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Immanuel Kant versus the Princes of Serendip: Does science evolve through blind chance or intelligent design?*

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Let me begin with an extract from the writings of Immanuel Kant. Toward the close of the 18th century, he expressed his view as to the nature of the scientific endeavor:

> *When Galileo caused balls, the weights of which he had previously determined, to roll down an inclined plane; when Torricelli made air carry a weight which he had calculated beforehand to be equal to that of a definite volume of water; or in more recent times, when Stahl changed metal into oxides, and oxides back into metal, by withdrawing something and then restoring it, a light broke upon all students of nature. They learned that reason has insight only into that which reason produces after a plan of its own; that reason must not allow itself to be constrained, as it were, by nature's reins, but must itself show the way... thereby constraining nature to give answer to questions of reason's own determining. Accidental observations, made in obedience to no previously thought-out plan, can never be made to yield a necessary law, which reason alone is concerned to discover... Reason must not approach nature in the character of a pupil who listens to everything the teacher has to say, but as an appointed judge who compels the witness to answer questions that he himself has formulated.*

Compare Kant's view of science with a brief extract from the Oxford English Dictionary:

> *SERENDIPITY: from a former name of Sri Lanka. A word coined by Horace Walpole, who says that he had formed it upon the title of a fairy tale called «The Three Princes of Serendip», the heroes of which ' were always making discoveries, by accidents and sagacity, of things they were not in quest for.'*

Kant lived too soon to experience the cascade of scientific discoveries, many of them quite accidental, that were about to take place. Science seemed to him as an entirely rational and methodological discipline. Science involved the formulation of explicit hypotheses, which are then demonstrated by experiment and thereby imposed upon Nature. Thus, Kant felt, we scientists must not remain under the dominance of experience, must not heed accidental observations, and must not listen to nature as if we were naive pupils. Is this a proper description of the scientific enterprise, or are we better described as Princes of Serendip: prepared minds in search of unanticipated wonders? I will argue that serendipity and rationality are as much intertwined with one another as are particles and waves, that some set out to circumnavigate the globe and do, while others set out for China and discover the Americas instead.

I shall focus on physics and chemistry because these are the sciences I know best. My talk consists of an eclectic selection of historical anecdotes, strung together chronologically and interpreted in terms of Kantian and serendipitous modes of discovery. As I tell my tale, please understand that I am not a qualified historian of science. Even less am I a philosopher.

Atoms as the supposedly indivisible constituents of all earthly matter were first imagined to exist by the ancient Greeks. Imagined is the key word. They offered little or no empirical evidence for their speculations. The modern-day atomic hypothesis was put forth and defended by John Dalton through his brilliant intuition and rather careless experimentation. He concluded that the atoms of each element «are perfectly alike» and «never can be metamorphosed, one into another.» It could be said that Dalton had imposed his views upon Nature, which for a time she conceded. Much later, Maxwell would use the then widely (but not universally) accepted atomic hypothesis to prove the existence of a Creator: he wrote that «a number of exactly similar things cannot each of them be eternal and self existent; they must therefore have been made.» By what or by whom Maxwell does not say.

Lavoisier listed twenty of what he regarded as chemical elements. Apart from the inclusion of heat and light, his list was a good one. However, the number of known chemical elements was growing rapidly. A few scientists came to believe that there were simply too many different kinds of atoms for them all to be equally elementary. Amongst them was William Prout, to whose work we will have several occasions to allude. In the early 19th century atomic weights of chemical elements began to be measured, and the results all seemed to be integer multiples of that of hydrogen. In a series of anonymously published articles, Prout suggested that all atoms were in some way made up of hydrogen atoms. Although we now know that atomic weights satisfy no such exact rule, there is a profound element of truth in Prout's hypothesis... and it was profoundly accidental that

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the elements then studied had approximately integer atomic weights: chlorine, whose mean atomic weight is about 37.5 had not yet been discovered!

One of Prout's less well-known endeavors, and one to which he did put his name, had to do with the age-old search for a cheap and effective purple dye. Unfortunately for him, the product he came up with in 1828, ammonium purpurate, was not much of a commercial success. Furthermore, Prout's new dye was made from uric acid, which itself was extracted from kidney stones or urine. Thus it was an 'organic compound' and not one that could be synthesized from scratch.

Until the middle of the 19th century, the doctrine of 'vitalism' placed a seemingly impenetrable barrier between organic and inorganic chemistry. Organic compounds, such as urea and acetic acid, could not be synthesized from inorganic materials because, so it was thought, they contained within them the 'vital force' of life which lay beyond the scope of the physical sciences. Organic chemicals had to be extracted from blood, urine or other such materials. In 1828, Frederich Wöhler was astonished when he found, quite by accident, that a compound he had synthesized, ammonium cyanate, was nothing other than urea. He wrote to one of his vitalist colleagues: «I must tell you that I have prepared urea without requiring a kidney or an animal, neither dog nor man.» Wöhler's serendipitous discovery, and quite soon afterward, the rather more Kantian synthesis of acetic acid from its constituent elements by Wöhler's student, were the first cracks in the organic-inorganic barrier.

Thus we are led to a short and happy story about the discovery of the first really useful artificial dye. In 1856, William Henry Perkin, a 17-year-old chemistry student, set out on his first research project. His mentor, the German chemist August von Hofmann, directed Perkin to attempt the synthesis of quinine from coal tar. Perkin did not succeed in this quest. Instead of producing the pure white crystals of quinine, he ended up with a dark and foul-smelling sludge. (Indeed, Perkin's assignment would not be completed for almost another century. The first total synthesis of quinine was accomplished in 1944, in a fully Kantian mode, by Robert Woodward and my friend and Harvard colleague Bill Doering.)

But Perkin was a true Prince of Serendip. Noticing that his noxious coal-tar derivative had a purplish tint, he forgot about quinine and abandoned his academic career. He set up a factory to manufacture the first aniline dye, to which French designers gave the name *mauve.* When Queen Victoria of England and Empress Eugenie of France publically flaunted mauve dresses, his new dye became so popular that the period became known as the Mauve Decade. As a rich man of 36, Perkin sold his business and returned to academic science, having laid the foundations to synthetic organic chemistry.

Incidentally, the second synthetic aniline dye was invented in 1859 by Perkin's mentor and given the name *magenta.* Only the historically literate will understand why a German scientist would name his discovery after a battle in that same year where the French defeated the Austrians. Subsequently, von Hofmann returned to Germany where he systematically developed a whole panoply of purple dyes and contributed mightily to his country's primacy in the new industry that emerged from his student's moment of serendipity.

As organic chemistry blossomed, so did its inorganic sibling. With the development of spectroscopy, the pace of discovery quickened. Some newly discovered elements were named after the colors of their most prominent spectral lines: Rubidium for red, Cesium for blue, and Thallium for bud-green. Mendeleev found a predictive pattern among the elements that was confirmed by the discoveries of Scandium, Germanium and Gallium. These new elements fit neatly into spaces in his table that Mendeleev had wisely reserved. They displayed just the chemical and physical properties that he had foreseen for them. To Mendeleev, the success of his periodic table of the chemical elements was yet another hint –beyond Prout's Law and the revelations of spectroscopy– of the structured nature of atoms. «Does not order imply structure?» his argument could be put. Mendeleev's great triumph resulted from a wholly Kantian approach and was not in the least serendipitous.

As Mendeleev was puzzling out his table, the French philosopher Auguste Comte declared that we could never learn the chemical composition of the stars. A few years later, astronomers, using the new technologies of spectroscopy and photography, managed to do just that. Philosophers should learn never to say never! However, some of the spectral lines seen in starlight had no known terrestrial counterparts. In 1868, Norman Lockyer interpreted certain otherwise unseen solar lines as those of a new element, which he called *helium.* The *-ium* suffix indicated Lockyer's suspicion that the solar element would turn out to be a metal. Several decades would pass before his error would be corrected.

In 1882, Lord Rayleigh returned to the nagging issue of Prout's Law. The then– measured density of oxygen gas was 15.96 times that of hydrogen. «The deviation of this number from the integer 16,» he wrote, «seemed not to be outside the limits of experimental error.» Rayleigh's precise experiments showed the density to be 15.88. It was most certainly not an integer. So much for Prout's Law! Rayleigh then turned his attention to nitrogen. Using two quite different approaches, he was surprised and perturbed to obtain two quite different results. The density of nitrogen in air seemed to be greater than its density when extracted from ammonia. He later wrote: «On the supposition that the air-derived gas was heavier than the 'chemical' nitrogen [from ammonia] on account of the existence in the atmosphere of an unknown ingredient, the next step was the isolation of this ingredient...» With the assistance of the chemist William Ram say, he succeeded in isolating and studying the not-so-rare gas that makes up fully 1% of our atmosphere. In the most serendipitous discovery of their careers, Rayleigh and Ramsay discovered the surprisingly nonreactive element *Argon* (the lazy one). In a last ironic twist, the density (or atomic weight) of nitrogen turned out to be experimentally indistinguishable from the integer 14! But by this time Rayleigh had lost interest in Prout's law.

The adventure continued as Ramsay and his coworkers went on to find several other inert gases in air: *Neon* (the new one), *Krypton* (the secret one) and *Xenon* (the foreign one). Finally, they discovered earthly helium within certain minerals. Helium turned out not to be a metal after all, but the lightest of the seemingly inert gases. (They did not know at the time that one more inert gas remained to be discovered: *Radon,* the radioactive one. And even less could they know that most of the helium on Earth was produced by the radioactive decay of uranium and thorium. Radioactivity had not yet been discovered.)

The work of Rayleigh and Ramsay forced a reluctant Mendeleev to add a whole new column to his periodic table, one to account for the newly found family of elements with zero valence. (Incidentally, Perkin's mentor von Hofmann, Mr. Magenta, was largely responsible for the notion of valence and coined an earlier version of the word.) For their work, Sir William Ramsay won the 1904 Nobel Prize in Chemistry, and Lord Rayleigh the Physics Prize of the same year. Never before and never again would the chemistry and physics prizes in a given year be so intimately related.

Aside from the isolation and identification of the inert gases, another two spectacular and unexpected scientific discoveries would take place in Mauve Decade. In 1895, William Conrad Röntgen had his moment of serendipity when he found something so entirely unexpected that he said to his wife, «People will say that Röntgen has probably gone crazy.» He was far from crazy. Röntgen had stumbled upon *X* rays, and he followed up his serendipitous discovery with the care and alacrity one expects of a great scientist.

A few years later, Henri Becquerel entered the serendipity sweepstakes. He had devoted himself to the study of luminescence and phosphorescence –the production of light by means other than heat– as had his father and grandfather before him and as would his only son. Soon after Röntgen found *X* rays, Becquerel suspected a possible linkage between the new radiation and his beloved phenomenon of cold light. As he later reminisced, «I thought immediately of investigating whether [*X* rays] could not... give rise to [luminescence] and whether all [luminescent] bodies could not emit similar rays. The very next day I began a series of experiments along this line of thought.» Rant would have approved!

Most of us know what happened next. Certain chemicals are phosphorescent. After being placed in sunlight for a few hours and taken to a dark room, they continue to glow. Becquerel chose his favorite phosphorescent chemical from his laboratory shelf. Through a quirk of fate, the particular material he chose was a compound containing uranium. Becquerel proceeded as follows:

> *One wraps a photographic plate in thick black paper. A piece of phosphorescent material is laid upon the paper and the whole is exposed, to the sun for a few hours. When the photographic plate is developed, one observes the silhouette of the phosphorescent substance... If a coin is placed between the phosphorescent substance and the paper, then its image can be seen to appear on the negative. The phosphorescent material emits radiations which traverse the opaque paper.*

Becquerel thought he had confirmed that phosphorescent substances produce *X* rays as well as light after being exposed to sunlight. A week later, to his amazement, he realized that the image on his film had nothing to do with sunlight or *X* rays, and not even anything to do with phosphorescence!

The sky was overcast when Becquerel attempted to repeat his experiment. He put his wrapped photographic plate along with his phosphorescent material in a dark desk drawer to await a winter sun that never came. A few days later (who knows why?) he developed the plate. His son Jean, who had collaborated with his father, wrote that «Becquerel was stupified when he found that his silhouette picture was even more intense than the ones he had obtained the week before.» Becquerel had discovered radioactivity! I've described Becquerel's work at some length because his initial discovery (which he followed up scrupulously in a more Kantian mode) was a rare instance of *triple* serendipity:

i. What if the Paris sun had come out on that fatefully dark December day?
ii. What if Becquerel had not developed the plate from the dark desk drawer?
iii. And what if he had used a phosphorescent material that did not contain uranium?

In the late 19th century, several arguments, quite aside from Prout's law and the periodic table, suggested that atoms have internal structure. Decades earlier Faraday showed how neutral atoms in solution behave as if they were electrically-charged ions bearing charges that were integer multiples of a fundamental unit of electric charge. If atoms did have electrically-charged constituents, as Faraday's work suggested, their vibrations could generate the characteristic spectral lines of each chemical element. In 1891, G. Johnstone Stoney wrote that «these charges, which it will be convenient to call *electrons,* cannot be removed from the atom.» His name for the then-hypothetical particle stuck. Just a few years later the electron was discovered through the careful and systematic study of cathode rays. The electron was the first known elementary particle, and it could quite easily be removed from atoms. But its tiny mass posed a weighty problem: What were the positively-charged constituents of atoms?

The answer depended on a series of experiments carried out by Ernest Rutherford. First, he showed that radioactivity produces three distinct kinds of radiation. He found that alpha rays consist of rapidly moving particles, and that «the alpha particle, after it has lost its positive charge, is a helium atom.» (Now we would say it differently: the helium atom, after it has lost its electrons, is an alpha particle.) Rutherford also identified beta rays as energetic electrons and gamma rays as energetic electromagnetic radiation. It was quite a *tour de force,* and I haven't even mentioned his epochal discovery (with Frederick Soddy) of the law of radioactive transformation which, among much else, put a full stop to the notion of the immutability of atoms.

Of all the forms of radioactivity, alpha particles were Rutherford's pets. In 1909, he and his collaborators, Geiger and Marsden, directed a beam of them from a radioactive source toward a thin gold foil target. «It seems surprising,» they understated, «that some of the alpha particles can be turned by 90 degrees, and even more.» Two years later, Rutherford formulated the notion of an atomic nucleus. Later he would describe his moment of serendipity:

> *«It was quite the most incredible event that has ever happened to me in my life... It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration... I saw that it was impossible unless you took a system in which the greatest part of the mass of an atom was concentrated in a tiny nucleus.»*

Rutherford's discovery of the atomic nucleus marks a great divide between the studies of atomic phenomena (and the development of quantum mechanics) and those of the subnuclear world and radioactivity. For want of time, I shall focus the latter. Systematic (*i.e.*, Kantian) studies of radioactive transformations and *X*-ray spectroscopy showed that the place of a chemical element in the periodic table, and hence its chemical properties, was determined by the positive charge of its nucleus: an integer multiple Z of the electronic charge, a quantity that became known as the atomic number.

Furthermore, the discovery of isotopes let us learn that the atomic weight of every nuclear species lay close to an integer multiple of that of hydrogen. (Today's atomic mass unit is defined by the mass of the most common isotope of oxygen, which is assigned an atomic weight of exactly 16.) Thus each atomic nucleus was uniquely characterized by two integers: Z (its electric charge) and A (the nearest integer to its atomic weight). These systematic properties, along with the fact that there were far too many different nuclear species for them all to be elementary, strongly suggested nuclei to be composite systems. But of what were they made?

Rutherford, again using alpha particles, succeeded in knocking particles out of nitrogen that seemed (and were) identical to hydrogen nuclei. He concluded that the hydrogen nucleus is a constituent of all atomic nuclei, that it is an elementary particle which he called the *prouton* (in honor of William Prout) or the *proton* (from Greek protos, meaning first). Only the latter name stuck. And so it was that Prout's hypothesis was reborn in a nuclear context. A nucleus with atomic number Z and mass number A was imagined to consist of A protons and $A - Z$ internal electrons. The proton-electron model of nuclear structure would persist until the year of my birth.

If two electrons bind four protons into a helium nucleus, Rutherford wondered whether one electron could form an intimate union with one proton to form a tiny electrically neutral nucleus, a conjectured particle to which he gave the name *neutron.* The story of its discovery would be a heady mix of serendipity and reasoned experimental analysis. In 1930, Bothe and Becker made the accidental discovery that alpha particles (once again!) impinging on beryllium produce an electrically neutral radiation which they assumed to consist of gamma rays. Then Irene Joliot-Curie and her husband Frederick Joliot showed that the beryllium rays would liberate energetic protons from paraffin. But they clung to the incorrect electromagnetic interpretation and missed their greatest research opportunity.

It remained for James Chadwick, in a series of carefully designed experiments, to show that the beryllium rays could not possibly be photons. Instead, he showed them to consist of neutral particles with about the same mass as the proton. Thus Chadwick discovered the neutron in 1932, but it was not at all the particle Rutherford had envisaged. The neutron is not made of a proton and an electron. It is a particle in its own right, an electrically neutral sibling of the proton. There are no electrons in atomic nuclei, just neutrons and protons. (Of course, we now know that neither particle is truly elementary. Each of them is made up of three quarks, but that is quite another matter.)

Today's discovery becomes tomorrow's research tool. Alpha particles, soon after they were found, were put to good use to discover atomic nuclei, neutrons, and induced nuclear reactions. Electrically neutral neutrons could far more readily enter larger nuclei. Immediately upon Chadwick's discovery, Enrico Fermi set out to see what happens when different elements were bombarded with neutrons. He found that a neutron striking a large nucleus is often absorbed. The heavier and unstable isotope thus formed would rapidly decay into an element one step higher in the periodic table.

What would happen, Fermi wondered, if neutrons impinged on uranium, which lay at the very end of the periodic table? In 1934, he concluded that he had synthesized elements number 93 and 94, to which he gave the names *Ausenium* and *Hesperium.* He was awarded 1938 Nobel Prize in Physics «for his demonstration of the existence of new radioactive elements» and for his investigations of slow neutrons. Now I would not for a moment question whether Fermi deserved his Nobel Prize, but in fact he had not discovered any transuranic elements.

Ida Noddack was an accomplished chemist who had discovered, along with her husband-to-be, the last of the stable chemical elements: *Rhenium.* (Could there have been a marital resolution to a potential priority dispute?) In 1934, responding to Fermi's claims, she published a paper entitled «Über das Element 93» in which she wrote, «It is conceivable that in the bombardment of heavy nuclei with neutrons, these nuclei break up into several large fragments which are actually isotopes of known elements, not neighbors of the irradiated element.» She pointed out that all the known elements must be excluded to draw the conclusion that element number 93 had been produced. Otto Rahn later claimed that Noddack's argument «was not taken seriously as it appeared to be in opposition to all physical views of nuclear structure.» And, after all, Ida Noddack was a woman... but she was the first person to foresee the possibility of nuclear fission.

And that portentous process will be last of the discoveries I will discuss. It was not so much a serendipitous discovery as it was anti-Kantian. Nature was trying to tell Fermi something when he found that uranium and thorium behave rather differently from other elements when irradiated with neutrons. But he listened neither to Nature nor Noddack. In December of 1938, just as Fermi was accepting his award from the hands of the Swedish king, the astonishing discovery of Rahn, Meitner and Strassman was announced. Working in collaboration, until Meitner was compelled to flee from the Nazis, they identified barium as a product of neutron absorption by uranium. The conclusion was inescapable: the uranium nucleus had been induced to split. «Oh what idiots we have been!» said Niels Bohr, «this is just as it must be.» The word describing this process, *nuclear fission* or *Kernspalung* in German, was coined by Lisa Meitner and her nephew whilst they were in Swedish exile. The 1944 Nobel Prize in Chemistry was awarded to Otto Rahn for its discovery.

So what should you conclude from these disjointed incidents of travel through the history of science? Perhaps you may begin to understand why modern scientists rarely consult the classical philosophers. In contradiction to the wisdom of Immanuel Kant and in paraphrase, we believe that –*Reason* may *act as an appointed judge who compels the witness* to *answer questions that he himself has formulated, but reason* must *approach nature in the character of a pupil who listens to everything the teacher has to say.*

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