

A BRIEF HISTORY OF CATALYSIS

Who'sWho in the Early Catalysis

Early Catalytic Processes

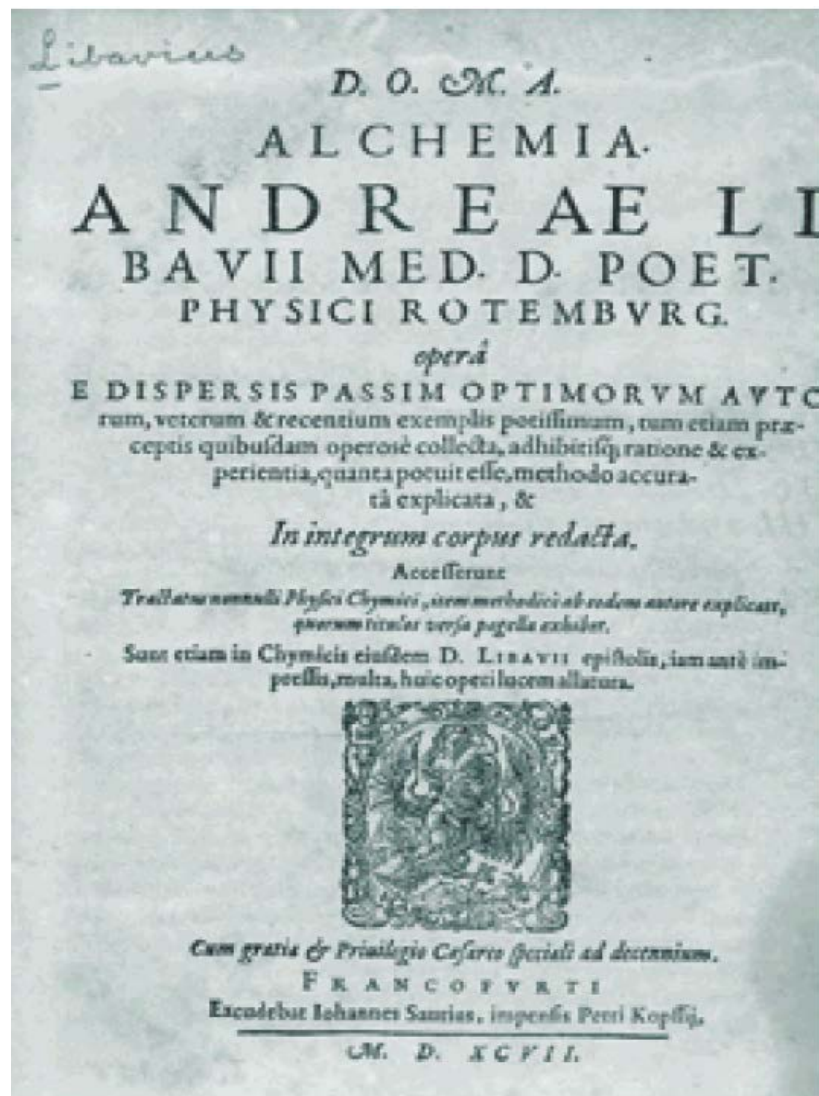
-6000	Beer brewing by malting procedure	Malt enzymes
-3000	Wine making by fermentative conversion of grape juice sugars	Yeast a.o.
-2000	Alcohol(ic drinks) by fermentation of various carbohydrate sources	Yeast a.o.
	Bread and other leavened bakery products by carbon dioxide and alcohol	Baker's yeast
	Vinegar (acetic acid) by aerobic fermentation of ethanol	Acetobacter
-800	Cheese making (coagulation) by casein hydrolysis with calf stomach extract	Calf rennet (chymosin)
1850	Yogurt formation from milk by lactose to lactic acid conversion	Lactobacillus

Kieboom, Moulijn, van Leeuwen, van Santen, Stud. Surf. Sci. Catal. 123 (1999)3-28

Andreas Libavius, "Alchemia", 1597

The first textbook of chemistry, first possible for the scientists to compare their work with others.

The first historical reference to catalysis as a chemical phenomenon; he, however, uses the term catalysis to describe the decomposition of base metals into silver and gold.



Johann Wolfgang Döbereiner (1780-1849)

Johann Wolfgang Döbereiner
1780–1849

Professor of Chemistry at Jena for thirty-nine years, a friend and protégé of Goethe, and the founder of the study of catalysis, his discovery of the power of finely divided platinum to ignite a stream of hydrogen caused a considerable stir in European chemical circles

From a portrait in the possession of Goethe-Nationalmuseum der Nationale Forschungs und Gedenkstätten, Weimar





apothecarian, studied chemistry later

1810 Chair for Chemistry and Pharmacy in Jena

exchanged letters with Goethe (and gave him one of his lighters as a gift)

obtained several kg platinum from Duke Karl August in Weimar

1816 conversion of alcohol to acetic acid / Pt wire

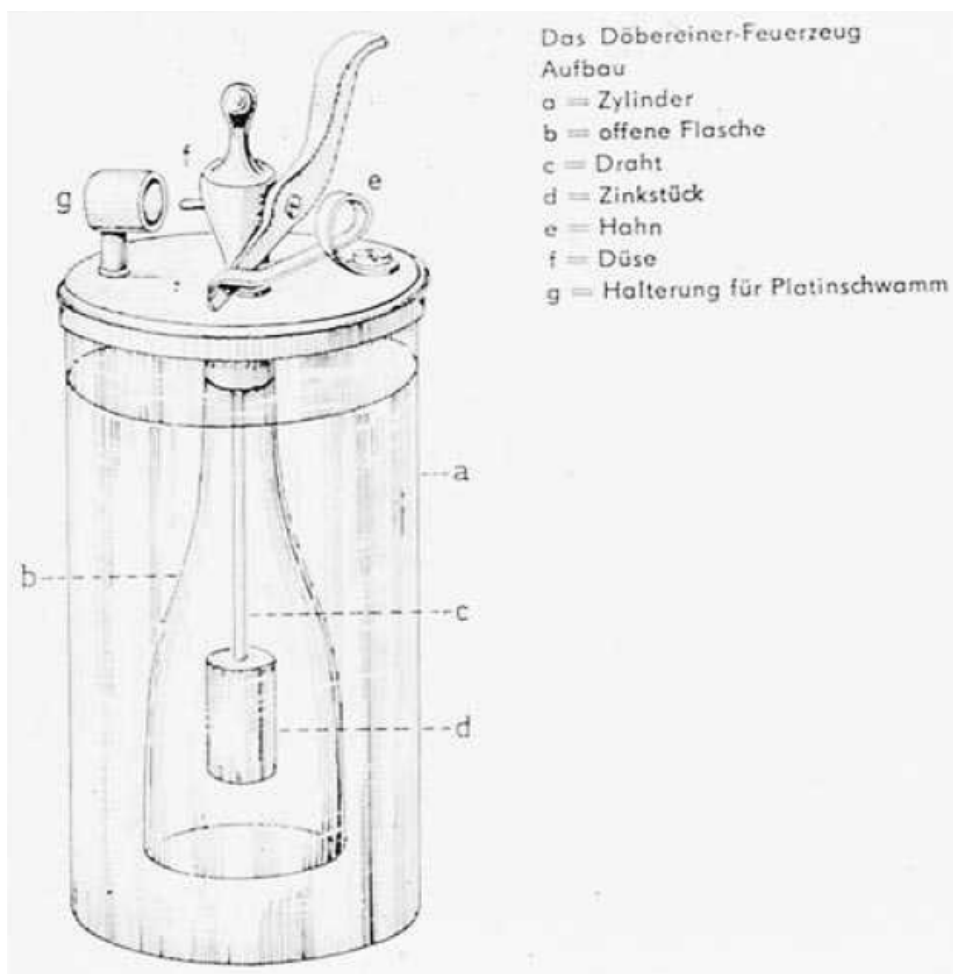
1832 conversion of alcohol to acetic aldehyde / Pt wire



An incidental result of Döbereiner's discoveries was his invention of the first lighter. This employed hydrogen, generated from zinc and sulphuric acid, passing over finely divided platinum which then glowed sufficiently to ignite the gas. A number of different types produced in Germany and in England became very popular and many thousands of them were in use over a long period of time. Many elaborate and fanciful designs on enamel or porcelain were also developed including the two models illustrated here

Courtesy of the Danish National Museum

The Döbereiner Lighter



Production of H_2
from Zn and
sulfuric acid (25%)
ignited at Pt
sponge on top

Humphry Davy (1778-1829)



- ❖ 1817 reactions of coal-gas and oxygen on Pt, Pd (active) and Co, Ag, Au, Fe (ineffective) wires
- ❖ developed safety lamp for miners
- ❖ detected anesthetic effect of N_2O (breathing it became the highlight of social events)

In 1817, the first observation that platinum induces the oxidation of hydrogen in air.

Michael Faraday (1791-1867)



- ☐ Catalytic properties of platinum for the oxidation of hydrogen
- ☐ Both the effects of pretreatment and poisons
- ☐ Required properties of platinum for ignition:

The only essential condition appears to be a perfectly clean and metallic surface, for whenever that is provided, the platina acts, whatever form and condition in other respects may be.

- ☐ Regeneration

Berzelius did not mention Faraday's works in the proposals of the catalytic phenomena.

Eilhard Mitscherlich (1794-1863)



- ☐ Prof. University of Berlin
- ☐ studied oriental languages, PhD on Persian texts
- ☐ discovered isomorphism “an equal number of atoms, combined in the same way, produce the same crystal forms: the crystal form does not depend on the nature of the atoms, but only on their number and mode of combination”
- ☐ synthesized benzene

Mitscherlich experiments provide critical clues in establishing a concept of “catalyst” and “catalysis” by Berzelius later.

□ E. Mitscherlich, “Ueber die Aetherbildung” (On the Formation of Ether)”, Pogg. Ann., 31 (1834) 273

- *Annalen der Physik* (English: *Annals of Physics*)

- *Gilberts Annalen*, *Poggendorfs Annalen*, *Wiedemann's Annalen* and so on, or for short *Gilb. Ann.*, *Pogg. Ann.*, *Wied. Ann.*

* on photons, on Brownian motion, on mass–energy equivalence, and on the special theory of relativity by Albert Einstein (1905)

** on the theory of blackbody radiation by Max Planck (1901)

□ Through careful studies on the *synthesis of diethyl ether from ethanol and sulfuric acid*, it was realized that *the acid was not being consumed during the production of the ether, although the reaction would not proceed unless the acid was present.*

Jöns Jakob Berzelius (1779–1848)



- ❖ studied medicine and chemistry in Uppsala, Sweden
- ❖ worked as medical doctor, became Professor of Medicine and Pharmacy, 1810 Professor of Chemistry and Pharmacy
- ❖ stopped teaching in 1829 to devote himself to research

□ a founder of modern chemistry along with Robert Boyle, John Dalton, and Antoine Lavoisier

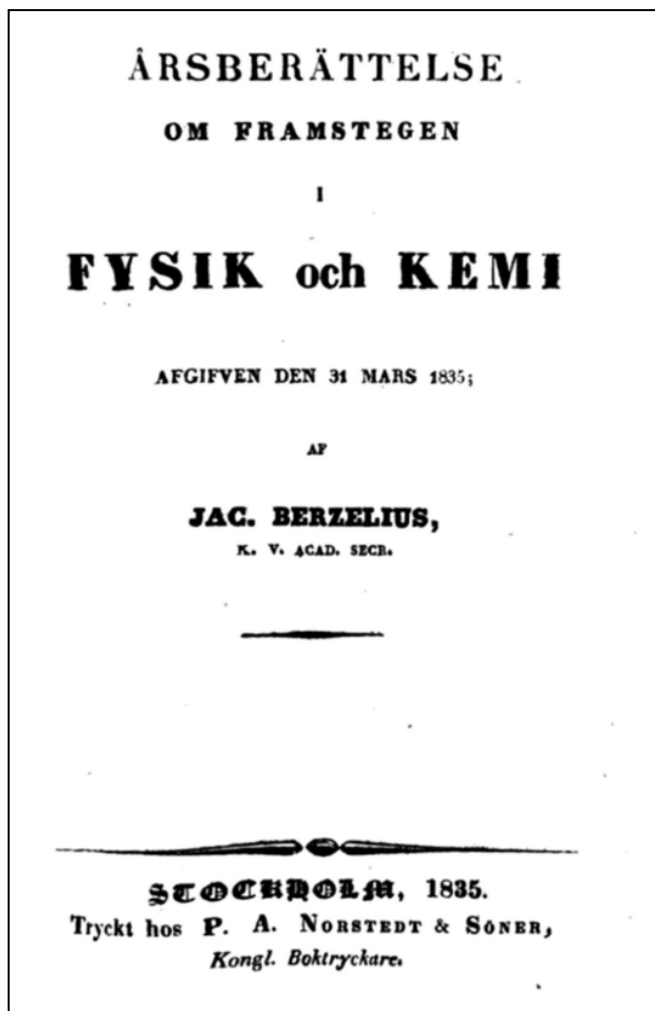


In Berzelii Park in Stockholm



German Baker's House

□ J.J Berzelius, Årsberättelsen om Framsteg i Fysik och Kemi
(Annual Report on Progress in Physics and Chemistry),
Royal Swedish Academy of Sciences, 1835



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Detta är en den oorganiska, likaväl som den organiska naturen tillhörig ny kraft att frambringa kemisk verksamhet, som säkert är mera utspridd än vi hittills tänkt, och hvars natur ännu är för oss förborgad. Då jag kallar den en ny kraft, är det dervid icke min mening, att det skall vara en af materiens elektrokemiska relationer oberoende förmåga, tvertom, jag kan icke förmoda annat, än att den är ett eget slags yttring af dessa, men så länge vi icke kunna inse deras inbördes sammanhang, lättar det våra forskningar att betrakta den, tills vidare, såsom en kraft för sig, likasom det skall lätta vårt afhandlande deraf, att dervid äga ett eget namn. Jag skall dervid, för att begagna en i kemien välkänd härledning, kalla den kroppars **katalytiska kraft**, sönderdelning genom denna kraft **katalys**, likasom vi med ordet analys beteckna åtskiljandet af kroppars beståndsdelar medelst den vanliga kemiska frändskapen. Den katalytiska kraften synes egentligen bestå deri, att kroppar genom sin blotta närvaro, och icke genom sin frändskap, förmå uppväcka frändskaper, som vid denna temperatur slumra, så att elementen i en sammansatt kropp, i kraft af dessa, ordna sig i andra förhållanden, genom hvilka större elektrokemisk neutralisering uppkommer. De verka dervid i det hela på samma sätt som värmets, och dervid kan den fråga uppstå, om en olika grad af katalytisk kraft hos olika kroppar kan uppväcka samma olikhet i katalytiska produkter, som värmets eller olika temperaturer ofta åstadkom-

It is then shown that several simple and compound bodies, soluble and insoluble, have the property of exercising on other bodies and action very different from chemical affinity. The body effecting the changes does not take part in the reaction and remains unaltered through the reaction. This unknown body acts by means of an internal force, whose nature is unknown to us. This new force, up till now unknown, is common to organic and inorganic nature. I do not believe that this force is independent of the electrochemical affinities of matter; I believe on the contrary, that it is a new manifestation of the same, but, since we cannot see their connection and independence, it will be more convenient to designate the force by a new name. I will therefore call it the “Catalytic Force” and I will call “Catalysis” the decomposition of bodies by this force, in the same way that we call by “Analysis” the decomposition of bodies by chemical affinity.

- besides “catalysis”, “polymer”, “isomer”, “protein”, etc
- discovered cerium (1803), selenium (1817), thorium (1829)
- Berzelius's group students: lithium, lanthanum, and vanadium



Elizabeth Fulhame (?-?)



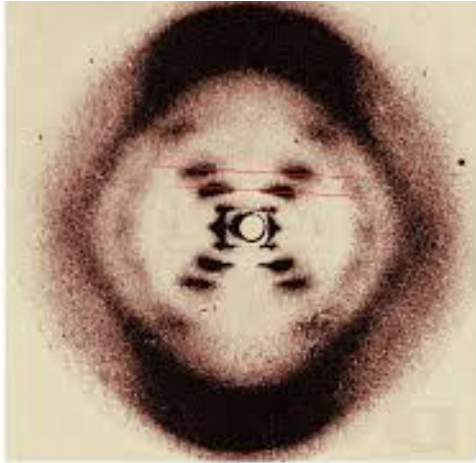
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Rosalind Elsie Franklin (1920-1958)

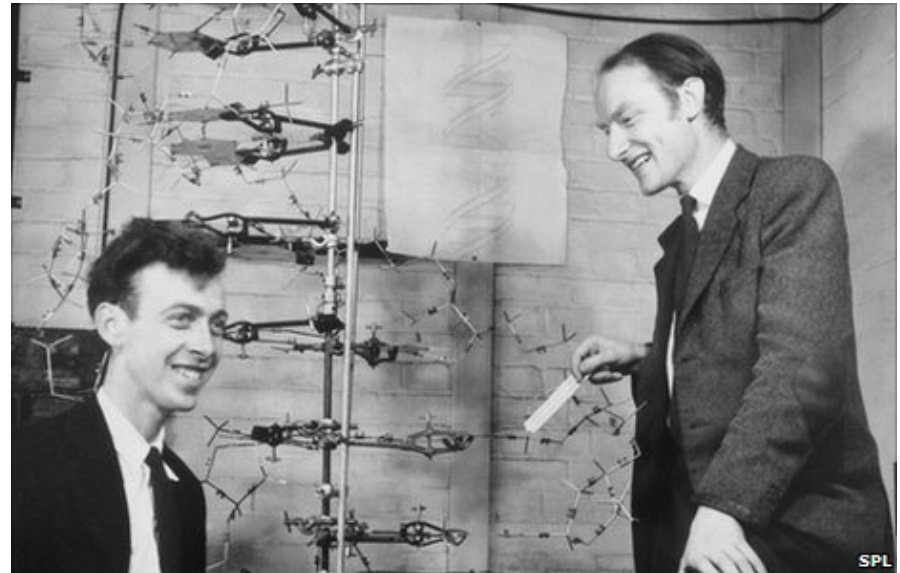
X-ray diffraction image
"Photography 51"



A sketch of the DNA
double helix by Francis
Crick (1953)



Worked at King's
College London



Francis Harry Compton Crick (1916-2004) and
James Dewey Watson (left) (1928-)
Cavendish Laboratory, University of Cambridge
Received the Nobel Prize (1962)

equipment, and to Dr. G. E. R. Deacon and the captain and officers of R.R.S. *Discovery II* for their part in making the observations.

*Young, F. B., Gerrard, H., and Jevons, W., *Phil. Mag.*, **40**, 149 (1920).

*Lougnot-Higgins, M. S., *Mon. Not. Roy. Astro. Soc., Geophys. Supp.*, **8**, 385 (1949).

*Von Arx, W. S., Woods Hole Papers in Phys. Oceanogr. Meteor., **11** (3) (1950).

*Eklund, V. W., *Arkiv. Mat. Astron. Fysik. (Stockholm)*, **2** (11) (1905).

MOLECULAR STRUCTURE OF NUCLEIC ACIDS

A Structure for Deoxyribose Nucleic Acid

WE wish to suggest a structure for the salt of deoxyribose nucleic acid (D.N.A.). This structure has novel features which are of considerable biological interest.

A structure for nucleic acid has already been proposed by Pauling and Corey¹. They kindly made their manuscript available to us in advance of publication. Their model consists of three intertwined chains, with the phosphates near the fibre axis, and the bases on the outside. In our opinion, this structure is unsatisfactory for two reasons: (1) We believe that the material which gives the X-ray diagrams is the salt, not the free acid. Without the acidic hydrogen atoms it is not clear what forces would hold the structure together, especially as the negatively charged phosphates near the axis will repel each other. (2) Some of the van der Waals distances appear to be too small.

Another three-chain structure has also been suggested by Fraser (in the press). In his model the phosphates are on the outside and the bases on the inside, linked together by hydrogen bonds. This structure as described is rather ill-defined, and for this reason we shall not comment on it.

We wish to put forward a radically different structure for the salt of deoxyribose nucleic acid. This structure has two helical chains each coiled round the same axis (see diagram). We have made the usual chemical assumptions, namely, that each chain consists of phosphate diester groups joining β -D-deoxy-ribofuranose residues with 3',5' linkages. The two chains (but not their bases) are related by a dyad perpendicular to the fibre axis. Both chains follow right-handed helices, but owing to the dyad the sequences of the atoms in the two chains run in opposite directions. Each chain loosely resembles Furburg's² model No. 1; that is, the bases are on the inside of the helix and the phosphates on the outside. The configuration of the sugar and the atoms near it is close to Furburg's 'standard configuration', the sugar being roughly perpendicular to the attached base. There

is a residue on each chain every 3.4 Å. in the z-direction. We have assumed an angle of 36° between adjacent residues in the same chain, so that the structure repeats after 10 residues on each chain, that is, after 34 Å. The distance of a phosphorus atom from the fibre axis is 10 Å. As the phosphates are on the outside, cations have easy access to them.

The structure is an open one, and its water content is rather high. At lower water contents we would expect the bases to tilt so that the structure could become more compact.

The novel feature of the structure is the manner in which the two chains are held together by the purine and pyrimidine bases. The planes of the bases are perpendicular to the fibre axis. They are joined together in pairs, a single base from one chain being hydrogen-bonded to a single base from the other chain, so that the two lie side by side with identical z-co-ordinates. One of the pair must be a purine and the other a pyrimidine for bonding to occur. The hydrogen bonds are made as follows: purine position 1 to pyrimidine position 1; purine position 6 to pyrimidine position 6.

If it is assumed that the bases only occur in the structure in the most plausible tautomeric forms (that is, with the keto rather than the enol configurations) it is found that only specific pairs of bases can bond together. These pairs are: adenine (purine) with thymine (pyrimidine), and guanine (purine) with cytosine (pyrimidine).

In other words, if an adenine forms one member of a pair, on either chain, then on these assumptions the other member must be thymine; similarly for guanine and cytosine. The sequence of bases on a single chain does not appear to be restricted in any way. However, if only specific pairs of bases can be formed, it follows that if the sequence of bases on one chain is given, then the sequence on the other chain is automatically determined.

It has been found experimentally^{3,4} that the ratio of the amounts of adenine to thymine, and the ratio of guanine to cytosine, are always very close to unity for deoxyribose nucleic acid.

It is probably impossible to build this structure with a ribose sugar in place of the deoxyribose, as the extra oxygen atom would make too close a van der Waals contact.

The previously published X-ray data^{5,6} on deoxyribose nucleic acid are insufficient for a rigorous test of our structure. So far as we can tell, it is roughly compatible with the experimental data, but it must be regarded as unproved until it has been checked against more exact results. Some of these are given in the following communications. We were not aware of the details of the results presented there when we devised our structure, which rests mainly though not entirely on published experimental data and stereochemical arguments.

It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material. Full details of the structure, including the conditions assumed in building it, together with a set of co-ordinates for the atoms, will be published elsewhere.

We are much indebted to Dr. Jerry Donohue for constant advice and criticism, especially on interatomic distances. We have also been stimulated by a knowledge of the general nature of the unpublished experimental results and ideas of Dr. M. H. F. Wilkins, Dr. R. E. Franklin and their co-workers at

King's College, London. One of us (J.D.W.) has been aided by a fellowship from the National Foundation for Infantile Paralysis.

J. D. WATSON
F. H. C. CRICK

Medical Research Council Unit for the Study of the Molecular Structure of Biological Systems, Cavendish Laboratory, Cambridge, April 2.

*Pauling, L., and Corey, R. B., *Nature*, **171**, 346 (1953); *Proc. U.S. Nat. Acad. Sci.*, **38**, 54 (1953).

*Furburg, S., *Acta Chem. Scand.*, **6**, 634 (1952).

*Chargaff, E., for references see Zamenhof, S., Frawerman, G., and Chargaff, E., *Biochim. et Biophys. Acta*, **8**, 402 (1952).

*Wyatt, G. R., *J. Gen. Physiol.*, **36**, 201 (1952).

*Astbury, W. T., *Symposium Soc. Exp. Biol.*, **1**, Nucleic Acid, 66 (Camb. Univ. Press, 1947).

*Wilkins, M. H. F., and Randall, J. T., *Biochim. et Biophys. Acta*, **10**, 192 (1953).

Molecular Structure of Deoxypentose Nucleic Acids

WHILE the biological properties of deoxypentose nucleic acid suggest a molecular structure containing great complexity, X-ray diffraction studies described here (cf. Astbury¹) show the basic molecular configuration has great simplicity. The purpose of this communication is to describe, in a preliminary way, some of the experimental evidence for the polynucleotide chain configuration being helical, and existing in this form when in the natural state. A fuller account of the work will be published shortly.

The structure of deoxypentose nucleic acid is the same in all species (although the nitrogen base ratios alter considerably) in nucleoprotein, extracted or in cells, and in purified nucleate. The same linear group of polynucleotide chains may pack together parallel in different ways to give crystalline^{2,3}, semi-crystalline or paracrystalline material. In all cases the X-ray diffraction photograph consists of two regions, one determined largely by the regular spacing of nucleotides along the chain, and the other by the longer spacings of the chain configuration. The sequence of different nitrogen bases along the chain is not made visible.

Oriented paracrystalline deoxypentose nucleic acid ('structure B' in the following communication by Franklin and Gosling) gives a fibre diagram as shown in Fig. 1 (cf. ref. 4). Astbury suggested that the strong 3.4-Å. reflexion corresponded to the inter-nucleotide repeat along the fibre axis. The ~34 Å. layer lines, however, are not due to a repeat of a polynucleotide composition, but to the chain configuration repeat, which causes strong diffraction as the nucleotide chains have higher density than the interstitial water. The absence of reflexions on or near the meridian immediately suggests a helical structure with axis parallel to fibre length.

Diffraction by Helices

It may be shown⁵ (also Stokes, unpublished) that the intensity distribution in the diffraction pattern of a series of points equally spaced along a helix is given by the squares of Bessel functions. A uniform continuous helix gives a series of layer lines of spacing corresponding to the helix pitch, the intensity distribution along the n th layer line being proportional to the square of J_n , the n th order Bessel function. A straight line may be drawn approximately through

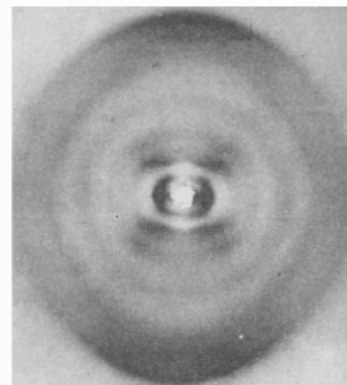


Fig. 1. Fibre diagram of deoxypentose nucleic acid from *B. coli*. Fibre axis vertical.

the innermost maxima of each Bessel function and the origin. The angle this line makes with the equator is roughly equal to the angle between an element of the helix and the helix axis. If a unit repeats n times about the helix there will be a meridional reflexion (J_0) on the n th layer line. The helical configuration produces side-bands on this fundamental frequency, the effect⁶ being to reproduce the intensity distribution about the origin around the new origin, on the n th layer line, corresponding to C in Fig. 2.

We will now briefly analyse in physical terms some of the effects of the shape and size of the repeat unit or nucleotide on the diffraction pattern. First, if the nucleotide consists of a unit having circular symmetry about an axis parallel to the helix axis, the whole diffraction pattern is modified by the form factor of the nucleotide. Second, if the nucleotide consists of a series of points on a radius at right-angles to the helix axis, the phases of radiation scattered by the helices of different diameter passing through each point are the same. Summation of the corresponding Bessel functions gives reinforcement for the inner-

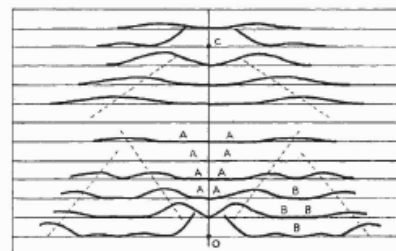
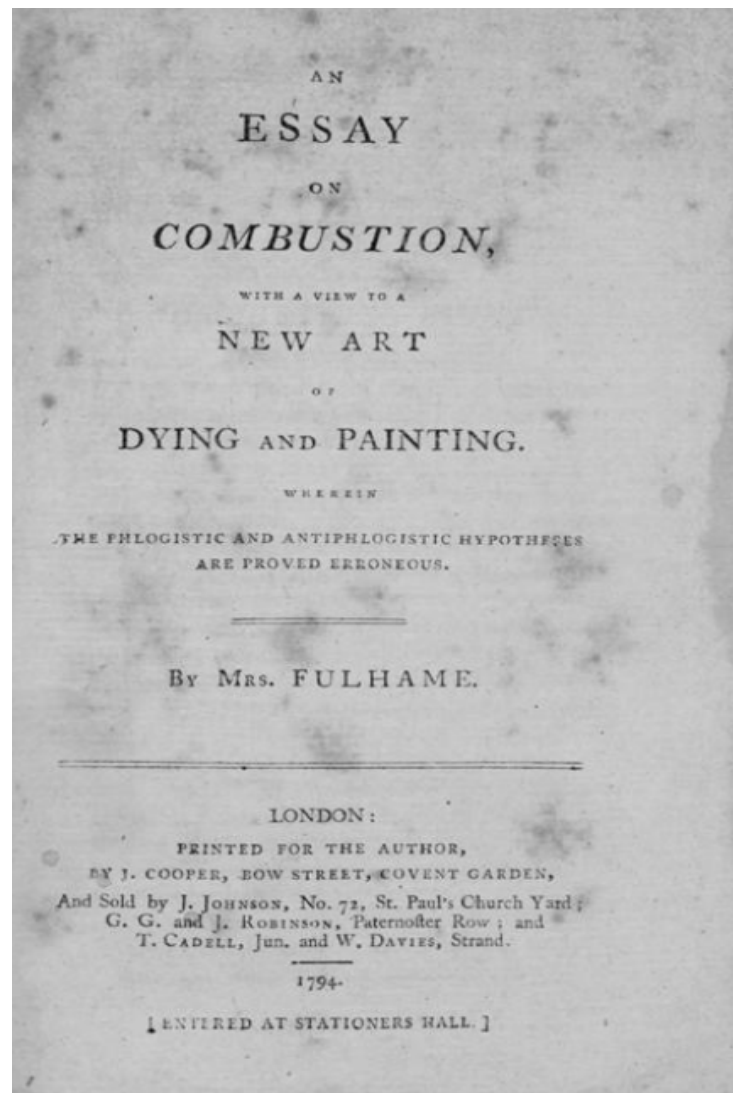


Fig. 2. Diffraction pattern of system of helices corresponding to structure of deoxypentose nucleic acid. The squares of Bessel functions are plotted about O on the equator and on the first, second, third and fifth layer lines for half of the nucleotide mass at 20 Å. diameter and remainder distributed along a radius, the mass at a given radius being proportional to the radius. About C on the seventh layer line similar functions are plotted for an outer diameter of 12 Å.

Elizabeth Fulhame: 'Franklin' in catalysis



Elizabeth Fulhame, "An Essay On Combustion with a View to a New Art of Dying and Painting, wherein the Phlogistic and Antiphlogistic Hypotheses are Proved Erroneous", 1794

- ☐ Invented the concept of catalysis
- ☐ Presented the principle features of catalysis:

the presence of small quantities of water is required for the oxidation of carbon monoxide but the water unaffected by the chemical reaction



- ☐ Bill Palmer, "**Elizabeth Fulhame: The Invisible Chemist**", *Teaching Science*, Vol. 54, No. 4, p. 12-16, December 2008
- ☐ Ida Emilie Steinmark, "**Elizabeth Fulhame: The Scientist the World Forgot**", *Education in Chemistry*, Royal Society of Chemistry, 10 October 2017
- ☐ In the preface of the essay,
"Some are so ignorant that they grow sullen and silent, and are chilled with horror at the sight of any thing, that bears the semblance of learning, in whatever shape it may appear; and should the spectre appear in the shape of woman, the pangs, which they suffer, are truly dismal."

DEFINE TO ALIVE!!!

MORE WOMEN IN CHEMISTRY HISTORY



ELIZABETH FULHAME
BORN ? DIED ?

The first person to describe catalytic processes in her only publication in 1794. She also stained cloth with light sensitive silver salts, later used in photography.



JANE MARCET
BORN 1769 DIED 1858

Published 'Conversations on Chemistry', the most popular 19th century chemistry textbook. A standard text in U.S. girls' schools, it also inspired Michael Faraday.



ANNA SUNDSTRÖM
BORN 1785 DIED 1871

Thought to have been the first woman chemist in Sweden. Worked with Jöns Jacob Berzelius, but her employment was forcibly ended when Berzelius married.



ANNA VOLKOVA
BORN ? DIED 1876

Claimed to have been the first woman to graduate as a chemist, in 1870. She was also the first woman to publish her own chemical research from a modern lab.



ELLEN SWALLOW RICHARDS
BORN 1842 DIED 1911

The first American woman to gain a chemistry degree. Her work led to the first water quality standards in America and the first modern sewage plant.



AGNES POCKELS
BORN 1862 DIED 1935

Had no education in chemistry, but carried out experiments in her kitchen on the surface tension of water. Now considered a pioneer of surface science.



LUCY EVEREST BOOLE
BORN 1862 DIED 1904

The first woman to research pharmacy in England, and the first woman to co-author a pharmaceutical research paper. Also the first female fellow of the RSC.



MARGARET SEWARD
BORN 1864 DIED 1929

Tutored, researched, and lectured in chemistry. Carried out vital work on food nutrition during the First World War, and was later awarded an MBE for her work.



ANNIE MALONE
BORN 1869 DIED 1957

Malone, a chemist and entrepreneur, developed hair care products for black women. Her success made her the first African-American woman millionaire.



EDITH HUMPHREY
BORN 1875 DIED 1977

The first British woman to obtain a PhD in chemistry. Carried out key research on inorganic complexes, but was forced out of a research career by sexist attitudes.



MAUD MENTEN
BORN 1879 DIED 1960

Carried out key research in biochemistry. In 1913, she co-devised the Michaelis-Menten equation for study of the rate of enzyme-catalysed reactions.



ELLEN GLEDITSCH
BORN 1879 DIED 1968

In her early career, Gleditsch worked under Marie Curie. She established the half-life of radium and contributed to the confirmation of the existence of isotopes.