden: das Benzanilid $C_6 H_5 . NH . CO . C_6 H_5$ und zwei näher noch nicht untersuchte Körper, ein nur wenige Grade höher schmelzendes und dem γ-Oxy-α-Phenyl-β-Chinolincarbonsäureester sehr ähnliches und ein anderes, bei 318⁰ schmelzendes Derivat.

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20. M. HUGO ZAPAŁOWICZ m. c. **Krytyczny przegląd roślinności Gałicyi. Część IV.** *(Revue critique de la flore de Galicie. IV partie).*

L'auteur donne la suite de son travail, qui comprend le reste des *Cyperaceae* et les *Juncaceae*, avec une quantité de nouvelles variétés et formes.

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21. M. A. BECK. **O działaniu promieni radu na nerwy obwodowe.** *(Über die Wirkung der Radiumstrahlen auf die peripheren Nerven).* *(Action des rayons du radium sur les nerfs périphériques).* Mémoire présenté par M. N. Cybulski m. t.

Die Angaben Dariers und Reymond's [1]) über die schmerzstillende Wirkung der Radiumstrahlen bei Neuralgien, bei lancinierenden Schmerzen der Tabetiker etc. haben den Verfasser auf den Gedanken geleitet, die physiologische Einwirkung dieser Strahlen auf den gesunden peripherischen Nerven und dessen Endigungen

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[1]) Action analgésiante des substances radioactives. Le Radium Nr. 3. 1904.

genauer zu untersuchen. Die Erforschung des Einflusses der akti-
ven Strahlen auf den Nervenstamm geschah hauptsächlich an Tie-
ren (13 Kaninchen, 5 Hunden) auch an Menschen, hingegen die
Untersuchung von deren Einwirkung auf die Nervenendigungen
der Haut hauptsächlich an Menschen. Als Quelle der Strahlen dien-
ten 10 Milligramm Radiumbromid von 100000 Einheiten, welche
von Armet de Lysle in Nogent sur Marne bezogen worden waren
und sich in der von dieser Fabrik gelieferten Dose eingeschlossen
befanden.

Behufs Einwirkung auf den Nervenstamm wurden die Tiere
aufgebunden und die das Radium enthaltende Büchse auf die den
N. ischiadicus einer Extremität bedeckende Haut vermittels Heft-
pflasters und leichten Verbandes befestigt. Auf diese Weise wurden
die Tiere verschieden lange Zeit behandelt. Die Dauer einer jeden
Bestrahlung betrug anfangs 30 Minuten, später 3 Stunden. Um die
eventuelle Wirkung der Radiumstrahlen von der etwaigen Wirkung
der Anlegung des Verbandes selbst unterscheiden zu können, wurde
in allen Fällen gleichzeitig auch die andere Extremität durch Be-
festigen einer entsprechenden runden Scheibe auf ähnliche Weise
behandelt.

Die Bestimmung der Sensibilität geschah vermittels des Induk-
tionsstromes, welcher durch entsprechende Nadelelektroden der Haut
zugeleitet wurde. Hiebei wurde die Reaktion des Tieres beobachtet
und mit der Reaktion auf Reizung der nicht bestrahlten Extremi-
tät verglichen.

Am Menschen wurde die Einwirkung der Radiumstrahlen auf
den N. ulnaris, hauptsächlich aber auf die Nervenendigungen der
Haut an verschiedenen Stellen derselben auf ähnliche Weise unter-
sucht, wobei ebenfalls immer die Reaktion von der Reizung der
bestrahlten und der symmetrischen Stelle beobachtet wurde.

Die Resultate der geschilderten Versuche können folgendermaßen
zusammengefaßt werden:

Von den 13 untersuchten Kaninchen wurde bei 8 Kaninchen
völliges Verschwinden der Sensibilität an der Pfote der bestrahlten
Seite beobachtet. Bei den übrigen Kaninchen wurde lediglich eine
mehr oder minder starke Herabsetzung derselben konstatiert. Bei
den Hunden war diese Herabsetzung sehr unbedeutend. Der ob-
jektive Nachweis des Verlustes, resp. der starken Herabsetzung
der Sensibilität konnte auch durch andere Symptome (wie z. B.

das Nichtkorrigieren künstlich hervorgerufener abnormer Stellun-
gen des Fußes etc.) gegeben werden.

Dabei wurde bemerkt, daß bei den Tieren, bei denen die Re-
aktion auf Reize nicht aufgehoben war, doch durch maximale Ver-
stärkung des Reizes (R A = O) die Reaktion nicht gesteigert wurde,
also keine Schmerzäußerung hervorgerufen werden konnte. Die
Herabsetzung, resp. das Verschwinden der Sensibilität war nur auf
den Fuß des Tieres beschränkt, während der Unterschenkel und
das Knie fast gänzlich von jeder Veränderung frei blieben.

Die konstatierte Veränderung tritt gewöhnlich bereits nach den
ersten zwei oder drei Bestrahlungen auf. Vollständige Abwesenheit
der Hautempfindung dauerte einige Tage an, nachher hob sich die
Sensibilität allmählich ohne jedoch den früheren Grad zu er-
reichen.

Nochmaliges Behandeln mit Radium hatte keinen sicher nach-
weisbaren Erfolg mehr, gerade als wenn die Folgen der ersten
Bestrahlungen auf den Nerven immunisierenden Einfluß gegen die
Wirkung der Radiumstrahlen ausgeübt hätten.

Den Umstand, daß die durch die Wirkung der Strahlen her-
vorgerufene Veränderung sich fast ausschließlich auf den Fuß selbst
beschränkte, glaubt der Verfasser dadurch erklären zu können,
daß die Radiumstrahlen in dieser Quantität, wie sie ihm zur Ver-
fügung stand, nur geringen Einfluß auf den tief gelegenen Ner-
ven ausübte, so daß nur an der Stelle, wo eine zweite Noxe (das
Umlegen der Schnur beim Fesseln des Tieres) zur ersten hinzutrat,
eine Schädigung hervortrat. Daß das Fesseln allein zur Hervor-
rufung einer solchen Schädigung nicht genügte, folgt erstens dar-
aus, daß dieselbe nur auf der bestrahlten Extremität, nicht aber
auf der anderen zu konstatieren war, zweitens aber wurde dies
durch Kontrollversuche an Kaninchen, die durch einige Tage auf-
gebunden, aber mit Radium nicht behandelt wurden, bestätigt.

Auf die Funktion der sensiblen Nervenendigungen in der Haut
hatte nach den Versuchen des Verfassers (am Menschen) die Be-
strahlung mit Radium keinen bemerkenswerten Einfluß. Wohl trat
in einigen Fällen eine geringe Herabsetzung der Sensibilität, in
einem Falle umgekehrt konstant eine ebenfalls geringe Steigerung
derselben auf, doch waren im ganzen die Veränderungen bei wei-
tem nicht so ausgesprochen wie die vorerst geschilderten.

Zum Schlusse berichtet der Verfasser kurz über Versuche,

welche den Zweck hatten zu eruieren, ob nach Einwirkung der Radiumstrahlen auf die Speicheldrüse (Glandula submaxillaris) irgend welche Störungen der Tätigkeit derselben auftreten. Es wurde nämlich nach längerer Bestrahlung der Drüse durch die dieselbe bedeckende Haut der Speichel beiderseits gesammelt, gewogen und auf Trockengehalt und Asche, auch auf dessen Gefrierpunkt untersucht.

Diese Versuche ergaben indessen keine positiven Resultate.

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22. M. TADÉE GODLEWSKI **O niektórych własnością promieniotwórczych Uranu.** *(Some Radioactive Properties of Uranium).* *(Sur certaines propriétés radioactives de l'Uranium).* Mémoire présenté par M. L. Natanson m. t.

1. The discovery of UrX.

In 1900 Sir William Crookes [1]) showed that it is possible to separate from uranium by a single chemical operation a small amount of a radioactive substance to which he gave the name UrX. This substance was, weight for weight, many hundred times more active photographically than the uranium from which it had been separated. The uranium deprived of this substance was almost inactive.

Similar results were afterwards observed by Becquerel [2]) who also noted the important fact that uranium recovered its activity with the time, while the activity of the separated substance decayed. This phenomenon was then quantitatively investigated by Soddy [3]), by Rutherford and Grier [4]) and by Rutherford and Soddy [5]).

These investigations proved that the activity of UrX, when measured by β rays, decayed with the time according to an exponential law, falling to half value in 22 days. In the same period uranium which, by removal of UrX, was deprived of all its β activity recovered it, and the recovery curve was complementary to the curve of decay of UrX. From the point of view of the

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[1]) Crookes: Proc. Roy. Soc. **66** p. 409, 1900.
[2]) Becquerel: C. R. **131** p. 137, 1900; **133** p. 977, 1901.
[3]) Soddy: Trans. Chem. Soc. **81** p. 860, 1902.
[4]) Rutherford and Grier: Phil. Mag. Sept. **1902** p. 315.
[5]) Rutherford and Soddy: Phil. Mag. Apr. **1903** p. 411.

disintegration theory this fact indicated that UrX is a successive product of uranium, and the change of UrX into its successive product was accompanied by the emission of β particles.

2. The experiments of Meyer and Schweidler on Uranium.

In 1904 Meyer and Schweidler[1]) repeated the quantitative measurements of Rutherford and Soddy with the difference, that while the latter used for separation of UrX the method of Becquerel, they made use of Crookes's method.

The aqueous solution of uranium nitrate was shaken with ethyl ether, and then the ether and water portions were separated from one another. The ether portion contained uranium nitrate deprived of UrX, and the β activity of this portion increased according to the theoretical curve, to half of its total value in 22 days. The uranium nitrate, however, when crystallized from the remaining water portion, lost its β activity at a different rate, decaying to half value in 2 days instead of 22 days. This unusual fact, that the recovery and decay curves of a radioactive product, were not complementary to one another, either pointed to the existence of a new product, or indicated some unknown radioactive phenomenon. In order to elucidate this question, Meyer and Schweidler started a series of investigations on the radioactive properties of uranium nitrate freshly crystallized from the water solutions. They substantiated the fact that uranium nitrate crystallized from the hot water solutions in the form of compact plates exhibited a peculiar radioactive behaviour. The activity of these plates decayed in the first few days after crystallization to about half of its original value, reaching a minimum after four or five days, and then increased slowly for a very long time. The time in which the minimum was reached and the initial form of the curve were both dependent on the thickness of the plate. As regards the meaning of this phenomenon, the authors suggest two possibilities; either that there is a change in the activity itself, or that the absorption of the rays is modified by the physical alteration of the crystallized pla-

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[1]) Meyer und Schweidler: Untersuchungen über radioaktive Substangen II: Über die Strahlung des Urans. Sitzber. der Wiener Akad. Mathem - naturwiss. Klasse Bd. 113 Abt II a. p. 1057—1079 Juli 1904.

tes [1]). Prof. Rutherford kindly suggested to me, that I should make some investigations to explain these phenomena.

3. The separation of UrX from uranium by means of fractional crystallization.

The experiments were first made in order to find out the conditions under which this first rapid decay of the β activity of uranium is obtained.

As in the experiments of Meyer and Schweidler, equal parts of uranium nitrate [2]) and water were taken and this solution was shaken with an equal weigth of ethyl ether. The ether solution, was then carefully separated from the water solution, and both were evaporated to dryness. In the case of water solution the evaporation was continued until even the water of crystallization was driven off.

The α and β activity of both portions were then measured.

The β activity was measured by means of an electroscope [3]) of the type of C. T. R. Wilson; the bottom of the electroscope was removed and replaced by aluminium foil 0·08 mm thick, which absorbed all the α rays.

The measurements showed that uranium nitrate from the aqueous solution which contained the excess of UrX, derived from the ether solution, lost the corresponding excess of its β activity according to an exponential law with the time, falling to half value in 22 days. The ether portion, which was at first almost completely inactive, when measured by β rays, recovered its activity according to a complementary curve [4]).

The only difference between my experiments and those of Meyer

[1]) Bezüglich der Deutung dieses Verhaltens ist zunächst die Möglichkeit gegeben, dass es sich um Änderungen der Aktivität selbst handelt, oder dass durch physikalische Zustandsänderungen der Kristallplatten ihr Absorptionsvermögen beeinflusst wird. Eine definitive Entscheidung zu geben wäre verfrüht. Meyer und Schweidler, Loc. cit. p. 1075 (19).

[2]) The uranium nitrate under the experiments was obtained from Merck in Darmstadt and was labelled „extra pure".

[3]) See Rutherford, Radioactivity p. 71 and Fig. 11.

[4]) I omit the detailed numbers obtained in these measurements because the results are completely normal; and further during the time when these investigations were being made Meyer and Schweidler published a short paper (Wiener Sitzungsber., Dec. 1904) in which they showed that when a very small amount of water was present in the solution, the decay of activity of UrX was quite regular.

and Schweidler was that my uranium nitrate was deprived even of its water of crystallization by evaporation, while in the experiments of the above named authors the uranium nitrate was crystallized from the solution. This proves that the rapid decay of activity occurs only when uranium nitrate is crystallized, but it does not occur when it was obtained from the solution by evaporation which had been carried so far that the water of crystallization was driven off.

This fact being established the subsequent experiments were made in the same manner as the experiments of Meyer and Schweidler. After separation of the ether solution, the aqueous solution containing an excess of UrX was concentrated on the water bath, and was then left for a short time at the temperature of the room. The great part of the uranium nitrate crystallized at the bottom of the dish forming a compact plate, on the surface of which the rest of the solution remained. This mother liquor was poured off into another dish and was kept on the waterbath until the solution lost all except the water of crystallization. The solution, after it was taken off the waterbath, crystallized at the temperature of the room forming a compact dry plate.

The whole process of preparation and measurement was repeated many times. Table I gives one of the series of experiments. T denotes the time in days from separation to measurement. The β activity is expressed as the ratio of the activity of the investigated product to the β activity of a standard amount of uranium oxide taken as 1000. The β activity is expressed in the same units throughout this paper.

Table I.

Ether portion		Water portion			
		First crystal plate		Plate of crystal from mother liquor	
T	Activity	T	Activity	T	Activity
0·25	19	0·10	366	0·12	2190
1	57	0·32	281	0·33	1370
2	84	0·75	210	0·75	1270
3	131	1·12	219	1·12	1125
5·3	190	1·64	236	1·68	1090
6·3	220	2·9	285	2·9	1090

	Ether portion	First crystal plate	Water portion		Plate of crystal from mother liquor
7·3	260	4·9	344	4·9	1100
8·3	273	5·9	368	6	1120
9·3	311	7·0	399	7	1180
13·3	420	8·1	427	8·1	1210
14·3	446	9·1	440	9·1	1210
15·3	460	12·8	529	12·9	1200
16·5	480	13·8	545	13·8	1210
		14·8	572	15·7	1190
		16·4	598	18·7	1200

These results are graphically represented in Fig. 1, where the ordinates give the activity, in the same units as before, the abscissae the time in days after separation. Curve I gives the activity of the ether portion, curve II that of the first plate of crystal, curve III the activity of the plate of crystal obtained from the mother liquor.
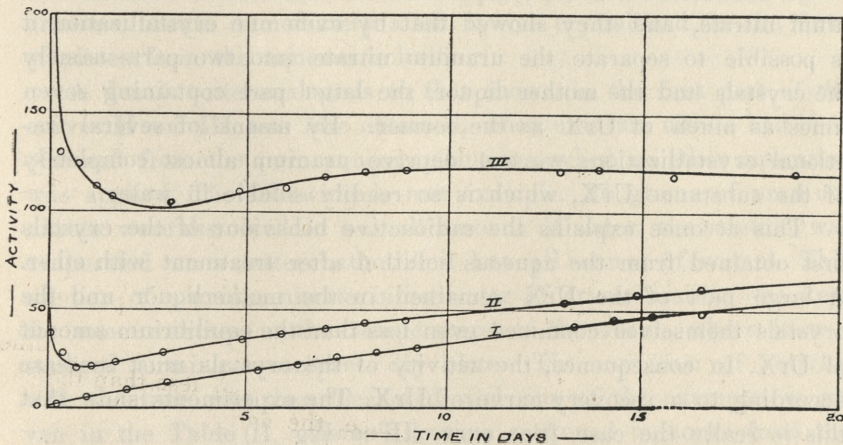

Fig. 1.

As we see the activity of the ether portion increases with the time according to the theoretical curve reaching half final value in 22 days. The activity of the first part of aqueous solutions, which contained the first crystals, falls to about half value in

about one day, this value being almost the minimum, and then increases slowly with the time. As we see from Fig. 1. the second part of curve II is parallel to curve I which shows that the activity of the first plate of crystal increases at the same rate as that of the ether portion.

The plate obtained from mother liquor (curve III), lost its activity during the first few days after crystallization. Its activity after reaching a minimum, and after a small increase remained practically constant. After two months it was observed to have decreased only 10%.

Disregarding for a moment the first rapid decrease of activity of both aqueous portions, which is exactly of the same nature as observed by Meyer and Schweidler, we see that we have the β activity in two cases increasing at the same rate i. e. the increase of activity of the ether portion and of the plate of crystal first obtained. This points to the fact, that UrX was removed not only from the ether portion, but also in some degree from first obtained crystals. The mother liquor must contain then the greater excess of UrX.

In connection with this, experiments were made with fresh uranium nitrate, and they showed that by even one crystallization it is possible to separate the uranium nitrate into two parts namely the crystals and the mother liquor, the latter part containing seven times as much of UrX as the former. By means of several fractional crystallizations we can deprive uranium almost completely of the substance UrX, which is so readily soluble in water.

This at once explains the radioactive behaviour of the crystals first obtained from the aqueous solution after treatment with ether. A large part of the UrX remained in the motherliquor and the crystals themselves contained even less than the equilibrium amount of UrX. In consequence, the activity of the crystals must increase according to a recovery curve of UrX. The experiments show that this is really the case. (See curve II on Fig. 1.)

In a similar way we can equally well explain the increase of activity observed by Meyer and Schweidler[1]) in the crystals of uranium nitrate obtained from water solution.

If in these experiments some part of motherliquor was poured

[1]) Meyer and Schweidler Loc. cit. p. 1074, Figs. 6 and 7.

off the surface of the plates of crystals, the uranium crystals would contain less of UrX than the uranium itself in a state of equilibrium. The increase of activity would thus be due to the recovery of the separated UrX. And in fact the authors state that this part of the curve corresponds to the constant of 22 days.

The activity of the crystals obtained from the motherliquor at first decayed very rapidly and, after reaching a minimum, increased a very small amount and finally remained almost constant falling only 10 per cent during two months. This is shown in curve III.

The percentage decrease observed in this experiment is smaller than the percentage rise observed in curves I and II. This is due to the fact the layer of crystals finally obtained from the mother liquor was about three times as thick as in the previous fractions. In other experiments, where the thickness of the plate was relatively very small, the excess of activity diminished regularly and in a more marked degree.

4. The effect of crystallization on the activity of uranium nitrate.

We shall return now to the initial rapid decay of activity of uranium nitrate immediately after it was crystallized in the form of plates from the aqueous solution.

A decay quite analogous to that shown in the first part of the curves II and III was also obtained, when uranium nitrate had been obtained from the pure aqueous solutions, when no ether separation was applied. The following is one example. 25 grams of uranium nitrate were dissolved in a small amount of water; the solution was evaporated on a water bath till it lost all excess of water. This solution of uranium nitrate in its water of crystallization was kept for some minutes at the temperature of the room, where it crystallized forming a compact dry plate. The variation of activity with the time was then measured and one of the examples is given in the Table II, where T is time reckoned in hours from the moment of crystallization to the measurement.

Table II.

T (in hours)	β Activity
0	1310
2·25	1130

2*

T (in hours)	β Activity
4·5	1030
23	895
44·5	880
52	885
71	875
95	880
120	890

We see that immediatelly after crystallization, the activity decays reaching a minimum after about two days.

The measurements of Meyer and Schweidler were then once more confirmed. The fact that the minimum was reached in a shorter time after crystallization in the experiments of the writer than in those of Meyer and Schweidler is fully explained by the difference in experimental conditions which greatly influence this period.

This decay of activity after crystallization at first suggests the existence of some other product besides UrX. But the absence of the complementary recovery curve contradicts this supposition. And further the rate of decay of radioactive products is generally independent of conditions. In these experiments, however, the time when the minimum was reached, as well as the form of the curve, was dependent upon many factors. In different experiments, the relative values of the activity at the minimum point and the rates of decay, were dependent upon the thickness of the plate of crystals, and upon the concentration of the solution from which the crystals were obtained. In consequence, it would be difficult to suppose the existence of some other product.

The supposition of Meyer and Schweidler [1]) that the phenomena are produced by some changes in absorbing power of the plates of crystals cannot explain the observed fact, when we take into consideration that the activity measured by α rays does not exhibit the same behaviour. The experiments of Meyer and Schweidler showed that the α activity remained practically constant. The writer made also experiments which completely confirmed this fact. And every change in absorbing power of the plates would be, of course,

[1]) Meyer and Schweidler Loc. cit. p. 1075 (19).

first of all shown by variation af α activity. Since these results can neither be explained by the existence of a new product nor by a change in absorbing power there remained the possibility that the process of crystallization alone influences the β activity of uranium nitrate. In order to show whether this was really the case, the following experiments were undertaken.

The hot solution of uranium nitrate containing only the water of crystallization was put under the electroscope. After about two minutes the disturbance of the gold leaf produced by heating effect ceased, and it was then possible to investigate the effect due to the process of crystallization by measurements of the activity. The experiments showed that at the moment when the crystallization started, the β activity commenced to increase very rapidly reaching the maximum when the crystallization was finished.

The following is an example of the experimental results obtained. 25 grams of uranium nitrate were dissolved in some water and evaporated in a flat glass dish on a water bath until it lost all the excess of water. The dish containing this hot solution of uranium nitrate in water of crystallization was then put under the electroscope. After three minutes the activity could be measured with accuracy. The results are shown in Table III where T is the time in minutes from the moment when the solution was taken off the waterbath.

Table III.

T (in minutes)	Activity
3	900
4	890
5	910
6	900

At this period the crystallization started.

8	1000
10	1180
12	1250
14	1350
17	1530
22	1710
27	1780

At this period the crystallization ended.

30	1780
35	1780

On the surface of the plate some drops of distilled water were now added, and the dish was placed again on the waterbath, so that the crystals melted in the water of crystallization. The measurements were repeated in the same manner as before.

In the moment when the second crystallization started, the activity of the solution was 1530; when it was finished the activity of the plate was 2830.

After the third crystallization the activity was 2940.

The fourth and fifth and sixth crystallization did not cause a further increase of the activity.

This maximum activity then decayed with the time and reached the value 935 after three days, and disregarding small irregular oscillations, remained constant at this value through many weeks.

Similar experiments were repeatedly made and gave exactly the same qualitative results.

These experiments show that the β activity of uranium nitrate is very considerably augmented by the actual process of crystallization and it will be proved later that the decay of activity, noted immediately after crystallization, is due to the loss of this excess of activity produced by crystallization.

The explanation of the increase of activity at the moment of crystallization is very simple. We know that all the β activity of uranium proceeds not from the uranium itself, but from UrX. But UrX is so readily soluble in water that it is possible, as we have seen, to separate UrX from uranium by fractional crystallization. If, as is usually the case, the hot uranium solution starts to crystallize from the bottom of the dish, first of all uranium itself crystallizes and UrX is pushed in the direction of the surface. When the whole mass is solidified we get a plate which contains on the surface an excess of UrX and in the lower layers a deficit of this substance. The β rays which come from the UrX, present near the surface, emerge with little absorption in the mass uranium itself, and thus the β activity must be larger than when UrX is uniformly distributed throughout the plate. In the same way we can explain the steady growth of activity during the actual pro-

cess of crystallization when UrX is continually passing to the upper layers.

Many observed experimental facts prove with certainty the correctness of this explanation of the increase of β activity produced by crystallization.

For instance we do not get the increase of β activity when the solution is continuously stirred during the crystallization so that instead of a compact plate there is a powder composed of very small crystals. Moreover, under suitable thermal conditions, the crystallization may be started at the surface instead of at the bottom, and then the increase of activity is not observed after crystallization, but on the contrary there is often a decay.

This last fact suggested to me a decisive test. If the increase of activity during the crystallization is due to the fact that UrX is pushed to the upper layers when the crystallization starts from the bottom of the vessel, then the lower layers of the plate of crystal should contain less of UrX. In order to see if this was really the case, I took a plate of crystal of which the activity was 1840. The plate was cut across so that it could be removed from the dish and it was then taken out and inverted so that the under surface faced the electroscope. The activity was found to be 528.

This experiment shows quite clearly the truth of the explanation of the rise of activity during the process of crystallization. By the crystallization UrX was pushed to the upper layers; when we turn the plate, the upper layers containing the excess of UrX are now underneath and, before reaching the electroscope, the β rays. which start from UrX, must pass through the whole thickness of the plate whereby they are to a great extent absorbed. And for this reason the activity of the plate, when it was turned over, was only one third of the activity measured from the upper side.

5. Diffusion of UrX.

The results obtained in the preceding section can now be used to explain the first rapid decay of β activity of uranium nitrate after crystallization from the water solution.

We saw that in the case wben uranium nitrate was obtained by evaporation from the solution, and not by crystallization, this first decay was not exhibited. Mereover, it was pointed out that

when the hot solution was stirred during crystallization, no increase of activity at the end of the crystallization was observed. It must now be noted that in this case we did not get any decay after crystallization.

We see then that the first rapid decay is the decay of the excess of activity produced artificially by crystallization, when the latter caused the uneven distribution of UrX throughout the plate.

This suggests the probability that the decay of β activity in the first days after crystallization is produced by the diffusion of UrX from the upper layers of the plate, where it was in greater concentration, to the lower, where its concentration is smaller. Thus if we observe the decay of activity when the upper surface is turned to the electroscope we should expect to see the analogous increase when the bottom of the plate faces the electroscope. Experiment showed this to be the case. Some of the experimental results are shown in Table IV where T gives the time reckoned in hours from the moment of crystallization to the corresponding measurements.

Table IV.

T.	β Activity of the plate when turned with the upper surface to the electroscope.	T.	β Activity of the plate when turned with the lower surface to the electroscope.
0	1840	0·1	538
16	1310	16	747
42	1030	42	731
68	1010	68	950

The same experiment made with a very thin plate

0	760	0·1	570
1	740	1	600
2	730	2	620
3·7	720	3·6	630
4·5	700	4·5	650
23	690	23	680

In order to completely establish that we here have to do with the diffusion of UrX through the plate from the layers of higher to lower concentration, the following experiment was made.

Fifty grams of uranium nitrate were treated with ether and from the remaining ether solution 15 grams were obtained consisting of uranium nitrate but almost completely free from UrX. When ether had been evaporated some drops of nitric acid were added to uranium nitrate and this was dissolved in hot water. The solution was evaporated till it lost all the excess of water, and then was kept at the temperature of the room for some minutes where it crystallized forming a dry plate of crystal. The activity of this plate measured 65.

In the other vessel 25 gr of uranium nitrate were heated on the waterbath till it melted in its water of crystallization. This solution was then taken off the waterbath and when the crysiallization started, 9 gr of the hot solution were poured on the surface of the first plate of crystal. The solution crystallized then in a few minutes forming the upper layer of the former plate.

In this manner a plate was made artificially which did not contain in the lower layers any UrX at all, but on the surface it did contain an excess of UrX.

The plate was cut off from the dish and the activity from both surfaces was measured. The results are shown in the table where T gives the time in hours after the crystallization.

Table V.

T (in hours)	Activity of the plate when turned with the upper surface to electroscope.	T (in hours)	Activity of the plate when turned with the lower surface to electroscope.
0	1035	0·1	196
2·5	865	0·8	221
18	665	2·5	239
20·7	637	18	367
27·5	619	20·7	417
43·3	585	27·5	430
		43·7	488

It is seen that the activity measured from the upper surface decreases, and that from the bottom surface increases both approximating to a common value.

This experiment shows that when we have a plate of crystal

of uranium nitrate in which the substance UrX is unequally distributed UrX diffuses from the places where it is in higher concentration to places where its concentration is lower.

This diffusion of UrX therefore explains the first rapid decay after crystallization. We see also that the period during which the minimum activity is reached should depend on the thickness of the plate, and such is the case.

6. The possible causes of the diffusion.

The question now arises in what manner and under the influence of what forces does this diffusion take place? Only two explanations appear possible.

It may be supposed that some part of the UrX is dissolved in a small amount of water and diffuses in a state of solution between the crystals under the influence of capillary forces. The crystal plates under investigation, however, seemed to be completely dry[1]) and the diffusion took place even when a part of water of crystallization had escaped from the crystals on the surface. Therefore the supposition that the UrX diffuses in the state of solution does not seem to be probable.

And if the diffusion does not take place under capillary forces we are here dealing with a „solid solution“. The crystals and the total mass of uranium are the solvent and UrX is the dissolved body. And then the UrX diffuses through the crystals from places of the higher to lower concentration.

We define the solution as a mixture of two substances, which is not a mechanical one, but is accompanied by the molecular penetration of both substances.

The process of formation of UrX points to the fact that we really have here a mixture of this kind. An atom of uranium breaking up by expulsion of one particle, changes into an atom of UrX. But it always remains surrounded by the other atoms and molecules of uranium. It is not possible to imagine deeper molecular penetration as existing for the atoms which previously were the atoms of the parent body.

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[1]) Meyer and Schweidler who first observed this decay of activity after crystallization, due as we saw to diffusion of UrX, pointed out that the plates investigated were completely dry (vollkommen trocken). Loc. cit.

Throughout a given mass of uranium, single atoms of UrX are dispersed. Thus if we consider the total amount of UrX present at a given moment in a given quantity of uranium, we may assume that all this UrX is „dissolved" in the uranium. The observed fact of the diffusion of UrX confirms this supposition. The diffusion of UrX goes in the direction from higher to lower concentration; we may conjecture from higher to lower osmotic pressure. But this osmotic pressure whilst it might control the diffusion cannot be imagined as completely analogous to the osmotic pressure as known in fluid solutions. In the case of extremely weak concentration of UrX the ordinary osmotic pressure would be a vanishing quantity. But in the present case the forces which guide the diffusion must be extremely great in order to overcome the immense resistance due to friction. These forces can only result from the reciprocal action between the molecules of the parent body and the atoms of its product and appear to be of a special radioactive type.

Just as UrX is dissolved in its parent uranium, so the other radioactive products should be dissolved in their parent. There are some experimental facts which confirm this supposition. We know that radium and thorium give out a gaseous emanation as one of their successive products. The emanation is produced at a constant rate, which does not depend on any physical or chemical agencies, but the escape of the emanation from the body is variable in character and dependent on different conditions. For instance, radium and most of the compounds of thorium give off little emanation when in a solid state. The emanation is stored in the body itself in considerable amount. We may suppose that in reality just as UrX was dissolved in uranium so the radium and thorium emanations are dissolved in radium and thorium.

When the parent body is dissolved the emanation is no longer held bound in the solid solution, and it can readily escape from the water. And it is a fact that all substances have the maximum emanating power when dissolved. The increase of emanating power in presence of moisture can be explained in the same manner.

We know further that generally the solubilities of gases decrease with the temperature. And indeed the emanating power of almost all radioactive bodies increases when the temperature is raised, reaching a maximum at a dull red heat. At this tempera-

ture the solubility should be minimum and all the emanation escape.

But the solubility of thorium emanation is not the same in all compounds of thorium. A compound like the hydroxide or carbonate possesses an equal emanating power in the solid state as in solution. This would indicate that thorium emanation so readily soluble in thorium nitrate and soluble in thorium oxide is not so readily soluble in thorium hydroxide or carbonate. We should then expect that in the last cases the emanating power should not be influenced by variation of temperature. The experiments of Rutherford and Soddy [1]) show that this is the case.

The existence of „deemenated" products after strong ignition whereby many physical and chemical properties of the compound are changed, can be also explained by the change in dissolving power of these compounds. Further investigations will show if this generalisation of the fact observed in the case of uranium is justifiable.

Further experiments on this subject are in progress. Analogous experiments will also be tried with other radioactive products in order to see if this explanation is general.

In conclusion I wish to express my best thanks to Prof. Rutherford for the interest he took in this work and for the encouragement I received from him.

[1]) Rutherford and Soddy, Phil. Mag. Apr. 1903 p. 453.

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