Supplementary Material

for

Julian Hirniak, an early proponent of periodic chemical reactions

by

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Contents

1 Julian Hirniak's publications

Some of Hirniak's research papers[1] were published in the Ukrainian journal *Збірник Математично-Природописно-Лїкарської Секциї Наукового Товариства імени Шевченка*, which also had the German title *Sammelschrift der Mathematisch-Naturwissenschaftlich-Ärztlichen Sektion der Ševčenko-Gesellschaft der Wissenschaften in Lemberg* at that time. The English translation is *Proceedings of the Mathematical-Natural Sciences-Medical Section of the Shevchenko Scientific Society in Lviv*. The journal was established in 1897 and published in Lviv until 1939.[2] Though the journal title and the table of content was bilingual, the actual articles were only in Ukrainian. This journal will be abbreviated as ЗМПЛС in the publication list. In Fig. 2 we show the cover page of the 1908, Vol. XII journal issue.

1. Юліян Гірняк, "Роля сталої, плинної і ґазової фази в хемічній рівновазї" ("The role of the solid, liquid and gas phase in chemical equilibrium"), ЗМПЛС (1903) [4].
2. Юліян Гірняк, "Ненастанна деґрадация енерґії конечна проява й причина всякого руху і житя в природі" ("Constant degradation of energy is an inevitable manifestation and cause of all movement and of life in nature"), Літературно-науковий вістник (Literary-Scientific Herald)[3] **21** (1903) [5].

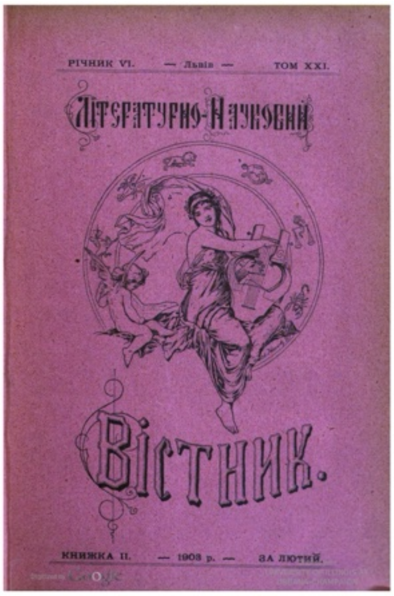


Figure 1 Cover page of *Літературно-науковий вістник*, Vol. XXI from 1903 (Public Domain. Digitized from original document provided by the Stefanyk National Scientific Library in Lviv).

[1] Other references, listing some of Hirniak's publications are [1–3].

[2] Digitalized archive of this journal is available at https://www.lsl.lviv.ua/index.php/uk/resursi-i-fondi/elektronni-materialy

[3] A monthly journal published in 1898–1906 in Lviv, in 1907–1914 and 1917–1919 in Kyiv, and in 1922–1932 again in Lviv. The cover page of volume 21 is shown in Fig. 1.

3. Юліян Гірняк, "О проводї тепла цукру у воднім розчинї" ("On the heat conduction of sugar in an aqueous solution"), ЗМПЛС (1907) [6].
4. Юліян Гірняк, "Про вплив синхронїчної зміни концентрациї на хід мономолекулярної реакциї" ("On the effect of a synchronous change in concentration on flow of the monomolecular reaction"), ЗМПЛС (1908) [7].
5. Юліян Гірняк, "Про періодичні хемічні реакциї" ("On periodic chemical reactions"), ЗМПЛС (1908) [8]. The cover page of this volume is shown in Fig. 2.

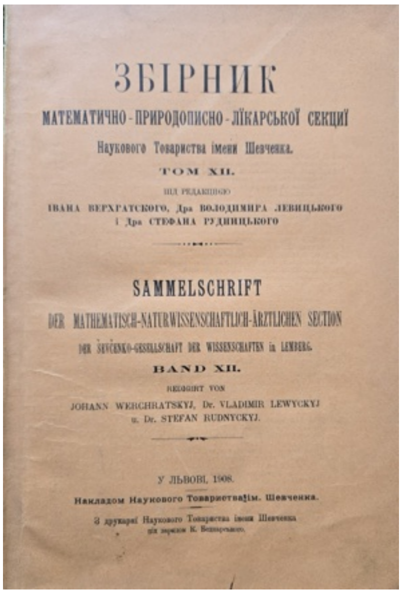


Figure 2 Cover page of *ЗМПЛС*, Vol. XII from 1908 (Public Domain. Digitized from original document provided by the Stefanyk National Scientific Library in Lviv).

6. Юліян Гірняк, "Замітки до рівнань моно- і бі-молекулярної хемічної кінетики" ("Notes on the equations of mono- and bi-molecular chemical kinetics"), ЗМПЛС (1909) [9].
7. Юліян Гірняк, "Вплив температури на скорість декількох хемічних реакцій" ("Effect of temperature on the rate of several chemical reactions"), ЗМПЛС (1909) [10].
8. Юліян Гірняк, "Вплив температури на скорість декількох хемічних реакцій (доповнене)" ("Effect of temperature on the rate of several chemical reactions (Supplement)"), ЗМПЛС (1910) [11].
9. Julius Hirniak, "Zur Frage der periodischen Reaktionen" ("On the question of periodic reactions"), Zeitschrift für Physikalische Chemie (1911) [12].
10. Julius Hirniak, "Beiträge zur chemische Kinetik. I. (In zwei Teilen)" ("Contributions to chemical kinetics. I (In two parts)"), Ševčenko-Gesellschaft der Wissenschaften

in Lemberg, pp. 101 (1911) [13].
[Note: This work was intended for his habilitation (from [14])].

11. Юліян Гірняк, "Мінеральоґия і хемія: Начерк мінеральоґиї і хемії для середних шкіл" ("Mineralogy and Chemistry: Outline of Mineralogy and Chemistry for Secondary Schools"), Руське Товариство Педагогічне (Ruthenian Pedagogical Society)[4](1912) [15].
12. Юліян Гірняк, "Дещо про теоретичне і методичне значінє сочинника температури скоростий процесів для хемічної кінетики" ("About the theoretical and methodical value of the temperature component of the rates of processes for chemical kinetics"), ЗМПЛС (1913) [16].
13. Юліян Гірняк, "Основи хемії для висших кляс гімназияльних" ("Basics of chemistry for upper classes in a gymnasium"), Українське Товариство Педагогічне (Ukrainian Pedagogical Society) (1914) [17].
14. Юліян Гірняк, "Кілька слів про наукову діяльність нашого земляка Володимира Бачинського" ("A few words about the scientific activity of our compatriot Volodymyr Bachynskyi"), ЗМПЛС (1919) [18].
15. Юліян Гірняк, "Організуймо великий рідний капітал для українських кооператив!" ("Let's organize a large native capital for Ukrainian cooperatives!"), Краєве товариство «Ощадність» (Regional Society «Oshchadnistj» («Frugality»)) (1927) [19].
16. Juljan Hirniak, "O zasadniczych pojęciach, nektórych nowszych kierunkach i ogónych paradoksach chemicznej kinetyki" ("About fundamental concepts, some new trends and general paradoxes of chemical kinetics"), Towarzystwo Aptekarskie we Lwowie (Pharmacy Society in Lviv) (1936) [20].
[Note: Odczyt wygloszony dnia 28 maja 1936 na I. posiedzeniu Oddzialu Lwowskiego Związku Chemików Polskich (Lecture delivered on May 28, 1936 at the first meeting of the Lviv Association Branch of Polish Chemists).]
17. Julian Hirniak, "Zur Kinetik der Folgereaktionen zweiter Ordnung" ("About the kinetics of second order subsequent reactions"), Acta Physicochimica U.R.S.S. (1941) [14].

In 1909 Hirniak also reviewed seven German publications for the Бібліографія (Bibliography) section of ЗМПЛС, the same volume he published his two 1909 articles in [9, 10]. These reviews appeared on pages 26 – 34 and included one book by Walter Nernst [21], three articles in *Annalen der Physik* by Grüneisen [22, 23] and Engler [24], two articles in the *Physikalische Zeitschrift* by Schlesinger [25] and Goldschmidt [26], and one article by Krüger in the *Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen* [27].

1. On page 26: W. Nernst – Theoretische Chemie vom Standpunkte der Avogadroschen Regel und der Thermodynamik. (VI. Auflage. Stuttgart, 1909).

[4]The Ruthenian Pedagogical Society [Rusjke Tovarysto Pedahohichne], later Ukrainian Pedagogical Society [Ukrajinsjke Pedahohichne Tovarystvo] (popular name - Ridna Shkola), was established in Lviv in 1881 to promote Ukrainian-language education.

2. On page 27: H. Schlesinger – Die spezifischen Wärmen von Lösungen. I., Physikalische Zeitschrift. **10**(6), 210-215 (1909).
3. On page 27: E. Grüneisen – Über die thermische Ausdehnung und die spezifische Wärme der Metalle, Annalen der Physik, **331**(7) 211-216 (1908).
4. On pages 28–30: E. Grüneisen – Zusammenhang zwischen Kompressibilität, thermischer Ausdehnung, Atomvolumen und Atomwärme der Metalle. Annalen der Physik, **331**(7) 393–402 (1908).
5. On pages 30–31: H. Goldschmidt – Über die Abhängigkeit der Reaktionsgeschwindigkeit von der Temperatur in homogenen gasförmigen Systemen, Physikalische Zeitschrift, **10**(6), 206–210 (1909).
6. On pages 31–33: F. Krüger – Zur Kinetik des Dissotiationsgleichgewichtes und der Reaktiongeschwindigkeit, Göttinger-Nachrichten, (4), 318-336 (1908).
7. On page 34: W. Engler – Über den Einfluß der Temperatur auf radioaktive Umwandlungen, Annalen der Physik, **331**(8), 483–520 (1908).

2 Favorable and critical citations of Hirniak's work

2.1 Favorable citations

The first decades viewed HIRNIAK's work very positive. LOTKA and BRAY cited HIRNIAK's publications when discussing the theoretical possibility of a periodic chemical reaction. Since then, many other authors followed their perception.

- The second article citing HIRNIAK hab been published by MAX TRAUTZ in October [28] (seven months after LOTKA's 1912 paper). He discusses the chemical kinetics and reaction velocities of reversible successive reaction steps and first presents the purely mathematical result published by JÜTTNER in 1911 that the equilibrium point will be approached aperiodically [29]. He continues describing a system of two simultaneous monomolecular reactions with an autocatalytic second step and states that the intermediate isomer concentration can't go through a maximum, citing LOWRY and JOHN's 1910 article [30]. But under certain conditions, the systems can show periodic behavior, as outlined by LOTKA in 1910 [31, 32]. He then describes the scientific discussion between HIRNIAK and LOTKA in

  > "Lotkas Rechnungen werden von Hirniak zum Teil nicht für ganz einwurfsfrei gehalten. Er behandelt den Fall gegenseitiger Umwandlung dreier Isomeren nach erster Ordnung, für den zurzeit noch kein experimentelles Beispiel vorliegt und findet, daß der Wert von „Schwingungsdauer" und „Dämpfung" von der Anfangskonzentration unabhaängig sein muß[4]), worauf Lotka wieder in sehr allgemeiner Weise die allgemeine Lösung für eine Reihe von Folgereaktionen mit autokatalytischem Verlauf gibt[5])."

  > "In some cases, Hirniak does not consider Lotka's calculations to be completely free of objections. He deals with the case of mutual conversion of three isomers to the first order, for which there is currently no experimental example, and finds that the value of "oscillation period" and "damping" must be independent of the initial concentration[4]), whereupon Lotka again presents, in a very general manner, the general solution for a series of subsequent reactions with an autocatalytic process[5])."

  while citing HIRNIAK's 1911 [12] and LOTKA's 1912 article [33] in the *Zeitschrift für Physikalische Chemie*. As a 'funny' typo one can find that he used the name *Journal für Physikalische Chemie* instead of *Zeitschrift für Physikalische Chemie* for HIRNIAK's paper.

- In 1913 ROBERT KREMANN published the book "Die periodischen Erscheinungen in der Chemie" ("The periodic phenomena in chemistry") [34] and discussed the work of HIRNIAK and LOTKA in section "*Theoretische Diskussionen über periodische Erscheinungen in der Chemie von Lotka und Hirniak*" ("*Theoretical discussions about periodic phenomena in chemistry by Lotka and Hirniak*"). In his first paragraph, he writes

  > "...gibt J. Hirniak[1]) ein Beispiel für die Möglichkeit einer periodischen Reaktion in homogenen System, eines Falles, der bis jetzt noch völlig unbekannt ist."

> "...J. Hirniak[1]) gives an example of the possibility of a periodic reaction in a homogeneous system, a case that is still completely unknown."

and cites both of Hirniak's articles, the 1908 and the 1911 article with the correct year. This is the first citation of Hirniak's 1908 article. It will take about 80 years until this publications will be cited again in Krug and Kuhnert's 1985 article [35]. But it should also be noted that Kremann followed the same idea Hirniak claimed already in his 1911 article: Lotka's theoretical model considers a heterogeneous system whereas Hirniak's reaction scheme describes a homogeneous system, which has later been shown to be not true.

Kremann reproduces the triangular reaction scheme from Hirniak's 1911 article (see Fig. 2 in main article) and discusses the problem of necessary positive rate constants, even uses several of the same equations as in Hirniak's 1911 article (see App. 4). He concludes subsection "*II. Reaktionen im homogenen System*" ("*II. Reactions in a homogeneous system*") with

> "Diese Ausführungen Hirniaks deuten also deutlich die Möglichkeit einer periodischen Reaktion auch im homogenen System an."

> "These statements by Hirniak clearly indicate the possibility of a periodic reaction even in a homogeneous system."

- In 1929 Nicolas von Raschevsky published the article "Beitrag zur Theorie der physikalisch-chemischen Periodizität" ("Contribution to the theory of physical-chemical periodicity"), discussing the possibility of periodic and rhythmic processes. [36] Before introducing the first differential equations, he writes

  > "Im Gebiet der homogenen Reaktionen ist das Auftreten von zeitlicher Periodlzit´at theoretisch sehr eingehend, besonders von A. Lotka untersucht worden *. Man kann wohl sagen, dass bei gekoppelten Reaktionen oszillierende L´osungen der Differentialgleichungen allgemein vorkommen. Jedoch sind diese Oszillationen allgemein positiv oder negativ ged´ampft. Eine echte Periodizit´at tritt nur dann auf, wenn die Reaktionen von sehr spezieller Art sind, und daneben noch die Reaktionsgeschwindigkeiten ganz speziellen Bedingungen unterworfen sind."

  > "In the field of homogeneous reactions, the occurrence of temporal periodicity has been studied theoretically in great detail, especially by A. Lotka *. One can probably say that oscillating solutions of the differential equations generally occur in coupled reactions. However, these oscillations are generally positively or negatively damped. Real periodicity only occurs when the reactions are of a very specific type and the reaction rates are also subject to very specific conditions."

  and lists seven of Lotka's articles [31–33, 37–40] and his *Elements of Physical Biology* book, Hirniak's 1911 article with the wrong publication year of 1910, and an article by Rakowsky [41], also with the stated publication year of 1906 to be one year before the actual year of 1907. This error indicates that he 'copied' this citation from Lotka's 1920 *JACS* article.

After emigrating to the USA, he used the name Nicolas Rashevsky and became an influential proponent of the nascent field of mathematical biology.

- Ernest Hedges and James Myers published their book "*The Problem of Physico-Chemical Periodicity*" in 1926 and briefly mentioned Hirniak's name in their 'Theoretical Discussions'. They distinguish clearly between all earlier heterogeneous reactions and 'true periodic chemical reactions' and start Chapter IV with

  > "The most important type of periodicity in many respects is a rhythmic time change and to this type belong all true periodic chemical reactions."

  They discuss the difference between damped and undamped 'vibrations', introduce the need for an autocatalytic reaction step, and present a formula for the 'period of vibration'. But then, they write

  > "Other mathematical expositions of how an autocatalytic system may become periodic are given by Lotka and by Hirniak."

  and citing Lotka's 1912 *Physical Review* paper [37] and Hirniak's 1911 paper [12], using the correct year. Although they used the correct publication year, it seems unclear if they actually read Hirniak's 1911 article because Hirniak's cyclic reaction scheme does not include any autocatalytic step.

- Maurice Copisarow published his 1931 article "*Periodizität und ihre Grundlagen*" ("*Periodicity and its foundations*") in the journal Kolloid-Zeitschrift [42] and discussed various phenomena in physical systems. He only touches shortly chemistry when writing

  > "...die verschiedenen Beispiele periodischer Strukturen aus dem Gebiete der Chemie[11–14]..."

  > "...the various examples of periodic structures from the field of chemistry[11–14]..."

  In [11], he cites four of Lotka's publications [32, 33, 37, 38], Hirniak's 1911 article [12] in [12] (using the correct year), two papers about rhythmic behavior in heterogeneous systems by Okaya [43, 44] in [13], and another heterogeneous chemical system by Hughes [45] in [14].

- Suzanne Veil published a small book in 1934 with the title "*Les phénomènes périodiques de la chimie. II. Les périodicités cinétiques*" ("*Periodic phenomena in chemistry. II. Kinetic periodicities*") [46], in which she discusses various temporal oscillatory chemcial systems. The first volume has the extension "*I. Les périodicités de structure*" ("*I. Structural periodicities*") [47] and discusses Liesegang rings and similar precipitation pattern. In Chapter *Autres périodicités suggestions d'ordre mathématique* (Other mathematically suggested periodicities) of Vol. I, she starts section *Suggestions d'ordre mathématique* (Mathematical suggestions) with

  > "Par la seule voie théorique, certain auteurs Lotka (93), Hirniak (94), Okaya (13) ont cherché si, par de hypothèses convenables sur la marche et le jeu de réactions engagées, il état possible de prévoir une allure rythmique des effets observés."

> "Through the theoretical approach alone, certain authors Lotka (93), Hirniak (94), Okaya (13) have sought whether, through suitable hypotheses on the progress and interaction of the reactions involved, it was possible to predict a rhythmic behavior of the observed effects."

She cited LOTKA's 1910 [31, 32] and 1912 [33, 37] papers for the damped oscillatory system, and only one 1920 paper [38] for the undamped system. In HIRNIAK's case, she cited his 1911 article [12] (with the correct year), and for OKAYA, his 1918 and 1919 articles [43, 44].

In the next paragraph, she presents LOTKA's autocatalytic reaction scheme and finishes with "...the oscillations to be expected are, depending on the case, either damped or maintained." But, dispite the fact that she discussed BRAY's result at the beginning of the book, she finishes with

> "Malheureusement ces spéculations, pour intéressantes qu'elles puissent être, se prêtent assez peu au contrôle de l'expérience, et n'ont pas encore reçu, jusqu'ici de confirmation directe."

> "Unfortunately these speculations, however interesting they may be, do not lend themselves well to experimental testing, and have not yet received direct confirmation."

which is interesting to read as BRAY published the experimental proof more than a decade earlier.

- In 1938, SHEMIAKIN and MIKHALEV published the book "*Физико-химические периодические процессы*" ("*Physico-chemical periodic processes*") [48] with more than 900 citations. In section "Chemical kinetics and periodic processes" on page 112, they write

  > "Математическое доказательство возможности существования химических реакций, протекающих периодически во времени, было впервые дано А. Лотка [616]."

  > "The mathematical proof of the possibility of the existence of chemical reactions occurring periodically in time was first given by A. Lotka [616]."

  citing four of LOTKA's articles between 1910 and 1920 and added 'Теория периодических реакций' ('Theory of periodic reactions') after the references.

  They also presented HIRNIAK's work in an interesting way. After showing the reaction scheme (very similar to Fig. 2 in the article but with the arrows of k_3 to k_6 in the wrong directions), they reproduced the first two equations from HIRNIAK's 1911 article before stating "For a periodic solution it is necessary that", followed by the forth equation in HIRNIAK's 1911 article. And based on the different rate constant numbering in their reaction scheme, this equation can't be correct. To distinguish HIRNIAK's work from LOTKA, they added 'Теория периодической реакции изомеризации' ('Theory of a periodic isomerization reaction') after the reference.

- In 1939, ANGÉLIQUE ARVANITAKI wrote an article about the squid giant axon [49] and discussed various oscillatory systems including chemical periodic reactions by simply citing Kremann [34], Lowry and John [30], Lotka [32, 33, 38], Hirniak [12], and Hedges and Meyers [50]. As often, all citations, except the more mathematically focused article by Lowry, contained the word 'periodicity'. Two pages later, they write

> "En suivant la voie de LOTKA (33, 34, 25), HIRNIAC (28), etc. on peut partir de deux réactions chimiques consécutives qui seraient ici, comme nous le dictent nos observations, électroactives, et qui rempliraient certaines conditions d'autocatalyse et de réversibilité."

> "Following the path of LOTKA (33, 34, 25), HIRNIAC (28), etc. we can start from two consecutive chemical reactions which would be here, as our observations dictate, electroactive, and which would meet certain conditions of autocatalysis and reversibility."

citing the same publications. But it seems that the reference (25) should actually be (35), as earlier, because the number 25 in the article refers to a 1933 physiology paper, not of interest there.

- In the 1939 article "*Периодические процессы в кинетике окислительных реакций*" ("*Periodic processes in the kinetics of oxidation reactions*") David Frank-Kamenetskii [51] writes

  > "Возможность колебательных процессов в кинетике окислительных реакций представляет общий интерес [см. ссылки на литературу (2-8)]"

  > "The possibility of oscillatory processes in oxidizing reaction kinetics is of common interest [see references to the literature (2-8)]"

  The citations list includes [2] Quincke, Wied. Ann., **35**, 614 (1888). [52] [Note: The citation uses page 614 but it should be page 580, as correctly used in [53].] [3] Bernstein, Pflüg. Zrch., **80**, 628 (1900) [53]. [4] Ostwald, Vorlesungen über Naturphilosophie, Leipzig. S. 274, 315, 352 (1902). [54] [5] Lotka, ZS. phys. Chemie, **72**, 508 (1910); **80**, 159 (1912). [31, 33] [6] Hirniak, ZS. phys. Chemie, **75**, 675 (1910) [12] [Note: Wrong publication year] [7] Skrabal, ZS. phys. Chemie, **6**, 382 (1930). [55] [8] Kremann, Die periodischen Erscheinungen in der Chemie, Sammlung chemischer Vorträge, **19**, 289, Stuttgart (1913) [34].

  In this list of citations, Frank-Kamenetskii mixes mechanical oscillations (page 274 in [54]), electrochemical oscillations [53], periodic phenomena in biological systems (page 315 in [54]) with the proposed periodic behavior in chemical systems by the last four authors.

- Herbert Pohl published two articles in 1981 and citing Hirniak's 1911 article, though as published in 1910. In both cases, it was one citation in a longer list with Bray, Lotka, and others when stating

  > "Early reports of even chemical reactions of periodic nature were largely ignored (Bray, 1921; Hirniak, 1910; Lotka, 1910, 1920)."

  in [56] or

  > "The study of oscillating reactions is presently in a growingly active state."

in [57]. After this statement, he lists articles from LOTKA, HIRNIAK, and BRAY but also includes 14 other publications from, for example, BELOUSOV, PRIGOGINE.

- In 1985, HANS-JÜRGEN KRUG and LOTHAR KUHNERT published an article about oscillating systems with an autocatalytic step in *Zeitschrift für Physikalische Chemie* [35]. In the introduction they write

  > "Dazu wurde bereits 1908 von Hirniak [1] und 1910 von Lotka [2] auf die Möglichkeit des Ablaufs periodischer chemischer Reaktionen in homogener Phase hingewiesen.
  > In den didaktischen Reaktionsschemata von Hirniak und Lotka sowie in weiteren Modellen (z.B. Lotka-II-Schema [3], Brüsselator [4], Oregonator [5], Lotka–Selkov-Schema [6]) wurde gezeigt, daß oszillatorisches Verhalten eng an die Beteiligung von Rückkopplungen in Form von zyklischer Kopplung, Autokatalyse, Autoinhibition oder Kreuzkatalyse gebunden ist."

  > "The possibility of periodic chemical reactions taking place in a homogeneous phase was already pointed out by Hirniak [1] in 1908 and by Lotka [2] in 1910.
  > In the didactic reaction schemes of Hirniak and Lotka as well as in other models (e.g., Lotka-II scheme [3], Brusselator [4], Oregonator [5], Lotka–Selkov scheme [6]) it was shown that oscillatory behavior is closely linked to the participation of feed backs in the form of cyclic coupling, autocatalysis, autoinhibition, or cross-catalysis."

  This is the second publication citing HIRNIAK's 1908 paper [8] in reference [1]. But they also added HIRNIAK's 1911 article [12], though still using the wrong year of 1910. In LOTKA's reference [2], they only cited the German article in *Zeitschrift für Physikalische Chemie* [31] but not the English version in *The Journal of Physical Chemistry* of the same year [32]. This might have been a conscious decision and is the earliest finding of placing HIRNIAK and LOTKA at the same 'scientific' level while indicating that HIRNIAK published one article before LOTKA and the other at the same year. The references [3-6] are [38, 58–60].

- P.E. RAPP cited LOTKA and HIRNIAK equally in his 1987 article "*Why are so many biological systems periodic?*" [61]. But he also highlights the initially difficult start

  > "Periodic chemical reactions were anticipated theoretically by Lotka and Hirniak in 1910 (Lotka, 1910, 1920; Hirniak, 1910). Accounts of an experimental example published in 1921 (Bray, 1921) seemingly attracted limited attention."

  As can be seen, they cited LOTKA's damped [32] and undamped [38] systems and HIRNIAK's 1911 article [12] with the year 1910 as used in LOTKA and BRAY's work [62].

- JASON GALLAS cited HIRNIAK's work in his 2015 article [63] while talking about

  > "The origins of the oscillator known as Brusselator can be traced to a work in 1956 by Prigogine and Balescu[5] showing that undamped oscillations[6−15] are supported far from thermodynamic equilibrium in open chemical systems governed by nonlinear kinetic laws."

  The references are [64] for [5] and a list of nine references with work from PRIGOGINE [58, 65], SCOTT [66], and seven early publications between 1910 and 1926 (books by Kremann and Hedges [34, 50] articles by Lotka [31, 33, 38, 40] and Hirniak [12] (using the 1910 publication year).

- Eberhard Bruckner's 1987 historical review article "*Die ersten theoretischen Modelle für oszillatorisches Verhalten in der Chemie von J. Hirniak und A. J. Lotka - zwei Publikationen in der Zeitschrift für Physikalische Chemie aus den Jahren 1910/11*" ("The first theoretical models for oscillatory behavior in chemistry by J. Hirniak and A. J. Lotka - two publications in the Journal of Physical Chemistry from 1910/11") [67] was published in conjunction with the 100th anniversary of the journal *Zeitschrift für Physikalische Chemie*. He presents the submission dates as January 31, 1910 for Lotka's and November 22, 1910 for Hirniak's articles in the same journal and uses 1910 as the publications year for both in the publication list. He quotes Hirniak's initial sentence with the reference to the 1908 article but does not provide any bibliographic information.

  Bruckner discusses the acceptance problems for periodic chemical reactions in the early 20th century with examples from Ostwald, Bray, Lotka, and Hirniak. He always refers to Lotka and Hirniak together as in, for example,

  > "...die in den theoretischen Modellen von Lotka und Hirniak ausgepr´agt ist. Beiden gelang die Entdeckung der reaktionskinetischen Bedingungen für oszillatorisches Verhalten ..."
  >
  > "...which can be found in the theoretical models by Lotka and Hirniak. Both discovered the reaction-kinetic conditions for oscillatory behavior ..."

- In a 2016 article by Alexander Pechenkin [68], with the title "*Две истории периодических процессов в химии* " ("Two stories of periodic processes in chemistry"), Hirniak is again cited while Pechenkin introduces Lotka's reaction scheme with its autocatalytic step, creating periodic behavior in section 2. While talking about Lotka's 1912 article, he writes

  > "В 1912 г. А. Лотка опубликовал статью, где сопроводил свой анализ химических колебаний ссылкой на статью Ю. Хирниака, опубликованную в 1910 г."
  >
  > "In 1912, A. Lotka published an article in which he accompanied his analysis of chemical oscillations with a link to an article by J. Hirniak, published in 1910."

  He continues in the next paragraph with

  > "Интересно, что сам Хирниак в своей статье 1910 г. сослался на свою статью, появившуюся раньше, чем первая статья Лотки. Однако эта первая статья Хирниака вышла на русинском языке и прошла незамеченной."
  >
  > "Interestingly, Hirniak himself, in his 1910 article, referred to his article appearing earlier than Lotka's first article. However, this first article by Hirniak was published in Rusyn and went unnoticed."

  With the second quote, Pechenkin points out that Lotka 'ignored' Hirniak's original 1908 paper, adding to the controversy about who published the first paper on the theoretical description of a periodic homogeneous chemical reaction. A more detailed discussion on the term русин (Rusyn) can be found in the article's Section *Ruthenian Language*.

But, as many other scientists, PECHENKIN uses the wrong publication year of HIRNIAK's 1911 paper. In addition, he used the year 2010 for LOTKA's 1910 article in the *Journal of Physical Chemistry* and his 'back transliteration' of HIRNIAK's last name from English to Cyrillic resulted in Хирниак. Here, the original name Гірняк, as used in all of HIRNIAK's Ukrainian articles, is barely recognizable.

- In another 2016 article by PECHENKIN [69], he discusses the 1938 book "*Физико-химические периодические процессы*" ("*Physico-chemical periodic processes*") by SHEMIAKIN and MIKHALEV and starts section 'Mathematical equations' with

  > "Already R. Kremann (1913, 411) describes A. Lotka's mathematical technique (1910, 1912) which shows that under certain conditions some of the complicated heterogeneous autocatalytic systems may show oscillatory behavior. As an example of the homogeneous oscillatory system Kremann refers to Hirniak's theoretical construction of a monomolecular interconversion of three isomers (Hirniak 1911)."

  and citing the three German publications by KREMANN [34], LOTKA [31], and HIRNIAK [12], though missing the citations for LOTKA's 1912 article. Here, PECHENKIN used the correct year for HIRNIAK's 1911, probably because KREMANN used it in his 1913 book.

  This quote is another example of scientist referring to LOTKA's 1910 model as heterogeneous whereas HIRNIAK's is considered homogeneous.

- In 2017, JOANA FREIRE, MARCIA GALLAS, and JASON GALLAS cited HIRNIAK's 1911 paper, as citation [8], in a paragraph when talking about the long history of periodic chemical reactions' [70]. On page 1989, they write

  > "In chemistry, periodic oscillations already have an almost two-centuries long history, dating back at least to the beginnings of the 19th century as evidenced by the many experimental works collected and described in almost forgotten books [5,6] and papers [7–9], a history that deserves to be better known."

  The two cited books are from KREMANN in 1913 [34] and from HEDGES and MYERS from 1926 [50]. The three articles are German publications in the *Zeitschrift für Physikalische Chemie* by LOTKA [31, 33] and HIRNIAK [12], with the publication year 1910.

- Some information about HIRNIAK's life and scientific work can be found in section "Julian Hirniak" in ALEXANDER PECHENKIN's 2018 book "*The History of Research on Chemical Periodic Processes* [71]. This section gives a short overview about HIRNIAK's live but contains several factual errors. For example, he discusses HIRNIAK's claim for priority presenting the first theoretical model for periodic chemical reactions and how it was related to LOTKA's work. But it is not clear how he comes to the conclusion when starting the section with "In 1910, Hirniak in "Zeitschrift für Physikalische Chemie" proposed that cyclic reactions can be oscillatory", using the year 1910, which, too often, had been used as the actual publication year. It's also confusing because he finishes the introductory Abstract of that chapter with

> "Besides Lotka, Hirniak (Lvov) contributed to the early mathematical studies of chemical periodical processes (1908, 1911)"

using the correct publication year. But after HIRNIAK's name, he uses the transliterated Russian spelling Львов [Lvov], not the correct English version of this Ukrainian city.

PECHENKIN also mentions HIRNIAK's 1908 publication but does not provide a reference. He only gives the German name of the journal, with a few typos, and presents the journal cover page of the 1908 edition, but stating that it's the issue of HIRNIAK's 1911 paper.

When discussing LOTKA and HIRNIAK's papers, he points out that LOTKA probably didn't know about HIRNIAK's 1908 article and suggests that HIRNIAK thought, while writing his 1911 article, that this was the same reason why LOTKA didn't cite his own work. Unfortunately, PECHENKIN falsely states

> "It should be noted that Lotka in his 1912 and 1920 papers referred to Hirniak's 1908 paper."

but no citation or reference can be found in any of LOTKA's 1912 [33, 37] or 1920 [38–40, 72] publications, except to HIRNIAK's 1911 (with the wrong year 1910 as mentioned earlier).

Notably, PECHENKIN also writes that HIRNIAK published his 1908 article in the "Rusyn language" and "Hirniak believed that Lotka did not refer to this paper because it was published in a rare periodical in the obscure language." We explain the differences between *Rusyn* and *Ruthenian* (the term HIRNIAK used in his 1911 German article) and *Ukrainian* in the article's Section *Ruthenian Language*. Perhaps due to the language confusion, PECHENKIN also wrote "Probably, Hirniak belonged to Rusyn (Ruthenians), a small ethnic group which belongs neither to Russians, nor to Ukrainians.", which is not correct. He also used three differently wrong versions for the long English and German names of the Shevchenko Scientific Society. The correct spelling can be found in the Supplementary Material Section 1 (*Julian Hirniak's publications*).

- CHRISTOPHE LETELLIER cites HIRNIAK in Chapter 5 "*Chemical Reactions*" of his 2019 book "*Chaos in Nature* [73]. He quotes a section from LOTKA's 1910 article and includes HIRNIAK's article

  > "The possibility of decaying oscillations had been announced after a study in 1904 of a hypothetical autocatalytic reaction[3] — since at the time "*no reaction is known which follows the* [mentioned]*law* [...] *of damped oscillations*" — by Alfred Lotka (1880-1949) and by Julius Hirniak.[4] Both studied the differential equations for the intermediary

reactions and, after a mathematical analysis, defined the conditions under which an oscillating chemical reaction could be seen."

Citation [3] lists LOTKA's 1910 article [32] and [4] refers to HIRNIAK's 1911 article [12], using the correct year.

- In a 2021 article by BERNOLD FIEDLER [74] one can find

  > "It is a lasting merit of [Hir1911] to point at the possibility of (damped) oscillations, once the Wegscheider constraints ... are strongly violated."

  This is an interesting approach to HIRNIAK's paper. FIEDLER clearly realized that HIRNIAK's reaction does not fulfill the WEGSCHEIDER constraints but rephrases it in a positive way.

- In a 2022 article by ROMAN CHERNIHA and VASYL' DAVYDOVYCH [75], they write in the introduction

  > "Following some earlier papers, in which linear ODEs were used for mathematical modeling of chemical reactions (in particular, see [3–5]), Lotka has shown that the densities in periodic reactions can be adequately described by a model involving ODEs with quadratic nonlinearities."

  while citing both of HIRNIAK's articles [8, 12] and LOTKA's 1910 German article [31]. No further discussion happens and it seems simply to be a citation with the first three articles including ODEs and having 'periodic reactions' in the title.

- JASON GALLAS cited HIRNIAK's 1911 article in his 2022 article [76], but it is completely 'hidden' within the five citations of the first sentence

  > "In pioneering works done in 1910–1920, Lotka [27–31] considered theoretically the problem of chemical oscillations. He was able to derive equations which produced sustained oscillations [31, 32]."

  The references [27-31] list four of LOTKA's papers [31–33, 38] and HIRNIAK's 1911 paper [12] as [28], though using the wrong year. The additional citation [32] refers to a 2018 article by ERNEUX [77].

2.2 Critical citations

- ANTON SKRABAL wrote in 1930 a 42-page article about the theory of periodic reactions in homogeneous systems. He starts with

  > "Im allgemeinen nähern sich die chemischen Reaktionen aperiodisch und asymptotisch ihrem Gleichgewicht[1]), doch kennt man auch periodisch verlaufende Vorgänge[2]). Unter den letzteren sind die periodischen Reaktionen im homogenen System am rätselhaftesten und daher von besonderm theoretischem Interesse. Die Möglichkeit solcher Reaktionen haben vor längerer Zeit Jul. Hirniak[3]) und A. Lotka[4]) theoretisch gezeigt. Beiden theoretischen Betrachtungen liegt ein System von Simultanreaktionen zugrunde."

  > "In general, chemical reactions approach their equilibrium aperiodically and asymptotically[1]), but periodic processes are also known[2]). Of the latter, the periodic

> reactions in the homogeneous system are the most puzzling and therefore of particular theoretical interest. The possibility of such reactions was shown theoretically a long time ago by Jul. Hirniak[3]) and A. Lotka[4]). Both theoretical considerations are based on a system of simultaneous reactions."

using the following citations: [1]) Siehe W. Nernst, Theoretische Chemie, 11. bis 15. Aufl., S. 634 und 766, Stuttgart 1926 [21]. [2]) Vgl. R. Kremann. Die periodischen Erscheinungen in der Chemie in Sammlung chemischer Vorträge **19**, 289, Stuttgart 1913. [34], [3]) J. Hirniak, Beiträge zur chemischen Kinetik, Lemberg 1911. Z. physikal. Chem. **75**, 675, 1911. [12] [4]) A. Lotka, Z. physikal. Chem. **72**, 508, 1910. **80**;, 159, 1912 [32, 33].

But SKRABAL realized already the 'problems' with HIRNIAK's math and chemistry. On page 388 he writes

> "In seiner Arbeit erwähnt J. Hirniak eine etwaige "unbekannte Gesetzmässigkeit", die das Negativwerden des Ausdrucks unter dem Quadratewurzelzeichen verhindert. Eine solche Gesetzmässigkeit wäre die Beziehung (22), falls die Zukunft lehren sollte, dass sie eine notwendige Beziehung ist. Im stärkeren Widerspruch zu dieser Beziehung stehen die sogenannten "Zirkularreaktionen", bei welchen die eine Seite der Beziehung (22) endlich, die andere Null ist."

> "In his work, J. Hirniak mentions a possible "unknown law" that prevents the expression under the square root sign from becoming negative. Such a law would be the relation (22), if the future should teach that it is a necessary relationship. In greater contradiction to this relationship are the so-called "circular reactions", in which one side of the relationship (22) is finite and the other is zero."

Equation (22) is given as $k_2k_4k_6 = k_1k_3k_5$ because he used the same reaction scheme as HIRNIAK in his 1911 article (see bottom sketch in the article's Fig. 2). He continued discussing WEGSCHEIDER's *Principle of Detailed Balance* and closes his article with

> "Periodische Reaktionen sind aus thermodynamischen und kinetischen Gründen möglich, aber aus denselben Gründen nicht wahrscheinlich. Damit im Einklang stehen die experimentellen Erfahrungen."

> "Periodic reactions are possible for thermodynamic and kinetic reasons, but not probable for the same reasons. The experimental experiences are consistent with this."

This quote is another indication about the difficult start of periodic chemical reactions in homogeneous systems. Even SKRABEL was still very skeptical, nine years after WILLIAM BRAY's experimental proof of oscillatory chemical reactions in 1921 [62].

- In 1947, WILHELM JOST published his article "Über den Ablauf zusammengesetzter chemischer Reaktionen - Systeme von Reaktionen I. Ordnung" ("About the process of compound chemical reactions - systems of first order reactions") and discussed a reaction scheme using first-order kinetics between three isomers, identical to HIRNIAK's system.

He starts his article with

> "Es ist bekannt, daß man bei der Berechnung der wechselseitigen Umlagerung dreier Stoffe nachnebenstehendem Schema von Reaktionen I. Ordnung Lösungen konstruieren kann, die einem Einstellen des Gleichgewichts durch gedämpfte Schwingungen entsprechen, sofern man beliebige Verhältnisse zwischen den sechs Geschwindigkeitskonstanten zuläßt[1]. Die Periodizität geht verloren, wenn man die Gültigkeit des Prinzips der mikroskopischen Reversibilität zugibt, wie ebenfalls seit langem bekannt, aber erst von L. Onsager[2] in allgemeinerem Zusammenhang diskutiert."

> "It is known that when calculating the mutual rearrangement of three substances according to the diagram of first-order reactions shown opposite, solutions can be constructed which correspond to establishing the equilibrium through damped oscillations, provided that arbitrary ratios between the six rate constants are allowed[1]. Periodicity is lost when one admits the validity of the principle of microscopic reversibility, which has also long been known but was only discussed in a more general context by L. Onsager[2]."

In reference [1], Jost cited articles by Hirniak [12] and Lotka [31–33, 78] and refers to Skrabal's work [55, 79] for numerical calculations and general overview about the topic. In reference [2], Jost cited Onsager's two famous articles from 1931 [80, 81]. He then gives the balanced rate constants equation and concludes that the system's eigenvalues are real, while, again, citing Skrabal's work. He continues with two exemplary four-component reaction schemes, generalizes his mathematical proof to n-component systems, and summarizes (which is actually his abstract) with

> "1. Es kann gezeigt werden, daß in beliebig kompliziert zusammengesetzten chemischen Umwandlungen nach der I. Ordnung keine Periodizität auftreten kann, sofern das Prinzip der mikroskopischen Reversibilität erfüllt ist. 2. Darüber hinaus gilt die schärfere Aussage: die Konzentration jeder Komponente dieses Systems kann als Funktion der Zeit höchstens $(n-2)$ Extrema durchlaufen, wenn n die Zahl der Komponenten ist."

> "1. It can be shown that no periodicity can occur in first-order chemical transformations of any complexity, provided the principle of microscopic reversibility is fulfilled. 2. Furthermore, the stricter statement applies: the concentration of each component of this system can pass through at most $(n-2)$ extremes as a function of time if n is the number of components."

These statements shows clearly that Hirniak's proposed periodic behavior wasn't possible in Jost's analysis.

- John Hearon included Hirniak's 1911 article (with the correct year) in his 1953 article "*The kinetics of linear systems with special reference to periodic reactions*" [82] in the introduction with

  > "The possibility of periodic reactions was early considered (Lotka, 1910; Hirniak, 1911; Lotka, 1920) and an experimental case was shortly reported (Bray, 1921)."

  After introducing Lotka's system, he continues with

  > "In all of the above cases, except that of Hirniak (*loc. cit.*), the differential equations which describe the system are *non-linear*, whether or not the system is open."

His mathematical analysis of different chemical reaction schemes is similar, but more general than our examination of HIRNIAK's work. The summary of his paper can be found in the first sentence of his abstract

> "It is shown on the basis of (1) conservation of mass, (2) positive concentrations, and (3) the principle of detail balancing that periodic reactions cannot occur in a closed system described by linear differential equations."

- 10 years later, in 1963, HEARON again cited HIRNIAK's 1911 article in his article "*Theorems on Linear Systems*" [83]. There, he wrote

  > "Hypothetical (but assertedly realizable), chemical systems, obeying *linear* kinetics, have been discussed (as early as 1911, Hirniak[38] and late as 1955, Landahl[39]; other references are given in Hearon[8]) as exhibiting periodic behavior. In all cases either the *Principle of Detailed Balance* has been assumed out of existence, or the equations used show that conservation of mass is infringed."

  with the two citations [12, 84] and his own article [82], clearly indicating the impossibility of the periodic behavior.

- In the 1973 article "*Oscillations, multiple steady states, and instabilities in illuminated systems*" by ABRAHAM NITZAN and JOHN ROSS [85], the authors state

  > "The possibility of oscillatory phenomena in a cyclic reaction scheme was long ago demonstrated by Hirniak.[10]"

  while citing HIRNIAK's 1911 paper correctly. They start similarly as in the article's Section *Analysis of Hirniak's work* but assume specific conditions for the rate constants,

$$k_1 \gg k_4, \quad k_5 \gg k_2, \text{ and } k_3 \gg k_6 \tag{1}$$

  which lead to a damped oscillation frequency of

$$\omega = \frac{1}{2}\left[4k_1k_5 - (k_1 + k_5 - k_3)^2\right]^{1/2} \tag{2}$$

  and a damping constant of

$$\gamma = \frac{1}{2}(k_1 + k_5 + k_3) \ . \tag{3}$$

  Because $\gamma > \omega$ they conclude that "in most situations the oscillatory behavior will not be amendable to experimental observation due to the large damping rate." Although they realize that the *Principle of Detailed Balance* rules out damped oscillations in a closed system on its way to chemical equilibrium, they write

  > "However, in an open system in a nonequilibrium steady state [the conditions proposed in Eq. (1)] may be achieved and one way of doing so is by optical excitation."

Though this might be possible, it is certainly not what HIRNIAK had in mind when proposing his reaction scheme.

- FONG *et al.* wrote in their 1982 photochemistry paper [86]

> "The feedback mechanism responsible for the oscillatory delayed fluorescence could conceivably be given by a cyclic scheme generically related to that discussed by Hirniak[51] and Nitzan and Ross,[52] although the large amplitudes of the oscillations are not easily accounted for by the description of an incoherent kinetic system."

while citing [12] and [85]. Here it is interesting that they cited HIRNIAK for a system the original work was certainly not intended for.

- ANATOL ZHABOTINSKY discussed HIRNIAK's "cyclic interconversion of three isomers" in his 1991 short historical review article "*A history of chemical oscillations and waves*" [87] and explains why periodic behavior seems to be possible but it thermodynamically impossible. He writes

> "In 1910, Hirniak[4] proposed that cyclic reactions can be oscillatory. He used the simplest example: the cyclic interconversion of three isomers."

citing HIRNIAK's 1911 article, but using the wrong year here and in the bibliography. He discusses that thermodynamics puts "strong restrictions on the rate constants in this system" and adds

> "This condition immediately forbids any oscillations in the system. Later, it was shown that it is impossible to have any concentration oscillations in the vicinity of the thermodynamic equilibrium state.[5] This thermodynamic analysis made a very strong impression on the majority of chemists, who interpreted it as being valid for all homogeneous closed chemical systems."

citing JOST (1947) [88], HEARON (1953) [82], and Gray (1970) [89] in reference [5]. With the last statement, ZHABOTINSKY gives an explanation for the continued diverse view of HIRNIAK's work. Many scientists see HIRNIAK as an early advocate for chemical oscillatory systems, similar to LOTKA, whereas others highlight the thermodynamic errors in his reaction scheme.

- In their 2017 article "*Periodic Reactions: The Early Works of William C. Bray and Alfred J. Lotka*, RINALDO CERVELLATI and EMANUELA GRECO [90] compared shortly HIRNIAK and LOTKA's work and HIRNIAK's claim of priority based on his 1908 article, though they dated both articles, in their references (31) and (33), as published in 1911.

They specifically addressed HIRNIAK's misunderstanding of LOTKA's work. They write

> "Hirniak distinguished his work from that of Lotka by insisting[34] particularly on the homogeneous nature of his model."

with the reference text

“Hirniak did not want to recognize that even the example of Lotka was hypothetical and concerned a homogeneous system. The presence of a condensed phase was perhaps misleading for Hirniak; however, Lotka’s hypothetical reaction then proceeded in a homogeneous phase, gas or solution.”

3 Translation of Hirniak's 1908 article

Translation from Ukrainian of the article "Про періодичні хемічні реакциї", *Збірник Математично-Природописно-Лікарської Секциї Наукового Товариства імени Шевченка* **XII** (1908) [8] by Юрій Головач (Yurij Holovatch).

Note: In this translation, we reproduce scans of the equations from the original publication. The articles have been provided by the Stefanyk National Scientific Library in Lviv, Ukraine, where originals of the journals are stored.

About periodic chemical reactions.
written by
Dr. Julian Hirniak.
(reported at the meeting of the Mathematical-Natural Sciences-Medical Section on September 10, 1908)

In this study I want to attract attention to one consequence that is very easy to derive from the equations of chemical kinetics. Making a closer look on the great interest to the problems in this field of physical chemistry, one has to conclude that the research is pursued exclusively in the experimental direction and that the studies with the help of mathematical analysis[1] appear in the literature almost as exceptions. If one adds to this that the very value of mathematical analysis in chemistry is very often directly or indirectly questioned, it is of no surprise that on some issues completely wrong views can be spread, although a simple and easy calculation can clarify the matter indisputably. I mean here the fact that in one, recently published place, the periodicity of a chemical process is considered a characteristic sign of catalysis. As I will show by the calculations below, periodicity can appear in processes in which there is no catalysis at all. And therefore, it is not in a causal relationship with catalysis, although such a phenomenon can be observed with the latter.

So far, I have very limited and fragmentary information about the extent to which periodic reactions have been studied experimentally, and I cannot now make it easier for myself to access the relevant literature sources. The work of Prof. Dr. W. Ostwald about the dissolution of chromium by mineral acids, which gave a periodic rate of this rather physical process, does not fit the analysis below.

Without resorting to premature assumptions about the significance of such reactions, either for chemical dynamics itself, or for application to the explanation of some subtler process in nature, I will try to use one theoretical example to show that in some cases they not only can, but must occur. Moreover, the possibility of such cases is not limited at all.

Let's take one well-known example. Prof. R. Wegscheider studied the relationship between reaction rate constants and chemical equilibrium constants. In his work,[2] he discusses, among others, the problem of three substances and presents the reaction equation between the three isomers. In this case, he considers unimolecular reactions, which essentially facilitates the calculations. There, the reaction occurs reversibly in

[1] R. Wegscheider – Chemische Kinetik homogener Systeme – Monatshefte für Chemie. B. XXI. 1900. page 693.
[2] Über simultane Gleichgewichte etc. – Monatshefte für Chemie. – B. XXII. 1901. p. 860.

all possible combinations. Substance M_1 turns to M_2, and M_2 to M_1, M_2 turns to M_3, and M_3 to M_2, M_3 turns to M_1, and M_1 to M_3. Thus, the total change

$$M_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} M_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} M_3 \underset{k_6}{\overset{k_5}{\rightleftarrows}} M_1$$

consists of as many as six reaction phases, or six separate component processes. Each of them has its own specific and separate rate, which is determined by the corresponding factors k_1, k_2, k_3, k_4, k_5, k_6.

Let's denote these phases with Roman numerals as follows:

I $M_1 \longrightarrow M_2$	II $M_2 \longrightarrow M_3$	III $M_3 \longrightarrow M_1$
I' $M_2 \longrightarrow M_1$	II' $M_3 \longrightarrow M_2$	III' $M_1 \longrightarrow M_3$

The initial concentrations of the three isomers M_1, M_2, M_3 will be denoted as A_1, A_2, A_3. Let the decrease of these concentrations during time t be ξ_1, ξ_2, ξ_3. We define individual reaction rates in a sequential order, and by subscribing individual factors for clarity, we obtain:

I	I'	II	II'	III	III'
$\frac{dx}{dt}$	$\frac{dy}{dt}$	$\frac{dz}{dt}$	$\frac{du}{dt}$	$\frac{dv}{dt}$	$\frac{dw}{dt}$
k_1	k_2	k_3	k_4	k_5	k_6.

Due to the mass action law the rates equal to:

$$\frac{dx}{dt} = k_1(A_1 - \xi_1), \quad \frac{dy}{dt} = k_2(A_2 - \xi_2), \quad \frac{dz}{dt} = k_3(A_2 - \xi_2)$$

$$\frac{du}{dt} = k_4(A_3 - \xi_3), \quad \frac{dv}{dt} = k_5(A_3 - \xi_3), \quad \frac{dw}{dt} = k_6(A_1 - \xi_1)$$

Considering these equations in more detail, it is easy to obtain the following decrease rates of individual concentrations:

$$\left.\begin{aligned}
\frac{d\xi_1}{dt} &= k_1(A_1 - \xi_1) - k_2(A_2 - \xi_2) - k_5(A_3 - \xi_3) + k_6(A_1 - \xi_1) \\
\frac{d\xi_2}{dt} &= -k_1(A_1 - \xi_1) + k_2(A_2 - \xi_2) + k_3(A_2 - \xi_2) - k_4(A_3 - \xi_3) \\
\frac{d\xi_3}{dt} &= -k_3(A_2 - \xi_2) + k_4(A_3 - \xi_3) + k_5(A_3 - \xi_3) - k_6(A_1 - \xi_1)
\end{aligned}\right\} \quad \ldots (A)$$

However, the following equations are obtained from the equations of hylotropic groups, in which reactions can be formulated according to Ostwald.[3] The mass conservation law is expressed here by the relation: $\xi_1 + \xi_2 + \xi_3 = 0$, from which it also follows that $\frac{d\xi_1}{dt} + \frac{d\xi_2}{dt} + \frac{d\xi_3}{dt} = 0$. The last connection indeed follows from the system of equations (A). The integration of this system gives the following result:

[3] See Wegscheider – Ibid.

$$\left.\begin{aligned}
\xi_1 &= \frac{1}{\lambda'-\lambda''}\left[\frac{\lambda''T'}{\vartheta'}\left(e^{-\vartheta' t}-1\right)-\frac{\lambda' T''}{\vartheta''}\left(e^{-\vartheta'' t}-1\right)\right]\\
\xi_2 &= \frac{1}{\lambda'-\lambda''}\left[-\frac{T'}{\vartheta'}\left(e^{-\vartheta' t}-1\right)+\frac{T''}{\vartheta''}\left(e^{-\vartheta'' t}-1\right)\right]\\
\xi_3 &= \frac{1}{\lambda'-\lambda''}\left[-(\lambda''-1)\frac{T'}{\vartheta'}\left(e^{-\vartheta' t}-1\right)+(\lambda'-1)\frac{T''}{\vartheta''}\left(e^{-\vartheta'' t}-1\right)\right]
\end{aligned}\right\}. \quad (B)$$

where the following notations have been introduced:

$$T_1=(k_1+k_6)A_1-k_2A_2-k_5A_3, \qquad S_1=k_1+k_5+k_6, \qquad T'=T_1+\lambda' T_2$$

$$T_2=-k_1A_1+(k_2+k_3)A_2-k_4A_3, \qquad S_2=k_2+k_3+k_4, \qquad T''=T_1+\lambda'' T_2$$

$$\vartheta'=\frac{S_1+S_2}{2}+\sqrt{\frac{(S_1-S_2)^2}{4}+(k_1-k_4)(k_2-k_5)}, \quad \lambda'=\frac{k_2-k_5}{S_2-\vartheta'}$$

$$\vartheta''=\frac{S_1+S_2}{2}-\sqrt{\frac{(S_1-S_2)^2}{4}+(k_1-k_4)(k_2-k_5)}, \quad \lambda''=\frac{k_2-k_5}{S_2-\vartheta''}.$$

Although the equations (B) look quite complicated, the calculations do not take much time, and the nature of the process, which is described by an exponentially decaying in time function, is such that it does not deviate at all from the current typical solutions to the problems of chemical dynamics. Prof. Wegscheider studied first of all the equilibrium to which such a system leads. He had no reason to delve further into the process itself, that is, into the way the state of equilibrium is approached. Therefore, he did not conduct a more detailed discussion of his equations (B).

However, it so happened that these equations belong to those which, under one condition, are nothing else but purely periodic reactions with increasingly smaller or decaying amplitudes. Therefore, in publishing this note before collecting more material, I will use the above equations for the calculations that are suitable for my purpose.

So let's see if the system of integral equations (B) can be physically interpreted in the case when the inequality holds:

$$\frac{(S_1-S_2)^2}{4}+(k_1-k_4)(k_2-k_5)<0. \quad \ldots\ldots\ldots\ldots \quad (C).$$

Let's put, for example, the following values for individual k:

$$k_1=1,\ k_2=20,\ k_3=2,\ k_4=30,\ k_5=1,\ k_6=20;$$

After calculations, we get:

$$\frac{(k_1+k_5+k_6-k_2-k_3-k_4)^2}{4}+(k_1-k_4)(k_2-k_5)=-326.$$

Condition (C) can be fulfilled as easily as the opposite condition, when the left side of the inequality is greater than zero. Therefore, it seems to me that the discussions of the last case until now have no advantage over the previous one (C), and it is this one that I want to take a closer look at, especially since there is no rational reason to reject it yet.

We will use shorter notations in the future:

$$\frac{S_1+S_2}{2}=a, \quad k_2-k_5=k, \quad S_2=S,$$

and the absolute numerical value

$$\sqrt{\frac{(S_1-S_2)^2}{4}+(k_1-k_4)(k_2-k_5)}$$

will be denoted as b.

Substituting these notations into the abbreviations given above (p. 3), we get:

$$\vartheta'=a+bi, \quad \lambda'=\frac{k}{S-(a+bi)}, \quad \lambda'-\lambda''=\frac{2kbi}{(S-a)^2+b^2}$$

$$\vartheta''=a-bi, \quad \lambda''=\frac{k}{S-(a-bi)},$$

where $i=\sqrt{-1}$.

Let's proceed to the calculation of integrals ξ_1, ξ_2, ξ_3. We obviously have here:

$$T'=T_1+\frac{k}{S-a-bi}T_2=\frac{T_1S+kT_2-T_1a-T_1bi}{(S-a)-bi},$$

or, with further shortenings

$$T_1S+kT_2-T_1a=\alpha, \qquad S-a=\alpha', \qquad T_1b=\beta,$$

instead of the former expression

$$T'=\frac{\alpha-\beta i}{\alpha'-bi},$$

and quite similarly

$$T''=\frac{\alpha+\beta i}{\alpha'+bi}.$$

Let's calculate the values of $\dfrac{T'}{\vartheta'}$ and $\dfrac{T''}{\vartheta''}$. The first one:

$$\frac{T'}{\vartheta'}=\frac{\alpha-\beta i}{(\alpha'-bi)(a+bi)}=\frac{\alpha-\beta i}{\alpha'a-abi+\alpha'bi-b^2i^2}=\frac{\alpha-\beta i}{(\alpha'a+b^2)+(\alpha'b-ab)i}$$

gives by definition $(\alpha'a+b^2)=\alpha''$, $\alpha'b-ab=\beta'$, the value $\dfrac{\alpha-\beta i}{\alpha''+\beta' i}$, and the second one in the same way $\dfrac{T''}{\vartheta''}=\dfrac{\alpha+\beta i}{\alpha''-\beta' i}$. From which it is easy to calculate again

$$\frac{\lambda'' T'}{\vartheta'} = \frac{k}{\alpha'+bi} \cdot \frac{T'}{\vartheta'} = \frac{k}{(\alpha'+bi)} \cdot \frac{(\alpha-\beta i)}{(\alpha''+\beta' i)}$$

Proceeding like this further

$$\frac{\lambda'' T'}{\vartheta'} = \frac{k}{\alpha'+bi} \cdot \frac{T'}{\vartheta'} = \frac{k}{(\alpha'+bi)} \cdot \frac{(\alpha-\beta i)}{(\alpha''+\beta' i)}$$

we get with simultaneous reduction

$$S' = \alpha' \alpha'' - b\beta', \quad S'' = \alpha' \beta' + b\alpha'',$$

$$\frac{\lambda'' T'}{\vartheta'} = \frac{k\alpha - k\beta i}{S' + S'' i}$$

and is the same way:

$$\frac{\lambda' T''}{\vartheta''} = \frac{k\alpha + k\beta i}{S' - S'' i}$$

Now let's take a closer look at exponential expressions $e^{-\varphi' t}$ and $e^{-\varphi'' t}$. By substituting there the values of φ' and φ'', we arrive due to the definition

$$e^{-at} \cos bt = \varphi$$
$$e^{-at} \sin bt = \chi$$

at the entirely new forms:

$$e^{-\vartheta' t} = e^{-(a+bi)t} = e^{-at-bti} = e^{-at}(\cos bt - i \sin bt) = \varphi - i\chi$$
$$e^{-\vartheta'' t} = e^{-(a-bi)t} = e^{-at+bti} = e^{-at}(\cos bt + i \sin bt) = \varphi + i\chi.$$

Using them, let us now calculate the following expression:

$$\frac{T''}{\vartheta''} e^{-\vartheta'' t} - \frac{T'}{\vartheta'} e^{-\vartheta' t} = \frac{\alpha+\beta i}{\alpha''-\beta' i}(\varphi+i\chi) - \frac{\alpha-\beta i}{\alpha''-\beta' i}(\varphi - i\chi).$$

Bringing to the common denominator $\alpha''^2 + \beta'^2$ we get the following value for the numerator:

$$\alpha\alpha''\varphi + \beta\alpha''\varphi i + \alpha''\alpha\chi i + \alpha''\beta\chi i^2 + \alpha\beta'\varphi i + \beta\beta'\varphi i^2 + \alpha\beta'\chi i^2 + \beta\beta'\chi i^3 -$$
$$- \alpha\alpha''\varphi + \beta\alpha''\varphi i + \alpha''\alpha\chi i - \alpha''\beta\chi i^2 + \alpha\beta'\varphi i - \beta\beta'\varphi i^2 - \alpha\beta'\chi i^2 + \beta\beta'\chi i^3 =$$
$$= 2i[(\beta\alpha'' + \alpha\beta')\varphi + (\alpha\alpha'' - \beta\beta')\chi],$$

resulting in

$$\frac{T''}{\vartheta''} e^{-\vartheta'' t} - \frac{T'}{\vartheta'} e^{-\vartheta' t} = 2i \frac{(\beta\alpha'' + \alpha\beta')\varphi + (\alpha\alpha'' - \beta\beta')\chi}{\alpha''^2 + \beta'^2}$$

Proceeding similarly, we can calculate easily as well

$$\frac{\lambda'' T'}{\vartheta'} e^{-\vartheta' t} - \frac{\lambda' T''}{\vartheta''} e^{-\vartheta'' t} = -2ki \frac{(\beta S' + \alpha S'')\varphi + (\alpha S' - \beta S'')\chi}{S'^2 + S''^2}$$

$$\frac{\lambda' T''}{\vartheta''} - \frac{\lambda'' T'}{\vartheta'} = \frac{2ki}{S'^2 + S''^2} (\beta S' + \alpha S'').$$

Having calculated in this way all the constituent terms of the system of integral equations (B), we can now easily write the equations describing the changes of individual ξ_1, ξ_2, ξ_3, over time, namely:

$$\left.\begin{aligned} \xi_1 &= \frac{(S-a)^2+b^2}{b} \cdot \frac{1}{S'^2+S''^2} \Big[(\beta S' + \alpha S'')(1-\varphi) - (\alpha S' - \beta S'')\chi \Big] \\ \xi_2 &= \frac{(S-a)^2+b^2}{k.b} \cdot \frac{1}{\alpha''^2+\beta'^2} \Big[(\beta\alpha'' + \alpha\beta')(\varphi - 1) + (\alpha\alpha'' - \beta\beta')\chi \Big] \\ \xi_3 &= \frac{(S-a)^2+b^2}{b} \Big\{ \frac{1}{S'^2+S''^2} \Big[(\beta S' + \alpha S'')(\varphi - 1) + (\alpha S' - \beta S'')\chi \Big] + \\ &\qquad + \frac{1}{k} \cdot \frac{1}{(\alpha''^2+\beta'^2)} \Big[(\beta\alpha'' + \alpha\beta')(1-\varphi) - (\alpha\alpha'' - \beta\beta')\chi \Big] \Big\} \end{aligned}\right\} (B')$$

Comparing the new form (B') of the system of integral equations with the form (B), we immediately see that all complex (imaginary) numbers marked in (B) with letters λ', λ'', T', T'', φ', φ'' fell out, and only real factors remained:

$$(S-a)^2+b^2,\ S'^2+S''^2,\ k, \alpha''^2+\beta'^2,\ \beta S' + \alpha S'',\ \alpha S' - \beta S'',\ \beta\alpha'' + \alpha\beta',\ \alpha\alpha'' - \beta\beta'.$$

Exponential terms $e^{-\vartheta' t}$ and $e^{-\vartheta'' t}$ have become periodic functions $e^{-at} \cos bt$ and $e^{-at} \sin bt$. Thanks to this, the integrals ξ_1, ξ_2, and ξ_3 became suitable for physical interpretation also under condition (C), and the integrals (B') in this case are nothing else than the dependence of changes in individual concentrations on time, expressed by one of the periodic functions, i.e., the goniometric one.

Let us consider a numerical example for a more convenient illustration. Let us put, for example, $k_1 = 1$, $k_2 = 601$, $k_3 = 1$, $k_4 = 501$, $k_5 = 1$, $k_6 = 2196.426$. Then $a = 1650.713$ and $b = 1$. Let us choose as well $A_1 = 1.3684$. $A_2 = 5$, $A_3 = 0.0002$, having in mind here such units that the solution comprising $A_1 + A_2 + A_3$ remains in a liquid state. After performing rather long calculation, we finally get:

$$\begin{aligned} \xi_1 &= 0{\cdot}6636 - 0{\cdot}6636\, e^{-1650t} (\cos t + 1{\cdot}647 \sin t) \\ \xi_2 &= 2{\cdot}428 - 2{\cdot}428\, e^{-1650t} (\cos t + 410 \sin t) \\ \xi_3 &= -3{\cdot}0916 + 0{\cdot}6636\, e^{-1650t} (\cos t + 1{\cdot}647 \sin t) + \\ &\qquad + 2{\cdot}428\, e^{-1650t} (\cos t + 410 \sin t). \end{aligned}$$

From the form of these equations it follows first of all that

a) $\xi_1 + \xi_2 + \xi_3 = 0$, that should be kept.
b) at time $t = 0$ we have $\xi_1 = \xi_2 = \xi 3 = 0$, i.e., the concentrations do not decrease by any amount, but only rest at the initial levels A_1, A_2, A_3.
c) in time $t = \infty$ the substance M_1 falls from the initial level 1.3684 by the amount 0.7048, M_2 from 5 by 2.572, and M_3 rises from 0.0001 to the height 3.0917.

This numerical example gives only a significant concentration shift, but due to the extremely high value of the exponent (1650) of the exponential function $e^{-\alpha t}$, deviation or periodic fluctuations of the initial composition of the entire system are so strongly damped from the first period that, for example, they could not be observed experimentally. As it is very easy to further calculate, the first deviation, which is also the maximal one, immediately has a value close to the composition at $t = \infty$. This does not surprise us at all, considering that there are relations as

$$\vartheta' = 1650 + \sqrt{-1}$$
$$\vartheta'' = 1650 - \sqrt{-1}$$

in which the value of b differs from zero by only one. The more the value of b increases, the more pronounced will be the periods and the longer they will be kept within the limits available for analytical observation.

We also immediately see that because of the relation

$$a = \frac{S_1 + S_2}{2} = \frac{k_1 + k_2 + k_3 + k_4 + k_5 + k_6}{2}$$

harmonic, that is, continuous periodic changes in the composition of the system are absolutely excluded, because a would be $= 0$ only if all k were $= 0$, which would be identical to the absence of any reaction.

Capitulating the matter, we must note that the most general equations of chemical dynamics, which have been discussed so far either on the basis of the formulation of experiments or for theoretical reasons, represented exclusively aperiodic processes. As we can see, one has not bypass solutions that may contain complex (imaginary) terms. It should first be checked whether they will not fall out of the equations due to the appropriate computational transformation.

It seems to me that there is little prospect and there is no great need to engage in general searches to predict in advance the possibility of periodic processes on the basis of appropriately combined reactions. Therefore, for now I will limit myself to the discussion of one arbitrarily chosen example given above.

4 Translation of Hirniak's 1911 article

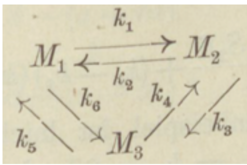
Translation from German of the article "Zur Frage der periodischen Reaktionen", *Zeitschrift für Physikalische Chemie* **75U** (1911) [12] by Niklas Manz.

On the question of periodic reactions.
by
Julius Hirniak.
(Received on 22.11.10.)

Mister A. Lotka published in the April issue of the 72nd volume of this magazine an article entitled: "On the theory of periodic reactions". I just recently read this publication and hence, I am only now getting around to pointing out that I dealt with the same question some time ago; my first note in this regard is in the "Proceedings of the mathematical-natural Sciences-medical Section"[1)], Vol. XII, 1908, of the Shevchenko Society of sciences in Lviv in Ruthenian language with the title: "The periodic chemical reactions", published. In Vol. XIII of the same publication, I addressed the same question again in the article "Remarks on the equations of mono- and bimolecular chemical kinetics".

Since my work in other languages has not yet been reviewed, they probably remained generally unknown. But it shows that the question is tackled independently from different sides, which may have something to do with its actuality.

I now consider it appropriate to present my first mentioned publication in more detail before adding a few words about the work of Mr. A. Lotka. I pointed out the possibility (even necessity) of a periodic chemical reaction using the example of a monomolecular mutual transformation of three isomers.



The kinetic system of differential equations was already integrated by Prof. Wegscheider for a long time[2)].

[1] Zbirnyk mat.-pryr.-lik Sekcyji.
[2] "About simultaneous equilibria, etc.", Journal of Physical Chemistry **39**, 268 (1902)

If we define the concentration decreases ξ_1, ξ_2, ξ_3 of the components M_1, M_2, M_3, the rate constants k_1, k_2, $\ldots k_6$, and the initial concentrations A_1, A_2, A_3, we find the kinetic system of differential equations of the reaction to be:

$$\left.\begin{aligned}
\xi_1 &= \frac{1}{\lambda' - \lambda''}\left[\frac{\lambda'' T'}{\vartheta'}(e^{-\vartheta' t} - 1) - \frac{\lambda' T''}{\vartheta''}(e^{-\vartheta'' t} - 1)\right] \\
\xi_2 &= \frac{1}{\lambda' - \lambda''}\left[-\frac{T'}{\vartheta'}(e^{-\vartheta' t} - 1) + \frac{T''}{\vartheta''}(e^{-\vartheta'' t} - 1)\right] \\
\xi_3 &= \frac{1}{\lambda' - \lambda''}\left[-(\lambda'' - 1)\frac{T'}{\vartheta'}(e^{-\vartheta' t} - 1) + (\lambda' - 1)\frac{T''}{\vartheta''}(e^{-\vartheta'' t} - 1)\right]
\end{aligned}\right\} \text{(A)}$$

with the introduction of the following abbreviations:

$$\begin{aligned}
T_1 &= (k_1 + k_6) A_1 - k_2 A_2 - k_5 A_3 , \\
T_2 &= -k_1 A_1 + (k_2 + k_3) A_2 - k_4 A_3 , \\
S_1 &= k_1 + k_5 + k_6 , \quad S_2 = k_2 + k_3 + k_4 , \\
\vartheta' &= \frac{S_1 + S_2}{2} + \sqrt{\frac{(S_1 - S_2)^2}{4} + (k_1 - k_4)(k_2 - k_5)} , \\
\vartheta'' &= \frac{S_1 + S_2}{2} - \sqrt{\frac{(S_1 - S_2)^2}{4} + (k_1 - k_4)(k_2 - k_5)} , \\
\lambda' &= \frac{k_2 - k_5}{S_2 - \vartheta'} , \quad \lambda'' = \frac{k_2 - k_5}{S_2 - \vartheta''} , \\
T' &= T_1 + \lambda' T_2 , \quad T'' = T_1 + \lambda'' T_2 .
\end{aligned}$$

All six rate constants k_1, k_2, $\ldots k_6$ must have positive values if the reaction is to retain its character.

It is now also easy to see that the values ϑ' and ϑ'' can become complex values in these integrals. Given the complete arbitrariness of the values k_1, k_2 $\ldots$etc. (within the limits of 0 to ∞), it can often happen that the expression under the square root sign:

$$\frac{(S_1 - S_2)^2}{4} + (k_1 - k_4)(k_2 - k_5)$$

becomes negative. A numerical example is easy to give. If we insert $k_1 = k_5 = 1$, $k_3 = 2$, $k_2 = k_6 = 20$, $k_4 = 30$, the value for the discussed expression is -326. Due to the connection between the symbols ϑ' and ϑ'' and the other expressions λ', λ'', T', and T'', all expressions of the integral system (A) may become complex, if necessary.

Without using probability calculus, we can assume that the only conditional equation between the six rate constants

$$\frac{(k_1+k_5+k_6-k_2-k_3-k_4)^2}{4}+(k_1-k_4)(k_2-k_5)<0$$

has a relatively large range of values. This means that the changes of the occurrence of the critical singular case, where everything within the integrals becomes imaginary, are also quite large.

We would come across an imaginary process.

However, it is clear that the case here is completely analogous to that of an electrical discharge, where the process sometimes runs aperiodically, depending on the values of the relevant factors, and at other times resolves into damped sinusoidal oscillations. Unless some yet unknown law prevents the expression under the square root sign from becoming negative, it is difficult to see how one could argue against this conclusion.

This is perhaps so self-evident that further proof is perhaps superfluous. But apart from the fundamental necessity, I also want to show here the simple transformation, on the basis of which the integral system (A) can be freed from all complex values and brought into the form of sine functions.

This should probably make the question a little more tangible.

Let us define:

$$\frac{S_1+S_2}{2}=a,\quad k_2-k_5=k,\quad S_2=S,$$
$$\sqrt{\frac{(S_1-S_2)^2}{4}+(k_1-k_4)(k_2-k_5)}=b\,i,$$

so follows first:

$$\vartheta'=a+bi,\quad \lambda'=\frac{k}{S-(a+bi)},\quad \lambda'-\lambda''=\frac{2k\,bi}{(S-a)^2+b^2},$$
$$\vartheta''=a-bi,\quad \lambda''=\frac{k}{S-(a-bi)},$$

with $i=\sqrt{-1}$.

Further is:

$$T'=T_1+\frac{k}{S-a-bi}\,T_2=\frac{T_1S+kT_2-T_1a-T_1\,bi}{(S-a)-bi},$$

or, with the introduction of

$$T_1S+k\,T_2-T_1a=\alpha,\quad S-a=\alpha',\quad T_1b=\beta,$$

also:

$$T'=\frac{\alpha-\beta i}{\alpha'-bi},$$

and similarly:

$$T'' = \frac{\alpha + \beta i}{a' + bi}.$$

Let us now calculate the expressions $\frac{T'}{\vartheta'}$ and $\frac{T''}{\vartheta''}$. The first one:

$$\frac{T'}{\vartheta'} = \frac{\alpha - \beta i}{(\alpha' - bi)(a + bi)} = \frac{\alpha - \beta i}{(\alpha' a + b^2) + (\alpha' b - ab) i}$$

gives with the following substitutions:

$$\alpha' a + b^2 = \alpha'', \quad \alpha' b - ab = \beta'$$

the value

$$\frac{\alpha - \beta i}{\alpha'' + \beta' i},$$

and the second similarly:

$$\frac{T''}{\vartheta''} = \frac{\alpha + \beta i}{\alpha'' - \beta' i},$$

from which again follows:

$$\frac{T'}{\vartheta'} - \frac{T''}{\vartheta''} = -\frac{2(\alpha'' \beta + \alpha \beta') i}{\alpha''^2 + \beta'^2}.$$

If we proceed with:

$$\frac{\lambda'' T'}{\vartheta'} = \frac{k}{(\alpha' + bi)} \frac{T'}{\vartheta'} = \frac{k}{(\alpha' + bi)} \frac{(\alpha - \beta i)}{(\alpha'' + \beta' i)}$$

and use immediately the abbreviations:

$$S' = \alpha' \alpha'' - b\beta', \quad S'' = \alpha' \beta' + b\alpha''$$

we obtain:

$$\frac{\lambda'' T'}{\vartheta'} = \frac{k\alpha - k\beta i}{S' + S'' i}$$

and also:

$$\frac{\lambda' T''}{\vartheta''} = \frac{k\alpha + k\beta i}{S' - S'' i}$$

Let's now take a look at the exponential expressions $e^{-\vartheta' t}$ and $e^{-\vartheta'' t}$. If we use the values ϑ' and ϑ'' in those, we come, due to the relationship:

$$e^{-at} \cos bt = \varphi,$$
$$e^{-at} \sin bt = \chi$$

to completely new forms:

$$e^{-\vartheta' t} = e^{-(a+bi)t} = e^{-at}(\cos bt - i \sin bt) = \varphi - i\chi,$$
$$e^{-\vartheta'' t} = e^{-(a-bi)t} = e^{-at}(\cos bt + i \sin bt = \varphi + i\chi.$$

Therefore, we obtain:

$$\frac{T''}{\vartheta''}e^{-\vartheta'' t}-\frac{T'}{\vartheta'}e^{-\vartheta' t}=\frac{\alpha+\beta i}{\alpha''-\beta' i}(\varphi+i\chi)-\frac{\alpha-\beta i}{\alpha''-\beta' i}(\varphi-i\chi).$$

If we use the same denominator $\alpha''^2+\beta'^2$ for the right side of the last equation, we obtain for the nominator the symmetrical polynomial:

$$\alpha\alpha''\varphi+\beta\alpha''\varphi i+\alpha''\alpha\chi i+\alpha''\beta\chi i^2+\alpha\beta'\varphi i+\beta\beta'\varphi i^2+\alpha\beta'\chi i^2+\beta\beta'\chi i^3,$$
$$-\alpha\alpha''\varphi+\beta\alpha''\varphi i+\alpha''\alpha\chi i-\alpha''\beta\chi i^2+\alpha\beta'\varphi i-\beta\beta'\varphi i^2-\alpha\beta'\chi i^2+\beta\beta'\chi i^3,$$

or immediately:

$$2i\,[(\beta\alpha''+\alpha\beta')\varphi+(\alpha\alpha''-\beta\beta')\chi].$$

Therefore, the result is:

$$\frac{T''}{\vartheta''}e^{-\vartheta'' t}-\frac{T'}{\vartheta'}e^{-\vartheta' t}=2i\frac{(\beta\alpha''+\alpha\beta')\varphi+(\alpha\alpha''-\beta\beta')\chi}{\alpha''^2+\beta'^2}.$$

Using the same path, we obtain:

$$\frac{\lambda'' T'}{\vartheta'}e^{-\vartheta' t}-\frac{\lambda' T''}{\vartheta''}e^{-\vartheta'' t}=-2ki\frac{(\beta S'+\alpha S'')\varphi+(\alpha S'-\beta S'')\chi}{S'^2+S''^2}$$

and:

$$\frac{\lambda' T''}{\vartheta''}-\frac{\lambda'' T'}{\vartheta'}=\frac{2ki}{S'^2+S''^2}(\beta S'+\alpha S'').$$

We now have all the necessary converted terms of the integral system (A), which we can simply write as:

$$\left.\begin{aligned}
\xi_1&=\frac{(S-a)^2+b^2}{b}\cdot\frac{1}{S'^2+S''^2}[(\beta S'+\alpha S'')(1-\varphi)-(\alpha S'-\beta S'')\chi]\\
\xi_2&=\frac{(S-a)^2+b^2}{k\,.\,b}\cdot\frac{1}{\alpha''^2+\beta'^2}[(\beta\alpha''+\alpha\beta')(\varphi-1)+(\alpha\alpha''-\beta\beta')\chi]\\
\xi_3&=\frac{(S-a)^2+b^2}{b}\left\{\frac{1}{S'^2+S''^2}[(\beta S'+\alpha S'')(\varphi-1)+(\alpha S'-\beta S'')\chi]\right.\\
&\qquad\left.+\frac{1}{k}\cdot\frac{1}{(\alpha''^2+\beta'^2)}[(\beta\alpha''+\alpha\beta')(1-\varphi)-(\alpha\alpha''-\beta\beta')\chi]\right\}
\end{aligned}\right\}\quad\text{(B)}$$

Calculating a numerical example is complicated. With the values (intentionally chosen for the short oscillation period):

$$k_1=k_3=k_5=1,\quad k_4=501,\quad k_2=601,\quad k_6=2196{\cdot}426$$

we obtain:

$$a=1650{\cdot}713,\quad b=1.$$

Let's add $A_1=1.3684$, $A_2=5$, $A_3=0.0001$. We need to consider units in a way to keep the solution, which includes $A_1+A_2+A_3$, diluted. After the insertion follows:

$$
\begin{aligned}
\xi_1 &= 0{\cdot}6636 - 0{\cdot}6636\,e^{-1650\,t}(\cos t + 1{\cdot}647 \sin t)\,, \\
\xi_2 &= 2{\cdot}428 - 2{\cdot}428\,e^{-1650\,t} \;(\cos t + 410 \sin t)\,, \\
\xi_3 &= -3{\cdot}0916 + 0{\cdot}6636\,e^{-1650\,t}(\cos t + 1{\cdot}647 \sin t)\,, \\
&\qquad\qquad + 2{\cdot}428\,e^{-1650\,t} \;(\cos t + 410 \sin t)\,.
\end{aligned}
$$

Because of $b = 1$, the oscillation period is short and, because of $a = 1650$, the amplitudes are extraordinarily damped. The process here is practically completely aperiodic, because the oscillation is completely destroyed after the first oscillations. Despite my original intention, I did not calculate any further examples[1]), but it seems to me that as b grows and a becomes smaller, we can expect "favorable" results. From the given example it can also be seen:

$$
\begin{aligned}
t &= 0, & A_1 &= 1{\cdot}3684, & A_2 &= 5{\cdot}0, & A_3 &= 0{\cdot}0001, \\
t &= \infty, & A_1 &= 0{\cdot}7048, & A_1 &= 2{\cdot}572, & A_3 &= 3{\cdot}0917.
\end{aligned}
$$

Furthermore, because of:

$$a = \frac{\Sigma k}{2} \qquad \text{and} \qquad b = \left| \sqrt{\frac{(S_1 - S_2)^2}{2} + (k_1 - k_4)(k_2 - k_5)} \right|$$

it is very generally to see that:

1. the process cannot be undamped under any condition,
2. the value of the oscillation period and the damping is independent of the initial concentrations.

Finally, I have to make the following comment:

My scheme is simpler and coincidentally more radical than that of Mr. A. Lotka, because it refers to a periodic reaction in a homogeneous system, and such a reaction is still completely unknown.

The case that Mr. A. Lotka is dealing with is perhaps more relevant, since we urgently need, I would say, a theory of periodic reactions for heterogeneous systems.

From a formal point of view, the circumstances in my example are more favorable since here the periodicity is calculated in a "finite" way, while in Mr. Lotka's case it is limited to the infinitely small concentration area directly at the equilibrium limit.

Also, some of the neglects/simplifications in Mr. Lotka's calculation do not seem entirely correct to me. But since their discussion would be too much, I rather forego it until further research in this area appears to make their considerations important.

Leipzig, Physical-Chemistry Institute, November 1910

[1] Originally, I intended to systematically carry out the calculation for various typical number combinations, but the work turned out to be so tedious that I decided against it.

5 Translation of Section IV of Wegscheider's 1901 article

Translation from German of section '*IV. Die gegenseitige Umwandlung von drei Isomeren*' in the article "Über simultane Gleichgewichte und die Beziehungen zwischen Thermodynamik und Reactionskinetik homogener Systeme" ("About simultaneous equilibria and the relationship between thermodynamics and reaction kinetics of homogeneous systems") by Rudolf Wegscheider, *Monatshefte für Chemie* **22**(8) (1901) [91][1] by Niklas Manz.

IV. The interconversion of three isomers.

If there are three isomeric types of molecules M_1, M_2, and M_3 in a homogeneous system that can convert into one another, then the following six reactions are possible:

$$\begin{array}{llllll} \text{I.} & M_1 \rightarrow M_2, & \text{II.} & M_2 \rightarrow M_3, & \text{III.} & M_3 \rightarrow M_1. \\ \text{I'.} & M_2 \rightarrow M_1, & \text{II'.} & M_3 \rightarrow M_2, & \text{III'.} & M_1 \rightarrow M_3. \end{array} \tag{4}$$

If the concentrations of the three substances are in equilibrium C_1, C_2, and C_3, then thermodynamics gives the equilibrium conditions

$$\frac{C_2}{C_1} = K_1, \qquad \frac{C_3}{C_2} = K_2, \qquad \frac{C_1}{C_3} = K_3. \tag{5}$$

with the well known relationship

$$K_3 = \frac{1}{K_1 K_2}. \tag{6}$$

In this case, the kinetics of the transformation can easily be developed, since we are dealing with simultaneous linear differential equations with constant coefficients.

If the rate coefficients of the six reactions I, I', II, II', III, and III' are denoted in sequence by k_1 to k_6, their rates are given by

$$\frac{dx}{dt}, \quad \frac{dy}{dt}, \quad \frac{dz}{dt}, \quad \frac{du}{dt}, \quad \frac{dv}{dt}, \quad \frac{dw}{dt}, \tag{7}$$

and with the initial concentrations A_1, A_2, and A_3 of the three molecules and the concentration decreases ξ_1, ξ_2, and ξ_3 at time t one can find the six reaction equations as:

$$\begin{aligned} \frac{dx}{dt} &= k_1(A_1 - \xi_1), & \frac{dz}{dt} &= k_3(A_2 - \xi_2), & \frac{dv}{dt} &= k_5(A_3 - \xi_3), \\ \frac{dy}{dt} &= k_2(A_2 - \xi_2), & \frac{du}{dt} &= k_4(A_3 - \xi_3), & \frac{dw}{dt} &= k_6(A_1 - \xi_1). \end{aligned} \tag{8}$$

[1] This paper was identically republished in *Zeitschrift für Physikalische Chemie* in 1902 [92] and in the initial journal 10 years later again in 1911 [93].

The rate of decrease of the concentrations of the molecules M_1, M_2, and M_3 are

$$\begin{aligned}
\frac{d\xi_1}{dt} &= k_1(A_1-\xi_1) - k_2(A_2-\xi_2) - k_5(A_3-\xi_3) + k_6(A_1-\xi_1),\\
\frac{d\xi_2}{dt} &= k_1(A_1-\xi_1) + k_2(A_2-\xi_2) + k_3(A_2-\xi_2) - k_4(A_3-\xi_3),\\
\frac{d\xi_3}{dt} &= k_3(A_2-\xi_2) + k_4(A_3-\xi_3) + k_5(A_3-\xi_3) - k_6(A_1-\xi_1).
\end{aligned} \tag{9}$$

The sum of the three $\dfrac{d\xi}{dt}$ is zero, since the law of mass conservation gives $\xi_1+\xi_2+\xi_3 = 0$. By introducing this relationship, the number of differential equations is reduced to two.

The result of the integration is the following. Introducing these abbreviations:

$$\begin{aligned}
T_1 &= (k_1+k_6)A_1 - k_2A_2 - k_5A_3,\\
T_2 &= -k_1A_1 + (k_2+k_3)A_2 - k_4A_3,\\
S_1 &= k_1+k_5+k_6,\\
S_2 &= k_2+k+3+k_4,\\
\vartheta' &= \frac{S_1+S_2}{2} + \sqrt{\frac{(S_1+S_2)^2}{4} + (k_1-k_4)(k_2-k_5)},\\
\vartheta'' &= \frac{S_1+S_2}{2} - \sqrt{\frac{(S_1+S_2)^2}{4} + (k_1-k_4)(k_2-k_5)},\\
\lambda' &= \frac{k_2-k_5}{S_2-\vartheta'},\\
\lambda'' &= \frac{k_2-k_5}{S_2-\vartheta''},\\
T' &= T_1 + \lambda' T_2,\\
T'' &= T_1 + \lambda'' T_2,
\end{aligned} \tag{10}$$

one can write

$$\begin{aligned}
\xi_1 &= \frac{1}{\lambda'-\lambda''}\left[\frac{\lambda''T'}{\vartheta'}\left(e^{-\vartheta' t}-1\right) - \frac{\lambda'T''}{\vartheta''}\left(e^{-\vartheta'' t}-1\right)\right],\\
\xi_2 &= \frac{1}{\lambda'-\lambda''}\left[-\frac{T'}{\vartheta'}\left(e^{-\vartheta' t}-1\right) + \frac{T''}{\vartheta''}\left(e^{-\vartheta'' t}-1\right)\right],\\
\xi_3 &= \frac{1}{\lambda'-\lambda''}\left[-(\lambda''-1)\frac{T'}{\vartheta'}\left(e^{-\vartheta' t}-1\right) + (\lambda'-1)\frac{T''}{\vartheta''}\left(e^{-\vartheta'' t}-1\right)\right].
\end{aligned} \tag{11}$$

The equilibrium conditions follow from these formulas by setting $t = \infty$. The equilibrium concentrations C_1, C_2, and C_3 are the concentrations of the three molecules $A_1-\xi_1$, $A_2-\xi_2$ and $A_3-\xi_3$ at $t = \infty$.

Therefore one obtains

$$
\begin{aligned}
C_1 = [A_1 - \xi_1]_{t=\infty} &= \frac{1}{\vartheta'\vartheta''}(k_2k_4 + k_2k_5 + k_3k_5)(A_1 + A_2 + A_3),\\
C_2 = [A_2 - \xi_2]_{t=\infty} &= \frac{1}{\vartheta'\vartheta''}(k_1k_4 + k_1k_5 + k_4k_6)(A_1 + A_2 + A_3),\\
C_3 = [A_3 - \xi_3]_{t=\infty} &= \frac{1}{\vartheta'\vartheta''}(k_1k_3 + k_2k_6 + k_3k_6)(A_1 + A_2 + A_3).
\end{aligned} \tag{12}
$$

The relationships between equilibrium coefficients and rate constants are as follows:

$$
\begin{aligned}
K_1 &= \frac{C_2}{C_1} = \frac{k_1k_4 + k_1k_5 + k_4k_6}{k_2k_4 + k_2k_5 + k_3k_5},\\
K_2 &= \frac{C_3}{C_2} = \frac{k_1k_3 + k_2k_6 + k_3k_6}{k_1k_4 + k_1k_5 + k_4k_6},\\
K_3 &= \frac{C_1}{C_3} = \frac{k_2k_4 + k_2k_5 + k_3k_5}{k_1k_3 + k_2k_6 + k_3k_6} = \frac{1}{K_1K_2}.
\end{aligned} \tag{13}
$$

The concentration ratios, which are, according to thermodynamics, independent of the total concentration, have a value independent of the initial concentrations according to the kinetic derivation.

The same equilibrium conditions can be obtained much easier as outlined in the second option of the previous section. Inserting the equilibrium concentrations C_1, C_2, and C_3 into the equations for the $\frac{d\xi}{dt}$, the $\frac{d\xi}{dt}$ must be zero. This gives the following three equations, which define the conditions for the constant concentration values of the three molecules in accordance with equation 18) of the previously mentioned article:

$$
\begin{aligned}
0 &= k_1C_1 - k_2C_2 - k_5C_3 + k_6C_1,\\
0 &= -k_1C_1 + k_2C_2 + k_3C_2 - k_4C_3,\\
0 &= -k_3C_2 + k_4C_3 + k_5C_3 - k_6C_1.
\end{aligned} \tag{14}
$$

The third equations is a result of adding the first two after a multiplication with -1.

From these equations one finds the same values for the equilibrium concentration conditions as before. For example, if one eliminates C_1 from two equations, one obtains a relationship between C_2 and C_3, which is identical to the one above.

The kinetically derived equilibrium conditions agree with the thermodynamic ones. All six rate constants can have arbitrary values. On the other hand, one can see that the relationships $K_1 = \frac{k_1}{k_2}$, $K_2 = \frac{k_2}{k_3}$, $K_3 = \frac{k_3}{k_1}$, which would hold at each individual equilibrium, would not need to be satisfied if there were simultaneous equilibria. The validity of the equation $K_1 = \frac{k_1}{k_2}$ would mean that at equilibrium, the reactions I and I' are also in equilibrium on their own, or that $\frac{dx}{dt} - \frac{dy}{dt} = 0$. The kinetic equilibrium condition derived above also includes the case discussed in Section II, that the simultaneous pairs of counteractions are not in equilibrium on their own, but that they only reach equilibrium through their interaction; then $\frac{dx}{dt} - \frac{dy}{dt}$ is not zero even at equilibrium.

In order for the individual pairs of counteractions to be in equilibrium on their own in simultaneous equilibrium, certain relationships between the rate constants must be followed. In equilibrium, one obtains the following values for the speed differences of the pairs of opposing reactions:

$$\begin{aligned}
\left[\frac{dx}{dt} - \frac{dy}{dt}\right] &= \frac{A_1 + A_2 + A_3}{\vartheta' \vartheta''}(k_1 k_3 k_5 - k_2 k_4 k_6), \\
\left[\frac{dz}{dt} - \frac{du}{dt}\right] &= \frac{A_1 + A_2 + A_3}{\vartheta' \vartheta''}(k_1 k_3 k_5 - k_2 k_4 k_6), \\
\left[\frac{dv}{dt} - \frac{dw}{dt}\right] &= \frac{A_1 + A_2 + A_3}{\vartheta' \vartheta''}(k_1 k_3 k_5 - k_2 k_4 k_6).
\end{aligned} \tag{15}$$

The three speed differences are therefore identical at equilibrium, as must be the case from Section II. But only for $k_1 k_3 k_5 = k_2 k_4 k_6$ they do become zero. Only then will the three reaction pairs be in equilibrium on their own and only then will the relationships $K_1 = \frac{k_1}{k_2}$ etc. apply. One can easily convince oneself that these simpler relationships arise from the previously derived general one if one sets $k_1 k_3 k_5 = k_2 k_4 k_6$.

The simpler form of the relationship between equilibrium constants and rate constants always applies, among other things, if one of the three reaction pairs is omitted, e.g., if $k_1 = k_2 = 0$.

Simple relationships also occur when equilibrium is reached without any counteracting effects. For example, if only reactions I', II', and III' take place, then k_1, k_3 and k_5 are zero and one obtains $K_1 = \frac{k_6}{k_2}$, $K_2 = \frac{k_2}{k_4}$, $K_3 = \frac{k_4}{k_6}$.

[Note: We are omitting translating the remaining page because it solely relates to Section I of this paper about the ester formation from acid and alcohol.]

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