From Solved Electrons to Shale Gas via the Liberal Arts

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I came to Juniata College fifty years ago as a dedicated explorer, which has included adventures with entomology, chemistry, physics, mathematics, philosophy, spelunking, mountain climbing, etc. After earning my Ph.D., I learned to fly, bought a small plane, and proceeded to expand my explorations of places such as the Grand Canyon. These experiences were vigorous but chaotic. Juniata has unusual and close relationships between faculty, and between faculty and students. These relationships, along with the focus of Juniata as a liberal arts teaching institution, brought order to my personal chaos. This essay is about that change.

THE ORIGIN OF MY INTEREST IN SOLVATED ELECTRONS

I came to Juniata married to both my wife and my chemical research interest. The former was born in Utah, the latter at the Chemistry Department of Yale University when I entered as a graduate student. The focus of the department was chemistry! It was as if nothing else mattered. Like most of the new graduate students, I went from professor to professor to choose a research advisor by listening to their ideas on what was important: electrical conductivity, diffusion, non-equilibrium thermodynamics, etc. I chose Dr. Andrew Patterson because of his presentation on solvated electrons, and as a result worked twelve hours per day for four years on a project examining the phase properties of metal ammonia solutions. My goal at that time was to find an institution that would allow me to continue work in this area for fifty more years. Why solvated electrons, and how did I end up doing research on shale? The answer lies in how the liberal arts focus of Juniata and the broad interests of most of its faculty helped me with my work.

Let me start by briefly describing solvated electrons; the very name sounds weird. Solvated electrons are, in a sense, the simplest of ions, just electrons wandering around in a solvent, nothing else. In some ways, this simplest of ions behaves like other ions; however, in other ways they are fascinatingly different. Sodium chloride dissolves in ammonia via the reaction $NaCl \rightarrow Na^+ + Cl^-$. Sodium metal dissolves by the similar reaction $Na \rightarrow Na^+ + e^-$, where e^- is simply an electron floating in the solution as if it were an ordinary non-metallic ion. In dilute solution, the chloride ion and the solvated electron behave similarly. However, in concentrated solutions, the electrons start to interact and the result is a solution that seems like a liquid metal—very different from a sodium chloride solution. If you try to make up a solution at intermediate concentrations, it gets complicated; the solution becomes in some sense ionic and metallic at the same time. Furthermore, at very low temperatures (e.g., -70^o C) the solution becomes partly like a metal and partly like a normal ionic solution. As an analogy, fill a test tube with two mixtures—one of water and blue ink, and the other with gasoline and yellow paint—and then shake it and wait. The yellow gasoline will float to the top, whereas the blue water will sink to the bottom. This result would be similar to a sodium metal ammonia solution with a bronze colored concentrated solution on top, and a blue dilute solution on the bottom.

This effect is due to three highly unusual features for a solution. First, at low concentrations electrons absorb red light and transmit blue light, which results in the blue color. However, at higher concentrations the electrons start to interact in a complicated quantum mechanical manner resulting in behavior that is similar to electrons in metals. One consequence of this is a change in the interaction with light resulting in high reflectivity similar to that of a metal. The second feature is that the electrons become very mobile, which results in high electrical conductivity and changes the magnitudes of the attractive forces between groups of sodium ions and electrons. This results in the formation of the second, more concentrated phase for some solutions of metal in ammonia. The third feature is that although an electron has very little mass, it nevertheless occupies as much space as a few ammonia molecules by virtue of having a diffuse wave function. This means that a concentrated sodium ammonia solution is lighter that the pure solvent or a dilute solution. At higher temperatures (above -41^o C for sodium) and intermediate concentration, this separation of the metal-ammonia solution disappears. Most people would say, it not only sounds weird, but it is weird. However, why should anyone care? In any event, my advisor, Dr. Andrew Patterson Jr. was interested, and so was a Nobel Prize winner at Yale, Lars Onsager. Inspired by them I chose to work in this area for my Ph.D. thesis. I got help in this respect from Gerard Lepoutre, a Catholic priest from the Catholic University of Lille, who had previously received his Ph.D. at Yale with a thesis on solvated electrons.

Dr. Lepoutre had two very practical interests. The first was promoting student and faculty exchanges between universities in different countries. He lived in a section of France that had been overrun by foreign military in two world wars, and saw academic exchanges as a means of preventing such disasters in the future. He was deeply involved, along with Bill Russey and myself, in getting an exchange started at Juniata, initially with the Catholic University of Lille. Bill Russey then expanded Juniata's exchanges to include Germany and England. Ruth Reed also did a lot of work in this area. This beginning led to Ei Ichiro Ochiai becoming a member of the Chemistry Department. Lepoutre's second interest was that of using solvated electrons to invent a new kind of powerful and light battery. His work was a precursor to the invention of the present-day lithium battery. Unfortunately, I ignored this research direction and retained my esoteric interest in the phase properties of sodium solutions mentioned above. Beyond arousing occasional intellectual curiosities, my work in this area has remained esoteric in that it has no direct economic or societal consequences.[1]

MY ARRIVAL AT JUNIATA COLLEGE

After obtaining my Ph.D. in solvated electrons, I worked for a few years as a post-doc, including teaching at a liberal arts college. As a result, I was especially excited when an opportunity arose to apply for a permanent teaching positon at Juniata. I was impressed by the intellectual diversity of the people that I met during my interview. Besides the Chemistry faculty, I met with Esther Doyle in English, Howard Crouch in Education, Bob Fisher in Biology, and Tom Nolan in Economics. That diversity encouraged me to come. Bob Fisher arranged to pick me up at the airport. He asked what time my plane landed; my response was to ask what time did he want it to land. This of course turned into a discussion of flying lessons and the equivalence of car and small plane prices (in those days), and that rolled into the beginning of a wonderful interview trip and all kinds of wild discussions, such as the nature of solvated electrons and how my plane could get better gas mileage than a car.

My small plane had good gasoline mileage, but it could not carry both my wife and I and the material we were moving. So we drove. Most people probably do not remember Mifflin Street back in 1967, but I do, and so does my wife. It was like “old Appalachia”—run down, to say the least. My wife burst into tears as we were driving up the street, and I told her that we would only be here for a year. I was obviously wrong on that account—by a factor of fifty! Starting at Juniata in 1967, I jumped into teaching physical chemistry, freshman chemistry laboratory, and general education, building equipment for doing solvated electron work, and raising kids with a fervor that now, fifty years later, seems impossible.

MY COLLABORATIVE RESEARCH ON SHALE GAS AT JUNIATA COLLEGE

In the 1970s, the country was running into an energy crisis. Petroleum engineers were declaring that the oil reserves of the United States would run out by the year 2020. This would result in a dramatic change in lifestyle, the return of corner grocery stores, horses instead of cars, cold houses, thick warm coats, etc. There were of course all kinds of governmental reactions. President Richard Nixon directed the National Science Foundation to begin a new program called Research Applied to National Needs (RANN) that funded research focused on national needs, rather than on topics of only academic interest. The Department of Energy was also founded during this period.

Juniata's president at that time, John Stauffer, was also on the board of trustees of Columbia Gas Corporation and engaged in a discussion with its research director concerning natural gas reserves. Columbia Gas owned most of the natural gas pipelines in the US and was actively involved in drilling gas wells. In particular, they were drilling through shale beds in Ohio, West Virginia, Pennsylvania, and other states to get to the sandstone underneath which contained natural gas. The strange thing was that sometimes the wells would start producing gas while they were still drilling through the shale! Every petroleum engineer at the time "knew" that shale was a solid rock; it could not contain gas, they claimed. As a result of his discussions with the Columbia Gas research director, Stauffer handed me a medicine vial full of what looked like dirt, of the kind you find anywhere around Juniata. This, however, came from a shale-drilling well in Ohio. At that time, I was working on an apparatus for measuring small pressure changes in ammonia gas above a solvated electron-liquid ammonia solution. Specifically I was using the ammonia gas pressure above a metal ammonia solution at equilibrium to provide thermodynamic information about the electron-ammonia-metal ion interactions in the solution in conjunction with standard thermodynamics. Why not determine the response of the "dirt" in the vial to small changes in methane gas pressure using the same apparatus? I did, and the result was unmistakable; the rock could hold gas. Specifically, if the pressure around the rock was decreased stepwise, the rock emitted gas! The quick result from Columbia Gas was many more vials of shale "dirt" from different wells at different depths. The results varied from sample to sample, but the overall result was confirmed; my research at Juniata discovered that shale holds natural gas. I reported the importance of this result at a scientific meeting sponsored by the Gas Research Institute (GRI), in a paper that showed that the experimental production data of one of these mysterious gas wells could be quantitatively explained by my medicine vial data by simply scaling up the volume of shale from a medicine vial to the volume of shale accessed by a well drilled into shale.[2]

My memory of that meeting was that GRI committed $50 million on the spot for further research. The USA needed new energy sources then, and shale occurred throughout the U.S.A.; had we been sitting on an energy gold mine without knowing it? I wrote a research proposal to try to get the National Science Foundation into the game. I received a telephone response that they wanted to fund the proposal, but they were not allowed to; the government wanted to get the new Department of Energy involved. I was told to send my proposal to DOE. In this manner, Juniata received funding, as did Columbia Gas and a variety of other companies, to develop shale gas.

What problems were we trying to solve? The problem was that not all shale was productive, and productive shale was not present at all depths of a shale well. In addition, once found, the productive shale layers usually needed to be specially treated by fracturing it in order to produce gas, and this could be done only for small spatial intervals of a well bore that might be 5000 ft. deep overall. After drilling, the next problem, then, was to locate the depths where productive shale intersected the well bore. Drillers in conjunction with specialized logging companies had a wide variety of instruments that could be lowered down the well and send measurements back to the surface to “log,” or create a graph of, instrument readings versus well depth. However, these logging instruments had been designed for use on ordinary well bores in sandstone; they did not work for shale. As a result, logging companies tried to create new logging tools or adapt existing ones for use in shale. Direct laboratory measurements of gas content, gas permeability, and specific degassibility were needed.[3]

My laboratory at Juniata College (alone) could make these specific measurements. However, it was impossible to lower Schettler, his apparatus, and/or Juniata College down well bores! The overall project then was to send samples obtained at specific depths to Juniata and use our results to calibrate the various logs from novel and standard logging tools that could be lowered down well bores after trial modifications for shale. Hopefully, a correlation could be found between the downhole logging data and the Juniata laboratory data on well samples. The next step was to decide what depths contained active shale and then to attempt to activate those depths by fracturing the shale at those depths. This partnership between Juniata, various logging companies, and Columbia Gas Corporation continued for about eighteen years with steady improvement of the ability of logging companies to locate active shale layers directly with their new logging tools and calibration efforts, using data from Juniata College.

The laboratory equipment at Juniata to do the fundamental measurements of gas content was very specialized. Its construction involved several Juniata faculty members in addition to me; specifically Dale Wampler (chemistry and computers), Tom Fisher (chemistry and electronic circuitry), Rick Parmely (chemistry), Loren Rhodes (computer science), Todd Gustafson (biology), Don Mitchell (chemistry), and Bob Zimmerer (biology). Dale Wampler initially suggested that my apparatus could be automated by connecting it to the new rack-mounted computers that were just coming out in the mid-1970s. The initial apparatus was thus replaced by one that we built in-house with computer-operated valves and pressure transducers. Since our laboratory at Juniata was the only one in the 1970s and ’80s that could make the measurements needed, we had all the work we could do in this area. Only later did Micromeritics Corporation, with the aid of one of our graduates, market a system similar to ours. The computer interfacing involved the expertise of Dale Wampler, Tom Fisher, and Loren Rhodes in our liberal arts environment with free (and interested) intellectual interchange between faculty of different disciplines. Rick Parmely was teaching some Freshman Chemistry sections at the time and used this connection to involve about 100 students over the years on the project: preparing samples, running the computers, compiling results, etc. All of this work involved much report writing and Bill Russey (Chemistry) devoted much time editing my drafts.[4] Figure 1 shows our laboratory results of the gas content of shale as a function of pressure for several gases.

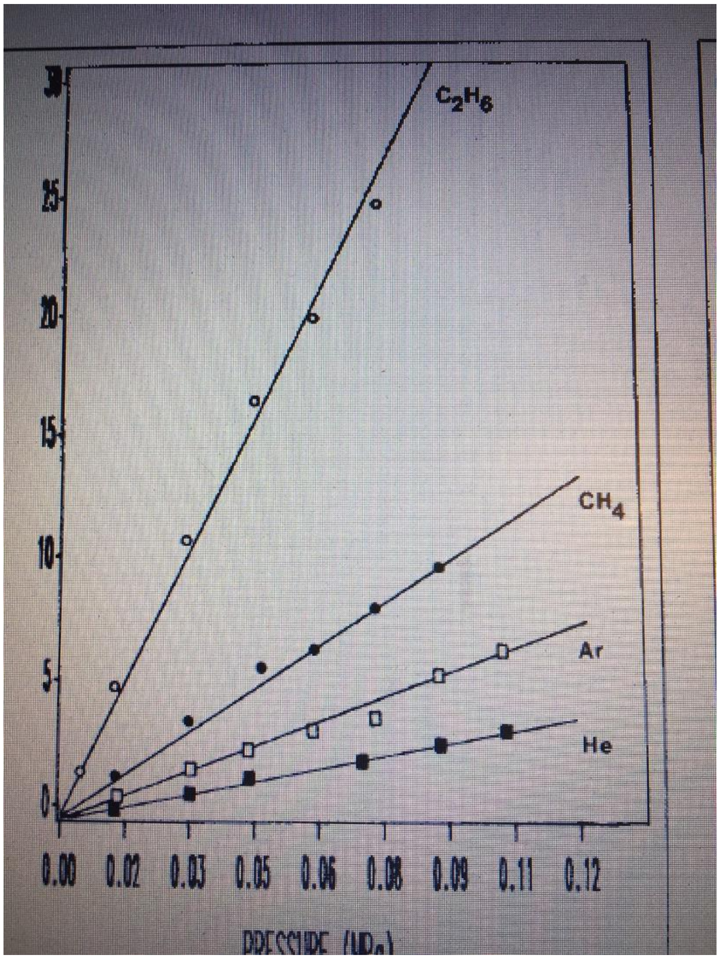

Figure 1: Graph of gas content in shale as a function of pressure as obtained by exposing the sample to different gasses in the laboratory.

Shale gas wells have some special properties for which well drillers were unprepared. After drilling, a shale well generally produces almost no gas. The next step was to locate potential hot spots (layers) along the well bore, i.e., layers of rock intersecting the well bore that have high effective porosity and permeability (and hence high gas potential). Fracking activates these hot layers. A standard way for a driller to find the hot layers is to log gas flow by lowering a flowmeter down the well to locate the depths that gas enters the well bore. However, in the 1970s, the standard flowmeters drillers used were not sensitive enough to work for shale wells; the flow produced by the hot layers was too low. To correct this, Todd Gustafson and I invented two new flowmeters, which were then patented and used to pinpoint the hotspots. One of these could measure the low flows quantitatively, but had a resolution of only about ten feet in locating the hot spots, which could be only a few inches thick. The other flowmeter had a high resolution of less than two inches, but at the expense of decreased flow accuracy. Both were successfully used to locate “hot spots” in the well bore. Once located these hot spots were then fracked to result in a producing well. Students, Gustafson, and I made several trips to gas wells to aid in these flow measurements using our flowmeters, built in Gustafson's laboratory.[5]

With the help of Tom Fisher, we got involved in measuring the Nuclear Magnetic Resonance (NMR) of shale samples. Our laboratory data suggested that gas porosity and the permeability of shale was correlated with the carbon content of the shale, which in turn can be measured by Magnetic Resonance Imaging (MRI), a form of NMR and a common instrument in a chemistry laboratory. We thus started a program to include taking NMR readings of our shale samples to see if they were correlated to our other laboratory measurements, and indeed found a correlation between laboratory degassing rate and the organic content of the shale. The Gas Research Institute picked up on this and developed a MRI instrument that could be lowered down a well bore to locate potential hot layers with high organic content.

Where did the hydrocarbon gas in shale come from? Shale contains clay minerals coming from mud that was laid down along with algae and other organic matter a long time ago, such as during the Devonian period, 400 million years ago. Clay minerals have catalytic properties that aided the decomposition of the organic material into hydrocarbons, including methane gas. This is believed to have taken place in the pores of the clay minerals, which are very small—dimensions only somewhat larger than atoms. Our laboratory measurements of shale degassing dealt with the flow through these very small pores. This left issues of how the gas could flow through many feet to a well bore at a feasible, economic rate to produce measureable amounts of gas.[6]

In addition to these very small pores, shale (fortunately for the energy business) typically contains fractures along the bedding planes. The presence of these fractures becomes evident when one breaks a piece of shale, and can be seen via an electron microscope (with help from Bob Zimmerer), or by dye penetrant analysis, a technique widely used to detect fatigue fracture in such structures as the spars in airplane wings (such as mine). In dye penetrant analysis, one coats the object with a powerful dye, waits for it to soak in (if it does), rinses off the surface, sprays the surface with a white powder, waits, then observes if and where the dye that had diffused into the rock (or wing spar) then diffused back out, leaving a mark on the powder. Figure 2 shows the result obtained on a shale slab.

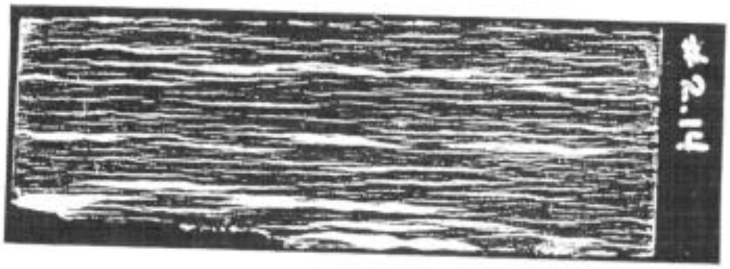

Figure 2: Dye penetrant analysis applied to a small slab of shale (1 inch by 3 inches). This is a photograph using a fluorescent dye. The light stripes are places where the dye leached back out of the shale. The very fine lines correspond to very thin fractures barely detectable under an electron microscope.

Figure 3: Gustafson and Schettler by a bed of shale just a mile from Juniata College. Note the fractured areas suggesting possible hot layers separated by very dense impermeable layers.

With the help of Tom Fisher and Bob Zimmerer (Biology and electron microscope), we produced data that encouraged Gas Research Institute to look for bedding plane fractures down well holes. They found them. The net result was a model of shale gas production that proceeded from a short migration of gas from the rock to a local fracture, and from there to progressively larger fractures (produced by fracking), which le~~a~~d finally to the well bore. This model is analogous to the flow of cars into the city in the morning; many individual cars travel slowly down driveways to streams of cars at higher speeds on streets, then to rivers of cars speeding down -ane super-highways, resulting in a flood of cars into city centers. Likewise with methane molecules traveling out of "solid" rock into micro fractures, to the larger fractures, to fractures produced by fracking, and hence to the well bore. Figure 3 shows a bed of shale found near Juniata College; it is easy to imagine that it contains a mix of hot layers separated by unproductive zones.[7]

EPILOGUE

The Juniata shale project ended when the politics associated with the energy crisis of the 1970s ended in about 1990.[8] The money to support well drilling and research dried up. However, representatives of the large oil companies had been attending our meetings and had quietly started on a development effort of their own: horizontal drilling. All wells prior to that time were straight vertical holes; what the oil companies were working on were ways to bend the well stem so that one could drill into a hot spot (or level) and then along that hot layer. In fact, this can now be done multiple times in one well so that the horizontal bores stem out from the central bore like petals on a flower. Fracking then augments the existing fractures by widening them by forcing high-pressure fluids down the well. These fracking fluids include sand grains to hold the fractures open when the fluid is removed. At the end of the fracking process, the fluid is released back to the surface, leaving the sand grains to keep the fractures propped open.

What has happened since Juniata's departure from the shale gas scene? Natural gas is now the second largest energy source in the United States and shale gas is a large proportion of that. Geologic maps indicate that about one-third of the surface of the U.S.A. is shale, which is suggestive of huge reserves. In some sense, the "energy crisis" has been replaced by new fears of global warming resulting from the burning of fuels. In any event, it has been a long road from President John Stauffer's receipt of a medicine vial containing shale from a well that Columbia Gas had drilled. The purpose of this essay has been to convey how a liberal arts institution, such as Juniata, can impact humanity by virtue of its broad-based intellectual approach.

NOTES

1. Paul D. Schettler Jr., “Liquid-Liquid Phase Separation in Metal Ammonia Solutions” (unpublished Ph.D. Thesis, Yale University, 1963); Paul D. Schettler Jr. and Gerard Lepoutre, “Interactions between Solvated Electrons. I. Electron-Electron, Electron-Solvent, and Solvent-Solvent Interactions in Ammonia. Valence Bond Approximation,” *Journal of Physical Chemistry*, 79 (1975): 2823-2827; Paul D. Schettler Jr., Patricia W. Doumaux, and Andrew Patterson Jr., “Liquid-Liquid Phase Separation in Alkali Metal-Ammonia Solutions. V. Model for Two-Component Systems, with Calculations,” *Journal of Physical Chemistry*, 71 (1967): 3797-3801.
2. Paul D. Schettler Jr., “Study of Hydrocarbon--Shale Interaction” (Progress Report No.1, Report #ORO-5197-1 on Morgantown Energy Research Center contract #(DOE): E(40-1)-5197, 1976).
3. Note that specific degassibility describes the rate of gas production of a shale sample in response to a step drop in surrounding gas pressure. The specific degassibility of a sample is a function of both its gas content and its fundamental permeability, and depends upon the detailed nature of the rock.
4. Paul D. Schettler Jr. and C.R. Parmely, “Physicochemical Properties of Methane Storage and Transport in Devonian Shale.” (Annual Technical report, June 1989-May 1990, Report #PB-91-109017/XAB, PB-91-109017/XAB, and PB-91-109009/XAB on Gas Research Institute Contract #5085-213-1143, 1990): 74 pp + 335 pp (data appendix I) + 383 pp (data appendix II).
5. R. Bennett, Paul D. Schettler Jr. and T.D. Gustafson, “Measuring Low Flows in Devonian Shale Gas Wells with a Tracer Gas Flowmeter,” (Proceedings of the SPE 1988 Eastern Regional Conference, Charleston, WV, USA, 1-4 Nov 1988).
6. Paul D. Schettler Jr. and C.R. Parmely, “Physicochemical Properties of Methane Storage and Transport in Devonian Shale” (Final report, April 1985-April 1991, Jan 1993, Report # PB-94-120359/XAB, Gas Research Contract GRI-5085-213-1143, 1993): 51 pp.
7. R. Bennett, Paul D. Schettler Jr., G.H. Bowles, C.R. Parmely and B.F. Morton, “Selection of Well Completion Zones Using the Dye Leachback Technique,” (Proceedings of the SPE 1989 Eastern Regional Conference and Exhibition, Oct 1989): pp. 303-308.
8. There was a lot of report writing during the period from 1976-1991. This included monthly, quarterly, and annual reports throughout this period. We presented most of the detailed data in the quarterly reports with summaries in the annual reports. In addition, we made one verbal presentation sponsored by DOE or GRI for petroleum engineers and other interested parties.