Polanyi's Physical Adsorption: One of the Early Theories of Quantum Chemistry

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Michael Polanyi is known as a philosopher who presented such ideas as tacit-knowledge or personal knowledge, generally speaking. But before changing his profession to philosophy, he had been an extremely active physical chemist, who dealt with diverse fields such as adsorption theory, chemical kinetics, X-ray diffraction, dislocation theory and so on. We find that he is even more extreme when we look at his key students and colleagues. Needless to say, John Polanyi is Michael's son. Eugene Wigner was his doctor student. Herman Mark, Karl Weissenberg, Egon Orowan, Henry Eyring, M. G. Evans, and Melvin Calvin were members of his research team, or colleagues. It could be said that it was Polanyi who raised the next generation of leaders in modern physical chemistry from the 1930's.

John Polanyi says this of his father:

> If he were ever boastful, Michael Polanyi would have described himself as a scientist of the second rank. The first rank, in his terminology, constituted the pillars on which the edifice of science rested…He was equally bold in his choice of topics. He was anxious to make use of the freedom that his amateur status gave him. His family cultivated young Hungarian painters, poets, novelists and scholars. "I grew up in this circle," Michael wrote, "taking it for granted that I could do great things."

This saying is actually supported by Michael Polanyi himself. Polanyi replied to Kuhn when he was asked why he left the sciences:

> I thought that I would make my discoveries in science before the Great War and afterwards I would go on and do something in philosophy of science. And actually when I wrote my theory of adsorption I thought I had made a great discovery. I had made a discovery, but not a very great one. And so that didn't help me to establish myself definitely as a scientist.

It is quite obvious that Polanyi was a first tier scientist, but the question of first or second is not really the point here. The point is that Polanyi thought his adsorption theory to be his greatest discovery, even though it is his reaction kinetics that is generally regarded to be his representative work as a scientist.

Polanyi's adsorption theory was not chemisorption but physisorption, in present terminology. He assumed porous solids to be adsorbent and gas to be adsorbate; the binding force to the adsorbent he thought to be potential spatially fixed, caused by intermolecular attraction; and multi-layer adsorption continuing to liquefy the compressed layer. At first, he proposed this theory in 1914 under the supervision of George Bredig when he studied at Karlsruhe TH, eventually basing his doctoral thesis on it in 1916. His theory was supported by other chemists such as Herbert Freundlich, but on the other hand resulted in severe criticism from Fritz Haber and Albert Einstein for reasons I will explain in just a moment. Polanyi kept developing this theory intermittently and presented the final version with Fritz London in 1930.

Although Langmuir proposed the adsorption theory at the same time Polanyi first proposed his theory, Polanyi was not aware of it, because of the communication difficulties under the influence of the war. Langmuir's theory assumed the plane surface of metal to be adsorbent and the binding force he thought to be electrostatic force. The adsorbates are captured in distant cite, so that the force between adsorbates is negligible, forming a mono layer on the surface. This theory was apparently conditionally limited for the phenomena but simple and easy to apply. An electrostatic view of chemical reaction was popular for the chemists at that time, and also G. N. Lewis proposed the chemical valence theory in 1916. Most physicists at that time, such as Haber and Einstein, followed this line of thinking.

In actuality, setting at that time was not so simple. Polanyi himself summarized the situation at that time:

> During the very years in which the theory was born, there occurred a dazzling series of insights into the nature of things. Debye's discovery of fixed dipoles, Bohr's atomic model, and the ionic structure of sodium chloride found by W. H. Bragg and W. L. Bragg, established the pervasive function of electrical interaction. A number of theories were put forward on these lines. Keesom suggested an electrostatic interaction of fixed quadrupoles; Debye, an interaction of quadrupoles with induced dipoles. Kossel's attempt to explain all chemical bonds as attraction between positive and negative ions also belongs to this period.
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> This view of atomic forces made my theory of adsorption untenable. Electrical interactions could not be derivable from a spatially fixed potential; they would be screened off by the presence of other molecules in the field.[1]

The electrostatic view was not uniquely created by chemists, but was also being approached concurrently by physicists as well. It was the result of the sudden development of atomic theory in accordance with the development of quantum theory in physics. Unlike chemistry, the idea of the "atom" was very new for physics. Although the existence of the electron was already accepted, the electron was not recognized as a part of the atom's structure. Atomic theory, more precisely atomic structure theory including electrons, was not accepted until Bohr's model in 1913. For physicists, the atom had been just a particle in their own mechanics. In 1911, the need for energy quanta was first confirmed during the famous Solvay Conference, and in the same year Rutherford proposed the atomic model on which Bohr expanded just afterwards. Valence theory was gradually accepted as an extension of the atomic structure theory in physics. As a result, Freundlich dealt with both Langmuir's theory and Polanyi's theory in his book in 1922. Even so, the fusion of valence chemistry and atomic structure physics was not yet to be.

Here, let us clarify the situation and terminology. There were two schools of chemists: those who referred to valency to explain chemical reaction or chemical structure, and those who did not during the 1910's. The latter included electrochemists, thermochemists, and scientists on kinetic theory of gases, mainly in Europe. They were physicists rather than chemists in that sense, or one might say chemical physicists. European chemistry at that time was organic synthetic chemistry. Ostwald already used the term "physical chemistry" with regards to his unique philosophical idea. However, it generally meant nothing more than to differentiate it from organic synthetic chemistry when it referred to a discipline.

But by the 1920's, as John W. Servos has pointed out, the former became powerful in the U.S.[2] They developed their theories independently of what was going on in Europe, which

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1 Polanyi Michael, p. 88.
2 Servos, pp. 202-250.

was the development of atomic structure theory in accordance with quantum theory. Valency was, however, gradually adopted in Europe during the 1920's as well. The final push towards fusion was given by the physicists' side; Heitler and London in 1927.

Polanyi was a chemical physicist. His approach to adsorption was completely through chemical physics, as I have explained. Indeed, Mary Jo Nye pointed out that "Polanyi's approach lay thoroughly within the framework of nineteenth-century classical thermodynamics."[3] But he was not "classical" in a Whiggish sense. His approach derived from the very heart of the topic at that time. In Polanyi's theory, gas molecules, through equation of state, would become liquefied when adsorbed under high pressure. This was the biggest difference from Arnold Eucken's theory, which assumed direct gas adsorption under high pressure. This hypothesis came from Polanyi's interest in early quantum theory.

As Scott pointed out:

> Polanyi's proposal to Bredig came out of a careful study of Planck's treatise on thermodynamics and of the work of Einstein in establishing the concept of the quantum of energy. His creative contribution was to see, by an act of the imagination, a joint consequence that was not separately obvious in either piece of work. Planck had explained Nernst's theorem that the entropy (the disorder of the component molecules) of a substance would approach zero as the temperature approached absolute zero. Polanyi's new idea was that the same would be true if, instead of lowering the temperature in order to decrease the random motion of the gas molecules, pressure were increased instead. The closer the pressure came to infinity the more motion of the molecules would be restricted, thus decreasing entropy to zero at infinite pressure.[4]

It is apparent that Polanyi applied Nernst's heat theorem, in the context of specific heat, to adsorption. He also took into account Van der Waals equation for application. Certainly he did not use quantum theory directly, but despite that at the time only few scientists such as Einstein and Nernst knew the significance between quantum theory, Nernst's heat theorem and low temperature physics, Polanyi was putting it into practice within the field of adsorption.

From 1900 to 1907, Max Planck's energy quanta were just a hypothesis. But in 1907, Einstein proposed a quantum theory on solids. Unlike the light quanta, this quantum theory had a quick reaction in the scientific community. Nernst noticed the significance of Einstein's theory, because for his heat theorem, which was proposed in 1906, he needed to clarify the reason how and why specific heat at low temperature goes down. By this time, quantum theory was no longer a mere hypothesis, but only for the select few. Also they needed more experimental evidence. It was brought by Kamerlingh Onnes in 1908. He liquefied helium through Van der Waals equation. It was due to this that they could examine quantum effects at low temperature. Thus, this became the main theme of the 1st Solvay Conference, which was organized by Nernst himself. This was the context under which Polanyi proposed his adsorption theory.

Even though Polanyi himself was not good at mathematics of quantum mechanics, he was one of its early adopters. This is why he could follow along with Einstein and Nernst's discussion on specific heat. Polanyi had been interested in specific heat since reading a book by Nernst during Gymnasium. Polanyi regarded the paper on specific heat he wrote at Gymnasium to be 'nonsensical', however, that was the year 1907 and according to Scott, there was a correspondent at the University of Vienna who offered to discuss it with him. As John Polanyi

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3 Nye, p. 89.

4 Scott & Moleski, p. 27

described, Polanyi was bold with his choice of topics. And the greatest topic for him had been adsorption[5].

Even after being attacked by Einstein and Haber, Polanyi did not abandon his adsorption theory. He contacted London right after London had proposed his dispersion theory in 1929. Polanyi immediately asked such questions of London: 'Are these forces subject to screening by intervening molecules? Would a solid acting by these forces possess a spatially fixed adsorption potential?'[6] Even though Polanyi himself was not good at mathematics of quantum mechanics, he recognized the impact of London's work and applied it with London to his adsorption in 1930; he proved that adsorption potential changes depending on the distance from the wall as he suggested in 1916.

As I have explained so far, Polanyi's theory only makes sense when applied within the context of early quantum theory. He was definitely an early adopter of quantum theory. This can be seen by his choice of topic and application of London dispersion force to his adsorption theory. Also as Gavrogru and Simoes argued, one is unable to follow any story by focusing on one discipline alone, especially during this era in history. It is for this reason I would like to propose in lieu of disciplines such as physics, chemistry, physical chemistry or chemical physics, a *topic* instead be used to describe this study. Perhaps quantum theory (not quantum mechanics) or property of matter would be good candidates.

When we intentionally remove the confines of discipline and examine Polanyi in the context of quantum theory, we can see intention behind Polanyi's choice of research topic. In previous studies, Polanyi's life seemed to be dictated by coincidence, however, he might have made very carefully planned choices. Study on colloids was one main theme of electro chemistry at that time. Colloid was a topic common to both mentors Tangl in the medical school of Budapest University, and Bredig in Karlsruhe TH. Even though Polanyi was forced to turn to medical study on the advent of his father's death in order to make a living, he began as an unpaid assistant to Tangl. Rare at that time, Tangl put emphasis on physics and chemistry. Polanyi had held interest in thermodynamics since his time in gymnasium.

Polanyi says to Kuhn in the same interview I quoted in the beginning:

> As to myself, it was an idea that although I had no change of becoming a scientist, at least I would have some form of scientific occupation—being a doctor—and then I could read and perhaps do some work on the side. But it turned out that I became scientist.

When we think from this perspective, we can understand how happy he was when his idea on liquefaction of gases was approved by Einstein. Polanyi wrote "Bang! I was created a scientist."[7]

To re-examine Polanyi in this way lead me to re-examine the history of early quantum theory as well. For example, it was in fact specific heat that was the central topic for early quantum theory, even though normal history of quantum mechanics had until now only been examined at the simplest level. During that time only a few scientists knew the significance of specific heat for quantum theory, and it was they who were its' paradigm builders.

With Polanyi as the catalyst, I started focusing on the history of quantum mechanics as the beginning of the research programs for property of matter.

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[5] Scott & Moleski, p.16.
[6] Polanyi Michael, pp. 89-90.
[7] Scot & Moleski, p. 28.

References

Interview of Michael Polanyi by Thomas S. Kuhn on February 15, 1962, Niels Bohr Library &Archives, American Institute of Physics, College Park, MD USA, www.aip.org/history/ohilist/4831.html.

Gavroglu, K., and Simões, Ana. 2012, *Neither Physics nor Chemistry: A History of Quantum Chemistry*, The MIT Press.

Nye, Mary Jo, 2011, *Michael Polanyi and his generation: origins of the social construction of science*, The University of Chicago Press.

Polanyi, John C., 2003, 'Michael Polanyi, The scientist', *Polanyiana: The Periodical of the Michael Polanyi Liberal and Philosophical Association*, Vol. 12, No. 1-2.

Polanyi, Michael., Grene, Marjorie eds., 1969, 'The Potential Theory of Adsorption'(1967), *Knowing and Being*.

Scott, William T., and Moleski, S. J., Martin X., 2005, *Michael Polanyi: Scientist and Philosopher*, Oxford University Press.

Servos, John W., 1990, *Physical Chemistry from Ostwald to Pauling: THE MAKING OF A SCIENCE IN AMERICA*, Princeton University Press.