

CARBON: THE TOOL OF THE

GODS

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M.S. Akanni

Professor of Chemistry

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An Inaugural Lecture Delivered at Oduduwa Hall, Obafemi Awolowo University Ile Ife Nigeria.

On

Tuesday 25th July 2000

Inaugural Lecture Series 143

Obafemi Awolowo University Press Ltd. Ile Ife, Nigeria.

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ISSN 0189-7845

Printed by
Obafemi Awolowo University Press Limited,
Ile-Ife, Nigeria.

INTRODUCTION

There is a religious event on Ash Wednesday in the Catholic Church that requires a priest to use ashes to make a sign of the cross on the forehead of every congregation member with the pronouncement, "from the dust you were made and to the dust you will return". The Yoruba translation of this is, "erupe ile ni iwo, iwo yio pada di erupe ile". The English version is a bit ambiguous but appears safe as dust can connote ashes, carbon particles or soil dust. Like a conservative Catholic, I believe rigidly in the doctrines of the church and so, do not ask my religious superiors questions about the mysteries of creation. Notwithstanding, I have spent time pondering about the Yoruba version of the Ash Wednesday's pronouncement as Yoruba is quite rich in expression and description of events which should be devoid of ambiguity. The question I had curiously raised is, is man made of silica, that is silicon(IV)oxide which is the chemical name for sand that forms about 95% of the earth crust? Science fiction stories would have us think so, but it is actually unlikely, if not impossible. Rather, over 97% of the mass of human body is constructed from six elements, C, O, H, N, P and S with (H₂O) constituting 65% by mass.

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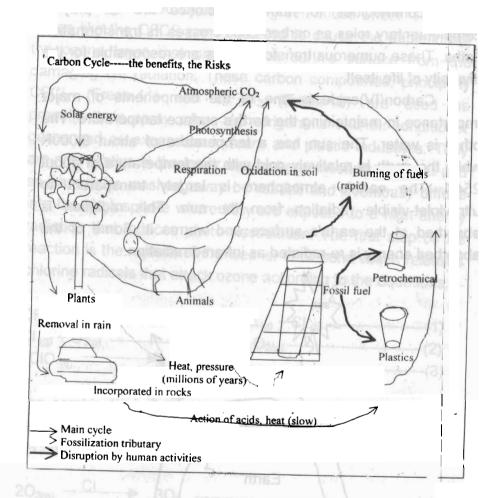
Carbon is the most prevalent by mass in the solid components of cells as carbon atoms are bonded to itself and to H, N, O, S and P. The five next most abundant elements in the body in form of ions are Na⁺, K⁺, Mg⁺, Cl⁻ and Ca²⁺. Calcium ions are necessary for the formation of bones and for the transmission of various signals such as those that trigger contraction of cardiac muscles causing the heart to beat. Fifteen other elements are found in trace quantities. These

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include the first row transition metals (except Sc and Ti), I, Si, F, Sn, As, Se and Mo. So, it can be observed clearly that silicon which constitutes 30.4% of sand is only found in trace amount in the body. Therefore, all living systems grow and reproduce on the earth, move gracefully in the ocean and float effortlessly in air and all are composed of compounds which include carbon as the central character and is the element implicated as the basis of the molecules of life.

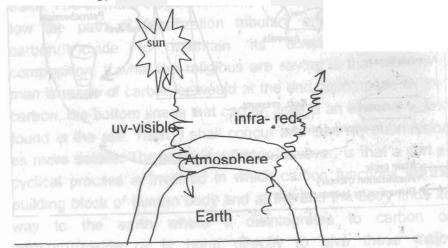
Dead bodies return to the earth differently in different places. In some Asian countries corpses are incinerated in a process known as cremation. The major products of such combustion are likely to be carbon, carbon(IV)oxide, some inorganic oxides and water. In places where tradition, time and land space permit the dead to be buried, there is the tendency to claim the absolute validity of the biblical injunction aforementioned because, at least, the body has returned to the earth. The ultimate stage however, is that the body will decay to tow the path of fossilization tributary and thus contribute carbon(IV)oxide to maintain its constant atmospheric composition. If what the religious are saying is that whether a man is made of carbon or would at the end decompose to give carbon, the bottom line is that carbon itself is an element that is found in the soil. Then, I shall concur and take my submission as mere details. The important factor however, is that a sort of cyclical process is involved in which carbon functions as the building block of human body and at the end the body finds its way to the earth where it disintegrates to carbon or carbon(IV)oxide or is burnt directly to give these major products. This cyclical process and some other natural phenomena gave birth to the carbon cycle in which

carbon(IV)oxide plays a central role in providing a vital link between the various carbon compounds such that carbon atoms are cycled through the ecosystems.



The composition of atmospheric carbon(IV)oxide stands approximately constant at 0.03% by volume. The various routes by which the natural balance of liberation and consumption of carbon(IV)oxide are maintained bring about the convergence of the entire Universe. The sun, the earth, water and air which are critical commodities to human existence are all playing complementary roles as carbon criss-crosses its transformation paths. These numerous transformations are responsible for the diversity of life itself.

Carbon(IV)oxide is one of the components of major importance in maintaining the earth's surface temperature. The other is water. The sun has a temperature of about 6,000K while the earth is relatively cold with the temperature of about 254K. The earth's atmosphere is largely transparent to ultraviolet-visible radiation from the sun. This radiation is absorbed at the earth's surface and warms it. Some of the absorbed energy is re-radiated as infrared radiation.



Certain atmospheric gases like carbon(IV)oxide, methane,

The combination of (2) and (3) forms a cycle for the chlorine radical catalysed decomposition of ozone to oxygen.

The rate of ozone depletion, $r = k[Cl.][O_3]$ shown by equation (2), increases linearly with chlorine radical and has a

rate constant of 7.2 x 109 dm3 mol-1 s-1 at 298K and so, the higher the CFCS in the atmosphere, the higher the ożone depletion and the greater the green-house effect. The Montreal protocol ratified by the U.S. Senate in 1988 and the Helsinki Declaration signed by 82 nations in 1989 pledged to phase out the use of CFCS by the year 2000 purely to eliminate or alleviate the environmental risks associated with these gases. However, the commercial significance of CFCS has subtly frustrated the implementation of this decision as the follow up meeting of November 1998 in Buenos Aires, Argentina decided to cut back on green-house gas emission by only 5% over the next ten years. The decision for low cut was taken despite the fact that the meeting implicated global warming as the cause of increased mosquito activities resulting in increased drug Global warming is resistant malaria parasites across Africa. also said to be the cause of increased waves, floods and tornadoes across the north and central America.

Carbon(IV)oxide is not considered an air pollutant because it is essentially non-toxic and remains fairly constant from the last ice age some 10,000 years ago until roughly the beginning of industrial revolution 300 years ago. Since that time the concentration of CO₂ has increased by about 25% and is now close to 360 ppm. This increase which emanates from slash-and-burn bushes, the solar radiation and the burning of all carbon-containing fuels (wood, coal, natural gas, gasoline etc) is responsible for the observed increase in the average global air temperature of 0.3 to 0.6 °C over the last century, 1880-1980. Computer prediction has estimated CO₂ level to double from its present value between 2050-2100 with a consequence of global temperature increase of 1.5 to 4.5 °C.

Such increase is expected to trigger a major change in the climate of the planet and humanity that has acquired the potential of changing the concentration of CO2 and other heattrapping gases will be the main victim of the disruption of the natural carbon cycle. Clearly then, man must weigh the costs versus the benefits of his action. Two phenomena may precipitate the predicted climatic change. On one hand, global warming could lead to the increased evaporation of water and increased cloud formation. Such increased cloud cover could reduce the amount of solar radiation reaching the earth's surface with the attendant cooling effect. On the other hand, a rise in the mean sea level brought about by thermal expansion of seawater and increased melting of polar ice caps could raise the sea level higher with profound effects on coastal cities and possibly a capture of significant land mass to tilt the existing 3:1 sea-land ratio and consequently alter the ecosystem.

A discussion on the importance of carbon(IV)oxide will be incomplete without reference to its role in photosynthesis which supports all life on this planet. The process takes place in a green plant as shown by the equation,

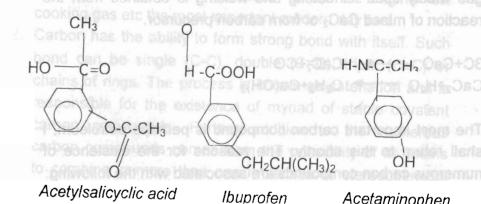
$$CO_2 + H_2O$$
 hv $^{1}/_{\mathbb{R}}(CH_2O)_n + O_2$, where

 $(CH_2O)_n$ denotes carbohydrate. The mediator for this reaction is the chlorophyll molecule which absorbs in the infrared region of light, $\lambda = 680$ nm. At this wavelength, a mole of light quantal is about 176 kJ. Photosynthesis is a reverse of respiration or combustion and about 630 kJ of energy is required. Thus the above equation is oversimplified and a multi-step is involved. The active unit in the plant cell, the chloroplast contains

stacked chlorophyll which funnel activation energy or electrons to a central site of the actual reaction. The current accepted mechanism, proposed by Melvin Calvin (Nobel Prize, 1961), involves about 100 sequential steps for the conversion of 6 moles of CO₂ to 1 mole of glucose. The other oxide of carbon, carbon monoxide enters the atmosphere mainly through the incomplete combustion of carbon or carbon-containing compounds. Carbon monoxide is an air pollutant and an inhalation poison because CO molecules bond to iron atoms in haemoglobin in blood and displace oxygen molecules that the haemoglobin normally carries. Thus toxic amount of CO can cause death by oxygen deprivation.

With the story so far, the pertinent question to raise is, what makes carbon unique among its electronic family of silicon, germanium, tin, lead and the other metal and non-metal congeners? The number of carbon compounds whose formulae are known to chemists was recently estimated and stands at about two and half millions. This figure outnumbers the known compounds of the rest 104 or more elements in the Periodic Table. Organic or carbon compounds are central to our lives. Hydrocarbons are used as fuel to power our vehicles and to heat our homes. Our bodies are fuelled with food in form of sugars, fats and proteins. The food is made palatable by organic flavouring, is wrapped in organic plastic and is kept from spoiling with organic preservatives (e.g. sodium benzoate). Our clothes are made of carbon containing compounds and the fabric is made colourful with organic dyes. One of the crucial roles of carbon is its involvement in the synthesis of new compounds with known structures and accurately predictable properties. Hence carbon is found in

high composition in drugs, anaesthetics and pesticides. For example, one of the earliest pain-killers was 2-hydroxybenzoic acid (salicylic acid). This acid was found to irritate patient's mouth, stomach and in severe cases, cause internal bleeding. In 1899, Hofmann, a German Chemist synthesised the ethanoyl (acetyl) derivative of salicylic acid which is equally therapeutic but less toxic. The trade name is aspirin and is still used today as antipyretic (fever-reducing) and analgesic (pain-releasing). Some common aspirin substitutes, ibuprofen and acetaminophen later came up.



Acetaminophen is the active ingredient in tylenol and datrin while ibuprofen performs the same function in advil and nupril. Some other common drugs like codeine that suppresses cough, diazepam (valium) that calms the nerves are carbon chemicals.

Three of the most important early anaesthetics were dinitrogen oxide, N_2O , ethoxyethane, $C_2H_5OC_2H_5$ and chloroform, $CHCl_3$. Nitrous oxide is non-toxic and non-flammable but it produces light anaesthesia. It is still used

effective anaesthetics but it is highly flammable and hence dangerous. Chloroform produces deep anaesthesia and is non-flammable but it is toxic and carries the risk of liver damage through the inducement of cancer growth. These problems led ICI in 1951 to begin a search for an ideal anaesthetics and in 1956, a carbon compound, F₃C-CHCIBr (2-bromo,2-chloro,1,1,1-trifluoroethane) was found and is in widespread use in hospitals today. Many petrochemicals, especially aromatics such as naphthalene, benzene, phenol, cresol, toluene, xylene etc are by-products of soft coal. Acetylene, a gas widely used for cutting and welding is obtained from the reaction of mined CaC₂ or from carbon precursor.

$$3C+CaO \longrightarrow CaC_2+CO$$
 $CaC_2+H_2O \longrightarrow C_2H_2+Ca(OH)_2$

The most important carbon compound is perhaps petroleum, I shall return to this shortly. The reasons for the existence of numerous carbon compounds are associated with the following:

1. The electronic configuration of carbon is, 1S² 2S² 2P². The 1S² is a closed inactive doublet while electrons in the 2S and 2P orbitals can undergo hybridization to produce four orbitals of equivalent energy required for bonding that conforms with the octet configuration. Thus carbon has no accessible low-lying d-orbital, no lone-pair of electrons and so cannot expand its co-ordination shell beyond four. Hence most carbon compounds are out of the orbit of the terror of corrosion by aggressive moist air in an hydrolytic-oxidative processes. Though many carbon compounds, especially the

hydrocarbons, are energetically unstable with respect to their oxidation products (CO₂ and H₂O) upon combustion at a high temperature, the high activation energy required for such oxidation reactions cannot be compensated for by the slight thermal provocations at the ordinary conditions. The consequence of this is that many carbon compounds are thermodynamically unstable but kinetically stable. The importance of this stability to society is that many hydrocarbons can be stored and the energy of their oxidation released as and when required. This makes hydrocarbon products, gasoline, kerosene, engine oil, cooking gas etc the most important modern day fuel.

2. Carbon has the ability to form strong bond with itself. Such bond can be single (C-C), double (C=C), triple (C=C) of chains of rings. The process is known as catenation and is responsible for the existence of myriad of stable covalent carbon compounds. Further addition to the numerous carbon compounds comes from the possibility of its atoms to combine in more than one molecular or stereochemical pattern (isomers) and for carbon to form stable covalent bonds to a large number of other atoms resulting into compounds of different functional groups. Two crystalline allotropes (phenomenon of the same element existing in different forms or shapes) of carbon are known. These are diamond and graphite. In addition, other forms of carbon, useful in various industrial processes, exist. They are known collectively as amorphous non-crystalline carbon and include animal, wood, sugar and gas charcoals, lampblack, coke and soot. Its common isotope is the naturally occurring radioactive carbon-14. This radiocarbon is brought about by |

the bombardment of atoms in the atmosphere by cosmic radiation to produce sub-atomic particles including neutrons. These neutrons then react with the nitrogen atoms in the atmosphere in a transmutation process to produce carbon-14.

$$^{14}N_7 + ^{1}n_0$$
 $^{14}C_6 + ^{1}H_1$ The rate at which carbon-14 is being formed is the same

with the rate at

which it is disintegrating to nitrogen by the emission of beta particle.

$$^{14}C_6$$
 $^{14}N_7 + {}^{\circ}\beta_{-1}$

Thus the simultaneous formation and decay ensure the constant concentration of carbon-14 in form of its oxide, ¹⁴CO₂ at about 6% in the atmosphere. The ¹⁴C-isotope has a half-life of 5,700 years and enters into the carbon cycle so that all living matters are to some extent radioactive and maintain a constant proportion of radiocarbon as a result of natural exchange process. When an animal or a plant dies, the renewal of carbon-14 ceases but the decay continues. Thus, by measuring the amount of radioactivity of any organic material, it is possible to estimate the time which has elapsed since it ceased to participate in the carbon cycle exchanges. This has been the valuable and scintillating method for dating organic remains and archaeological excavations. Mr. Vice-Chancellor sir, I now wish to focus the discussion on my work on carbon compounds.

During the chemistry experiment in my first year in H.S.C. in 1970, we ran out of soap for washing glassware in the laboratory. I innocently dashed to the school kitchen, collected some quantity of vegetable oil and heated it with the laboratory sodium hydroxide in a beaker. Upon cooling, the resulting content solidified and was used to wash our glassware. It foamed fairly well but contained the by-product, glycerol as impurity which was not removed. Little did I know in 1970 that I had unconsciously begun my work in the area of the exciting system called metal carboxylates, otherwise known as soaps. Six years after, as a postgraduate student, I started research into the properties of metal carboxylates. My doctoral thesis was written on the system and sixteen of my published articles were on the properties of soaps.

Metal carboxylates are salts of long chain organic acids. The organic acids of my interest are the relatively cheap even chain length (compared to odd chain length) acids from the dodecanoic acid, C₁₂ to octadecanoic acid, C₁₈. The carbon contents in these acids stand at the lowest of 72.0% in dodecanoic acid to 76.1% in octadecanoic acid. Thus carbon forms the preponderant composition of the material involved in my research and it is my long usage of carbon compounds that triggered the choice of my topic for this lecture.

Soaps have long history of existence. It was believed that soap production was first carried out during the ancient civilization around the Mediterranean Sea. The Phoenicians were among the early producers and around 600 BC they used soaps as articles of barter with the Gauls. They took

soaps to the south of France from where it spread to Spain, Italy and Germany. Cair Museum reported around 1400 BC that the deposits taken from the axle of a chariot contained quartz, iron and a sufficient quantity of fat and lime from which lime soap was produced. After the fall of Rome, the history of soap temporarily got lost until 1758 when Macquer proposed that metallic soap could be produced by combining oil with lead metal. Pratt, between 1879 and 1882, patented soaps such as lead and manganese linoleates by dissolving the metals in linseed oil to produce liquid paint dryers. Cobalt soaps were produced around 1901 while naphthenic acid soaps were produced for sale in 1925. Africa was not entirely left out while soap production was spreading in Europe. The shortage of cheap raw materials for the soap industries in Europe led Lever Brothers Limited to develop palm oil and coconut tree plantations in the Solomon Islands (South Pacific) and Belgian Congo very early in this century. On the home front, the Yorubas and Binis are known for long to be engaged in soap industry on a small scale. The traditional soap bears various names depending on the locality. Thus in Ekiti, Ondo and Kwara states, the soap is known as "ose dudu" (black soap) or "ose abuwe" (bathing soap), in Oyo town, it is called "ose oyo" while in Ago-Iwoye, Ogun state, it its referred to as "ose ago". The colour of all the soaps in these areas is either dark gray or black due to thermal decomposition arising from excessive heating during preparations. Prior to the advent of detergents and soap tablets, the Nigerian traditional soaps were widely used for bathing and washing and it was believed that the were among the early producer soaps have medicinal efficacy.

Saponification, which is one of the oldest chemical

processes, is the method employed in the Nigerian traditional society for soap production. Certain plants are cut, dried and burnt to ashes in air. The plants commonly used include palm kernel bunch, cocoa pods and unripe banana or plantain stems. The ash so obtained is wrapped in some fabrics or cloth and soaked in water. The fabrics is then squeezed for a clear solution to ooze out. In most cases the ashes contain a high percentage of the salts of alkali metal especially the carbonates which on addition of water give basic solutions of the metals.

Akanni and Ogugbuaja (1985) confirmed the high composition of the alkali metals from the result of their study on the major, work and trace elements in Nigerian traditional soaps obtained from different locations across the country using the method of Instrumental Neutron Activation Analysis, INAA. The work revealed potassium to be thirty times higher in composition than the closest element in all the soaps sampled. Thus the soaps derive their soft and creamy physical state from the high potassium content. It is a common practice to evaporate the clear ash solution to obtain a concentrated solution prior to boiling it with palm oil or palm kernel oil. The mixture is vigorously stirred until it starts to foam indicating the formation of soap. In most cases cassava flowers or other starchy materials are added to serve as builders. Garet (1972) reported this procedure in his book titled, Surface and Active Chemicals, in which he stated that the early preparation of soaps entailed the heating of goat tallow and wood ash, the product of which was salted out using edible salt. It is noteworthy that the raw materials employed in the manufacture of soaps

natural fats and oils and the fatty acids from them are present as triglycerides of aliphatic carboxylic acid. The common names of many of these carboxylic or fatty acids clearly indicate their natural product origin. Thus palmitic acid, CH₃(CH₂)₁₄COOH is present as its glyceride at about 35-40% of palm kernel oil. The preparation of Nigerian traditional soaps and in fact any soap follows a simple chemical reaction of the type,

Glycerol, the by-product is used extensively in the manufacture of cosmetics, foodstuff, plastics and anti freeze agents. The principal fats and oils used in most commercial houses are grouped according to their properties.

- 1. Tallow, grease and Palm Oil. These contain primarily an ester of stearic acid. They can be saponified by weak alkali solutions to yield firm soaps that can be easily salted out with 7-10% salt. The soaps have low solubility in water but give persistent lather.
- Coconut and Palm kernel Oils. They contain a large proportion of low molecular weight acids like lauric acid (ca 50%). So, they require much alkali, release much

- glycerol (12%) and give high yields of white, hard and brittle soaps that foam quickly and profusely but the lather is unstable with fresh and salt water.
- Olive, Cottonseed, Corn and Peanut Oils. These are non-drying and semi-drying oils. They are saponified by moderate concentration of alkalis to produce toilet soaps like castile soaps. The soaps are very soluble in water because they contain a high percentage of oleic acid (70-85%). They give a thin but abundant latter and have good detergent power. The yield of glycerol by them is about 10%.
- 4. Linseed and Soyabean Oils. These are drying oils and are rich in unsaturation. They give very soluble soaps with rich lather but the soaps are sticky and the lather is greasy. Hard soaps (using caustic soda) made from them become dark with time and easily develop a bad smell.
- 5. Hardened Oils. These are hard fats unsuitable for soap preparation. They can be hydrogenated to give hard fats similar to tallow. The soaps produced from the hydrogenated product are hard, insoluble in water and do not lather well. Yet, hardened fats are often added to other oils and fats to enhance the consistency of their soaps.
- 6. Castor and Rape Oils. They contain ricinoleic acid, the soap of which is difficult to salt out. Rape oil contains crucic acid which is extremely sensitive to electrolytes. These oils are only useful upon addition to other oils. Castor oil enhances the transparency of soaps.

The difference in the traditional and modern commercial

method of soap preparation is small and can be regarded as merely a degree of improvement. Today, many Nigerians are engaged in soap industry, the small-scale venture outnumbers the big commercial companies and so, the method of preparation should be allowed to bear repetition such that the evolved minor modification can be brought to focus. Perhaps in so doing some individuals in this audience may take home a profession in making soaps of high quality.

Fats or oils and the required quantity of alkalis are passed through a mixer into a soap pan, an open tank with a capacity of about 5000kg and boiled together with steam for several hours. Mixing is usually done rapidly between 15 to 30 minutes and the temperature is commonly kept under 70°C. Glycerin (glycerol) is removed by boiling the soap mixture with a large quantity of hot brine of controlled strength. Glycerin dissolves in salt water forming lye with a layer of soap curd on top. The glycerin is run off and the curd is boiled with a measured amount of water to give a desired degree of hydration. It is then cooled to remove excess salt from it. The soap is skimmed off and perfumes, dyes and disinfectants may be added prior to pumping for conversion into tablets, flakes or powders. Floating soaps have air beaten into them as they solidify. A hard soap contains a high percentage of sodium. A soft or liquid soap is obtainable by saponification with potassium hydroxide, with the liquidity increasing as the carbon chain of the fatty acid decreases. Ammonium soaps are commonly found in the liquid state.

General Properties of Soaps

The principal use of all washing soaps is to remove dirt. Dirt has been defined as matter in the wrong place. For instance, fried sausage is a delicacy but the oil of it in one's shirt constitutes dirt. Some soaps are associated with specific uses. For example, a strong solution of soft soap like potassium oleate in alcohol (2 parts in 3) is used as a liquid shampoo for cleansing the skin and hair. Many antiseptic or germicide or generally disinfectant soaps are now common in the market. They are domestic soaps impregnated with chemicals such as phenol, cresol and formaldehyde. Boracic soaps are used to free the skin from freckles, blackheads and rheumatic pains. Mercuric chloride (corrosive sublimate) soap is one of the strongest antiseptics, the dilute solution of which can destroy virulent bacilli. It is prepared by grinding 1 part by weight of HgCl₂ (previously dissolved in 8 parts by weight of rectified spirit) to 32 parts by weight of dried and powdered castile soap. Mercuric iodide antiseptic soap normally contains 0¹/₂-3% mercuric iodide. It is prepared by mixing equal parts of Hgl2 and KI and milling the mixture into castile soap. The mercury soaps possess the property of skin etching and hence females intensely and ignorantly apply them for beauty enhancement in a process wrongly coined bleaching. Detergents are particularly powerful dirt removal as the sulphates and hydrogencarbonates of calcium and magnesium implicated as the sources of hardness in natural water, the universal solvent widely employed for washing, have no effect on detergents. The structure of detergents consists of a long oil-soluble hydrophobic and a water-soluble hydrophilic groups. The hydrophilic groups include the sulphate (-OSO₃-), sulphonate

(-SO₃-), hydroxyl (-OH), ammonium (-NH₄⁺) and phosphate [-OPO(OH)₂] groups. The early detergents were mostly sodium dodecyl sulphate prepared from cottonseed or coconut oil. The first step is hydrogenation of oil glyceride followed by esterification of the hydroxyl group using tetraoxosulphate(VI) acid and then neutralization of acidic lauryl hydrogen sulphate with sodium hydroxide. Other common synthetic detergents are sodium alkylbenzenesulphonates. Builders (fillers) such as the carbonates, phosphates, silicates of sodium and rosins often added to detergents give basic solutions that serve to boost the detergency of soaps.

Soaps owe their importance to their ability to modify the surface of the liquids in which they are dissolved. Hence they are classified as surfactants or surface- active agents. Soaps are complex mixtures of the salts of the fatty acids contained in the oils and fats used for their preparations. The main sources of impurity in soaps often come from the inability of most producers, especially the small scale ones to strike a stoichiometric balance of the reactants in the neutralisation process, as the exact glyceride composition in the natural fats and oils they use is not accurately known. A complete removal of glycerol and fillers from soap curds is often not achievable by some soap producers. In addition, soaps usually contain a variable amount of water and a small amount of impurities, inherent in the raw materials, or introduced through the process of manufacture. Thus, most common soaps either contain excess acid [to give acidic soap, $R(CO_2)_nM.RCO_2H$] or base [to give basic soap, $(RCO_2)_y(OH)_xM$] and other impurities which may be sufficiently significant to impair foaming capability and cause irritation or burning of skins.

Generally, potassium soaps are deliquescent while sodium soaps are non-deliquescent. The soaps of saturated fatty acids are crystalline in texture while unsaturated acids produce partly crystalline but somewhat sticky soaps. Potassium soaps are highly soluble in water. Sodium soaps dissolve in hot water but on cooling, the solution becomes turbid due to slight hydrolysis and a fairly strong solution of 1-2% of sodium soaps may cool to give a jelly like mass. Aqueous solutions of soap froth on shaking to give alkaline solution. The alkalinity was previously believed to be due to ionization into the alkali and acid ions. The ions then interact with water to give the hydroxides and weakly dissociating organic acids, which are insoluble in water and thus appear as turbidity in dilute cold solution. McBain disputed this theory and affirmed that the turbidity was due to the formation of an acid salt according to the equation,

2RCOONa + H₂O RCOONa.RCOOH + NaOH

It was found that one part of neutral sodium stearate in 2000-3000 parts of boiling water would yield an acid soap and that sodium oleate and lower fatty acid soaps require a larger quantity of water and lower temperature before hydrolysis is initiated. The technical importance of this behaviour is that soaps of the solids, high molecular weight fatty acids have little washing power in cold water while those of liquid fatty acids, as well as the lower molecular weight acids have high lathering and cleansing power in cold water. Thus, the number of carbon atoms in a fatty acid is of critical importance in determining whether or not its salt will exhibit a soapy property. Soap-like properties begin to appear in a salt with the aliphatic chain of eight carbon atoms even though soaps of carbon atoms

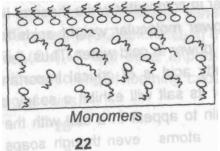
between eight and twelve are irritant to the skin. This is because the paraffin chains in them are too weak to counterbalance the strong polar action of the hydrophilic head group. At the other extreme, soaps with the carbon atoms higher than twenty are too insoluble and are not useful. Thus the optimum carbon range, for practical purposes of usefulness of soaps, is between twelve and eighteen carbon atoms.

The surface tension, at ordinary temperature, of the aqueous solutions of most soaps is much less than that of water. Soaps of unsaturated acids are most powerful reductants of surface tension, followed by those of *lauric*, myristic and palmitic acids. Soaps of higher paraffin chains such as arachidic, behenic (C₂₂), legnoceric acids, etc yield insoluble sodium salts and thus do not affect the surface tension of water.

The electrical conductance measurements have given deeper insight into the mode of aggregation of soap solutions. A typical study has shown that the conductance of many soap solutions decreases to a minimum for about 0.1 mol dm⁻³ and increases with the concentration up to about 1.0 mol dm⁻³. This behaviour was interpreted to be due to three states of aggregation interchangeable according to the following conditions.

1 Soap molecules exist as dissociated monomers in dilute

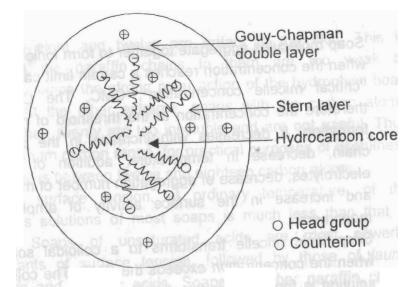
solutions.



Soap molecules aggregate together to form ionic micelle when the concentration reaches a certain limit called the "critical micelle concentration", CMC. The CMC is therefore the concentration at the threshold of micellar formation. It decreases with increase in the paraffin chain, decrease in temperature, addition of strong electrolytes, decrease of aggregation number of micelles and increase in the surface activity of amphiphilic monomers.

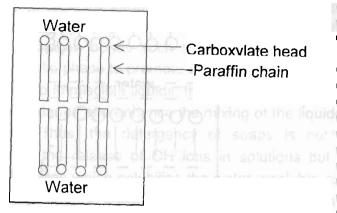
3. Soap ionic micelle transforms to a colloidal solution when the concentration exceeds the CMC. The colloidal solution is formed from the dispersed particles with a diameter of about 450 millimicrons.

The ionic micelle is believed to consists of about 10 monomers or molecules which subsequently increases to about 50 with increase in concentration. These numbers are known as the aggregation numbers. The aggregation number for ionic soaps is generally less than that of non-ionic soaps because the electrostatic repulsion between the ionic head groups is greater than the steric repulsion between the non-ionic head groups. Addition of salts usually increase the aggregation number in response to a decrease of the CMC. Hartley painted the picture of a micellar aggregate as roughly spherical.



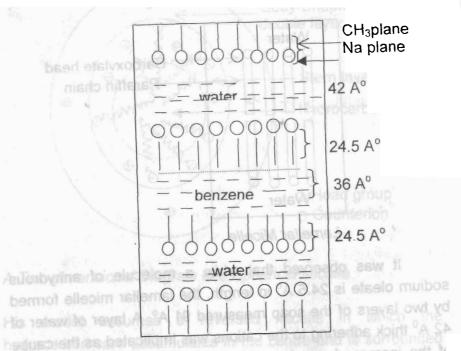
A Two-dimensional Diagram of a Spherical Micelle

His model assumes a reversed micelle in which the hydrocarbon core accumulates in the centre and is surrounded by a compact Stern layer which contains the polar heads, water and more than half of the positive electric charge or counterions called the ionic cloud or ionic atmosphere. The Gouy-Chapman double layer is next to the Stern layer and it contains water and the remaining counter-ions. The number of such ions is dependent on the number of aggregating molecules in each micelle. McBain employed the evidence of X-ray analysis to propose a lamellar structure for a micelle. His model consists of molecules arranged in double layers with the hydrocarbon chains oriented towards each other while the polar groups projected outwards. X-ray data revealed that the micelles seem to have a thickness of four or more of the double layers.



Lamellar Micelle

It was observed that while a molecule of anhydrous sodium oleate is 24.5 $\ensuremath{\text{A}^{\circ}}$ in length, the lamellar micelle formed by two layers of the soap measured 91 Ao. A layer of water of 42 A⁰ thick adhering to the cations was implicated as the cause of the increased spacing. Upon addition of benzene, sodium oleate appeared to dissolve in it but a closer observation revealed that the lamellar micelle actually expanded to accommodate the benzene between the paraffin ends of the soap molecules such that the X-ray spacing increased to 127 A°. However, the lamellar micellar theory has been faulted on the premium that such a structure could only exist in concentrated solution (ca 10%) in which thermal agitation that could disrupt aggregation is minimal and in which X-ray data are more meaningful. Various structures had since been proposed that ranged from cylindrical, disc shape, rod shape to ellipsoidal structure.



Micelle of Sodium Oleate in Water and Solubilized Benzene

Modern theory relates the surface activity of soaps to the specific molecular structure of the higher fatty acids composed of 12 to 20 carbon atoms. Upon reacting such an acid with a base, an amphiphile with the duality of the lypophilic and hydrophilic properties is produced. When the amphiphile is in a mixture of water and oil, it will station itself at the boundary layer, the interface between the two liquids and orientate the salt group to mix with water and the hydrocarbon tail to embed in the oil. Such operation at the interface naturally tends to interrupt the surface energy and is commonly referred to as the surface tension. If the two phases involved are a liquid and a

gas, the disturbance of the interface will produce foaming. If the phases are a solid and a liquid, weakening of the film will break some of the hydrogen bonds such that water molecules are adhered to the solid phase to promote wetting of the solid. If the case is that of two immiscible liquids, the disturbance will break the surface boundaries and enhance the mixing of the liquids to form emulsion. Thus, the detergency of soaps is not the consequence of the release of OH ions in solutions but the formation of micelles which solubilise the water insoluble oil or grease. Several factors collaborate in such mechanism of detergency. The first step in the removal of a thin film of oil or grease from a fabric is the wetting of the surface by the detergent solution such that the oily film is dislodged in the form of minute droplets. The second step is the solubilization or emulsification (if large) of the droplets in the micelle. The last step is the dispersion (dragged away) of the captured prey (the dirt) and the captor (the paraffin tail) by the hydrophilic portion of the detergent aided by the mobile water phase

The soaps discussed so far are those of group I elements, particularly sodium and potassium, they are highly soluble in water and are used purely for washing purposes. There is another class called the heavy metal non-washing soaps. They are insoluble in water but soluble in organic solvents. This class of soaps has been the main focus of my research interest because of the way they arrange themselves internally to compensate for their dual hydrophobic and hydrophilic properties. Besides, non-washing soaps have enormous industrial and technological applications such as:

Fungicide and Herbicide

Many non-washing soaps are soluble in organic solvents and hence they are useful in stabilizing some industrial chemical processes such as in fungicide preparation and as emulsifying agents in the polymerisation of paints. For example, fungicides of copper carboxylates are used for timber protection while those of zinc carboxylates are used in the treatment of athlete's foot. Mercuric ethylstearate in kerosene is used to eradicate certain weeds. Some other fungicidal soaps are used in the treatment of ropes and fishing nets. Some serve as antifouling agents in ship paints.

Dryers, Catalysts and Rubber Formulation

Dryers are compounds used in paint, varnish and printing ink industries to accelerate the change of the liquid oil to elastic solids. Soaps of iron, zinc and copper are used as auxiliary dryers to boost the actions of primary dryers. Lead, cobalt, vanadium and cerium carboxylates easily produce cations in organic solvents which acts as polymerisation catalysts. For example, cobalt naphthenate acts as a catalyst for the air oxidation of toluene to benzoic acid. In rubber industry, lead and zinc carboxylates are used as accelerators and softening agents respectively in the vulcanization of rubber.

Protective Covering

Some metal carboxylates possess low chemical reactivity and fairly high stability to radiation. They therefore exhibit non-corrosive property and are used in the manufacture of protective and decorative coatings to

prevent corrosion. For example, manganese stearate is used for coating sodium bicarbonate to prevent caking in fire extinguisher while manganese naphthenate is used for protecting electro-luminescent phosphorus from deterioration. The non-corrosive nature makes some soaps suitable as fluid reactor fuels. The low solubility of some, like zinc oleate, makes them useful in water-proof fabrics such as papers, mansory concrete and wooling materials.

4 <u>Lubricants</u>

Some soaps are gelling agents. In petroleum and plastic industries, calcium and barium soaps are added to grease to increase its thickening, durability and lubricity. Upon addition to waxes in the manufacture of candles and crayons, soaps are found to increase the melting points and prevent sagging and softening of these materials at high temperatures. Incorporation of some soaps to lead pencils has been found to enhance their lubricity and smoothness.

5. <u>Cosmetics and Pharmaceutics</u>

Some metal carboxylates can be produced in powders of very fine particle size with high smoothness and considerable adherence and water repellency to the skin. Hence zinc and magnesium octadecanoates are used extensively by the cosmetic industries in the preparation of face and body powders. Magnesium octadecanoate in particular is used in preparing water-in-oil emulsions for cosmetic creams and as lubricant and binder for tablet preparations.

Standards, Films and Display Systems

Some applications of metal soaps are associated with their solution properties and the exhibition of mesophases (liquid crystals) or the release of metals or metal oxides upon electrical or thermal heating. Thus solutions of metal (e.g. lanthanum) decanoates. naphthenates, ethylhexanoates and cyclohexybutanoates are frequently used in analytical chemistry as standards for the determination of metal content in organic systems by atomic absorption spectroscopy. Manganese stearate shows highly two-dimensional magnetic properties, either as a powder or Langmuir Blodgett, LB film. The LB multilayer of lead(II) soaps such as the tetradecanoate. are valuable as soft X-ray crystal analysers. Cerium(III) soaps have been used to make photosensitive polymer films. Some carboxylates of indium, aluminium and chromium have been used as precursors to produce high quality epitaxial growth on quartz and glass substrates. These thin films find wide applications in photovoltaic devices for the conversion of solar energy to electricity, in decoration and protection of materials, in conductors, capacitors and resistors in microelectronic circuits, in selective absorbers and heat mirrors, in coating lenses to reduce the amount of reflected light from the surface of lenses and in protecting lenses. Furthermore, many of the metal carboxylates exhibit one or more thermotropic liquid crystalline phases and there is currently a tremendous interest in the applications of such metallic mesogens (metal-containing crystals). At the threshold of phase transition, some

optical phenomena are known to occur which promote reflection and refraction properties. Thus it is common to find liquid crystals being used as pressure and temperature sensors and as components in the display systems such as thermometers, wristwatches, pocket calculators and laptop computers. For example, cholesteric liquid crystals can be described as a flat rod with a flexible tail. In the liquid crystal state the molecules sit side by side in layers. The tail induces a layer to twist relative to the next. The slight motion causes a change in the orientation of successive layers and this imparts colours to the liquid crystals. Changes in temperature and pressure often alter the order of the layers and hence the colour. Thus the liquid crystals of these compounds have been used to monitor temperature and pressure changes in situations where conventional methods are known to have failed. Such are the cases in their uses to detect hot spots in microelectronic circuits, which may signal flaws and as thermometric liquid for measuring the skin temperature of infants.

Soaps of heavy metals are prepared by metathesis in alcohol solutions and purified by recrystallisation in hot suitable organic solvents such as benzene, toluene, hexane, alcohols etc. I had studied over the last twenty years the thermodynamic and transport properties of the decanoates, dodecanoates, tetradecanoates, hexadecanoates and octadecanoates of lead, zinc, cadmium, mercury, manganese, cobalt, nickel, copper and vanadium. A few odd chain length carboxylates of some of

these metals had also been studied. The properties of interest include:

- (i) conductivity, viscosity, molar volume and density of the systems as functions of temperature.
- (ii) decomposition kinetics leading to the **evaluation** of the rate constants and the orders of reactions.
- (iii) identification of the products of pyrolysis leading to the formulation of the mechanism of degradation.
- (iv) evaluation of thermotropic mesomorphic transitions and construction of binary phase diagrams.
- (v) measurement of surface tension leading to the evaluation of atomic parachor.
- (vi) preparation and characterisation of thin oxide films deposited on soda lime glass supports.

This seemingly multidimensional approach had made it possible to establish:

(I) A model for the dissociation mechanism in the organic ionic melts in which upon thermal heating the metal ions are released to carry the major current with little or no contribution to conductance by the carboxylate moiety. e.g.

$$MA_2^- + 2A^-$$

M is a divalent metal and A, the carboxylate anion.

(II) A model for the viscous flow in which 5-6 molecules constitute the micellar unit of flow for the pure molten soaps while the unit is considerably reduced in binary soap-additive mixtures. The presence of an additive often leads to a change in the microscopic structure of

the pure soap. For example, addition of small amount of lead oxide as contaminant perturbed the essentially small spherical structure of the pure soap and changed it to long cylindrical micelles. The unit of flow correspondingly changed from 5-6 in the pure soap to just one molecule at about 0.22 mole fraction of the additive, PbO. Deviations from ideality were observed for some of the mixtures especially at high contaminant compositions and the behaviour was associated to the formation of complexes. Akanni and Burrows (1980), Akanni et al (1982), Akanni and Mbaneme (1986), Akanni and Adeosun (1989).

A model for the degradative pathways in which the initiation step for decomposition is the rupture of the oxygen-metal bond followed simultaneously by the abstraction of β -hydrogen by the carboxylate anion.

Akanni, Begun and Burrows (1984), Akanni, Lambi and Ajayi (1986).

R-CH₂-CH₂-C H H R-CH - CH₂ - C - O

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M + CO₂ + RCH=CH₂ + RCH₂CH₂COOH where M is a divalent metal below hydrogen in the activity series.

In a soap in which M is above hydrogen in the activity series the decomposition should produce a metal oxide and a ketone in place of a metal and an acid obtained in the above scheme.

(IV) A melting behaviour in which the soaps upon heating either pass through a solid-solid transformation or through mesophases before melting to isotropic liquid, i.e.

Solid I Solid II Mesophase Liquid or Solid Liquid

The results of such studies made it possible for the construction of temperature-composition binary phase diagrams in which the region within which a mesophase or liquid crystal is stable was identified. Such phase stability is crucial to the applications of liquid crystals. Adeosun and Akanni (1978), Akanni (1987).

A process for the pyrolytic deposition of thin films on (V) suitable substrates. A thin film does not have a precise definition. In general a thin film has a thickness of about 10⁻⁶ to 10⁻⁴ m and is commonly referred to as the 4th state of matter. A useful thin film should be chemically stable in the environment in which it is to be used. adhere well to the substrate which gives the structural support, have a uniform thickness, be chemically pure or of controlled composition and have a low density of imperfections. Various methods of preparation are known such as vacuum deposition, sputtering, chemical vapour deposition but the one employed by the Ife group is called metal organic chemical vapour deposition, MOCVD. The films obtained from MOCVD technique have comparable purity and consistency as those prepared from the above well documented techniques. Ajayi, Akanni et al (1986), Ajayi, Akanni et al (1990).

In the course of these studies, copious data, the eventual practical benefits of which are rarely predictable, have been contributed to literature on the activation enthalpies and entropies for dissociation, conductance, viscous flow, decomposition and phase transitions. Surface tension data were provided which revealed the dominant role of the hydrophobic chain and the importance of the unsaturation centres in the surfactant actions of metal carboxylates. The surface tension data in combination with the molar volumes are useful for estimating parachors, a property that was first observed by Sugden to be primarily additive and constitutive and was calculated from atomic and bond parachors. Akanni and Burrows (1987). In my effort to link the mechanism of solubility to phase transitions in soaps, two models of solubility were presented. In some solvents the behaviour was consistent with the solubilisation of the mesophases while in others, Krafft type of behaviour was followed where solubility was low up to a certain critical temperature and then increased dramatically at the threshold of micellisation. The overall picture showed that the solvation energy required for the disrupture of the soapsolvent aggregates, formed by the co-ordination of the orbital of the metal ion with the solvent molecules, dictates the type of solubility mechanism. Akanni, Burrows et al (1984), Akanni and Abass (1989).

Mr. Vice-Chancellor sir, I wish to report that the quality of our work in Ife on the chemistry of metal carboxylates is high. Our efforts to date have yielded more than 40 published articles in reputable international journals on this system, 20 out of which I played a key role. Notwithstanding, the quality and quantity would have been improved upon if we had the required tools, encouragement and conducive environment to sustain our seventies and early eighties research efforts. Burrows and Ellis of the Universities of Coimbra, Portugal and West Indies, Kinston, Jamaica respectively took away research into the chemistry of metal carboxylates from Ife. They are doing better than our team at the moment because of the availability of research facilities. I was so impressed by an article sent to me in 1986 authored by Burrows and nine others that I wrote to Burrows, "you have assembled eminent chemists in different branches of chemistry and employed sophisticated machines to produce a research output that is of better quality than our previous work on metal carboxylates". Today the situation is worse than it was in 1986. Chemistry among the basic sciences is wasteful, in the sense that apart from the constantly changing techniques and equipment, most of its needs are consumables. In Physics and Biology, a potentiometer or microscope can still be found functioning after 10 or more years of purchase whereas in Chemistry the tetraoxosulphate(VI) acid and caustic alkali bought today and reacted together to form a salt in a titration experiment are gone for good with the formation of a new chemical compound. Chemistry constitutes a pivot on which all science based disciplines revolve, it is a central science and so, more attention should be focussed on it in terms of allocation of funds. On this front, I shall take a full responsibility of the charge of a biased opinion. However, I shall submit that the argument for more resources for chemistry bears no prejudice to the fact that all science courses require continuous huge capital and if the nation is interested in technology development, it has to invest heavily in science. I shall return to this shortly.

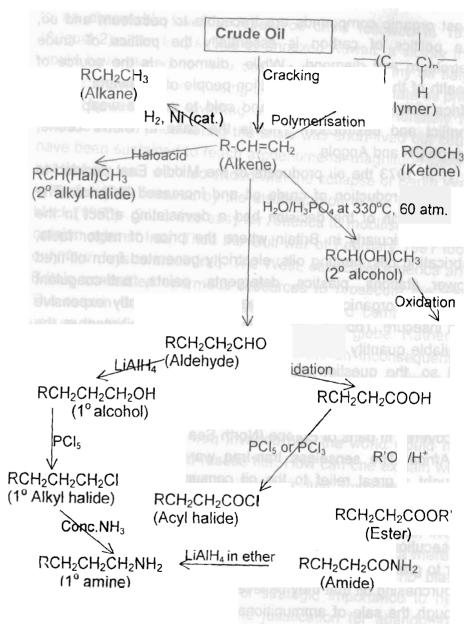
The Politics of Carbon

I have delved briefly into the importance of carbon from the point of view of Chemistry, Biology, Geography, Physics and the Medical Sciences. I shall now endeavour to allude to the politics of carbon. In discussing this, I must confess that I can only claim a lay man's view of international politics since I had no privilege of being tutored in the school of international relations. Notwithstanding, science tends to be methodical and follows established rules for gathering and evaluating information and so, it is a powerful tool for developing an understanding of the natural world, but it cannot analyse international politics. This does not mean that a scientist cannot comment on international politics, the crucial factor is that he should not be regarded as being more knowledgeable on issues in this area just because he is a scientist. He must struggle with the same moral and ethical questions that confront all disciples of international diplomacy and his judgement can be just as faulty as anyone else. So, my comments on the politics of carbon may generate controversy in some circles. They are to be evaluated along the line of a personal opinion and perception of a scholar in the School of Chemistry who is interested in focussing a search light on carbon from all perspectives. This is because this ubiquitous element is a major constituent of many organic compounds of domestic, commercial and chemical importance. A few of the compounds of carbon are products of the fractional distillation

of crude petroleum. The fractions and some of their uses are:

Carbon Atoms	Boiling Point Range °C	Major Uses
1 - 5	0-80	Home heating, cooking and factory fuel.
5 - 7	30-110	Solvents.
6 - 12	40-200	Gasoline for automobile fuel.
12—16	175-275	Jet fuel, kerosene for stoves and lamps.
15—18	250-400	Heating oil, diesel fuel.
18 (and above)	Above 300	Lubricants, waxes, petroleum jelly.
Residue	rot. toot lutiesy	Asphalt, coke etc.

Many compounds are derivatives of one of these fractions or the other. The synthetic routes of some derivatives having crude oil as a precursor are:



Close to 96% of all oils and gases are burnt as fuel while only 4% is used to produce chemicals. Thus virtually all fuels and

most organic compounds are traceable to petroleum and so, the politics of carbon is essentially the politics of crude petroleum and diamond. While diamond is the source of wealth of the one and half million people of Botswana, across Africa diamond it is mined and sold to acquire weapons of conflict and destruction. This is the case in Sierra Leone, Congo DR and Angola.

In 1973 the oil producers of the Middle East decided to cut back production of crude oil and increased its price. The reverberation of the decision had a devastating effect in the West, particularly in Britain where the price of motor fuels, lubricating oils, heating oils, electricity generated from oil-fired power stations, plastics, detergents, paints, anti-coagulant fluids and organic chemicals became significantly expensive and insecure. Though America fell back on her oil reserve, the available quantity could not meet the local consumption alone and so, the question of bailing her allies in Europe out of shortage was out of the card. Thus high oil price lingered on till the tail end of the seventies when new oil fields were discovered in parts of Europe (North Sea Oil in 1979) and more in Africa. The senseless Iran-Iraq war that started in 1979 brought a great relief to the oil consuming countries as the warring factions had to pump more oil, albeit OPEC control of production, to earn more money to procure armaments for the prosecution of the war. The West seized the opportunity of the war to grab back from both countries part of the money wasted in purchasing oil that they believed was priced beyond its value through the sale of ammunitions to both sides to prolong the war. Ironically, the same West turned round to stop the war after the satisfaction that the oil price had reasonably stabilised

to an acceptable level. A repeat oil crisis followed in 1990 (August 2) when Iraq seized or annexed Kuwait, a victory that would have placed her in a position to control many oil fields with the consequence of using the advantage to dictate oil price at will by raising or lowering of production. Unfortunately for Iraq the rise in price during the crisis was short-lived but could have been sustained to reach a phenomenal magnitude were it not that the cold war had ended with the collapse of Berlin Wall in winter 1989 followed by the disintegration of the communist block (1990) . So, it was easy for America to mobilise the world opinion against Iraq. Thus the Gulf-war of February 1991 took only four days to crush Iraq. The West, especially America and Britain committed enormous resources to prosecute the war. The reason was not the supposedly avowed commitment to ensure that Kuwait was not erased from the globe. Rather, it was because the West could not tolerate an inconsequential and erratic government in Iraq to be in a position of switching on and off the button of oil production and be causing fluctuating fortunes for the economy of the entire world. If Kuwait had no oil and Iraq invaded her, the world would not have moved so swiftly to rescue her. How can one explain why America gave up easily in Somalia just immediately she suffered a slight casualty while she stayed on in Saudi Arabia when her military position was bombed and 19 American lives were lost. For the case of the oil rich country, America merely resolved to apprehend the terrorists behind the bomb blast claiming that Saudi Arabia is of strategic importance to her interest in the Middle East. The justification for abandoning Somalia is that the country had no central government and therefore the level of chaos was beyond anybody's control. It

can be argued that oil was not involved when the West pounced on Yugoslavia and bombed the country for 80 days between April and June 1999. The Yugoslavia-Kosovo issue was a clear example of the West inconsistency in response to crisis in the troubled spots across the globe and the American President associated it to a special NATO interest in Kosovo. The oil field in Angola did not allow for a clear decision. Despite the ravaging war, the West could not abandon Angola completely because of their nationals prospecting for oil. Thus pressure was put on the warring factions to engage in murky cease- fires and peace accords while the West switched sides as events unfolded. It will be recalled that America supported Portugal against the Angolan nationalists during the war of independence. As soon as independence was gained, America supported UNITA to destabilise the new nation. Savimbi was not a winner and so, the West changed his status from a freedom fighter to a warlord. Consequently, support was switched to MPLA government that controls the oil fields. In August 1997 a French company discovered a large quantity of off-shore (Caspian Sea) oil in Angola which is more exciting than anywhere in the world. Peace is not too crucial in Angola for the drilling of oil in the location as the America Exxon and the French Chevron oil companies are actively lifting crude oil while the war rages on. It is expected that production in the next five years would exceed two million barrels a day. The United Nations finally pulled out its peace mission in Angola in failure on March 15, 1999 and inspite of the pull out the war has not disrupted the shipment of 7% oil need which America gets from Angola.

The Algeria situation is close to that of Angola where it is believed that the oil wealth is the factor that has intimidated the Human Right defenders from violating the integrity of Algeria by issuing caustic remarks on the civil-gorilla war in the country. While the killing of innocent citizen in the most bizarre manner was going on in all towns and villages unabated, the locations of the oil fields enjoyed relative peace and stability sufficient to keep the oil workers in the field. However, an effort was made in July 1998 by the international community to send a peace mission to Algeria after more than five years of unrest. The mission returned to base with no solution to the crisis. The civil war in Sudan started in 1983 and has raged on since then with no serious effort by the world powers to stop it. Although Sudan was an ally of the West during the cold war, she was of little economic interest to the block as her main export to the U.S.A., Gum Arabic is insignificant in value to oil. This would explain the ease with which America imposed a comprehensive economic sanction on Sudan in 1997 giving a flimsy excuse that Sudan engaged in terrorism, the magnitude of which was perceived to be on a low scale in comparison to what obtains in Gaddafi's Libya. An oil refinery was commissioned in Sudan on June 30, 1999 and the first shipment of crude oil was exported (through the port of Bassai on the Red Sea) from Sudan to Singapore on August 30, 1999. Sudan is now in a position to export about 150,000 barrel of crude oil daily with a reserve of about 800 million barrels. It will be interesting to observe from now on, how the international politics plays out towards Sudan and the oil money may as well be a potent factor for changing the dynamics of the war in favour of Kartoun Islamic government. Libya was declared a terrorist state by the

Reagan administration in 1982 but the process of sanitising and isolating her had to await the cessation of the East-West pendulum of confrontation. For instance, it was alleged that Libya sponsored the bombing of a discotheque in Germany in 1986 where two American service men died. The prosecution of this event was embarked upon eleven years (1997) after because it was envisaged that no useful result would be achieved as long as the Berlin Wall separated Germany. This is because the vital information on the case could only be retrieved from the security outfit of the former East Germany. In a similar circumstance, France in 1999 indicted six Libyans of been responsible for the blown off of the Air France 772 flying across the Saharan Desert in 1989. Libya in July 1999 dramatically conceded to the indictment and paid millions of dollars in compensation to the families of the victims of the air crash. In April 1992 the decision was tabled to impose a flight embargo on Libya over the Lockerby, Scotland bombing of Panam plane103 in which 270 people died in December 1988. Libya refused to hand over the two suspects of the plane crash for trial and sustained her position for ten years. However, on April 5, 1999 Libya bowed to pressure from his friends, South African, Nelson Mandela and the Saudi Arabia monarch and handed over the suspects to the United Nations authority for transportation to the Netherlands. Iran is now being suspected as the architect of the crash. It is commendable that Libya did not succumb to threats by America and Britain for the seven able to stay afloat, years of the UN sanction. Sh tantalising the big powers as her enormous oil wealth made it difficult for her economy to be easily ruined. Actually some European countries like Italy, Belgium and Spain continued to prospect for oil during the period of the flight embargo. Recently (1997) strong ties started between America and Azerbaijan because of the huge quantity of oil discovered in this former USSR enclave. Unfortunately, by December 1998 there was already a dwindling interest in Japan and the U.S.A. because the oil wells sunk into the Azerbaijan shore of the Caspian Sea were not yielding the expected quantity of oil.

The four months-carnage between June 5 and October 18, 1997 in Congo Brazzaville had the undertone of oil politics. General Denis Sassou Nguesso was known to have made a generous oil deal with the French oil company, ELF when he was the head of government. His successor, Pascal Lissouba invited the American oil company, Ossy to the country, a move that infuriated France. When war broke out France tacitly supported Nguesso and ELF gave him material resources close to \$150 million. With this strong support (Nguesso denied receiving any sort of help from ELF two months after the war) and the help of Angola, Nguesso private militia called 'Cobra' defeated the Congo National Army. Like all the troubled spots in Africa where oil is found, Congo Brazzaville was reduced to rubbles during the war. The location of the oil field where the French company was prospecting for oil did not taste the bitter pills of the war and lifting of oil continued throughout the period of the war. For reasons predicated purely on strengthening internal security at home through a friendly neighbour, the Angola troops that came to assist Nguesso capture the oil rich city of Pointe Noire, the second largest city in Congo, behaved like typical Africans and compounded people's suffering by massively looting their properties. Equatorial Guinea was a colony of Spain and up till the eighties the Spanish influence

was visible everywhere in the country. The Americans and South Africans have now almost displaced the Spaniards following the recent discovery of oil fields and the 'golden liquid' has suddenly transformed Equatorial Guinea to a regional leader. She was the architect of the meeting of the Central Africa Economic Community, the inaugural meeting of which she hosted in Malabo on June 24. 1999

The role of the Organisation of Oil Producing and Exporting Countries, OPEC in dealing with crisis where petroleum interest is involved is quite amusing. OPEC seems to have a silent unwritten agreement that borders on bizarre diplomacy. The organisation rarely opposes or supports member nations on global issues. Apart from meeting to deliberate on oil quota allocation to members for natural constraint to dictate the price or for the big buyers to manipulate the price, members are of little or no political and economic interest to each other. For instance, it was intensely rumoured in 1984 that Saudi Arabia would bail Nigeria out of economic depression by giving a huge soft loan to the Buhari-Idiagbon administration. The cookie was said to have crumbled following the warning by America that Saudi Arabia should not circumvent the efforts of the International Monetary Fund, IMF, the body saddled with the responsibility of administering healing pills to nations in deep economic crisis. The frustration of the failure of this purported Saudi Arabia assistance was probably responsible for the rush of the Nigerian government at the time to strike a primitive and outdated deal of trade by barter which involved the exchange of oil for goods. Radio Kudirat reported on September 7, 1999 that the Babangida administration continued the barter policy and exchanged crude

oil at \$10.00 a barrel for the execution of projects at a time crude oil was being sold at \$19.00 a barrel in the world market Nigeria and Cameroon had for long barked at each other in the oil rich Bakassi Peninsula, they had bitten each other twice or more in what could be described as mere skirmishes. Perhaps Cameroon would not have stretched her lean resources to engage a bigger nation in an open confrontation that could lead to a full scale war if the controversial Bakassi Peninsula was just a piece of open grassland where massive aid is required for the inhabitants to feed and survive. After all, there was no serious conflict over the Peninsula between the two countries prior to the discovery of oil. It is also inconceivable if France would want to support the liberation of a piece of land, far away from home, just to secure it and thereafter channel enormous resources to develop it without the prospect of a good return. This view is strengthened by the refusal of France to accept the offer of Anjouan and Moheli Islands when they seceded from the Comoro Islands and opted for re-colonisation after 25 years of independence secured in 1975. Though a little quantity of oil insufficient to seduce France is found in Anjouan Island, the people of both rebellious Islands are predominantly farmers and fishermen. In fact the Anjouanese oil was the main factor that gave impetus to the August 3, 1997 secession. With the rejection of re-colonisation by France, the Anjouanese presumed that they could bail themselves out of a chain of poverty if they could control the little quantity of oil in their domain. This may explain the rejection of confederation by the Aniouanese while the Mohelis accepted it during the OAU organised peace talk in Ethiopia to resolve the Comoro Islands crisis in November 1997. The consequence of the rejection was

of course political chaos in the rebellious Island. However, Anjouan Island finally agreed to a loose confederation with the other Islands on April 23, 1999 in a peace talk in Antananarive, Madagascar. This agreement is yet to be implemented. A referendeum on it held on January 23, 2000 favoured the seccessionists.

The contrived crisis and instability in Nigeria stemmed in large part from the oil fortune God bestowed on the nation. Prior to the discovery of oil, the regional governments were strong and stable. With virile components, the seemingly weak government at the centre was able to weld the nation firmly together. This feat of stable government should however be credited to our colonial power as the legacy of good governance handed over was bastardised almost immediately after the exit of the colonial administration. The flow of oil in our wells followed the exit closely, then came the military coup, counter coup, civil war, state creation and centralisation of virtually everything including the unfortunate take over of this great University by the Federal Government. Thereafter, many higher institutions were established inproportional to the capacity of the economy. Of course the consequences were enormous, insufficient funding, lack of infra-structure, poor condition of service, brain drain, fall of standard etc. The very week some academic gurus cried foul aloud and alerted the nation that educational institutions were crumbling under the weight of numbers, but more were established based on the criterion of women pressure. Work ethics, merit and resourcefulness were thrown to the winds and everybody started to scramble to share in the oil money. Indigenes of some states vowed to fight to finish should any section of the

country canvass for a weak centre, an arrangement that might allow each state or region to substantially preside over its revenue. The agitation of the Ogoni and Ijaw youth of the Niger-Delta for monetary compensation for the ecological damage of their environment that started during the Babangida-Abacha regime (August 1985-July 1993 and November 1993-June 1998 respectively) assumed a different dimension of hostage taking for ransom. The crisis climbed a step further to a demand for the outright control of resources (the Anjouanese experience) so that the region will merely be paying taxes to the Federal Government. The policy in the oil industry tends to complicate problems. The place became the centre of intense intrigues during the Babangida-Abacha regime where technocrats were frequently replaced with favourites of inadequate professional competence to balance ethnic quota. Consequently, chaos and apathy set in and what followed was the perennial shortage and epileptic supply of refined oil. The shortage of gasoline in the country became so acute that the Daily Sketch of June 25, 1997 screamed in a headline, "Ivory Coast to rescue Nigeria for the supply of gasoline". Ordinarily, the headline would have made little impression on Nigerians were it not for the following reasons.

- (i) Nigeria at the time exported daily close to two million barrels of crude oil.
- (ii) She supplied the only private refinery in Ivory Coast with crude oil.
- (iii) Nigeria had four refineries as against one in Ivory Coast.
- (iv) Granted that it is pardonable that the country could run into deep shortage of gasoline because of the relatively

high population of users, it is painful and ridiculous that many of the companies prospecting for crude oil in Nigeria had shares in the Ivory Coast refinery. It was thus the case of the same people taking cheap crude oil to a neighbouring African state and bringing back expensive refined oil, it was a solid business of exporter and importer of the same commodity in a double gain.

(v) On a different note, Nigerians virtually owned the refinery in Sierra Leone to which crude oil was diverted or siphoned regularly during the Abacha regime. Gambia voted against the suspension of Nigeria from Commonwealth over the Ken Saro Wiwa and his Ogoni colleagues saga. Abacha allocated barrels of crude oil to Gambia to manage on his behalf in appreciation or compensation. Gambia made close to \$3,000,000.00 from the windfall. BBC reported on January12, 2000 that the money ended up in the Switzerland personal accounts of top Gambian government functionaries.

Corruption and greediness made it impossible to check this and many other sharp practices in the oil sector. Thus, the oil business or deal became so jucrative that people could get to any length to secure employment in the sector, obtain licence to lift oil, become oil marketers or gasoline station owners or even petrol attendants. In fact some petrol attendants were much more economically comfortable than the University professors. This development was mimicked by a Yoruba programme aired on Radio Nigeria, Ibadan on 17th. November 1997. The programme centred on a University professor who impregnated a girl. The mother of the girl vowed

to prevent her daughter from marrying a poor professor who had been working for more than 20 years without a house to his credit or a plot of land to build one. She threatened to kick the foetus out of the girl's womb if she failed to swarp an oil worker or a banker or a military or custom man for the professor as the father of her baby. The professor made his case worse by insisting that he must recover his purse containing N150.00 and an identity card he forgot when he visited the girl the previous night. Sensing the state of increasing contempt for him by his would-be mother in-law, the professor boosted that he had another N350.00 in his savings account in addition to the lost N150.00. The picture painted by this satire showed accurately the reality of our times and demonstrated beyond doubt that all academics in this country are living unenviable life. The army has stuck to power for too long because there was oil money to manage. The frequency of coups, botched or successful attested to the interest of men in uniform to continue to push for power. As earlier said, Nigeria exports about two million barrels of oil daily and earned conservatively about 25 million dollars daily from oil export alone. The 1997 earning from oil export stood at about 166 billion naira, about 7.5 billion dollars at the then official government exchange rate of N22.00 to a dollar. It is naïve to think that a man who has the privilege of presiding over this huge amount of money in a country where objectivity is obscured due to ethnic rivalry and where there is the prerogative to disburse funds arbitrarily will not employ foul play to continue to stay in power. It is such arbitrariness in money disbursement that made it possible for a military government functionary to literarily convert his house to the central bank. Nigerians deserved the praise for checking the military out of

power. In the process of sorting out our self-inflicted mess, the government of the day should be flexible in access, active in redress and rigorous in success. The first step towards redress and success is to invest in science. Many of our well-trained scientists are ageing and are checking out of the University system. The brain drain has robbed the nation of replacements. Thus a big vacuum has been created as scientists cannot be produced on short notice. Whoever becomes a professor after about twenty years of first degree is considered a flier in academic circles. Scientists have to labour for long hours in the laboratory performing experiments, making observations and drawing conclusions. They differ basically in operational procedures from their counterparts in some other disciplines who formulate theories or document events while cogitating at desks. Today in our University, the number of applicants for admission to read Economics or Accounting is more than doubled those applying for the eleven basic sciences in the Faculty of Science. In some years, the cut-off mark for Economics or Accounting was higher than for Medicine, Technology or Pharmacy. This is a type of scandalous social disorder brought by the misuse of oil wealth. Such a dangerous development that has shifted the interest of our youths to pursue get-rich-quick courses, sometimes turning potentially brilliant academic materials to criminals in pursuit of quick money should not be sustained for long if Nigeria has to survive her present paroxysm.

As early as 1967, Chief Obafemi Awolowo realised the uniqueness of science as the basis for social upliftment. Hence he signalled a warning in his inaugural lecture as the Chancellor of this University and said, "the feat of social

rocketry is feasible provided that Science is the booster and Humanities the controller." Late Adeleye Adegite in his inaugural lecture in 1989 indirectly echoed this opinion when he stated that, "Science moves forward while other disciplines move about." Most of our social and economic problems today would have been averted if the oil wealth had been invested to power scientific findings. This misplacement of priority has highlighted in different fora. The Transparency International report of 1997 rated Nigeria first among the most corrupt nations of the world. She was in the third position the previous year, 1996. Barbara Judichee of Radio France International on 26th December 1998 asserted that Nigerian crude oil had continuously been massively smuggled out and that this had contributed significantly to ruin the economy. Sharma Brown of VOA in Africa Perspective of 4th March 1999 reported that Abacha's regime was characterised by corruption, kick-backs and outright theft. The Zambian Sunday Mail of 26th April 1998 reported that the Kenyan Finance Minister admitted that corruption had ruined the economy of his country and that corruption had done an incalculable harm to many African countries with the potential to perform wonders. Corruption always denies the most vulnerable, access to national resources as what is meant to improve their living standards ends up in the pockets, or is in the bank accounts of a few greedy individuals. The revolting thing about the faith of such accumulated wealth is that it is usually abandoned in the foreign banks when death knocks to take its toll. The culprits in this regard in Nigeria are those who had the opportunity to preside over the affairs of the nation. The crucial decision to challenge them for ruining our economy was difficult to take.

The constraint in taking such a decision was that before the implementation of a hatched confrontation, some few individuals having been "settled" would have organised demonstrations in support of our looters. Thus, a few privileged people continued to plunder the wealth of the nation leaving the majority in a state of M³, micro-management of misfortune. It is hoped that the anti-corruption bill recently signed into law (June 13,2000) will be vigorously enforced such that this scandalous and criminal culture is reversed.

Summary

Carbon-12, defined as a naturally abundant non-metallic element that occurs in many inorganic and all organic compounds, is one of the most abundant elements in the universe. It exists in amorphous, graphite and diamond allotropes and lately C_{60} called fullerene was found to exist in space. Fullerenes are used as superconductors and lubricants. Carbon is capable of chemical self-bonding to form numerous chemically, biologically and commercially important long chain molecules. The atomic number and weight are 6 and 12.01115 respectively. It sublimes above 3500°C and boils at 4827°C. Its diamond allotrope has a specific gravity of 3.15 to 3.53, graphite has a value of 1.9 to 2.3 while the amorphous forms have values of 1.8 to 2.1. The valency is predominantly four and does not extend its co-ordination shell beyond the octet configuration. However, carbon nanotubes have been prepared by the laser-vapourisation of carbon with an admixture of nickel/cobalt. They are regarded as molecular quantum wires.

Carbon nanotubes-epoxy composite fibres are used in high performance aircraft and carbon nanotubes can be dispersed into polymer matrices to strengthen them. Carbon-14 isotope produced by the neutron bombardments of the atmospheric nitrogen enters the carbon cycle through 14CO2 and is useful for dating dug-up sub-merged matters. The excess of CO2 in the atmosphere is implicated as the cause of global warming or green house effect. The other oxide of carbon, carbon monoxide is odourless, toxic and a complete nuisance except where it is used as a reducing agent in the preparation of some useful compounds. Carbon and its compounds find enormous use in technology, medicine, pharmacy and the sciences. Steel, a composite of carbon and iron, is indispensable in the construction industry. For example, carbon nanotubes have high length-to-diameter ratio and can be incorporated into the steel sheets useful for the building of car bodies. The body of such a vehicle permits an efficient spray painting by giving the paint spray an electrostatic charge, which is then attracted to the car body by the high voltage passing through it. However, the constraint in this usage is that carbon nanotubes are very expensive, a gram costs about \$100.00 which is 10 times the cost of a gram of gold. Thus incorporating it to the body of a vehicle may be more costly than the vehicle itself. The natural exchange of carbon through CO2 in respiration-photosynthesis sustains all lives on this planet. Carbon is indeed a ubiquitous element, it is the most treasured matter and it is a tool bestowed by the Gods on mankind to keep his life alive on the earth. Inspite of the abundance of this life-line element in one form or the other in Nigeria, its influence on the wealth of the nation looks like a

mirage to the generality of our people. It is a tale of woe, a tale told to an idiot, full of sound and fury, signifying nothing. Carbon and by extension crude oil is the most important of all modern raw material. The possession of it is yet to make a positive impact on the quality of life of our people and the question is, will our descendants curse or bless us for the legacy of carbon, the tool from the Gods? On this note I rest my case and I thank you for listening.

References

- 1. L.W. Codd et al, J. Chem. Tech. <u>5</u> (1972) 271.
- 2. Encyclopedia of Polymer Science and Technology, <u>5</u> (1965) 126.
- 3. J. R. Partington, History and Chemistry, vol. 4 (1971).
- 4. H.E. Garret, Surface Active Chemicals, Pergamon Press, Oxford (1972) 62.
- 5. M.S. Akanni and V.O. Ogugbuaja, J. of Radioanaly and Nucl. Chem. 91 (1985) 395
- 6. M. M. Jones et al, Chemistry and Society, 5th Edition, Saunders College Publication (1987).
- 7. F.E.S. Mohammed and M.M. Amer, Oil, fats, waxes and surfactants, "Chemistry and Analysis" Anglo-Indian Bookshop, Cairo (1965) Part IV P₁₈₅₋₂₁₈.
- 8. M. O. Oladimeji, M. S. Akanni and O.A. Afolabi, Nig. J. of Science. 25 (1991).
- 9. S. O. Adeosun and M.S. Akasnni, Thermochim. Acta, 39 (1980) 35.
- 10.S. O. Adeosun, M. S. Akanni and H. D. Burrows, Thermochim. Acta 42 (1980) 233.

- 11. M. S. Akanni, H. D. Burrows, F. Oshodi and H. C. Sine, Thermochim. Acta, 54 (1982) 289.
- 12.M. S. Akanni and P. C. Mbaneme, J. Chem. Soc. Farad. Trans. I, <u>82</u> (1986) 3357.
- 13. M. S. Akanni, P. B. Begun and H. D. Burrows, Thermochim. Acta <u>81</u> (1984) 45.
- 14. M. S. Akanni, O. B. Ajayi and J. N. Lambi, J. of Thermal Analys. <u>13</u> (1986) 131.
- 15. M. S. Akanni and B. F. Adeosun, Thermochim. Acta, <u>152</u> (1989) 259.
- 16. S. O. Adeosun and M. S. Akanni, Thermochim. Acta, <u>27</u> (1978) 133.
- 17. M. S. Akanni, Thermochim. Acta, <u>122</u> (1987) 355.
- 18.O. B. Ajayi, M. S. Akanni, J. N. Lambi, O. Osasona, B. Podor and H. D. Burrows, Thin Solid Films, 136 (1986) 91.
- 19. O. B. Ajayi, M. S. Akanni, J. N. Lambi, C. Jeynes and J. P. Watts, Thin Solid Films, 183 (1990) 123.
- 20. S. Sugden, J. Chem. Soc. 175 (1929) 1177.
- 21.N. K. Adams, Physical Chemistry, Clarendon Press, Oxford (1956) P₂₃₂.
- 22. S. Glasstone, Textbook of Physical Chemistry, 2nd Edition, Macmillan, London (1960) P₅₂₆.
- 23. M. S. Akanni and H. D. Burrows, Thermochim. Acta <u>115</u> (1987) 351.
- 24. M. S. Akanni, H. D. Burrows, H. A. Ellis, D. N. Asongwed, H. D. Babalola and P. O. Ojo, J. Chem. Tech. Biotechnol, <u>34</u> (1984) 127.
- 25. M. S. Akanni and N. A. Abass, Liquid Crystal, Vol. 6, <u>5</u> (1989) 597.
- 26.N. Pipel, Properties of organic solution of heavy metal

- soaps, Chemical Review <u>63</u> (1963) 221.
- 27.K. S. Markley, Fats and Oils- Fatty acids 2, Wiley Inter-Science Publications, New York (1961).
- 28.A. R. Ubbelohde, Some problems concerning chemical reactions in ionic melts, Chemistry and Industry, 10 !968) 313.
- 29. Encyclopadia of Chem. Technol. 7 (1967) 272.
- 30. Eldon D. Enger and Bradley F. Smith, Environmental Science- a study of interrelationship, 4th Edition, (1992) Wm. C. Brown Publishers, U.S.A.
- 31. Y. Lin, J. Rare Earth, <u>10</u> (1990) 98.
- 32. D. M. Aranaz and T. R. Lomer, J. Phys. C. <u>2</u> 91969) 2431.
- 33. M. Pomerantz, F. H. Dacol and A. Segmuller, Phys. Rev. Lett. <u>40</u> (1978) 246.
- 34. A. Aviram and M. Pomerantz, Solid State Commu. <u>4</u> (1982) 297.
- 35.I. A. Asaolu, B. H. Blott, W. I. Khan and D. Melville, Thin Solid Films, 99 (1983) 263.
- 36. B. L. Henke, R. C. C. Perera, E. M. Gullikson and M. L. Schattenburg, J. Appl. Phys. 49 (1978) 480.
- 37. H. Adams, N. A. Bailey, D. W. Bruce, R. Dhillon, D. A. Dunmur, S. E. Hunt, E. Lalinde, A. A. Maggs, R. Orr, P. Styring, M. S. Wragg and P. M. Maitlis, Polyhedron 7 (1988) 1861.
- 38. G. S. Hartley, J. Chem. Soc. Trans. Farad., 30 (1934) 44.
- 39. L. Mcbain, J. Amer. Chem. Soc., <u>25</u> (1948) 77.