



Energeia

Adventures in Surface Science: A Personal History

By Kenneth S W Sing

I was fortunate to be able to begin my Ph.D. research immediately after World War II. This was a good time to start work on adsorption and the surface properties of solids. The first signs of a rapid development of new catalysts and industrial adsorbents were clearly evident, but there was little understanding of the surface chemistry and physical texture of the new materials. My research interests have continued to be mainly concerned with the pore structure of adsorbents and the modes of attachment of molecules to solid surfaces. We now know that adsorption at a fluid-solid interface (i.e. an increase in concentration or density) can involve a wide range of different molecular interactions. In fact, it is this specificity of adsorption which provides a scientific basis for heterogeneous catalysis and the separation and purification of gases and liquids.

Before I could make my first gas adsorption measurements 52 years ago, it was necessary to design and construct a suitable apparatus. There were no research technicians available and therefore the research student had to learn the basic skills of glass-blowing, metal working and electrical engineering. When the adsorption equipment was eventually constructed and calibrated, long hours were spent in taking readings - sometimes through the night - because there was always the possibility of a loss of power or mechanical failure. Of course, this was before the computer age and therefore mathematical calculations were made with a large slide rule or a hand-operated calculating machine. All of this experience was good training, although it could be frustrating when the

vacuum pumps failed or a slow air leak into the vacuum system occurred! However, there was a real feeling of adventure and scientific discovery, which I suspect is not as strong today. Of course, there were also hidden dangers. For example, we were not aware of the carcinogenic activity of some common organic solvents, or the hazards involved in the use of liquid oxygen, asbestos or mercury.

An objective of our work in the early post-war period was to prepare solids with large surface areas, which could then be used as stable and highly active adsorbents. The three most important industrial adsorbents at that time were activated charcoal, alumina and silica



(From left) Drs. John Gregg, Stephen Brunauer, and Ken Sing at Brunel University, London, England, 1969)

gel, but very little was known about their surface structures and it was even difficult to reproduce the properties of an adsorbent. The particular aim of my Ph.D. work was to convert aluminum hydroxide into an active adsorbent and then study the surface properties of the 'activated alumina.' This was probably the first investigation of its kind and has been followed by many other, more

elegant studies of the thermal decomposition of various hydroxides and oxide-hydroxides. At present, the main objectives are to produce tailor made adsorbents and model pore structures.

I completed my PhD work in 1948 and after a brief period of industrial research, I set up my first research laboratory. Since then, my colleagues and I have carried out extensive investigations of the pore structures and surface chemistry of a wide range of
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Molecular Structure and Energetics: A Changing Paradigm

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The concept of molecular structure embraces three components. The first component is the molecular geometry, characterized by the relative nuclear positions in the molecule. It can be described by a set of coordinates of all nuclei in the molecule. A chemically more amenable description of molecular geometry is by the so-called 'internal coordinates' comprised of the bond lengths, bond angles, and angles of internal rotation. The presence of symmetry may considerably simplify the description of molecular geometry. Another component of molecular structure is the electron density distribution, and the third is the intramolecular motion. To many, molecular structure is simply the atomic connectivity in the molecule but this is an incorrect oversimplification.

The concept of molecular structure has proved to be a most useful model in the physical sciences, but it is a model only. The drawback of models is that they have limitations, while their advantage

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adsorbents and other materials including the oxides of Cr, Ti, Co, Fe and Si and also activated carbons and molecular sieve zeolites. Much of this work was undertaken in collaboration with various academic and industrial laboratories in Britain and abroad. These experiences have convinced me that scientific partnership is of great importance.

In 1945 it seemed that gas adsorption could be used as a routine procedure for determining the surface area of a powder or a porous solid. The method was based on the Brunauer-Emmett-Teller (BET) theory, which had been published in 1938. However, as happens so often in scientific research, this was not the end of the story. By 1950 we realized that, although it represented an important development, the BET theory was based on an oversimplified model of gas adsorption. It therefore became necessary to discover why the BET method is not always reliable and to investigate adsorption within pores of well-defined size and

was readily available and research targets were not too difficult to hit! My colleagues and I were encouraged to move into some new multi-disciplinary areas, which involved solid state and colloid chemistry, pigment technology and surface chemistry. Over the next 25 years, we were able to make some of the first gas adsorption measurements on such materials as inorganic and organic pigments and carbon cloth.

In scientific research, as in other fields of human endeavor, one thing often leads to another and the stages of conception, birth and growth of ideas are impossible to separate. For example, the pioneering measurements of Fred Baker, Don Carruthers, Bob Day, Lyn Stryker, Danica Turk and other co-workers in the 1960s and 1970s provided standard adsorption data, which we and others have made use of in many more recent investigations. Without these early studies we would not have been able to interpret recent experimental results obtained with MCM-41 and other novel adsorbents.

who are perhaps not as well known outside their own research fields. Over the past 50 years, I have known a number of such leading surface scientists: Barrer, Brunauer, de Boer, Dubinin, Everett, Gregg, Kiselev and Rideal are a few of the distinguished names that spring to mind. I will now refer briefly to the character and work of a few of these leading surface scientists.



Dr. A. V. Kiselev in England, 1968

It was on my first visit to the USA in 1967 that I met Professor Stephen Brunauer. Although we had previously corresponded and exchanged reprints, for me that first meeting was an exciting occasion. Stephen Brunauer was born in Hungary in 1903. He emigrated to the USA in 1921, when he joined an uncle who owned a grocery store in New York. Through determination and hard work (much of it part-time), he gained his Ph.D. degree in 1933. A few years earlier, he had met Paul Emmett and they had begun their pioneering work on gas adsorption. A little later Brunauer was able to persuade Edward Teller (the so-called “father of the hydrogen bomb” and also Hungarian) to collaborate and I think that it was Teller’s mathematical skill which enabled them to formulate the BET theory and later the more general treatment of multilayer adsorption (the BDDT theory), which appeared in 1940.

During the war, Brunauer was given a commission in the U.S. Navy and he told me that overnight he was expected to become an expert in high explosives and that one of his proudest achievements as a naval officer was the appointment of Albert Einstein as his consultant. In 1951, Brunauer’s career underwent another

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shape. In fact, this has turned out to be a more difficult task than was originally thought and is still incomplete!

In 1965 I became chairman of the Department of Chemistry at Brunel University, the new technological university of West London, England. Those were halcyon days when funding

One of the pleasures derived from scientific research is the opportunity to meet fellow scientists. Of course, it is always fascinating to encounter colorful and world-famous scientists like Linus Pauling or controversial former scientists like Margaret Thatcher. In my view, however, there are many other equally distinguished and interesting scientists,



*Dr. Brunauer (center) in the Sing’s garden in 1969.
Ruby Sing and her dog Dougal on the left and Dr. Lyn Stryker on the right.*

Surface Science, continued

marked change of direction when he became manager of basic research in the Portland Cement Association and was soon recognized as a leading authority on



Sir Eric Rideal and Professor Kiselev in Wales, 1968

the microstructure of hardened cement and related materials. Finally, he returned to the academic world in 1965, when he was appointed chairman of the Chemistry Department of Clarkson College of Technology. He continued to publish a series of stimulating research papers until his death in 1986.

In my view, Professor Brunauer was a remarkable man in many respects. In an obituary, I wrote "Stephen Brunauer's spoken delivery was slow and deliberate, even painstaking; in contrast, his writing was always fluent, stylish, and eminently readable. His book *The Adsorption of Gases and Vapours*, first published in 1943, has been widely acclaimed as his masterpiece and still remains one of the best monographs ever written on surface science." After re-reading Brunauer's book many times, I have not changed my opinion of it.

The other surface scientist who had a great influence on my work was the Russian chemist Andrei Vladimirovich Kiselev, who was a professor of physical chemistry in the M.V. Lomonosov State University, Moscow. I met Kiselev when he came to Britain for the first time in 1957. He took part in the Second International Congress of Surface Activity, which was held in London and gave three important papers on gas adsorption and the energetics of adsorption. I was very impressed by the fact that, although at that time his spoken English was imperfect, his ideas were so important that they dominated the discussion sessions on gas adsorption.

Kiselev returned to England in 1958 and once more in 1967 and I was also able to see him in Moscow in 1965 and again in 1968. Although he received many further invitations to give plenary lectures in Western Europe, it seemed that he was not allowed to leave the former Soviet Union.

Kiselev's research output was extraordinary: he and his many co-workers produced over 900 original papers and reviews and at least 8 books - all within 30 years. One might imagine that he had very little time for other activities, but in fact he had wide-ranging interests in the arts and crafts and his apartment in Moscow was

like a small museum, filled with objets d'art of all kinds. After his death in 1984, I wrote "Looking back over a period of thirty years, one can admire the work of master craftsman and it is tempting to compare Kiselev's approach to science with that of the architect setting out to design a great cathedral."

Academician Mikhail Mikhailovich Dubinin was very different in personality and status. I became aware of his

work on the adsorptive properties of microporous carbons in the mid 1950s and met him briefly during my first visit to Moscow in 1965. The long-standing rivalry between Dubinin and Kiselev was already well known when I made my second visit in 1968 and since I was a Kiselev supporter I did not expect to have the opportunity to meet Dubinin. It was a pleasant surprise therefore to receive an invitation to join him for a discussion. In fact, this turned out to be a strange experience: our scientific discussion lasted no longer than 1 hour and was followed by coffee, vodka and a 3-hour lunch in the exclusive Academicians' restaurant. I



Mikhailovich Dubinin in Moscow, 1988

remember the generous hospitality but very little of our conversation! At that stage, Dubinin was evidently a very powerful member of the Soviet scientific establishment. He lived in a luxury apartment, had a large dacha and was able to travel outside the Soviet Union and even take his wife abroad. I subsequently met Dubinin again at various conferences in Western Europe, but in my eyes he continued to be an enigmatic figure and I never felt entirely comfortable in his presence. Towards the end of his long life, things changed drastically: the Dubinins still had their spacious apartment, but they were apparently cold and short of food. Of course, this decline in the status of senior scientists reflected other changes which accompanied the disintegration of the Soviet Union.

What do I conclude from my adventures in surface science? In my view, we should always remember that scientific research is a human activity. Scientists are not magicians or superior people and very few have the exalted intellectual powers of Einstein. Of course, a research scientist must have some creative ability; in addition, the three essential qualities are intellectual honesty, enthusiasm and patience. We cannot predict the needs of society or even the full impact of computer simulation and theoretical developments in the years to come, but one thing is certain: there will continue to be exciting and demanding scientific challenges to be faced.

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consultant. He was recently a visiting scientist at the UK Center for Applied Energy Research.

Molecular Structure, continued

is that they can be improved as necessitated by the progress of the field. The molecular structure model has proved to be usefully adaptable to improvements. The information on molecular structure is pivotal to our understanding of all chemical and biological functions of a substance. Changes in the molecular structures can be correlated with changes in other properties, which makes the concept useful and widely applicable.

One of the most important conceptual changes in the molecular structure model has been the recognition of the intimate relationship between geometrical changes and their energy costs. This might appear trivial in hindsight, but the utilization of this relationship has not even reached its full potential.

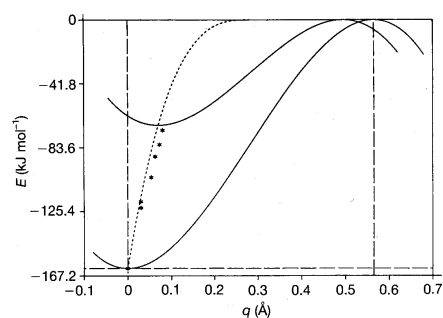
The purpose of the present communication is to shed some light on the availability and utility of information on small structural differences and the benefit of a unified structure/energy approach in viewing some potential of crystallography, supramolecular chemistry, and the potential of small structural changes in biological function.

Decades ago the knowledge of molecular structure was rather esoteric and of theoretical importance only. The molecular structure concept was detached from actual situations, such as whether the molecule was isolated in the gas phase or resided in a crystal. It was also detached from the means, by which it was determined. In other words, it was generally assumed that the molecule of a substance had one unique structure regardless of the possible interactions of the molecule with others and regardless of the nature of the physical techniques by which it has been determined. In the 1950s attention was called to the importance of different ways of averaging over various motions in the molecule in different techniques, but the experimental data had to improve considerably before those differences could show up in the actual information. In the most demanding studies today careful distinction is made in the data as to their origin with respect to the experimental techniques used, while in the bulk of published reports this difference is still being ignored. Similar care should be exercised in making comparisons of computed structures with experimentally determined ones. We are witnessing a computational chemistry revolution, but most workers have yet to

recognize that a computed structure refers to the minimum position in the potential energy function, which is different from any average amenable to experimental determination unless the molecule is diatomic and performs strictly harmonic motion.

Let us turn now to the energy costs of structural changes. Unfortunately every kind of change and every single substance is different. Thus we have to restrict our introductory discussion to some simplified model. Take a carbon-carbon bond in a carbon chain; it has been estimated that it takes some 15 kJ/mol to stretch or compress such a bond by 0.1 Å. A bond angle deformation of 10 degrees costs about 5 kJ/mol, and a torsional distortion of 15 degrees costs about 1 kJ/mol. These amounts of geometrical changes are about ten times the magnitude of typical experimental errors of good structure determinations. It is obvious that a noticeable change in a bond length costs much more than a conformational change, with the angular change costing something in between.

The consequences of the geometrical change/energy cost correlation can be interpreted in two opposite ways. Let us confine the discussion to the extreme changes: the bond length and the torsion. One way of interpretation is that when small interaction energies are available, it suffices to consider conformational changes and ignore bond stretch and compression due to the lack of the necessary energy for such changes. The other way is that ignoring bond length changes, however small, will introduce relatively large systematic errors in the rest of the considerations because of the heavy energy price associated with such changes. In any case, the availability of higher precision makes more demanding insight possible and vice versa.



Correlation between change in ground-state structure (q) and activation energy (E) in tetrahydropyranyl acetals (Domenicano and Hargittai, 1992)

Until some time ago the structure of a molecule was assumed to be the same in

its isolated gaseous state and in the crystal. Today considerable efforts are being directed towards uncovering and understanding the magnitude and nature of intermolecular interactions in the crystal, and proper comparison of the gaseous and crystalline structures of the same molecule is a promising technique in such a quest. The intermolecular interactions are weaker than the usual chemical bond so the resulting structural changes are relatively small but carry revealing information. Often very similar molecules build very different crystal structures. This is not surprising because in polymorphism even the same substance appears in different crystal modifications.

In one of today's success stories, supramolecular chemistry, it is, again, the relatively weak interactions between the participating molecules whose structural consequences are to be studied in order to uncover the magnitude and nature of interactions in supramolecular formation. Both in molecular crystals and in supramolecular formations, the spatial arrangement of the molecules is complementary. This is probably the single most solid piece of information available of a priori describing crystal structures and supramolecular formations. It has been called an almost scandalous state of affairs that having determined and stored a huge amount of crystal structure data, it is still difficult to predict the crystal structure of a new substance. There is, of course, always the possibility of the computational approach leading to the structures via energy minimization, but this is merely obtaining the facts rather than understanding them. The Russian crystallographer Alexander I. Kitaigorodskii said that a first rate theory predicts, a second-rate theory forbids, and a third-rate theory explains after the fact. Even a third-rate theory is useful, of course, but the first-rate theory signifies our understanding of the subject matter and the interactions involved.

There is yet another aspect of the molecular structure/energetics paradigm change, and that involves the understanding of chemical events in their dynamics. Chemistry is about making and breaking chemical bonds. On the level of nuclear motion this means a femtosecond time scale. Femtochemistry has been pioneered by Ahmed H. Zewail at the California Institute of Technology who showed how the chemical happenings break down into elementary steps. The electron diffraction technique with its extremely short interaction time is

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COMMENTARY

Unburned Carbon on Fly Ash: A Burning Issue for Coal-Fired Utilities

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Tom Ruppel

The phenomenon of unburned carbon on utility fly ash has become a major problem for the electric utility industry. The problem was hardly mentioned ten years ago. But NO_x-reduction regulations were not imminent then either. Today, it is an important environmental/regulatory/technical/economic issue.

First, it is an environmental issue because the Environmental Protection Agency (EPA) is considering further lowering NO_x emission limits under Title I and Title IV of the Clean Air Act Amendments of 1990 (CAAA). Under Title I, the Ozone Transport Commission has recommended to the EPA 0.15 lb NO_x/mmBtu or 75% reduction for the 12 states in its northeast region and the Ozone Transport Assessment Group (OTAG) advocates 0.15 lb/mmBtu or up to 85% reduction for 17 "fine grid" states in its 37-state region. The EPA, under Title IV Phase II (2000 AD) limits for utility boilers, has proposed ratcheted down Phase I (1995) limits further. Combustion modification alone cannot meet these severe limits and it also introduces an undesirable increase of unburned carbon in the fly ash.

Second, it is a technical issue because combustion and power plant engineers are attempting to reduce NO_x emissions without increasing unburned carbon formation. While this objective can be accomplished in more than one way, the number three reason, economics, places the utility industry squarely between a rock and a hard place.

The problem of incomplete combustion in coal-fired utility boilers has resulted in a number of measures taken to achieve reduction of NO_x emissions by control of combustion conditions inside the boiler. These measures, which take some form of reduced excess air or a modified excess air or fuel profile in the combustion zone, reduce temperature in the boiler with resultant decreased carbon burnout. It has been referred to variously as loss-on-ignition (LOI), unburned carbon, and unburned carbonaceous material. It reduces the efficiency of boilers, may render previously salable fly ash unsalable and expensive to dispose of, and - in addition to the CAAA - could con-

ceivably even trigger regulatory restrictions under the Resource Conservation & Recovery Act (RCRA).

The LOI and air toxics or hazardous air pollutants (HAPs) issues are related. With respect to the CAAA, polycyclic organic matter (POM) is on the HAP list of Sec. 112. The presence of at least some POM in unburned carbon can be inferred logically. If the concentration was considered by EPA to be significant enough to regulate, it could require the facility to install Maximum Achievable Control Technology (MACT) under Sec. 112. However, there is accumulating evidence that the POM content of unburned carbon on fly ash is low, generally in the parts per billion range. There is no reason to believe that LOI on fly ash should be a concern under Sec. 112.

Fly ash containing unburned carbon is not a hazardous waste under RCRA. In a final regulatory determination on August 9, 1993, the EPA "... concluded that regulation under Subtitle C of RCRA [hazardous waste] is inappropriate for four large-volume fossil fuel combustion waste streams: fly ash, bottom ash, boiler slag, and flue gas emission control waste because of the limited risks posed by them and the existence of generally adequate state and federal regulatory programs..." Further, even in the absence of the exemption, there are no reports that a utility fly ash containing higher mounts of unburned carbon has failed a Toxicity Characteristics Leaching Procedure (TCLP) extraction test. Thus, unless there are reports to the contrary, the higher LOI fly ash should not be classified as a hazardous waste. But there may be reports to the contrary. Currently, there are indications that the EPA may revisit the exemption in view of the increased utilization of low-NO_x burners to reduce NO_x emissions.

However, because coal combustion wastes were temporarily exempted from hazardous Subtitle C by Congress under RCRA through the Bevill Amendment in 1980 and because EPA had delayed final classification of utility wastes as nonhazardous until August 9,

1993, states have been proceeding with their own regulations. From 1993 data, in the last several years, the top 11 coal-burning states (which account for more than 50 percent of the total coal-fired electric utility capacity of the entire United States) placed requirements on new, expanded, or changed utility waste landfills as hazardous (and thus subjecting utilities to high disposal costs), five of the states require testing of coal combustion wastes for toxicity (TCLP) prior to permitting an electric utility, nine require clay or synthetic liners, seven require some type of leachate collection system, 10 require groundwater monitoring, and all 11 require some form of clay or synthetic cover to be installed once the disposal unit is closed.

A strategy that could circumvent the low-NO_x burner/LOI conundrum is to accept the high level of unburned carbon on fly ash that occurs with combustion modification technologies and remove it later by means of post-combustion treatment technologies. This approach has merit when it is realized that the unburned carbon that has been removed from fly ash can likely be used further as a supplementary feedstock for the furnace, thus recovering much of the lost heating value.

There are three NO_x-reduction methods: combustion modification, post-combustion technologies, and fuel switching. Fuel switching and blending are practiced widely, but industrial and utility boiler incompatibility with fuels that a unit was not designed for precludes an otherwise obvious solution in many cases.

Realizing the growing problem and how it applies to some of the Clean Coal Technologies that DOE has developed in cooperation with industry, sponsors an Annual Conference on Unburned Carbon on Utility Fly Ash. One hundred sixty-six representatives from academia, boiler manufacturers, DOE, entrepreneurial companies, industry, and utilities attended the third conference in Pittsburgh, Pennsylvania in May 1997 to address economic, regulatory, and technical ramifications of the problem.

The speakers addressed experiences and observations of the phenomenon, effects on specifications and sales, characterization of the material, control measures, post-combustion treatment, and regulatory implications.

A message gleaned from the three conferences held to date is that the regulatory/technical/economic system for NO_x reduction may need to be viewed in a

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capable of detecting such steps separately. These studies yield detailed energy mappings of reactions for which heretofore only global representation was possible.

Probing into small structural differences and their energy correlation necessitates a critical approach of the assessment of information originating from different techniques and on different states of matter. This research carries the promise of a deeper understanding of the intricacies of structure/property relationships.

Molecular structures of biological importance have been determined with lower resolution than those of the

simplest systems. However, this is a consequence of logistical expediency rather than of any indication that subtle structural differences would not carry vital information. Looking back at the staggering historical development of our knowledge about, for example, the chemical identity and structure of the substance of genetic information, it is not too bold to anticipate considerable progress in this direction. Recent computational work on the intricacies of DNA base-pair structures may be a first sign of meeting this challenge.

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Commentary, continued

larger framework if utilities can be expected to meet anticipated Title I and Title IV NO_x emission regulations within reasonable economics. Short of fuel switching, it appears that this can only be achieved if post-combustion technologies are included in the optimization matrix. Selective Catalytic Reduction and Selective Noncatalytic Reduction technologies are becoming less expensive and better designed as further operating experience is gained. Thus the NO_x-reduction/combustion modification/LOI/post-combustion/heat rate/economics system may have to be optimized.

More information on this year's conference on Unburned Carbon on Utility Fly Ash can be found on the CAER web page at www.caer.uky.edu.

Energieia is published six times a year by the University of Kentucky's Center for Applied Energy Research (CAER). The publication features aspects of energy resource development and environmentally related topics. Subscriptions are free and may be requested as follows: Marybeth McAlister, Editor of **Energieia**, CAER, 2540 Research Park Drive, University of Kentucky, Lexington, KY 40511-8410, (606) 257-0224, FAX: (606)-257-0220, e-mail: mcAlister@caer.uky.edu. **Current and recent past issues of Energieia** may be viewed on the CAER Web Page at www.caer.uky.edu. Copyright © 1998, University of Kentucky.



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