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### History of Science

Error and Discovery: Why Repeating Can Be New



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The fascinating story of the discovery of nuclear fission began with an error that earned Enrico Fermi (see picture) a Nobel Prize for the apparent but incorrect discovery of the transuranic elements. Careful repetition and extension of the experiments finally led to the correct interpretation by Hahn, Meitner, Strassmann, Frisch, and Bohr as an effect from nuclear fission of the "small impurity" of  $\frac{235}{92}$ U (0.7%) contained in natural uranium.

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# Error and Discovery: Why Repeating Can Be New\*\*

Martin Quack\*

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Dedicated to the Bayer company on the occasion of its 150th anniversary

### Motto

The Romans used to place pillars in the Forum Romanum for those men during their lifetime who had served Rome in an outstanding fashion, the "Roman Nobel Prize of Politics" so to speak, but not so for Cato. When Cato was asked by his friends: "Why is there no pillar for Cato in the Forum Romanum?" his reply was: "I prefer that they ask 'why is there no pillar for Cato in the Forum Romanum?' than that they would ask 'Why is there a pillar for Cato in the forum Romanum?"" (cited after reference [1])

### 1. Introduction: A Nobel Prize for an Erroneous **Discovery**

This Essay might also be entitled "Which Nobel Prize in Physics was given for an erroneous discovery?", that is, explicitly for a result that later turned out to be wrong. It tells one of the most fascinating stories in the history of science, which has been in fact extremely well investigated by historians of science and documented in many articles and books. However, when asking this question to a large number of physicists and chemists with the side-remark: "that is probably something one should know", I found that, interestingly, only a very small number of the scientists asked know the answer (less than a handful out of more than certainly several hundred I have asked over the last decades or so). It is also quite instructive that while there are many papers and books about debates on Nobel Prizes, these mostly concern quarrels about priorities, stolen ideas, omitted first or codiscoverers, and so on, but none (to the best of my knowl-

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edge) seems to tell this particularly striking story of the erroneous Nobel Prize discovery.

Thus while this part of the history of science is perfectly well known, it is not at all widely appreciated. The purpose of this Essay is to help in changing this situation on the occasion of the 75th anniversary in 2013 of this Nobel Prize of 1938.[2] We are talking about the history of the discovery of nuclear fission, which is not only of interest because of its enormous practical importance, but also because it shows very well how science works. We are used to standard comments of referees stating that "Repeating is not new" (and then suggesting rejection of the paper). This kind of statement misses an essential aspect of science, particularly well demonstrated by the history of nuclear fission. Scientific work really has two very different components, which one may call the "creative" and the "critical". The creative component tries out new ideas and unexplored avenues often guided by speculation (sometimes by theory). It sells well under the fashionable term "novel". However, the critical component is as important as the creative component. The critical component questions the "novel" result, subjecting its weaknesses to harsh criticism, repeating and testing the results in long investigations involving hard work, often rejecting or correcting the original result and sometimes leading to an even more striking discovery than previously assumed by the wildest speculation. This was precisely the route followed in the history of the discovery of nuclear fission, which started with an enormous error in the "novel" discovery of new elements (guided by theory), and, after years of careful checking, led finally to a much more revolutionary discovery than originally anticipated.

The answer to the question at the beginning of this Essay is that it is the Nobel Prize for Physics given in 1938 to Enrico Fermi for the discovery of the "new transuranic elements" (then named "ausenium" and "hesperium") with charge numbers  $Z = 93$  and 94, respectively, thus larger than  $Z = 92$ for the previously "last" known element uranium. The literal citation of the short Nobel Prize citation in French is:

"L'Académie royale des sciences a décidé, le 10 novembre 1938, que le Prix Nobel de physique pour l'année 1938 serait attribué à Enrico Fermi pour sa découverte de nouveaux éléments radioactifs, développés par l'irradiation des neutrons, et sa découverte à ce propos des réactions de noyaux, effectuées au moyen des neutrons lents.

<sup>[\*\*]</sup> Based on a lecture "Was wäre, wenn niemand nachgemessen hätte: Irrtum als Weg zur Erkenntnis (grosse und kleine Irrtímer in der Wissenschaft, je ein Nobelpreis fír ein falsches Resultat und dann fír seine Korrektur)", Diskussionsforum Molekulare Wissenschaften, Collegium Helveticum, Semper Sternwarte, Friday October 19, 2012 (see also Vorlesung Chemische Reaktionskinetik M. Quack, HS 2012, Kapitel 2.10, Zur Entdeckungsgeschichte der Kernspaltung).

Le même jour l'Académie a décidé de ne pas distribuer le prix Nobel de chimie pour l'année 1938 et de le réserver pour l'année suivante."<sup>[2][\*]</sup>

That a Nobel prize for Chemistry was not awarded in this year is particularly amusing, as it would later be chemists who showed that Fermi had not discovered new elements but something very different, which he did not realize. It is worthwhile to also cite from the extensive laudatio of the President (H. Pleijel) of the Nobel Prize Committee for Physics, which stresses towards the end the discovery of the new transuranic elements:

"Fermi a en effet réussi à produire deux nouveaux éléments, dont les numéros d'ordre sont 93 et 94, éléments auxquels il a donné le nom d'ausénium et d'hespérium."<sup>[3][\*\*]</sup>

### 2. The Error is Based On a Correct Theory in Connection with an Unexpected "Artifact" Reaction from a Small Impurity

In 1934, Fermi had investigated nuclear reactions of uranium with the then newly available neutrons, $[4]$  which just two years before had been discovered by Chadwick.<sup>[5]</sup> Fermi's theoretical idea behind these investigations was in principle correct and we know today that the reactions which Fermi anticipated for these experiments actually do occur [in Eqs. (1)–(4), written in modern notation].

$$
{}_{92}^{238}\text{U} + n \rightarrow {}_{92}^{239}\text{U}^* \rightarrow {}_{92}^{239}\text{U} + h\nu(\gamma) \tag{1}
$$

 $^{239}_{92}U \frac{\beta^2}{93}Np$   $(t_{1/2} = 23.5 \text{ min})$  (2)

 $^{239}_{93}Np \rightarrow ^{239}_{94}Pu \t (t_{1/2} = 3391.2 \text{ min})$  (3)

$$
{}_{94}^{239}\text{Pu} \xrightarrow{\alpha} {}_{92}^{235}\text{U} + {}_{2}^{4}\text{He} \quad (t_{1/2} = 24400 \text{ a}) \tag{4}
$$

The idea for these experiments was brilliant, as the uncharged neutrons are not subject to Coulomb repulsion and thus can easily penetrate heavy nuclei. However, as Fermi and his co-workers at the time could generate only minute amounts of the suspected reaction products, they identified the product nuclei by their radioactive decay paths and lifetimes. Finding some radioactive substances with lifetimes, which were not known from previous studies of radioactive elements, supported by some studies of chemical properties, was taken as sufficient evidence for the new elements with  $Z = 93$  and  $Z = 94$ . The original report on these results was actually phrased rather cautiously, $[4]$  but over the years

[\*] The Royal Academy of Sciences has decided on November 10, 1938 to attribute the Nobel Prize for Physics for the year 1938 to Enrico Fermi for his discovery of new radioactive elements, obtained by irradiation with neutrons, and his discovery on this occasion of new nuclear reactions initiated by means of slow neutrons. The same day the Academy has decided not to give the Nobel prize for Chemistry in the year 1938, but to reserve it for the next year.

[\*\*] Fermi has actually succeeded in producing two new elements with atomic numbers 93 and 94, to which elements he has given the names ausenium and hesperium".

caution was reduced.<sup>[6]</sup> Fermi's results were criticized rather quickly by the co-discoverer of rhenium,<sup>[7]</sup> Ida Noddack, as giving insufficient proof for new elements in a short communication to *Angewandte Chemie*,<sup>[8]</sup> where the possibility of the production of new radioactive isotopes of much lighter elements by fragmentation was mentioned as a possibility, but the criticism and suggestion was not taken seriously by Fermi, Hahn, Meitner, and others.<sup>[9,10]</sup>

It turned out, however, that the criticism was fully justified. The radioactive isotopes, which Fermi and his coworkers had seen, originated in fact from the reactions of a small impurity of  $^{235}_{92}U$  (in 0.7% abundance), which has a high probability to undergo fission and generate highly radioactive isotopes of several light elements, which also have stable isotopes, such as in Equations (5) and (6).

$$
{}_{92}^{235}U + n \rightarrow {}_{37}^{93}Rb + {}_{55}^{141}Cs + 2n \tag{5}
$$

$$
{}_{92}^{235}U + n \rightarrow {}_{56}^{140}Ba + {}_{36}^{93}Kr + 3n \tag{6}
$$

These unexpected "artifact" Reactions (5) and (6) generated much more signal than the expected Reactions (1)–(4), in spite of the low abundance of the "impurity". Thus Fermi was fooled by these initial results and did not pursue this sufficiently further to provide more compelling evidence, although it is reported that he initially was worried that the results on the transuranium elements might be wrong.

### 3. Repeating Can Be New

Other research groups initiated experiments to continue and improve upon Fermi's experiments. This was not done in the suspicion that Fermi's results were actually wrong, but rather in the hope to better characterize the products and extend Fermi's research. This classic type of careful research is often today disqualified as "repetitive" and "not new". Lise Meitner convinced Otto Hahn to revive their collaboration on radioactive isotopes from many earlier years in starting to work on this question.<sup>[11,12]</sup> They were later joined by Fritz Strassmann. Irène Curie (the daughter of Marie Curie), who had already previously worked with her husband Jean Fréd¦ric Joliot on artificial radioactivity, collaborated with P.



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kinetics and spectroscopy at the frontier with physics, and fundamental symmetries in nature leading to conservation laws and their subtle violations.

Savitch on the repetition and continuation of Fermi's experiments. The idea in all cases was to characterize the results more carefully by "nuclear chemistry", where the reaction products were investigated using chemical methods of separation and enrichment using reactions of possibly related elements.

Table 1 gives a subsection of the periodic table as it was used at the time. Element 93 was called Eka-Re and element 94 Eka-Os, given the expected corresponding chemical similarities. We know today that another arrangement of the periodic table is appropriate, where uranium and the transuranic elements are part of the actinide series (Table 2).

Table 1: Subsection of the periodic table of 1934.

$_{20}$ Ca	215c	$22\text{Ti}$	22V	$_{24}$ Cr	$25$ Mn	$_{26}$ Fe					
$38$ Sr	$_{39}Y$	$_{40}Zr$	$_{41}$ Nb	$_{42}$ Mo	$_{43}$ Ms	$_{44}$ Ru					
56Ba	$57$ La	$_{72}$ Hf	$73$ Ta	74W	$75$ Re	$_{76}$ Os					
$_{88}$ Ra	$_{89}$ Ac	$_{90}Th$	$_{91}$ Pa	<sub>92</sub> U	$_{93}$ Eka-Re	$_{94}$ Eka-Os					
Lanthanides											
$57$ La	$_{58}$ Ce	$_{59}$ Pr	$_{60}$ Nd	61 P	$_{62}$ Sm	$63$ Eu					

Table 2: Subsection of the modern periodic table of the elements.



It is a historic curiosity that in 1934 the element masurium (Ms) appeared between manganese and rhenium, as "Ms" was believed to have been discovered as well by the discoverers of rhenium, but masurium turned out to be an error. We know today that element 43 is unstable (technetium; Table 2). On the other hand, rhenium had been prepared in substantial amounts and thus proven.[7]

We shall not tell all the details of the history of various discoveries and errors between 1934 and 1938. Quite a large number of publications appeared from the two groups mentioned, and also others. The isotope  $\frac{^{239}}{^{92}}U$  was proven by Hahn and Meitner, new thorium isotopes were proposed by I. Curie and P. Savitch, but rejected by Hahn and Meitner. Quite a few erroneous associations were also made because of the incorrect arrangement of the periodic table at that time. In essence, all these investigations led to dead ends, as far as the proof for the new transuranic elements was concerned. A nice survey of the difficulties is found in the papers by Hahn, Meitner, and Strassmann.<sup>[13,14]</sup>

In July 1938, Lise Meitner had to leave Germany because she was threatened by the Nazi racism after the occupation of Austria (she was previously protected by her Austrian citizenship, which worked as a safeguard for persons with Jewish confession). Thus Hahn and Strassmann in Berlin had to continue the experiments alone, with frequent contact by letter to Lise Meiter. After some time, they came to the conclusion that neutron bombardment of uranium resulted in an alkaline-earth element, because of the observed chemical properties. Their first assumption was that new radium isotopes would be produced, but then they realized that these new "radium isotopes" actually behaved like radioactive barium isotopes as they could not be separated chemically from barium. In their first publication on this discovery, they phrased this completely unexpected result very cautiously (literally from the original): "Wir kommen zu dem Schluss: Unsere 'Radiumisotope' haben die Eigenschaften des Bariums; als Chemiker mîssten wir eigentlich sagen, bei den neuen Körpern handelt es sich nicht um Radium, sondern um Barium, denn andere Elemente als Radium oder Barium kommen nicht in Frage."[15][\*]

### 4. A Fast Course of Events after the Ignition by **Discovery**

The timing of events in the very difficult times of 1938 and 1939 is also fascinating. Whereas progress had been slow for four years, things go explosively fast after ignition by discovery. Fermi gives his Nobel Lecture "Artificial radioactivity produced by neutron bombardment" (on "Ausenium" and "Hesperium" among other things) on December 12, 1938, and thereafter leaves for the United States, not returning to Italy because he is afraid of prosecution under the Mussolini government, his wife being Jewish.<sup>[6]</sup> On the same day, the laudatio of Pleijel is given, honoring the wrong discovery.<sup>[3]</sup> One week later on December 19, 1938 Otto Hahn writes in a private letter to Lise Meitner (shortened; and not quite literally) "that the radium isotopes behave like barium isotopes and we must come to the terrible conclusion that they are barium isotopes. I have agreed with Strassmann that at present we tell this only to you. Perhaps you can propose a fantastic explanation. We know in principle that uranium cannot break up ('zerplatzen') into pieces such as barium." Lise Meitner replies from Copenhagen in a letter dated December 21, 1938 that such a breakup appears difficult but that she cannot exclude it as impossible. This letter arrives in Berlin on December 23. Meanwhile Hahn and Strassmann had submitted their manuscript (on December 22, 1938). It appears in print already on January 9, 1939, obviously without much refereeing and revision.<sup>[15]</sup> A second, more detailed description of the proof for barium appears already on January 28, 1939.<sup>[16]</sup> A nice historical summary of the events in Berlin can be found in reference [17].

Over the Christmas holidays, Lise Meitner discusses with her nephew Otto Frisch in Kungälv (near Göteborg) a possible theory of "nuclear fission" (a term coined by Otto Frisch<sup>[11,12,18]</sup>) based on Bohr's liquid droplet model of the

<sup>[\*]</sup> We conclude: Our "radium-isotopes" have the properties of barium; as chemists we should say, these new substances are not radium, but barium, because elements other than barium and radium are excluded.

nucleus. They submit a paper on "A New Type of Nuclear Reaction" to Nature on January 16, 1939 (published on February 11). Upon return from the Christmas holidays, Otto Frisch tells the story to Niels Bohr, who is just leaving to take a boat to the United States. Niels Bohr's comment was "Oh, what fools we have been, we ought to have seen that before". (cited in reference[18]). On January 13, 1939, Otto Frisch carries out an experiment to prove the high-energy fragments resulting from fission (paper submitted to Nature on January 16, 1939, where the word "fission" is used). Niels Bohr works on the theory during his journey. In his second paper on the theory of fission, already submitted on February 7, 1939 to Physical Review he gives the essentially correct theoretical interpretation of the observations. The small amount of  $^{235}_{92}$ U is responsible for the observed fission products, because the excitation energy in the compound nucleus  $^{236}_{92}U^*$  is much higher than in the fairly stable  ${}^{239}_{92}U^*$ . The reason for this is the much lower stability of  $^{235}_{92}U$ , an "even-odd" nucleus with an odd number of neutrons (and nucleons) compared to the "even–even" nucleus  $^{238}_{92}U$ . Thus there is much more energy available in  $^{236}_{92}U^*$  to overcome the in principle very high coulombic barrier for fission into two highly charged components.[19] 26 years after his understanding of atomic electronic structure on the basis of the "old quantum theory", for which we celebrate the 100th anniversary in 2013,<sup>[20–23]</sup> and after several years of thinking about the quantum structure of the atomic nucleus, Niels Bohr is the person with the deepest insight into atomic structure.

When Bohr arrives at New York's harbor, he meets Fermi and informs him of the news. Fermi adds a footnote to the printed version of his Nobel Lecture: "The discovery by Hahn and Strassmann of barium among the disintegration products of bombarded uranium, as a consequence of a process, in which uranium splits into two approximately equal parts, makes it necessary to reexamine all the problems of the transuranic elements as many of them might be found to be products of a splitting of uranium". In essence, in this footnote, Fermi withdraws the results that led to the Nobel Prize in the first place.

Many activities on nuclear fission started from early 1939. It was also quickly recognized that the production of two or more neutrons in reactions such as (5) and (6) allows for branched "chain reactions", the concepts of which were known from chemical reaction kinetics.<sup>[24–26]</sup> Consequently S. Flîgge published a paper in June 1939 "Can the energy content of atomic nuclei be used by technology".[27] After the start of World War Two, most investigations on nuclear fission were kept secret. Under the direction of Fermi, the first chain reaction in a nuclear reactor was achieved on December 2, 1942, and it is well known that the first nuclear weapons were used in 1945 (a recent guide to the vast literature on the Manhattan project can be found in reference [28]). Personal, philosophical, and political aspects of these developments have found their way into the play "Copenhagen" by Michael Frayn,[29] apart from many books on history, as this is clearly not just part of the history of science, but of mankind. What had started out with an enormous error has become "one of the two greatest known risks for mankind".[30]

### 5. Error and Discovery: A Summarizing Assessment

In an assessment of the history of the discovery of nuclear fission one can see at first, how Fermi's error was in part induced by a theory, which was, in principle, correct. What he expected from theory actually does exist for  $^{238}_{92}U$ , but in his experiments it was overshadowed by the totally unexpected effects arising from the "minor impurity" (0.7% of  $^{235}_{92}$ U). Fermi's mistake is one of the most frequent mistakes in science (over-interpretation of the data). The data that he actually had available were quite insufficient to prove his point for the transuranic elements. This was easy to see, and it was actually seen immediately,<sup>[8]</sup> but Fermi, Hahn, Meitner, Strassmann, Curie, Savitch, and others were blind towards this aspect of the problem. They dismissed the criticism with the typical arrogance of experts.<sup>[9,31]</sup>

Nevertheless, it was understood that more careful investigations into this matter were desirable and these were undertaken as repetition and extension of Fermi's experiments, not in order to disprove them (nor to discover fission). Only when the experiments showed conclusively after many careful investigations that products such as barium had to be present, Hahn and Strassmann could not escape from the conclusion concerning such products, and initially they phrased this with the greatest reluctance. Repetition had become very new, indeed revolutionary. The correction of Fermi's result led to another Nobel Prize to Otto Hahn.<sup>[9,10]</sup> Also Fermi's original theoretical idea for producing transuranium elements was further pursued in more careful experiments leading to the true discovery of the new elements now called neptunium and plutonium by following the course of Reactions (1)–(4). This also led to a further Nobel Prize to McMillan and Seaborg in 1951.

The history of the discovery of nuclear fission is one of the many examples showing that carefully repeating, reproducing, extending, or rejecting earlier results is at the heart of good scientific work. Another aspect of the tedious route towards discovering fission is the blindness of the scientists involved towards the possibility of the new type of nuclear reaction of breakup into large fragments. There were good theoretical reasons to exclude such a breakup. The "Coulomb barrier" is proportional to the product of charge numbers  $Z_1 Z_2$  of the two fragments, where obviously  $Z_1 Z_2$  is larger at given  $Z = Z_1 + Z_2$ , when  $Z_1$  and  $Z_2$  become more similar. Also the then-known tunnel effect<sup>[32]</sup> explaining  $\alpha$  decay<sup>[33,34]</sup> would be much smaller for fragments of higher mass, thus greatly decreasing the rate for such fragmentation processes.

On the other hand, if one looked at the process of fission from the point of view of its statistical aspects,[35–37] a point of view common in the theory of chemical reaction dynamics at the time,<sup>[38, 39]</sup> as today,<sup>[40, 41]</sup> then fission into larger fragments appears to be a much more likely process. This interdisciplinary transfer of ideas did not work in the early history of nuclear fission, but it worked perfectly for transferring ideas from the theory of chemical chain reactions to the nuclear chain reactions.<sup>[24–27]</sup> In any case, it is clear that the history of nuclear fission is one of a close interplay between physics and chemistry, with discovery being made possible by investiga-



tion at the frontier combining these two traditional fields of science.

Returning to our initial statement on the importance of combining the "creative" and the "critical" components in scientific work, one might also phrase this in terms of scientific personalities: the enthusiast and the sceptic. Only the combination of the two personalities results in good science. In research, enthusiasm without scepticism leads to nonsense. Scepticism without enthusiasm leads to … nothing. In the best case, a scientist combines the two qualities in one person. In practice, a typical scientist will lean more towards one or the other of the two personalities. Then it is the interaction of many scientists of different orientations and backgrounds in the scientific community by discussion and publication that generates success, and certainly, the discovery of nuclear fission provides a good example for this as well.

It seems appropriate to conclude this section with a modern IUPAC version (2012) of the periodic table (Table 3), which shows the many transuranic elements as part of the overall picture. While Fermi's early experiments were incorrect, the basic ideas were followed in later work (reviewed in reference [42] for example). About 20% of the elements discovered and named until today are "transuranic" elements, including those with the names of Fermi (Fm), Bohr (Bh), Meitner (Mt) as well as those with the names of the places where many of the new elements were discovered (Berkeley giving berkelium, Bk; Dubna giving dubnium, Db; and Darmstadt giving darmstadtium, Ds).

### 6. Scientists at Work: Fermi, the Scientists, and the **Bureaucrats**

One might ask whether the Nobel Prize given for an erroneous result should not be withdrawn (at least in terms of historical perspective). However, in spite of Fermi's great mistake (followed by the even greater mistake of the Nobel Prize Committee), most scientists in the field would agree that Fermi as one of the greatest scientists of the 20th century deserves a Nobel Prize, even though definitely not for the discovery of ausenium and hesperium. Fermi has many great achievements to his credit, some of them worthy of a Nobel Prize. Perhaps his greatest achievement was his theory of radioactive  $\beta$  decay, published in Zeitschrift für Physik in 1934,[43] the same year when the erroneous experiments on the transuranics were published. The publication on  $\beta$  decay is a wonderful piece of work, well-written (in excellent German by an Italian), leading to the discovery of the weak interaction, the Fermi coupling constant (about correctly estimated already in this paper), and finally electroweak theory as a major stepping-stone to the modern standard model of particle physics (SMPP)<sup>[44-46]</sup> with some relevance even for the stereochemistry of chiral molecules. [47]

Furthermore, Fermi was the major driving force (together with Leó Szilárd) in building the first functioning nuclear reactor.[48] In this large enterprise, some other qualities of Fermi's were important, not only scientific but also organizational, administrative, and political. In that context I will report an anecdote, in the version I remember it being told by Per-Olov Löwdin at a summer school in 1973,<sup>[49]</sup> but there is also some printed record.

				$\lambda$		$\overline{\phantom{a}}$											18
$\overline{1}$ $\overline{1}$																	$\overline{c}$
н																	He
hydrogen																	helium
[1.007; 1.009]	$\overline{c}$		Key:									13	14	15	16	17	4.003
3	$\overline{4}$		atomic number									5	$\,$ 6	$\overline{7}$	$^{\rm 8}$	$\overline{9}$	10
Li	Be		Symbol									B	C	N	O	F	<b>Ne</b>
lithium	beryllium		name									boron	carbon	nitrogen	oxygen	fluorine	neon
[6.938, 6.997]	9.012		standard atomic weight									[10.80; 10.83]	[12.00; 12.02]	[14.00; 14.01]	[15.99; 16.00]	19.00	20.18
11	12											13	14	15	16	17	18
Na	Mg											AI	Si	P	S	<b>CI</b>	Ar
sodium 22.99	magnesium 24.31	3	$\overline{4}$	5	6	$\overline{7}$	8	9	10	11	12	aluminium 26.98	silicon [28.08; 28.09]	phosphorus 30.97	sulfur [32.05; 32.08]	chlorine [35.44; 35.46]	argon 39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
κ	Ca	<b>Sc</b>	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	<b>Se</b>	<b>Br</b>	Kr
potassium	calcium	scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38(2)	69.72	72.63	74.92	78.96(3)	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
<b>Rb</b>	Sr	Y	Zr	<b>N<sub>b</sub></b>	Mo	<b>Tc</b>	Ru	<b>Rh</b>	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
rubidium 85.47	strontium 87.62	yttrium 88.91	zirconium 91.22	niobium 92.91	molybdenum 95.96(2)	technetium	ruthenium 101.1	rhodium 102.9	palladium 106.4	silver 107.9	cadmium 112.4	indium 114.8	tin 118.7	antimony 121.8	tellurium 127.6	iodine 126.9	xenon 131.3
55	56	$57 - 71$	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	lanthanoids	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
caesium	barium		hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon
132.9	137.3		178.5	180.9	183.8	186.2	190.2	192.2	195.1	197.0	200.6	[204.3; 204.4]	207.2	209.0			
87	88	89-103	104	105	106	107	108	109	110	111	112		114		116		
Fr	Ra	actinoids	Rf	Db	Sg	<b>Bh</b>	Hs	Mt	Ds	Rg	Cn		FI		Lv		
francium	radium		rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		livermorium		
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
		La	Ce	Pr	<b>Nd</b>	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		lanthanum 138.9	cerium 140.1	praseodymium 140.9	neodymium 144.2	promethium	samarium 150.4	europium 152.0	gadolinium 157.3	terbium 158.9	dysprosium 162.5	holmium 164.9	erbium 167.3	thulium 168.9	ytterbium 173.1	lutetium 175.0	
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
		Ac	Th	Pa	U	<b>Np</b>	Pu	Am	$\mathsf{C}_{\mathsf{m}}$	<b>Bk</b>	Cf	Es	Fm	Md	<b>No</b>	Lr	
		actinium	thorium 232.0	protactinium 231.0	uranium 238.0	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium	lawrencium	

Table 3: Periodic table as of June 2012 (after IUPAC).



Figure 1. Fermi (left) and his friends Nello Carrara and Franco Rasetti at work (from Mario Agio, see also R. V. Caffarelli, Enrico Fermi, Imagini et Documenti, Edizioni Plus, Università di Pisa, 2002).

In the large project on nuclear power (and later nuclear weapons) in World War Two, Enrico Fermi (Figure 1) was at the connection between scientists and technicians on one side and the relatively large bureaucracy installed by the United States government on the other, with quite different cultures of these two communities. The bureaucracy noted at some point that some scientists did not arrive at the expected working times. Being questioned on this matter, Fermi replied for his fellow scientists: The scientists come to work at times when they can do the best creative work, and this differs from person to person, some come early, some come very late in the day, but they then stay late into the night as well. The bureaucracy responded to this by installing "time clocks" (for punching the time), so the scientists could document their arrival and departure times, and thus monitoring their overall working hours was possible. It turned out, however, that some of the theoreticians spent less than the expected 8 (or 9 or 10?) hours per day in the office buildings. When questioned again, Fermi replied: Well, theoreticians often do better work at home, where they are not disturbed so much, and can think more deeply and creatively. This problem could be solved as well by bureaucratic means, by giving small portable time clocks to the theoreticians, to be operated at home, whenever they were working there. No more questions were asked by the bureaucracy, but now Fermi came with a question to them: He, as well as other theoreticians he knew well, had the habit of often waking up in the middle of the night, they would get up and work on a pressing problem on their mind, which had been waking them up, and when finishing after a few hours, they would get to sleep again. Were they allowed to operate the mobile time clocks during these hours in the

night? The answer from bureaucracy was: Yes, because the scientists were doing work in these hours, they could punch the times as working hours.

After a few weeks, Fermi came up with yet another question. This concerned only himself, but he nevertheless would like to know the answer. He personally had many of his best ideas during his dreams. Was he then allowed to operate the mobile time clock before going to sleep? At this point he was understood and the whole project of precisely measuring the working hours of the scientists was stopped. Perhaps the story is true, but in any case it fits Fermi's genius. Se non è vero, è ben trovato.

As we have already identified nuclear weapons as one of the two greatest known risks of mankind (the other being climate change<sup>[30]</sup>) one might then perhaps at this point identify the unlimited growth of bureaucracy as one further major risk, certainly for scientific research,<sup>[50]</sup> perhaps for mankind.

### 7. Other Examples of Error and Discovery in Science

Nuclear fission provides one example for the tedious route through error towards discovery. Readers are invited to find further examples from their own experience. A few more examples are given here very briefly and without any details.

A most prominent example is the transition from a geocentric to a heliocentric picture (sometimes called Copernican revolution with a somewhat inappropriate historical connotation). Indeed, it is well known, but again not so widely appreciated, that already in early Greek astronomy there



existed a debate between astronomers such as Aristarchos who proposed a heliocentric world picture around 260 BC, and others who maintained the—both before and thereafter—more generally accepted geocentric system. With the accurate determination of the Earth's radius by Eratosthenes around 240 BC, and the ratios between the Earth's radius and the distances to the moon and the sun, as well as the ratios of their radii, early Greek astronomy at the time of Hipparchos around 150 BC had a fairly good geometry of the solar system at hand. They had obtained by perfectly correct procedures essentially the correct (rough) magnitudes, limited mainly by the limited accuracy of the naked-eye observations. Even the mathematical theory of the ellipse would have been available from Apollonius around 200 BC to correctly describe the planetary motions around the sun.

However, Hipparchos decided to use his extensive astronomical observations in the framework of the geocentric system later incorporated in the so-called Ptolemaic astronomy (summarized in the "Almagest" after 100 AD). This erroneous route was thus followed for about 1700 years until Copernicus reformulated the heliocentric model of Aristarchos around 1530. It was not a "rediscovery" because Copernicus knew about Aristarchos's work. Heliocentrism was still not accepted by the best astronomers such as Tycho Brahe, who rejected the Copernican model because of its known deficiencies. Brahe described from 1583 until his death in 1601 his extensive and by then much-improved astronomical observations by the geocentric "Tychonian" system, an improved Ptolemaic model (publicly available as a book after 1603). Geocentric systems remained popular throughout the 17th century. However, true discovery came in this context around 1600, with Johannes Kepler using a heliocentric system with elliptical motions of the planets, based essentially on the accurate data from Brahe and observations by Galileo. This discovery then paved the way for the modern celestial mechanics of Newton. Compared to the four-year delay between error and discovery in nuclear fission, the unnecessary 1700-year delay in an erroneous route towards the description of our solar system can indeed seem extreme.

Another telling example, now from chemistry, concerns the understanding of the mechanism of unimolecular reactions. Here, the apparent pressure independence of the rates of gas-phase unimolecular reactions led to the erroneous "radiation theory of chemical action" pursued for more than 10 years after 1910. Assuming that thermal black-body radiation provided the mechanism to generate excited, reactive molecules did, indeed, seemingly explain the apparent pressure independence of the reaction rates. Discovery arrived when Lindemann pointed out in 1922 that an alternative collisional mechanism would explain this pressure independence at high pressures and would predict a pressure dependence at sufficiently low pressures. This prediction was quickly confirmed by experiment and the "Lindemann mechanism" has since then been used to describe unimolecular reactions, radiation theory being rejected and forgotten (revived much later for situations at very low pressures , see reference [51] for a recent account of the history).

An error that led rather quickly to a very striking discovery is related to the so-called Theta–Tau  $(\Theta - \tau)$  puzzle in particle physics in the early 1950s. At that time, two particles with supposedly different parities but otherwise exactly the same properties were postulated, decaying into products of different parities [two or three pions; Eqs. (7) and (8)]. Because of the different parities on the product side

$$
\Theta \to \pi + \pi \quad \text{(positive parity)}\tag{7}
$$

 $\tau \to \pi + \pi + \pi$  (negative parity) (8)

and assuming the then generally accepted law of parity conservation,  $\Theta$  and  $\tau$  had to be different particles. But attempts to otherwise distinguish between  $\Theta$  and  $\tau$  failed. Lee and Yang then suggested in 1956 that parity might not be conserved in the weak interaction leading to the decay process, and thus  $\Theta$  and  $\tau$  were the same particle (today called the  $K^+$  meson) decaying by two competing channels into products of different parities. This suggestion of parity violation was quickly confirmed by several independent experiments following 1957. Since then parity violation in the electroweak interaction is a central aspect of the SMPP.[44–47]

Another puzzle involving electroweak interactions concerned the detection of solar neutrinos  $(\nu_e)$ . When this became possible in the experiments of R. Davis using Reaction (9),

$$
\nu_e + {}^{37}_{17}Cl^{17+} \rightarrow {}^{37}_{18}Ar^{18+} + e^-
$$
\n(9)

fewer neutrinos were found than predicted by all models of fusion reactions in the sun, which generate the neutrinos. The experiment is difficult (one obtains less than one <sup>37</sup>Ar atom per day from about 600 tons of  $C_2Cl_4$ , detected by the radioactive decay of  $37$ Ar, the reverse of Reaction (9)). Thus flaws in the experiment were suspected. However, repetition and refinement of the experiments over many years confirmed the "lack of solar neutrinos". From recent results we know now that the explanation is provided by the neutrino oscillations, which transform the  $v_e$  into other neutrinos not detected through Reaction (9). These stories from particle physics have entered textbooks,[52] however, this last chapter of history is not yet closed.

Parity violation in the electroweak interaction also has consequences in chemistry. In the recent theory of parity violation in chiral molecules, which predicts a parity-violating energy difference between enantiomers of chiral molecules, deficient theoretical methods were used continuously for about 15 years after the first quantitative calculations by Hegström, Rein, and Sandars in 1980. When we reinvestigated the theory in the 1990s, we had realized the weakness of the earlier calculations. It nevertheless came as a surprise that our improved theory changed the calculated parity-violating energy differences by two orders of magnitude for the benchmark molecule  $H_2O_2$ , and also for many other typical cases by one to two orders of magnitude. Once this dramatic increase was discovered in 1995, it was quickly confirmed by many independent calculations. The history is told in references [47, 51, 53, 54]. The large increase in the predicted magnitudes for molecular parity violation has important



consequences for possible experiments, but the story is not yet quite finished as the experimental confirmation for these very small predicted energy differences (about 100 aeV or  $10^{-11}$  J mol<sup>-1</sup>) remains to be achieved.<sup>[47, 51, 53, 54]</sup>

A final example is the recent report on long-lived nuclearspin isomers of water in the condensed phase, namely "ortho" and "para"  $H<sub>2</sub>O$ , which are apparently similar to ortho and para  $H_2$ .<sup>[55]</sup> This observation could not be reproduced by other research groups, in spite of considerable effort in repeating the experiments.<sup>[56,57]</sup> Of course, the inability to reproduce such a result might arise, for instance, from a lack of experimental skill, or from catalytic impurities on the walls of the experimental setup. However, the recent discovery of fast interconversion between ortho and para  $H_2O$  in molecular beams with formation of  $(H<sub>2</sub>O)<sub>n</sub>$  clusters but in the absence of any wall effects settles the matter: $[58, 59]$  the observation of long-lived nuclear-spin isomers of  $H<sub>2</sub>O$  in the condensed phase must be erroneous.

Many more examples for error and subsequent discovery in science could be given. Returning to nuclear fission, this Essay should be concluded with a statement outside the realm of pure science. It seems clear that the enormous stocks of nuclear weapons built and maintained as a consequence of the discovery of nuclear fission constitute a gigantic risk to mankind. While nuclear weapons have not been used in war for decades, it is easy to predict that maintaining large arsenals of these weapons will sooner or later lead to a catastrophe. Maintaining nuclear weapons is an erroneous and extremely dangerous policy, leading to a dead end in the literal sense of the word. This Essay thus concludes with a Catonian Ceterum Censeo: "Nuclear weapons must be destroyed".

The vast literature on the history of nuclear fission could not be cited, but the reader's attention is drawn to two reviews that can serve as a guide to that literature.<sup>[60,61]</sup> Figure 1 was a gift from Mario Agio, Zîrich and Florence. The 2012 IUPAC periodic table is reproduced by permission of the International Union of Pure and Applied Chemistry (see also reference [62]). I am grateful to Ruth Schîpbach for her help in preparing a clear manuscript from my handwritten notes. Our work is supported by ETH Zurich, SNF, and ERC.

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- [1] R. Marquardt, M. Quack, Z. Phys. D 1996, 36, 229 237.
- [2] Les Prix Nobel en 1938, Imprimerie Royale, P. A. Norstedt and Söner, Stockholm, 1938, p. 6.
- [3] H. Pleijel in Les Prix Nobel en 1938, Imprimerie Royale, P. A. Norstedt and Söner, Stockholm, 1938, pp. 19-23.
- [4] E. Fermi, Nature 1934, 133, 898-899.
- [5] J. Chadwick, Proc. R. Soc. London Ser. A 1932, 136, 692-708.
- [6] "Artifical radioactivity produced by neutron bombardment, Nobel Lecture 12 Dec 1938": E. Fermi in Les Prix Nobel en 1938, Imprimerie Royale, P. A. Norstedt and Söner, Stockholm, 1938, pp. 414 – 421.
- [7] W. Noddack, I. Tacke, O. Berg, Sitzungsber. Preuss. Akad. Wiss. Phys.-Math. Kl. 1925, 400-409. Ida Tacke married Walter

Noddack, which explains the name Ida Noddack in References [8] and [31].

- [8] I. Noddack, Angew. Chem. 1934, 47, 653 655.
- [9] "From the natural transmutations of uranium to its artificial fission (Nobel Lecture 13 Dec. 1946)": O. Hahn, Les Prix Nobel en 1945, P. A. Norstedt and Söner, Stockholm, 1946, pp. 51 – 66.
- [10] O. Hahn, *Helv. Chim. Acta* 1953, 36, 608-619.
- [11] L. Meitner, Adv. Sci. **1963**, 19, 363 365.
- [12] L. Meitner, Naturwiss. Rundsch. 1963, 16, 167-169.
- [13] O. Hahn, L. Meitner, F. Strassmann, Ber. Dtsch. Chem. Ges. 1937, 70, 1374 – 1392.
- [14] L. Meitner, F. Strassmann, O. Hahn, Z. Phys. 1938, 109, 538-552.
- [15] O. Hahn, F. Strassmann, Naturwissenschaften 1939, 27, 11 15.
- [16] O. Hahn, F. Strassmann, Naturwissenschaften 1939, 27, 89 95.
- [17] W. Seelmann-Eggebert, Chimia 1979, 33, 275 282.
- [18] O. R. Frisch, J. A. Wheeler, *Phys. Today* **1967**, 20, 43–52.
- [19] N. Bohr, Phys. Rev. 1939, 55, 418 419.
- [20] N. Bohr, *Philos. Mag.* **1913**, 26, 1-25.
- [21] N. Bohr, Philos. Mag. 1913, 26, 476 502.
- [22] N. Bohr, *Philos. Mag.* **1913**, 26, 857-875.
- [23] "Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation": F. Merkt, M. Quack in Handbook of High-Resolution Spectroscopy, Vol. 1 (Eds.: M. Quack, F. Merkt), Wiley, Chichester, 2011, pp. 1 – 55, (see also preface to this Handbook).
- [24] M. Bodenstein, Z. Elektrochem. 1916, 22, 202 206.
- [25] C. N. Hinshelwood, H. W. Thompson, Proc. R. Soc. London Ser. A 1928, 118, 170 – 183.
- [26] N. Semenoff, Z. Phys. **1928**, 48, 571 582.
- [27] S. Flîgge, Naturwissenschaften 1939, 27, 402 410.
- [28] C. Reed, *History Phys. Newsl.* **2012**, 12, 3-4.
- [29] M. Frayn, Copenhagen, Anchor books, New York, 1999.
- [30] M. Quack, Bunsen-Magazin 2011, 13, 138-143.
- [31] I. Noddack, Naturwissenschaften 1939, 27, 212 213.
- [32] F. Hund, Z. Phys. **1927**, 43, 805-826.
- [33] G. Gamow, Z. Phys. 1928, 51, 204 212.
- [34] R. W. Gurney, E. U. Condon, Phys. Rev. 1929, 33, 127 140.
- [35] N. Bohr, J. A. Wheeler, *Phys. Rev.* **1939**, 56, 426-450.
- [36] J. M. Blatt, V. F. Weisskopf, Theoretical Nuclear Physics, Wiley, New York, 1952.
- [37] V. Weisskopf, Phys. Rev. 1937, 52, 295-303.
- [38] H. Eyring, J. Chem. Phys. 1935, 3, 107-115.
- [39] E. Wigner, *Trans. Faraday Soc.* **1938**, 34, 29-41.
- [40] M. Quack, J. Troe, Ber. Bunsen-Ges. Phys. Chem. 1974, 78, 240 252
- [41] "Statistical Adiabatic Channel Model": M. Quack, J. Troe in Encyclopedia of Computational Chemistry, Vol. 4 (Eds.: P. von R. Schleyer, N. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, P. R. Schreiner), Wiley, New York, 1998, pp. 2708 – 2726.
- [42] G. Herrmann, Angew. Chem. 1988, 100, 1471 1491; Angew. Chem. Int. Ed. Engl. 1988, 27, 1417 – 1436.
- [43] E. Fermi, Z. Phys. 1934, 88, 161-177.
- [44] S. Weinberg, Phys. Rev. Lett. 1967, 19, 1264-1266.
- [45] "Weak and electromagnetic interactions": A. Salam in *Elemen*tary Particle Theory: Relativistic Groups and Analyticity (Hrsg.: N. Svartholm), Almkvist & Wiksell, Stockholm, 1968, S. 367 – 377.
- [46] S. L. Glashow, Nuclear Phys. 1961, 22, 579 588.
- [47] "Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy": M. Quack in Handbook of High-Resolution Spectroscopy, Vol. 1 (Hrsg.: M. Quack, F. Merkt), Wiley, Chichester, 2011, S. 659 – 722.
- [48] E. Fermi, Am. J. Phys. **1952**, 20, 536-558.
- [49] "Time and Time Reversal Symmetry in Quantum Chemical Kinetics": M. Quack in Fundamental World of Quantum



Chemistry. A Tribute to the Memory of Per-Olov Löwdin, Vol. 3 (Eds.: E. J. Brändas, E. S. Kryachko), Kluwer Adacemic Publishers, Dordrecht, 2004, pp. 423 – 474.

- [50] M. Quack, Bunsen-Magazin 2012, 14, 181 189.
- [51] M. Quack, Faraday Discuss. 2011, 150, 533 565.
- [52] C. Amsler, Kern- und Teilchenphysik, vdf Hochschulverlag Zîrich, 2007.
- [53] M. Quack, Angew. Chem. 2002, 114, 4812-4825; Angew. Chem. Int. Ed. 2002, 41, 4618 – 4630.
- [54] M. Quack, J. Stohner, M. Willeke, Annu. Rev. Phys. Chem. 2008, 59, 741 – 769.
- [55] V. I. Tikhonov, A. A. Volkov, Science 2002, 296, 2363 2363.
- [56] S. Albert, B. H. Meier, M. Quack, G. Seyfang, A. Trabesinger, Chimia 2006, 60, 476.
- [57] S. L. Veber, E. G. Bagryanskaya, P. L. Chapovsky, J. Exp. Theor. Phys. 2006, 102, 76-83.
- [58] C. Manca Tanner, M. Quack, D. Schmidiger, Faraday Discuss. 2011, 150, 118 – 122.
- [59] C. Manca Tanner, M. Quack, D. Schmidiger, J. Phys. Chem. A 2013, DOI: 10.1021/jp400958f.
- [60] E. Amaldi, Phys. Rep. 1984, 111, 1 332.
- [61] G. Herrmann, Angew. Chem. 1990, 102, 469 496; Angew. Chem. Int. Ed. Engl. 1990, 29, 481 – 508.
- [62] E. R. Cohen, T. Cvitas, J. G. Frey, B. Holmström, K. Kuchitsu, R. Marquardt, I. Mills, F. Pavese, M. Quack, J. Stohner, H. L. Strauss, M. Takami, A. J. Thor, Quantities, Units and Symbols in Physical Chemistry, 3rd ed., third corrected printing, IUPAC and Royal Society of Chemistry, RSC Publishing, Cambridge, 2011.