JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

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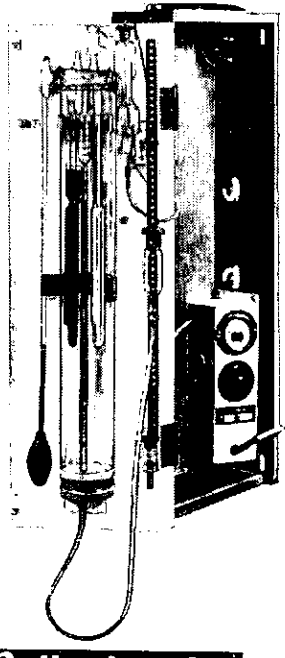

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Editorial

THE BACK PAGE

One of the obvious problems in editing a journal such as this is that of getting sufficient material of the right sort. Less obvious, perhaps, is the time at which the material is received. With two-monthly publication, it is difficult to publish topical material, particularly as the normal production period is about six weeks. Like any other publication, such as a newspaper, there are deadlines to meet. Publishers and printers must fit the *Journal* into a publishing complex, and the normal closing date for copy is the 1st of the month preceding publication. However, unlike a newspaper, processing of a technical publication involves such features as submitting proofs to authors which use up a considerable part of the production period. Thus, material which just misses a deadline may be denied publication for nearly three months.

In an attempt to overcome this difficulty in some degree, arrangements have been made to reserve space for late announcements, such as notices of meetings, overseas congresses, or position vacancies with a set date for application. Such notices will be accepted up to three weeks after the normal closing date. Although it will not always be required (as in this issue) the final page of the *Journal* will be used when necessary to cope with this material.

Thus the last page could well merit your early attention. It could include something of importance which requires immediate action.

THE CHEMICAL BASIS OF HEREDITY

R. E. F. MATTHEWS
Microbiology Department, University of Auckland

Nearly all organisms begin life as a single cell — the fertilized egg. The two most basic questions in biology are: (1) In what form is all the information needed to specify the adult organism packed into the fertilized egg? (2) How is this information used in cell division to produce new cells, and ultimately the completed adult? This is a very complex problem in organisms such as higher plants and animals where there is a very large number of different types of cells, serving different functions and organized into characteristic tissues and organs.

If we are prepared to discard statements like "a spirit enters the seed and guides it" as being merely a play with words, we must look for an explanation in terms of chemistry and physics. Biologists have been interested in these problems for a long time but it is only during the last 15 years that real progress has been made. New techniques drawn from various branches of physics and chemistry have made new kinds of experimentation possible. Biologists have sought and used relatively simple biological systems such as bacteria and viruses that have allowed one aspect of the problem at a time to be brought under control and investigated. We now have a fairly clear answer to the first question noted above, and rapid progress is being made with the second.

This explosive growth of new knowledge has led to the emergence of a new branch of science known as Molecular Biology. The study of Molecular Biology is not only giving us a clear understanding of the chemical basis of heredity, but is also throwing new light on many biological phenomena of great practical importance such as virus disease, cancer, the ageing process, the mechanism of action of drugs, and the effects of radiation on living material.

Size Range to be Considered

In thinking about these problems, it is important to try to form some idea of the relative sizes of the objects being examined and discussed. Some approximate representative sizes are listed in Table 1. This table gives linear dimensions. The actual volume occupied will, of course, be roughly the cube of the linear dimension given, so that in terms of

volume the size range covered is very large indeed. To take an over-simplified example, if a protein molecule were a cube one millimicron in each dimension, and a bacterium were a cube one micron in each dimension, then 1,000,000,000 protein molecules could fit into the space occupied by the bacterium.

TABLE 1: Linear Dimensions of Various Biological Objects of Interest

Size Unit	*Fraction of a Metre*	*Example*	*Size Ranges, and Instruments or Techniques used for Study*
metre	10^{1}	man	*macroscopic* (unaided human eye)
decimeter	10^{-1}	rat	
centimeter	10^{-2}	snail	
millimeter	10^{-3}	small insect	
—	10^{-4}	giant nerve cell	
—	10^{-5}	average cell	*microscopic* (light microscope, electron microscope)
		large chromosome	
micron (μ)	10^{-6}	chromosomes, bacteria	
—	10^{-7}	mitochondria	
—	10^{-8}	viruses, ribosomes	*colloidal molecular and atomic* (electron microscope, X-ray crystallography, techniques of organic chemistry, biochemistry and genetics)
millimicron ($m\mu$)	10^{-9}	protein molecules	
Angstrom (A)	10^{-10}	distances between atoms in organic molecules	

MOLECULAR BIOLOGY

Molecular biology is the study of the structure, function and interrelationships between large molecules and molecular aggregates in living material. The major classes of large molecules in cells are carbohydrates, fats, deoxyribonucleic acids (DNA), ribonucleic acids (RNA) and proteins. Carbohydrates and fats are primarily involved in the storage of energy or in the structural properties of cells. The nucleic acids and the proteins are of fundamental importance in the replication of cells and organisms, and it is the study of these classes of molecule that constitutes the "hard core" of the subject of molecular biology.

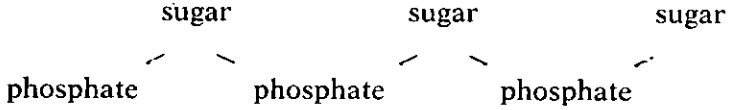
The study of genetics, which began about seventy years ago, showed by breeding experiments that: (1) The heredity material is made up of discrete unit characters or "genes"; (2) these genes are located in the chromosomes — small bodies that can be seen in the nucleus of a cell, using light microscopy; (3) the various genes are arranged in a definite linear order along the chromosomes.

It had been known for a long time that all or almost all the DNA in cells was located in the chromosomes of the nucleus. DNA was implicated in a vague way, combined with protein in the form of deoxyribonucleoprotein, as the physical carrier of the genetic information.

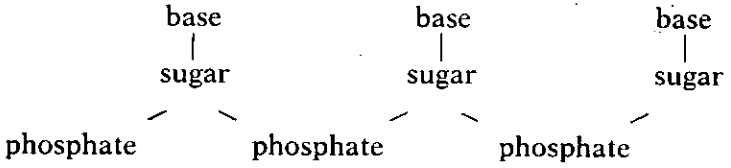
Twenty years ago a group of American biologists isolated purified DNA from one particular type of pneumococcus, a bacterium that causes pneumonia. By adding this DNA to pneumococci of another type they were able to transform them into the first type, with respect to a particular well-defined genetic character, the nature of the polysaccharide capsule surrounding each bacterium. Since then, it has been established beyond doubt that DNA is the material that carries the genetic information in all cells.

The Structure of DNA

DNA is a very long, thread-like molecule made up of phosphoric acid, a sugar, and four organic bases. The sugar (which is deoxyribose) and the phosphate molecules are joined together in an alternating fashion to form a regular backbone for the molecule:

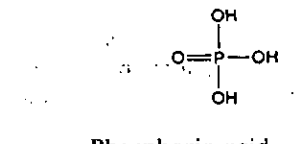


To each of the sugar molecules is joined one of the four organic bases:

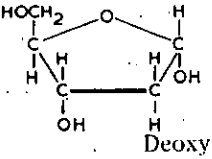


The four organic bases in DNA are called adenine (A), guanine (G), cytosine (C) and thymine (T).

STRUCTURAL COMPONENTS OF DNA



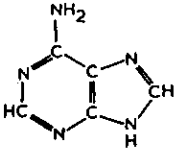
Phosphoric acid



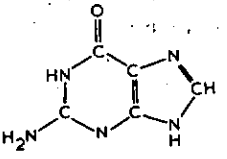
Deoxyribose

Organic Bases

Purines

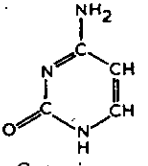


Adenine

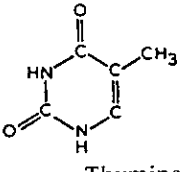


Guanine

Pyrimidines



Cytosine



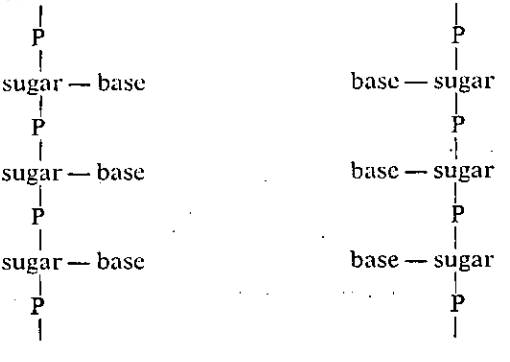
Thymine

DNA molecules may be very long indeed. The entire genetic material of the bacterium *Escherichia coli* has recently been shown to be in one piece about 500 μ long containing about 4,000,000 bases arranged in two strands as described below.

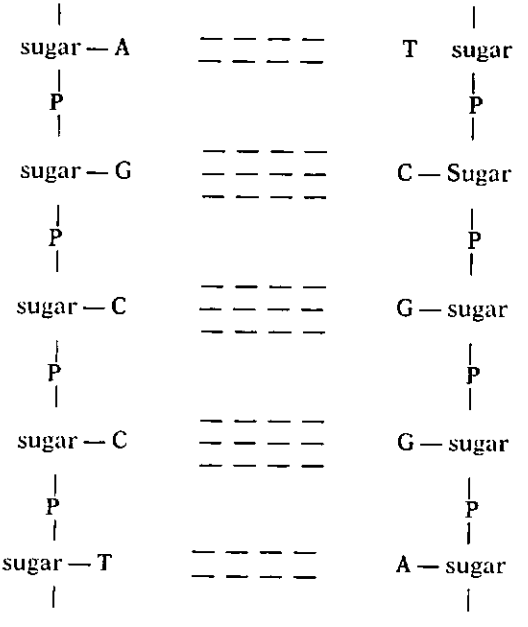
The sugar-phosphate backbone of all organisms is the same. It is the sequence of the bases along the DNA that gives each organism its unique genetic material.

HOW DOES DNA REPRODUCE ITSELF?

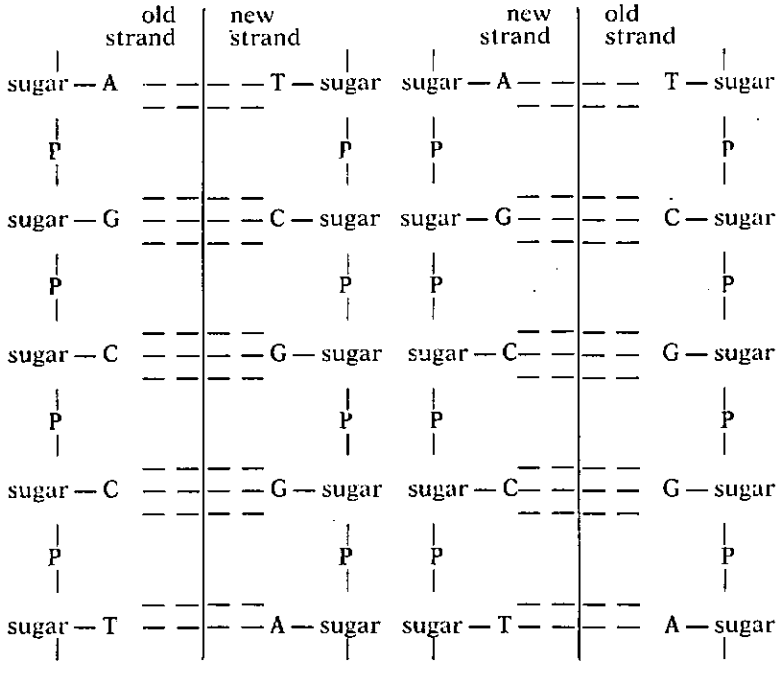
The most basic requirement for genetic material is that it should be able to reproduce itself exactly, or nearly exactly, so that the information can be carried correctly from cell to cell and from parent to progeny, without the need for outside guidance and without being influenced to any significant extent by environmental factors. DNA has two features which make such self-replication possible. First, the molecule is a double-stranded structure in which two of the phosphate-sugar strands with their attached bases lie side by side.



The two strands are in fact twisted together into a double helix, but this aspect of the structure need not concern us at present. The second vital feature is that the pairs of bases in the double structure lie close together, and because of their detailed chemistry only two kinds of pairs of bases are possible. Adenine (A) in one chain can pair with thymine (T) in the other, and guanine (G) can pair with cytosine (C). This specific pairing takes place through the formation of a weak type of chemical bond called the hydrogen bond. Two hydrogen bonds can form between A and T and three between G and C. No other combinations are normally possible so we get the following kind of structure (dashes indicate the hydrogen bonds):



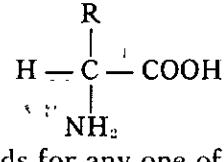
When the genetic material replicates itself in preparation for cell division the two strands come apart. Each base in the two strands then attracts to itself the appropriate hydrogen bonding partner from the supply available in the cell. (The "free" bases are already attached to a single sugar-phosphate unit.) Thus for the two sections of the double strand set out above, we get after one cycle of replication:



Thus two new double strands are formed, each identical with the parent double strand and each containing one of the strands from the parent in an intact state. This method for the replication of DNA, which was put forward by Watson and Crick in 1953 as a theory, has since been amply confirmed by experiment.

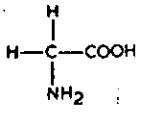
THE STRUCTURE AND FUNCTION OF PROTEINS

In their fundamental structure proteins are also long thread-like molecules with a regularly repeating backbone structure, but with 20 possible different building blocks, compared with the four bases in DNA. These twenty building units of proteins are the amino acids which have the following general structure:

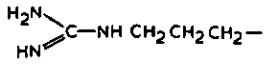


The R— here stands for any one of 20 different chemical groupings corresponding to the 20 amino acids. The 20 groups vary widely in their complexity, size and chemical properties.

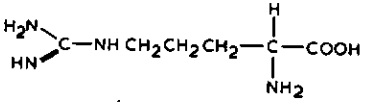
Thus for example R=H gives the simplest amino acid, glycine:



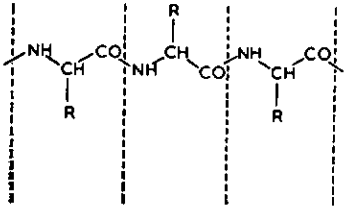
while R =



gives the much larger, basic amino acid, arginine



In proteins the $-NH_2$ group of one amino acid is joined to the $-COOH$ group of the next in a strong chemical bond to give the regular backbone structure:



Amino acid Amino acid Amino acid

The chain of a protein may be twisted and folded in various ways to give the final functional molecule, but this secondary structure is dependent in the first place on the sequence of amino acids in the chain. Some proteins carry out protective, structural, or other special functions for the organism such as those of hair, wool, skin and silk. However, the most important proteins are those which are enzymes. Every cell contains a large number of different enzymes which are the catalysts that allow all the specific chemical reactions in the cell to take place — enzymes for the breakdown and synthesis of sugars, for the manufacture of amino acids and hundreds of other reactions necessary in the metabolism of the cell. Differences between different cells reside in the different sets of enzymes they possess. Thus we can now reword the question, "In what form is all the information needed to specify the adult organism, packed into the fertilized egg?" and ask: "How does DNA contain the information for the synthesis of specific proteins?"

THE GENETIC CODE

The specificity of DNA lies in a sequence of four bases, while the specificity of proteins depends on a sequence of amino acids — there being twenty to choose from. The problem of the genetic code has been reduced to the question: "How can four letters (G, A, C, T) be used to code for 20 different words (amino acids)?" After a great deal of theoretical speculation and a number of most elegant experiments, it now seems almost certain that the genetic code has the following properties:

(1) It is universal from viruses to man.

(2) A triplet of bases in DNA codes for one amino acid in a protein.

(3) Triplets for neighbouring amino acids are adjacent and do not overlap.

(4) There are no bases functioning as "commas" between adjacent triplets.

(5) The code for each protein is read in one direction from a fixed starting point in the DNA chain.

(6) During the reading of the code it is probable that only one of the pair of DNA strands is used.

Expressed diagrammatically:

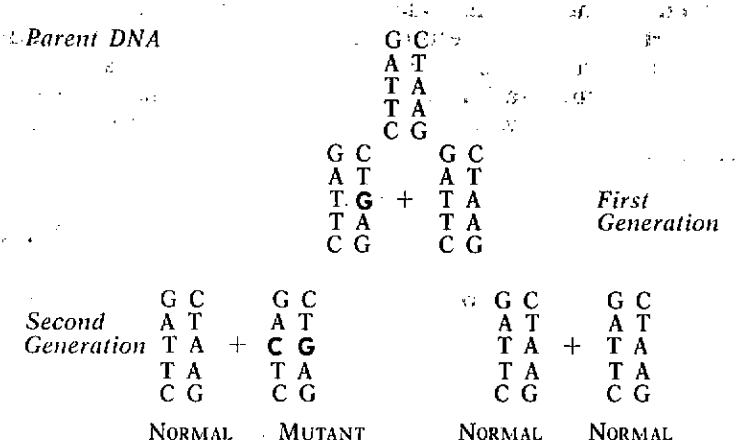
DNA	G A T	C C A	A T T	A G T	— — — —
Protein	AA_1	AA_2	AA_3	AA_4	— — — —

There are 64 possible triplets of 3 bases from a collection of 4, but only 20 amino acids. It has been possible to determine the actual triplets with fair certainty for most of the amino acids. One feature which is somewhat puzzling at present is that, for some amino acids at least, more than one triplet or bases can be used as the code-word.

THE NATURE OF MUTATION:

Geneticists have known for a long time that the genetic material is not entirely constant — that mutations or stepwise changes can take place. It is now clear that the fundamental unit of change in the genetic material is the base pair in the DNA. If for any reason — such as the action of a chemical mutagen or of radiation — a mistake should occur in base pairing during one cycle of DNA replication,

then in one of the progeny lines the DNA will contain an altered base pair. Two cycles of DNA replication giving rise to such a mutation can be illustrated schematically as follows (the mutant bases are in bold type):



This altered base pair will change the triplet of bases in which it occurs and may thus lead to a protein with one amino acid replaced by another at one particular place in the molecule. If this change was in a critical part of the protein molecule, it could lead to an altered or deficient enzyme. An example of this with human haemoglobin is discussed later. It is believed that mutation may also occur by addition or deletion of a base pair in the double-stranded DNA. This would lead to misreading of all the triplets in the code beyond the point of addition or deletion.

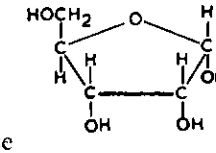
THE ROLE OF RNA

It has been known for some time that much of the protein synthesized in a cell is made in the cytoplasm, not in the nucleus where the DNA is located. How is the coded information in DNA actually used in the synthesis of proteins? It is here that RNA is important. RNA has a structure basically like that of DNA — a regular backbone of sugar and phosphate — the sugar being ribose instead of deoxyribose. Three of the four bases are the same (adenine, guanine and cytosine) but uracil replaces thymine.

STRUCTURAL COMPONENTS OF RNA

(a) Phosphoric acid

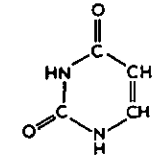
(b) Ribose



Ribose

(c) Organic Bases

Purines: Adenine and Guanine
Pyrimidines: Cystosine
and Uracil



Uracil

RNA has a much shorter molecule than DNA and is chemically less stable. The first direct evidence that RNA was important in the synthesis of proteins came from the study of certain viruses attacking plants. These consist of only the bare essentials necessary for self-replicating entities — a core of RNA surrounded by a protective coat of protein.

In 1956 it was shown that the RNA of tobacco mosaic virus could be stripped of its protein coat under mild conditions and that such RNA by itself was capable of initiating new infections that led to the production of new virus particles complete with the normal protein coat. This was the first evidence demonstrating that at least some kinds of RNA, like DNA, could carry the code for the synthesis of protein.

In cells three major classes of RNA can now be distinguished. They all have the same basic structure but serve different functions in the process of protein synthesis. The RNA classes are known as ribosomal RNA, messenger RNA and transfer RNA.

The synthesis of cellular RNA is controlled by DNA by a base-pairing mechanism similar to that involved in the replication of the DNA itself. In RNA synthesis one strand of the DNA acts as a template and the bases for RNA (already attached to ribose and phosphate) are lined up along the DNA according to the base-pairing specificity:

DNA BASES		RNA BASES
Adenine		Uracil
Guanine		Cytosine
Thymine		Adenine
Cytosine		Guanine

Ribosomal RNA makes up about 70 to 80% of the total RNA of the cell. Its DNA template forms a very small proportion of the total DNA of the cell. Ribosomal RNA occurs in small bodies known as ribosomes which consist roughly of a 50/50 mixture of protein and RNA. Very large numbers of ribsomes occur in the cytoplasm of cells. They are the sites where new proteins are synthesized. At least in some types of cell the ribosome is a non-specific body and can function in the synthesis of many different kinds of protein. The role of the ribosomal RNA in this process is not yet understood.

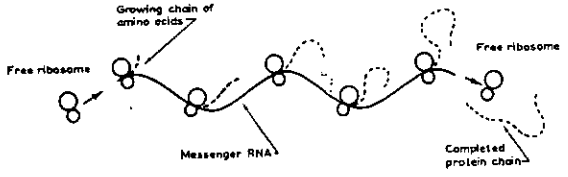
Messenger RNA. Messenger RNAs are copies, in RNA form, of stretches of the DNA that code for a particular protein. Thus, if a particular protein had 100 amino acids in its structure, we would expect its messenger RNA to have 300 bases. Since there are hundreds of different proteins in a cell, it is thought that a good proportion of the DNA of the cell is concerned with the production of messenger RNA. It has recently been calculated that the DNA complement of a human cell must contain enough information for the coding of between 60,000 and 6,000,000 different proteins of average size. In the mature organism cells in different tissues have specialized functions and produce different proteins. Thus not all the DNA in any particular cell is making messenger RNA. During protein synthesis messenger RNA becomes bound to the ribosomes.

Transfer RNA. There are at least 20 different transfer RNAs, one for each of the amino acids. Some amino acids associate with more than one transfer RNA (up to five) for reasons not yet clearly understood. A small proportion of the DNA is involved in the production of these amino-acid-specific transfer RNAs. These RNAs are much smaller than the other kinds. They contain only about 80 bases. Their detailed structure is not well known, but their function has been established. They pick up free amino acids in the cytoplasm and bring them to the site of protein synthesis at the ribosome. Here they recognize in some way the triplet of bases in messenger RNA that codes for the particular amino acid they carry. Thus each transfer RNA probably has two specific "recognition" sites — one for the specific amino acid which it picks up from solution (with the aid of a specific enzyme) and another for recognizing the appropriate triplet of bases in messenger RNA.

Polyribosomes. About two years ago it was discovered that more than one ribosome can become attached at once to

one piece of messenger RNA. Such a collection of ribosomes (often about five) on one strand of messenger RNA is known as a polyribosome. This makes the process of protein synthesis much more efficient since more than one protein strand can be being made at once on the same piece of messenger RNA. The details of the chemical events that occur at or near the surface of the ribosome as it is moved with respect to the messenger RNA, and as the transfer RNAs bring their appropriate amino acids to the ends of the growing protein chains, are not at all well understood at present.

The polyribosome can be represented schematically as follows (the transfer RNAs are not shown):



Thus, although there are many important problems of chemical detail to be solved, the general way in which the genetic information is stored, replicated in cell division, and used to make specific proteins is now fairly well understood.

The Regulation of Cell Growth

The major problem that remains is the question of the regulation of cell growth. How do cells grow in a controlled way and adapt themselves chemically and morphologically to their environment? How is the same complement of DNA in different parts of an organism during embryonic life used to produce the wide variety of cells and tissues found in the adult organism?

The details of these processes are far from being fully understood but rapid progress is being made. In particular, a most fruitful theory was put forward by two French biologists, Jacob and Monod, about four years ago. They postulated that there exist in the DNA two kinds of gene — *structural* genes and *regulatory* genes. A structural gene is the sort already discussed — a stretch of the DNA that codes for the amino acid sequence in a particular enzyme or structural protein. When the cell requires this protein, copies of the DNA are made in messenger RNA form which are then used to specify the protein. A regulatory gene, according to the theory of Jacob and Monod, is another

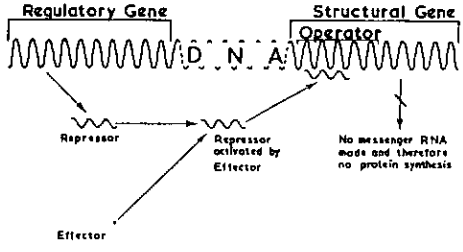
stretch of DNA which codes for the production of a *repressor*. The chemical nature of repressors is not established but there is some evidence that repressors may themselves be proteins.

The repressor is able to combine with and block the action of a section of the DNA called the *operator*. The operator is assumed to be the first part of the DNA of the sructural gene that is used in transcription, or to be next to it in the same DNA strand.

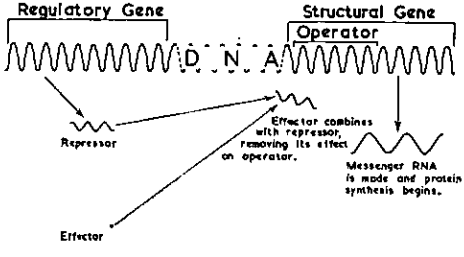
Whether or not the repressor blocks transcription is determined by substances of small molecular weight called *effectors*. Some effectors activate the repressor leading to the repression of synthesis of the particular protein. Other effectors may inactivate a repressor allowing protein synthesis that was previously blocked to proceed.

Put schematically:

For repression of enzyme synthesis:



For induction of enzyme synthesis:



There are two most important points about the small molecules in this scheme, the effectors. First, there is no necessary structural relationship between the effector and any part of the protein whose manufacture it can repress or induce. Secondly, effectors can originate either internally within the cell as a product of the cell's own metabolism or they can be absorbed by the cell from its surrounding

medium. Thus through this mechanism cells can adapt to changes in either their internal or external chemical environment. The stretch of DNA that codes for a single protein is known as a *cistron*. Jacob and Monod termed a cistron or group of cistrons, controlled by one operator, an *operon*. In many cases, the cistrons in the DNA that code for a series of enzymes that catalyse related biochemical reactions, occur one after the other along the DNA and are under the control of a single operator. In this way it is possible for a single small molecule (the effector) to turn on (or off) a whole sequence of biochemical steps in the synthetic or degradative machinery of the cell.

The basic theory of Jacob and Monod which was put forward on the basis of experiments with micro-organisms, is undergoing continuing revision and refinement. It will undoubtedly play a major part in unravelling in chemical terms the problems of embryology and development.

"Applications" of Molecular Biology

The description of the most fundamental processes of living material in chemical terms, as outlined above, is making it possible to take a fresh look at many important biological phenomena. Only a few examples can be briefly mentioned here.

Viruses cause important diseases in man, animals and plants. New insight is being obtained into the way the viral DNA or RNA takes over the synthetic machinery of the cell and dictates the replication of more virus particles.

The mechanism of action of drugs is coming to be understood in detailed chemical terms. For example, the potent antibiotic actinomycin D acts by binding specifically with the guanine bases in DNA. This prevents DNA-dependent RNA synthesis — *i.e.*, no new messenger RNA can be made and cell growth stops.

The problem of ageing in animals and man has been studied intensively for many years, but it is only recently that any clear idea about the process has emerged. The discovery that radiation accelerated ageing has provided a new way of studying the process experimentally. The idea that ageing is due to "stress" or "wear and tear" now seems untenable. It is much more likely that, as time goes by, random mutations occur in the DNA of the body cells. These mutations, which are almost all harmful to some degree, accumulate particularly in tissues where cells are not dividing rapidly. This accumulation of mutations leads

to decreased efficiency in the production of proteins and to lowered efficiency in the functioning of the cells.

Cancer is a disease of major importance to man. The basic steps in the conversion of a normal cell to a cancer cell are not yet understood in chemical terms. However, it seems very probable that the primary events take place in the genetic material — the DNA of the cell. A mutation in a regulatory gene may alter the production of certain key types of protein in the cell, leading ultimately to the uncontrolled growth and cell division characteristic of cancer tissue.

Many important genetic diseases affect man and animals. Some of these are now understood in chemical terms. For example, in the disease "sickle cell anaemia" which is particularly frequent in certain populations of Asia and Africa, the red blood cells are a sickle shape instead of the normal shape. This is due to the production of a defective type of haemoglobin, the oxygen-carrying protein of red blood cells. This abnormal haemoglobin has been found to be due to a single mutation in the DNA — a change from one base pair to the other — in the structural gene that codes for haemoglobin. The mutation leads to a substitution of a particular glutamic acid residue in the normal protein molecule by a valine in the mutant. This change in a single amino acid out of the 600 in haemoglobin is sufficient to alter the net electric charge on the intact protein. This change in charge leads to an abnormal aggregation of the haemoglobin molecules within the red blood cell, with consequent collapse into the "sickle cell" shape and reduced oxygen-carrying capacity. Other mutant haemoglobins have now been discovered which involve changes in single amino acids in the molecule.

Research in the Microbiology Department at Auckland

In conclusion, a few remarks will be made about the work going on in the Microbiology Department in Auckland. Many of the advances in basic knowledge outlined above have been made possible by the application of new and improved chemical and physical techniques. This involves the use of much expensive equipment. Through the support of various organizations, we have been fortunate in obtaining most of the modern apparatus that is required for research on nucleic acids and proteins. This includes such items as high speed centrifuges, equipment for the fractionation of nucleic acids and their constituents, an elec-

tron microscope, and sensitive automatic equipment for measuring radioactive isotopes in large numbers of samples. A group of biologists, biochemists and chemists is working on various aspects of the problem of how nucleic acids control normal cell growth, tumour cell growth, and virus multiplication.

Structure of Transfer RNA

The full sequence of bases is not yet known for any intact natural nucleic acid. Transfer RNAs, because of their relatively small size (about 80 bases), offer perhaps the most favourable kind of RNA for attempting to determine a complete base sequence. Work is in progress using the transfer RNA that takes the amino acid serine to the site of protein synthesis. The first problem is that, to obtain meaningful results, it is necessary to isolate one single species of transfer RNA in pure form in sufficient quantity for analysis. It was already known that there were three different kinds of serine transfer RNA. Recently in Auckland five have been separated using a more refined fractionation of transfer RNAs from yeast cells. While a complete sequence of bases is not yet in sight, it has been possible to show that all five species differ in some of their base sequences.

Replication of Viral RNA

Another line of work concerns the mechanism by which the nucleic acids of viruses containing RNA replicate themselves. We have recently isolated from virus-infected plants a material with the properties of double-stranded base-paired RNA. Such material does not appear to occur in normal cells. From the way in which this double-stranded material becomes labelled with radioactive phosphate we have concluded that the double-stranded structure contains a viral RNA strand and a base-paired complementary strand (A: U and G: C). The "anti-viral" strand then acts as a template for the production of a large number of viral RNA strands, by the base-pairing mechanism. As a new viral RNA strand is laid down it displaces the pre-existing strand from the template. This mechanism probably occurs in the replication of RNA viruses in animals, such as polio virus.

Protein Synthesis in Leaves

As noted earlier, protein synthesis occurs on polyribosomes which are strands of messenger RNA to which

several ribosomes are attached. We have recently developed methods for studying polyribosomes in plant tissues. We have found that the proportion of ribosomes in the polyribosome form is very dependent on the light and dark periods to which the plant is subjected. Polyribosome levels are highest during sunny days and lowest at the end of the night period. We have also found that there is a separate polyribosome system in the chloroplasts, based on a smaller type of ribosome that had been discovered by Dr J. W. Lyttleton at Palmerston North a few years ago. It has recently been shown in other laboratories that chloroplasts contain small amounts of DNA. The fact that they also contain a separate ribosome-polyribosome system for making proteins lends support to the idea that chloroplasts may be genetically autonomous organelles within the cell.

Perhaps enough has been said to show that the breakthrough of physics and chemistry into biology, with the consequent development of molecular biology, has opened up all sorts of new possibilities for experimentation on basic biological problems. The next twenty years should prove just as exciting as the past fifteen have been.

SUGGESTIONS FOR FURTHER READING

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ADSORBED MOLECULAR FILMS

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This lecture is concerned with thin films, or layers of molecules, adsorbed on surfaces. The properties of a surface, solid or liquid, are different from those of the bulk substance because of the unequal valence or Van der Waal attractive forces which occur at the surface. For example, imagine a single molecule within the bulk of a liquid (see Fig. 1a); the surrounding molecules will all exert attractive forces but because they occur on all sides, on average these forces will cancel out and the molecule will not be subjected to a net force in any particular direction. However, if the molecule is at the surface of the liquid, there is a net attractive force inwards, towards the bulk liquid (see Fig. 1b). Consequently, any surface tends to contract to the

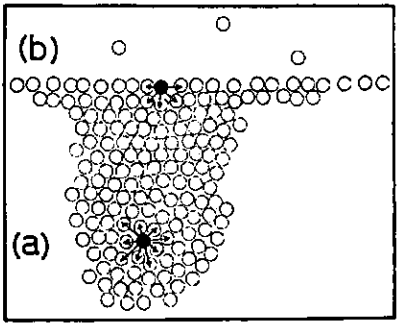


FIG. 1: (a) *Attractive forces roughly cancel out within the bulk liquid.* (b) *A net force, directed towards the bulk liquid, exists at the surface.*

smallest possible area, and because a liquid surface can move, it adopts a spherical form, as the surface is then the smallest possible for the given volume. Thus drops of liquid are spherical, and bubbles of gas in a liquid are spherical, for the same reason. Solid surfaces are not able to move, of course, but they are able to reduce these unequal surface forces somewhat by adsorbing other types of molecules in the vicinity. For example, if the solid surface is in air, it may adsorb oxygen or carbon dioxide, or water vapour. A nickel surface goes one step further; after adsorbing a film of oxygen on to its surface, chemical reaction occurs so that a film of nickel oxide is produced. The latter process is called

chemisorption, but more usually chemical reaction does not occur and the process is then called physical adsorption, or physisorption.

Such adsorbed films (whether chemisorbed or physisorbed), only one or two molecules thick, are attached to all solid surfaces unless special precautions are taken, like forming a new metal surface *in vacuo* by vaporization of a heated metal filament, or by heating an existing solid *in vacuo*. Silica gel, for example, has to be heated at about 200°C *in vacuo* (10^{-5} to 10^{-6} mm Hg) for about eight hours in order to remove adsorbed water. Silica gel is made up of particles each consisting of a three-dimensional network of —Si—O—Si— bonds due to the condensation of silicic acid molecules:

$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

At the surface, however, $-\overset{|}{\underset{|}{Si}}-OH$ groups remain, and water molecules are adsorbed on to these groups, unless the gel is heated in a vacuum.

A fairly recent technique used to investigate the properties of adsorbed films on solids is to measure the dielectric behaviour of the adsorbed molecules. The adsorbent, usually powdered, is packed into the space between two stainless steel coaxial cylinders which act as a capacitor, so that the adsorbent (silica gel, for example) can be considered as the dielectric. The whole dielectric cell is placed in a glass container which can be evacuated and heated. The electrical capacitance of the cell, containing the evacuated adsorbent, is next measured accurately by meaus of a known technique, one of which is called the "heterodyne beat method".

In brief, the unknown capacitor, or dielectric cell, is connected in parallel with a precision variable air capacitor and an inductance coil, to form a "tuning circuit" (see Fig. 2) which governs the frequency of a variable frequency oscillator. The frequency depends on the value of the total capacitance $= C_{cell} + C_{PVAC} + C_L$, where C_{PVAC} is the capacitance of the precision variable air capacitor and C_L is all the additional constant capacitance in the circuit, which

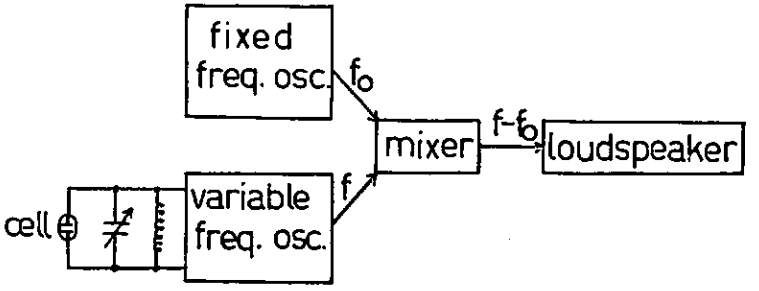


FIG. 2: *Schematic circuit of "heterodyne beat" method for measurement of capacitance.*

includes that of the leads. The frequency output is then "mixed" with a fixed frequency (say, 1 Mc/s) from a quartz crystal oscillator, and the difference between the two frequencies ($f-f_o$) is heard as "beats" over a loudspeaker detector. When $f=f_o$, no beats are heard and the value of the precision variable capacitor can be adjusted to obtain this condition. Now if the tap of the dielectric cell is opened and a measured quantity of water allowed to be adsorbed on to the silica gel, the dielectric constant of the gel will be increased, and since $C_{cell}=\varepsilon_{app} C_o$ where ε_{app} is the apparent dielectric constant of the gel and adsorbed water and C_o is the capacitance of the empty cell, then C_{cell}, the electrical capacitance of the cell, will also be increased. This increase in capacitance causes a corresponding change in the frequency and beats will now be heard over the loudspeaker, and the value of the precision variable condenser must be readjusted (*i.e.*, capacitance taken out) in order to reach zero-beat again. If this change in electrical capacitance, or ε_{app}, is plotted against the amount of adsorbed water, curves of the type indicated in Fig. 3, are obtained, in which an initial linear region is found to be practically independent of frequency (*i.e.*, the value of f_o), but the slope of the following region varies with frequency, being greater than that of the first region at low frequencies (2.5 kc/s to 100 kc/s, say) but being of smaller, and constant slope at higher frequencies (1 Mc/s and above). The point at which a change in slope occurs is considered to indicate the amount of water adsorbed in a monolayer on the adsorbent surface. Interpretation of these curves is still controversial and further research of this nature is being carried on, at present, at Auckland University.

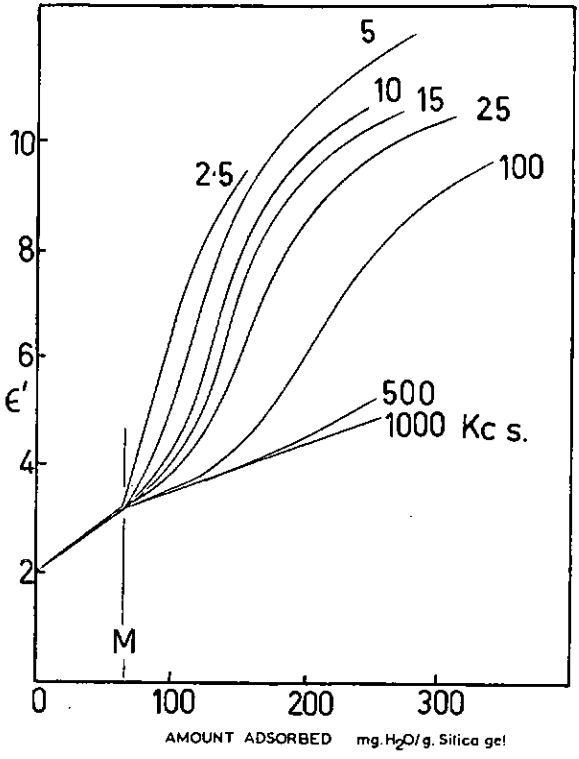


FIG. 3: *Apparent dielectric constant of the gel + adsorbed water* (ϵ') *plotted against the amount of water sorbed on silica gel at 25°, for various fixed frequencies from 2.5 kc/s to 1 Mc/s (M indicates monolayer completion.) (Nair and Thorp, Univ. of Auckland, 1964.)*

Adsorption can take place at liquid surfaces as well as solid surfaces, since any adsorption at an interface will reduce the uneven attractive forces at the surface, and this, in turn, reduces the surface energy, or surface tension. The adsorption of a single layer of stearic acid molecules on to the surface of water can be illustrated experimentally. The layer is only about 25×10^{-8} cm (*i.e.*, 25A) thick. Since 2.5 cm is approximately equal to 1 in., then the stearic acid monolayer is only about 10^{-7} in. thick, or ten million layers would be required to form a film 1 in. thick.

If a drop (say 0.1 ml) of a very dilute solution, containing only about 0.05 g stearic acid ($C_{17}H_{35}COOH$) in 100 ml benzene, is put on to a clean surface of water, a layer of

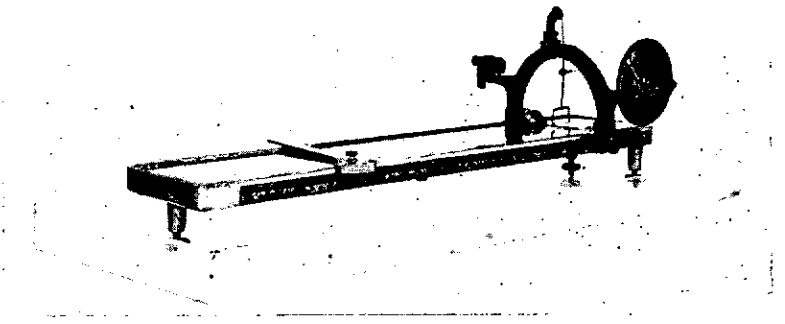


FIG. 4: *Langmuir trough.*

molecules will spread over the surface. The benzene molecules quickly evaporate leaving only insoluble stearic acid molecules. A shallow trough (see Fig. 4) (frequently known as a Langmuir trough, after one of the earlier workers in this field) is filled to the brim with water, and the film of stearic acid so formed is confined between a floating barrier attached to a torsion wire and a movable barrier which can be advanced along the surface towards the floating barrier, thereby compressing the adsorbed film. The film will obviously exert a force on the floating barrier as it is compressed and this can be measured by rotating the torsion wire, connected to a pointer which moves over a scale, so that the floating barrier remains in the same position. The scale is calibrated so that the position of the pointer gives a direct measure of the force exerted by the stearic acid film on the floating barrier. Now for every position of the movable barrier (and hence for every scale reading) the area of the film can be obtained (*i.e.*, each position of the barrier is noted on a rule attached to the side of the trough, the width of the trough being known). As the amount of stearic acid added in the drop is known, the area occupied by each molecule in the film can therefore be calculated as follows.

Suppose 0.1 ml of a solution containing 0.05 g stearic acid in 100 ml benzene or 0.05/100 g stearic acid per ml had been added. Then the amount of stearic acid added = $0.1 \times 0.05/100$ g $= 5.10^{-5}$ g. Hence the number of g moles added $= 5.10^{-5}$/M.Wt. $= 5.10^{-5}/284$, and, therefore, the number of molecules added $= (5.10^{-5}/284) \times N = X$ where N is about $60.0.10^{23}$ and is equal to the number of molecules in a g mole (*i.e.*, the Avogadro number). If the measured area of the film is A, then the area per molecule $= A/X$.

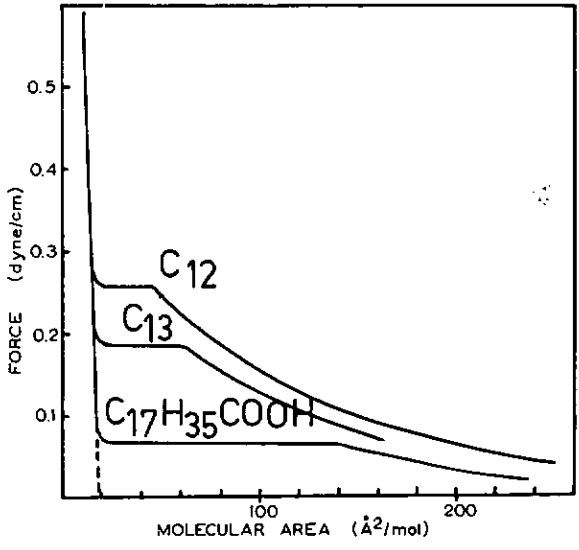


FIG. 5: *Force-area curves for a series of fatty acid monolayers on water.*

If the area per molecule is plotted against the force exerted on the barrier, a curve of the type illustrated in Fig. 5 is observed. In the near vertical region, where a small decrease in area corresponds to a large increase in force, the molecules in the monolayer have become closely packed together and are under compression. Thus extrapolating this linear region to zero force gives the area occupied by a molecule in a close-packed monolayer which is not under compression. This value is found to be about 20.5A^2 for stearic acid.

Remarkably, the same value is obtained for other carboxylic acids with long paraffin chains, such as myristic acid ($C_{13}H_{27}$.COOH) and palmitic acid ($C_{15}H_{31}$.COOH). Further, although a hydrophylic group, such as $-$COOH, appears to be necessary for the molecules to spread over the water surface, an alcohol group may be substituted for the carboxylic acid group and thus cetyl alcohol ($C_{16}H_{33}OH$) is also found to have a close-packed molecular area of 20.5A^2. The explanation is that the molecules in the adsorbed layer must be oriented with the hydrophilic groups dipping into the water and the paraffin chains sticking vertically out of the water, so that 20.5A^2 is the cross-sectional area of the paraffin chain, which is independent of the chain length, of course.

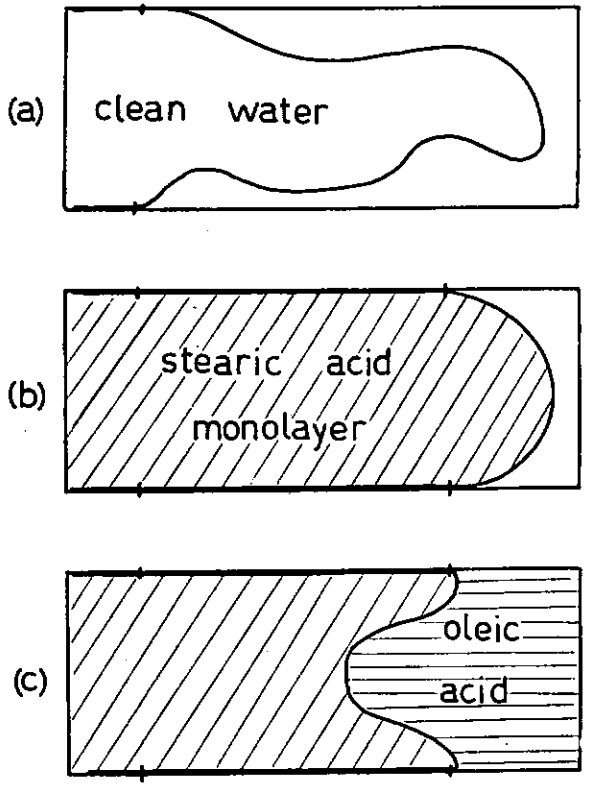


FIG. 6: (a) *Waxed thread is laid on clean water surface and fastened to sides of trough at one end.*
(b) *The thread is pushed by the stearic acid monolayer to form a parabolic curve. (Additional clips are finally added to fasten the thread to the sides of the trough, as shown.)*
(c) *Opposing force exerted by an oleic acid film on the other side of the thread.*

To demonstrate the movement of an adsorbed layer on water, the film (itself invisible) can be made to show its presence by the movement of a waxed silk thread boundary placed on the surface. This involves simpler equipment than before, and although it is described here merely as a means to illustrate the presence of an adsorbed monolayer of stearic acid molecules, it has a more practical use in that such films may be transferred on to glass or metal surfaces, one layer at a time. The equipment consists of a shallow trough with waxed edges, a waxed silk thread (the thread is dipped into a solution of paraffin wax in benzene and dried in air) and some clips. The trough is filled to the brim

with water and the surface is swept clean with a waxed barrier. The waxed silk thread is then laid on the surface carefully with forceps (to avoid contamination) and both ends are clipped to the sides of the trough at one end as shown in Fig. 6(a). Next, one or more drops of a dilute solution of stearic acid in benzene are added to the surface within the area bounded by the thread, and immediately the thread will move. When enough stearic acid has been added to form a close-packed monolayer, the thread forms a parabolic curve as shown in Fig. 6(b). (Should too much stearic acid solution be added, the excess remains as a visible "lens" on the surface. The surface would then have to be swept clean again and a fresh start made since only a monolayer must be formed.) Next, a drop of oleic acid is added to the surface, on the other side of the barrier, which also spreads over the surface to form a monolayer and exerts an opposing force which pushes the thread back again, as shown in Fig 6(c).

In this case a few extra drops of oleic acid are purposely allowed to remain in excess as "lenses" on the surface, since these act as reservoirs and keep a close-packed monolayer of oleic acid molecules pressing against the thread. Oleic acid, $CH_3.(CH_2)_7.CH=CH.(CH_2)_7.COOH$, has a double bond about half-way along the paraffin chain and this causes the molecule to be adsorbed lying flat on the surface. Thus a much greater area is occupied per molecule than in the case of the corresponding saturated paraffin chain. However, although this is of interest, the oleic acid is used in these circumstances only as a sort of "piston oil" — *i.e.*, to keep the stearic acid monolayer under constant pressure, so that the stearic acid molecules remain close-packed.

When the apparatus is used to transfer a monolayer of stearic acid on to a glass slide or metal plate, the slide or plate is initially immersed below the surface of the water before the stearic acid solution is added. On slowly drawing the slide (vertically) through the film a monolayer of stearic acid is deposited on both sides, and this can be followed by watching the movement of the thread, which is forced inward as the film is removed, some of the oleic acid molecules from the reservoir lenses spreading over the new surface, temporarily bared. Then on dipping the slide into the water again, another stearic acid layer is deposited on top of the first, and in drawing the slide out again, a third layer is deposited. In fact, any number of layers of molecules can be built up in this way, provided the film is large enough. Further, it has been found that odd

layers are deposited with the carboxylic acid group downwards, towards the surface, while even layers are oriented with these groups uppermost — a sort of head-tail, tail-head, head-tail arrangement. Although a single layer is invisible, as a number of layers are built up the film appears coloured. A film of 21 layers deposited on glass appears to be a yellow-brown colour, 41 layers appear as a dark blue film, 61 as light blue, 81 as yellow, 101 as red, and so on.

In order to illustrate the enormous importance of such adsorbed films, whether on solid or liquid surfaces, and often only one or two molecules thick, I am going to indulge in science fiction for the rest of this lecture, and guess what life would be like if such adsorbed films did not exist.

Let us imagine a typical day in your life without molecular films. You would get up at 7.0 a.m., say, put on your slippers and struggle to the bathroom. I say "struggle" not because you are still half-asleep but because the friction between your slippers and the floor might be as much as ten times more without the usual adsorbed surface films. A tremendously important use of adsorbed films is that they can act as lubricants, and a single layer of stearic acid molecules, 25Å thick, chemisorbed on to a metal surface can reduce the coefficient of friction by as much as one hundred times.

This can be demonstrated with quite simple equipment — two brass bars and a brass disc. For single molecules to be most effective as a lubricant they must be adsorbed on to an "atomically smooth" metal surface, so that the bars and disc should be polished to at least a mirror polish. One bar is supported on a block at such an angle that when the smooth polished disc is placed on the upper end it is just on the point of sliding down the bar; normally it "stays put", although now and again it may just start to slide. The second identical bar is coated with molten stearic acid, excess being removed by rubbing hard with filter paper, a technique which is supposed to leave only a chemisorbed monolayer behind. However, since the surface is bound to be full of "pot holes" and "crevices" (in terms of molecular distances) these will be filled with bulk stearic acid. If the disc is now placed on the upper end of the treated bar it will slide down, the coefficient of friction having been reduced considerably.

To return to our imaginary day: Having reached the bathroom, you would find no soap or tooth-paste — not because they were forgotten on the shopping list last week, but

because neither would be able to remove grease and dirt! Soap is normally able to remove grease by forming a molecular film around grease particles so that the latter become soluble in water. A soap molecule consists of a hydrocarbon chain containing about 17 carbon atoms in a zig-zag paraffin-type chain with a polar group, such as $-COO^-Na^+$, at one end. Now the hydrocarbon chain is able to "dissolve" in the grease particle, while the polar end-group is able to "dissolve" in water, so that a monolayer of soap molecules surrounds the grease particle, as shown in Fig. 7, and the whole particle thus becomes soluble in water. Well, in our "science fiction day" we do not allow molecular films, so if we tried to wash with soap we would get covered with a sticky, fatty substance which would not dissolve in water — rather like trying to wash with butter! The same would happen with tooth-paste. So you would have to "dry clean" with carbon tetrachloride, or alcohol, or acetone! Similarly, your clothes could never be washed but would always have to be dry cleaned.

Having had breakfast, you would set out for school, either on foot, or by transport of a different nature from that used at present — perhaps by hovercraft. Why not cycle, you say? — or go by bus or car? Without adsorbed films metal surfaces are not able to slide over each other without "seizing", or wearing excessively. Why not use oil? To explain this, I must first mention that there are normally two types of lubrication, known as hydrodynamic and boundary lubrication. Oils usually consist of glycerol

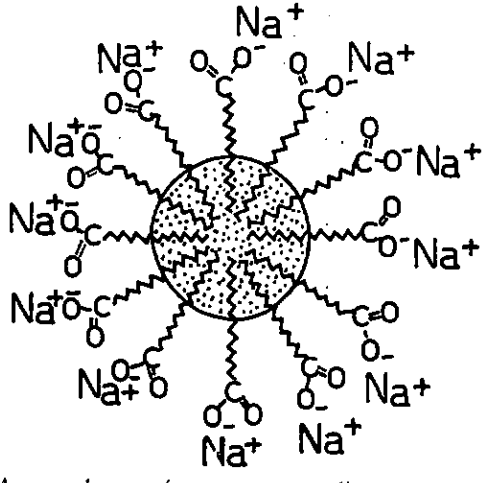


FIG. 7: *A monolayer of soap surrounding a grease particle.*

esters and are mostly hydrodynamic lubricants — *i.e.*, they are only efficient when hydrodynamic lubrication is possible, that is when the surfaces in motion are separated by a lubricant layer of appreciable thickness and the resistance to motion is then entirely due to the viscosity of the oil. However, such conditions only occur (1) at high sliding speeds, (2) with low loads and (3) usually when the design is such that a wedge of lubricant is involved. Thus the design of journal bearings is such that an oil wedge of lubricant of appreciable thickness is involved (see Fig. 8) and hydrodynamic pressure are developed which

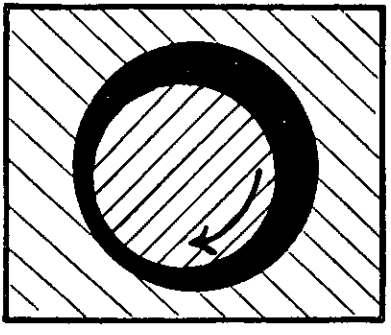


FIG. 8: *Schematic diagram of hydrodynamic lubrication in journal bearings.*

keep the metal surfaces apart and prevent wear. However, even when this type of hydrodynamic lubrication occurs measurements of electrical resistance have shown that intermittent metal-to-metal contact is still present at all times, which causes small fragments of the surfaces to shear off, causing wear, the metal dust collecting in the oil. Further whenever you start or stop a machine working on the basis of hydrodynamic lubrication (and this applies particularly to piston engines at the end of each stroke, for example) then the thick layer of lubricant is squeezed out and what is termed "boundary lubrication" becomes important.

A film of lubricant that can attach itself firmly to a metal surface (preferably by chemisorption) and is only one or two molecular layers thick is known as a boundary lubricant. An efficient boundary lubricant must not only be chemisorbed on to the metal surface, to prevent it from being swept aside by the sliding surface, but the molecules should also be oriented on the surface so that there is strong lateral adhesion between the adjacent molecules in the

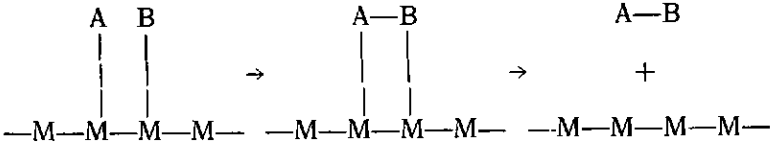
layer. Thus fatty acids, such as stearic acid, are able to react with metal surfaces to form oriented soap films which reduce wear, provided the temperature does not exceed the melting point of the metal soap, when the lateral adhesion forces between the molecules in the film are broken down. Although an oriented chemisorbed film reduces metal-to-metal contact considerably, so that the load is now supported, in part, by the film, the shear strength of the film must also be low to enable the contacting surfaces to slide over each other easily. Such boundary lubricants are normally added to hydrodynamic type oils. Sometimes they occur naturally in an oil, such as palm oil, which has been used for centuries in the steel industry in "cold" rolling thin sheets of steel between giant rollers. Palm oil contains about 8 to 11% of fatty acids, which take care of the boundary lubrication at low roll speeds, whereas, at high speeds, a type of hydrodynamic lubrication occurs in which the high viscosity of the oil becomes of importance. Unfortunately, soaps melt at about 110° to 250°C, according to the metal, and so other lubricants have to be used at higher temperaures. Solid films such as molybdenum sulphide and graphite make fairly good boundary lubricants since these solids have a layered structure and will shear easily in one direction, but the attachment of the film to the metal surface is weak, however.

This fascinating topic cannot be discussed further here, but at least the importance of molecular films in lubrication should now be clear, and so in conditions where adsorbed films are not possible, transport would have to be of the compressed-air-type or, possibly, with jet engines.

The effect on industry would be almost impossible to predict. Cold rolling steel, for example, to obtain steel plate for cars, refrigerators, metal cans, etc., would be near impossible, since roll wear would be enormous and the rolled sheet would be pitted badly — if it was possible to roll it at all. At this point I think I have already stretched the imagination pretty far, but perhaps a few industries could be named that would be non-existent if the phenomenon of adsorption on porous solids did not occur. First, all those that use catalysts for the manufacture of chemicals. Much use is made of what are called "heterogeneous" reactions where adjacent adsorbed molecules react together on a surface and the product is later desorbed. Such catalytic processes are used on a large scale in the chemical industry in the preparation of both inorganic and organic substances; well-known examples are the contact process for

the oxidation of SO_2 to SO_3 (in the manufacture of H_2SO_4) using a platinum catalyst surface, or the combination of H_2 and N_2 to form NH_3 on a ferric oxide surface (Haber process).

The production of petrol from coal by the Fischer-Tropsch synthesis is another example (CO combines with H_2 in the presence of a promoted cobalt oxide catalyst) and the production of methanol (also from CO and H_2) with a zinc oxide catalyst, the catalytic hydrogenation of ethylene on a nickel catalyst, and so on. The mechanism of such surface reactions is not always clear but it is thought that an "activated complex" occurs between adjacent molecules adsorbed on the catalyst surface, which requires less energy than in a homogeneous reaction because the adsorption process has caused a rearrangement of electrons, thereby facilitating chemical reaction. This may be indicated as follows:



The adsorption of water on porous solids, such as silica gel and alumina, is another important application of adsorption, which affects not only the chemical industry, but also the electronic and radio industries and instrument manufacturers, where use is made of such drying agents in order to maintain accurate measurements. An example is the perforated disk containing silica gel which is an essential part of a pH meter or an accurate balance.

Thirdly, considerable use is made of charcoal, alumina and other adsorbents (often packed in chromatographic columns) in the purification and separation of various chemicals.

Finally, to give an example of one important use of films on liquid surfaces, besides that of soaps and detergents, etc., a film of cetyl alcohol ($C_{16}H_{33}OH$) is often used on the surface of water in reservoirs, especially in Australia, in order to reduce the evaporation which may cause considerable loss of water in hot dry weather.

There has been opportunity here only to "scratch the surface" of this phenomenon of adsorbed molecular films, but at least I hope I have shown that such films play an essential part in everyday life and are far from being a theoretical concept, or just the concern of scientists. You might think of that next time you clean your teeth!

NUCLEAR STUDIES IN CHEMISTRY AND BIOLOGY

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Perhaps, at the end of four or five years at College, accumulating a tremendous amount of knowledge, the student has a greater feeling of the breadth of knowledge than at any future time in his career. With the start of university, begins the chiselling away of old facts as the depth in one or more disciplines of the block of knowledge increases at the expense of width.

Eventually, some twenty-five years later, he reaches the stage which this paper hopes to display — a stage of work in a world that is only slowly reaching textbook acceptance, a world of part-proven facts, of much speculation, and of possibilities of research from the snow mine at the South Pole to the face of the moon. The examples given here, then, are not drawn from the world of fantasy but are an attempt to convey an idea of the story to be read in the submicrogram realm of matter.

Most are familiar with the Periodic Table, so only that part of the table that is relevant to the rest of the paper is reproduced here.

PERIODIC TABLE

H							*He*
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	A
K							

Some of the chemistry of all these elements will be well known even if interests lie mainly in the biological sciences, the elements shown here are some of the most important.

It is intended to take two of the best known elements in this table and to indicate how we go about accumulating additional scientific information about our planet. First, consider hydrogen and oxygen in the following equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The atomic weight of hydrogen is generally known to be 1.009; this is because hydrogen is made up of the isotopes hydrogen and deuterium in the ratio 99.985H to 0.015D. But there is a third isotope of hydrogen called tritium, which was first discovered in 1934 by Lord Rutherford,

when he bombarded deuterated compounds with high energy deuterons to give the nuclear reaction:

$$^{2}_{1}H\,(d,p)^{3}_{1}H$$

He also initiated the search for tritium in natural water by using electrolysis and he hoped to measure the tritium in a mass spectrometer. To do this, however, because of the relative insensitivity of mass spectrometry, he would have had to enrich the tritium 10^{12}-fold, or, as a comparison, to reduce all the water in Lake Taupo to only a thimbleful of enriched water — an impossible task.

In 1951, Professor Libby of the University of Chicago showed that tritium was radioactive and, using the water that Rutherford had enriched, he was able to detect the minute level of radioactive tritium in this water, even though there is only one tritium atom for every 10^{18} hydrogen atoms. In fact, in all the water of the earth, there are only a few kilograms of tritium.

The second element in the Table is helium. This is a noble gas and is found not only in the atmosphere but in gas from oil wells. This element also has isotopes ^{4}He, approximately 100%, and ^{3}He, approximately 0.00013%. If the helium gas in the atmosphere is examined and compared with the helium gas of the oil wells, it is found that there is more ^{3}He in the atmospheric helium. As ^{3}He is a stable isotope, it was believed that bombardment of air by cosmic rays produced tritium which, by emitting an electron, would form ^{3}He by the reaction:

$$^{3}_{1}H \rightarrow {}^{3}_{2}He + \beta^{-}$$

Thus it was found that tritium is being continuously produced in the atmosphere by cosmic rays. After production, it forms tritiated water THO, so that all surface water is radioactive. This radioactivity of tritium decays away in the half-life of 12.5 years. It is now possible to measure this minute radioactivity of water because of its tritium content. How small this concentration of tritium is can be gauged from the fact that for every 10^{18} hydrogen atoms there is only one tritium atom.

So hydrogen (H) is not only hydrogen but also deuterium (D) and tritium (T), and:

- the isotope hydrogen is stable approx. 100% in abundance;
- the isotope deuterium is stable approx. 0.015% in abundance; and
- the isotope tritium is radioactive; 1 T atom to 10^{18} H atoms in abundance; and has a T½ 12.5 years.

Now consider the element, oxygen. Not very many years ago, it was taught that its atomic weight was 16,000, which was taken as the standard for the atomic weight table. It is now known that oxygen is made up of three isotopes having approximately the following relative abundance:

^{16}O	99.59
^{17}O	0.037
^{18}O	0.204

These are all stable isotopes, but there is a radioactive isotope ^{15}O with the half-life of only 126 seconds. Now if the formula for water is written with the various possible isotopic species, it can be seen how complicated even this formula becomes, for one can write it as:

$H_2{}^{16}O$	$H_2{}^{17}O$	$H_2{}^{18}O$
$HD^{16}O$	$HD^{17}O$	$HD^{18}O$
$HT^{16}O$	$HT^{17}O$	$HT^{18}O$

Take another common element, carbon, which has the following isotopes:

^{12}C of isotopic abundance 98.89 and a stable isotope.
^{13}C of isotopic abundance 1.11 and a stable isotope.
^{14}C that exists to the extent of 1 ^{14}C atom in 10^{12} ^{12}C atoms.

This latter isotope of carbon is radioactive with a half-life of 5,800 years.

^{14}C was also discovered by Dr Libby only a few years ago and, because of the relative long life of its radioactivity, a very successful method of dating carbonaceous material has been developed. ^{14}C is produced by the action of cosmic ray-produced neutrons on nitrogen of the atmosphere, by the nuclear recation:

$$^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + \beta^{-}$$

Prior to 1951, the amount of ^{14}C and tritium in the world produced by cosmic rays was only a few kilograms. However, since 1954 and at too frequent intervals since that time, nuclear and thermonuclear bombs have been detonated and these have injected into the atmosphere, a much greater quantity of man-made tritium and ^{14}C.

It is now realized that the three common elements, carbon, hydrogen and oxygen, are found in nature in a variety of isotopic forms having either stable or radioactive nuclei.

The equations for the precipitation of calcium carbonate can be written as follows:

$$H_2O + CO_2 \rightarrow CO_3^{--} + 2H^+$$
$$Ca^{++} + CO_3^{--} \rightarrow \underset{\downarrow}{CaCO_3}$$

But because of the various isotopes of carbon and oxygen, the formula for calcium carbonate can also be written as:

$Ca^{12}CO_3$ or $Ca^{12}C^{16}O\ ^{16}O\ ^{18}O$
$Ca^{13}CO_3$ $Ca^{13}C^{16}O\ ^{16}O\ ^{18}O$
$Ca^{14}CO_3$

not to mention many other combinations. Now, because of the different masses of the isotopes of oxygen, it can be shown that the ratio of oxygen isotopes in the calcium carbonate formed is a function of the temperature at the time of formation. It was Dr Urey of the University of Chicago who first conceived the idea of using this principle for the measurement of paleotemperatures, as will be explained later.

At the Institute of Nuclear Sciences, we can measure the ratio of the stable isotopes of oxygen in machines called mass spectrometers.

We can also measure the concentration of the radioactive isotopes ^{14}C and tritium because of the much greater sensitivity that can be achieved in the detection of the radioactive atoms in heavily shielded counters with the associated elaborate electronic counting equipment that has been constructed in the laboratory.

Now what can be done with this information? Well, we now know that water is not just H_2O but that the ratio of both the hydrogen and the oxygen isotopes can vary. We also know that water is radioactive with a half-life of 12.5 years and if this water goes underground additional radioactivity cannot be added to it so that the initial radioactivity decreases. Thus an estimate can be made of the age of water that could have been on the surface of the earth as far back as ninety years ago. Furthermore, the rain that has fallen this week over Wellington is more radioactive than rain water that fell in the same month last year. This radioactive water vapour has come either from the last big Russian tests in the North Polar area or from the American Johnston Island tests. Thus, there is a method available for studying the movement of vapour between the hemisphere and from the stratosphere to the troposphere.

Water is an important commodity, but we in New Zealand just cannot appreciate it because we fortunately have so much of it. But consider for a moment what would happen to the central districts of the South Island if this unprecedented dry spell continues. How long can the reservoirs under the plains last — in fact, how large are these reservoirs? The radioactive hydrogen isotope can help to provide an answer to such problems.

There are many other problems about water that have recently been found out. If snow is collected from Mt. Cook at various altitudes, it is found that the tritium concentration is greatest at the highest altitude. This summer one of my staff hopes to be able to use a helicopter to take samples of snow from various altitudes on Mt. Erebus in Antarctica. We have already examined ice from the snow mine at the South Pole. This snow should have fallen 100 years or so ago and as such should have undetectable amounts of tritium in it. We found, however, a considerable amount of tritium, which could mean either that the samples were contaminated in some way, or that the snow breathes and water vapour is carried by air to depths in the ice cap.

These are just a few comments in the fascinating story of the hydrogen isotopes. The carbon isotopes are just as exciting. Carbon-14 with its half-life of 5,800 years has enabled us to tell the archaeologists how long ago the first moa-hunters came to New Zealand. This can be found from the radioactivity remaining in the carbonaceous deposits of the middens of those early warriors.

At the moment I am trying to solve an interesting problem in New Caledonia where there are mound-like structures about which no legends or knowledge exist. These structures appear to have been made by some prehistoric man who at least knew something about mortar. Shells that are known to be extinct land snails have been bonded with mortar to form these structures. The land snail shell is made of calcium carbonate which, at the time of its formation, if in an environment such as existed on earth before A.D. 1900, had in it its quota of radioactive ^{14}C. This activity can be traced back for 45,000 years. Thus, if the early explorers in New Caledonia made the mortar by heating coral limestone that then recarbonated, the age of the mortar and the shell aggregate should be the same. At present, we are comparing the radioactivity in these fossil land snails with land snails living today in the same area. Using the same mortar technique we are going to "age" some of the ancient struc-

tures of Israel. From Jerusalem we have samples that go back to 2800 B.C., from the Bronze Age through the Iron Age ±800 B.C., and into the Roman Period.

The ^{14}C in the atmosphere has already increased 50% above pre-bomb levels. This carbon is in trees, food, and in you and me. The radioactivity of this carbon can be used in the study of plant physiology, atmospheric gas movements, or the age of bones, both human and animal.

A fairly well-known fossil remain called a belemnite is a hard calcium carbonate deposit that used to be part of an ancient squid, a close relative to the present-day octopus. This squid existed in considerable numbers around the shores of New Zealand and its ancestors can be traced by geologists back through India and into Iran. In ancient times there must have been a free water passage across this area.

All have heard about the glacial periods of the past ages, though how these came about is still a source of argument. The mean temperature at the Equator does not have to change by many degrees to bring about the melting of the ice caps in the polar regions with a consequent rise in sea-level, or the building up of the ice caps with a fall in sea-level.

Now, if the temperature of the surface water changes, the ratio of the oxygen isotopes in the calcium carbonate deposited by marine animals also changes. By these oxygen isotope variations, nature has built in a geological temperature scale, recording for us paleotemperatures over millions of years. These temperatures can be measured within ½°C, if the oxygen can be got out of the carbonate and into a mass spectrometer which is sensitive enough to this temperature differential. This looks simple enough for the equation can be written:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

However, this does not work. Hydrochloric acid already has water in it, with an oxygen isotope ratio possibly different from that in the calcium carbonate. One of the oxygen atoms is also in the H_2O. To overcome the problem of the water in the HCl, this acid is replaced by syrupy phosphoric acid. Then the equation becomes:

$$3\ CaCO_3 + 2\ H_3\ PO_4 \rightarrow Ca_3(PO_4)_2 + 3CO_2 + 3\ H_2O$$

and we have learned that the oxygens in the phosphate ion do not exchange for the oxygen atoms of the carbonate. Even so, one can only measure the ratio in two of the three

oxygen atoms, and one has to know the fractionation factor between the oxygen isotopes in the carbon dioxide and in the water.

Recently a most corrosive compound has been made, bromine pentafluoride BrF_5, which has the great advantage that it will dissolve substances, releasing oxygen. This could never be done before. The equation for the reaction taking place at 400° can be written:

$$CaCO_3 + 3BrF_5 \rightarrow 3/2\ {}_2 + CF_4 + CaF_2 + 3BrF_3$$

It is from the ratio of the isotopes of oxygen that it is possible to tell today the temperature of a sequence of belemnites found in New Zealand at Kawhia. They cover a time range of 25 million years commencing 140 million years. The same technique is being used to study temperature of formation of volcanic rocks and of carbonates in the geothermal area.

There is a story to be told in the isotopic variation of any of the elements. It is now known that nitrogen is made up of isotopes ^{14}N, 99.63%, and ^{15}N, 0.37%. At the price of £100 a gram, can be bought $^{15}NH_4NO_3$ or enriched ammonium nitrate, and from this nitrogen gas can be formed. This gas can be placed in special containers to form an artificial atmosphere for pine seedlings to grow in. If this nitrogen can be assimilated by the pine seedling, and the nitrogenous compounds of the trees are later examined and the $^{15}N/^{14}N$ ratio measured, then, if the ratio is greater than the normal ratio quoted above, it is known that nitrogen from the artificial atmosphere has in some way been fixed within the tree system. It is already known that fixation has taken place, but the mechanism by which it is fixed is still unknown. New Zealand scientists are at present working on this problem.

Let us look for a moment at the isotope of sulphur because I should like to conclude with a few words on the Moon Programme. Sulphur has the isotopes:

^{32}S	95.018	stable
^{33}S	0.750	stable
^{34}S	4.215	stable
^{35}S	—	T½ 87 days radioactive
^{36}S	0.017	stable

The meteorites and the earth almost certainly have a common origin in a gas and dust cloud that at one time was not at a very high temperature. If the sulphur isotopes in meteorites are examined, no matter which type, the

results are always very close to the same ratio for $^{34}S/^{32}S$ or $^{36}S/^{32}S$. The stars are, of course, at very high temperatures and within their core the elements are being synthesized. Physicists say that, from the normal neutron-capture star reactions, the ^{32}S, ^{33}S, and ^{34}S isotopes alone could be expected, since the chain of manufacture would be broken under ordinary stellar conditions by the disintegration of ^{35}S with its half-life of 87 days. However, if meteorites originate in a super-nova (a cataclysm in which a huge star disintegrated, producing very high neutron fluxes) the heaviest stable ^{36}S isotope is likely to be formed in significant quantities in such a disintegration. This is because we are now dealing with neutron capture reaction in which the whole disintegration process is over very rapidly. Before the sulphur isotope ^{35}S has time to decay, it is changed to a sulphur ^{36}S isotope. One of my Staff, Dr J. Hulston, recently examined 25 meteorites for the ^{36}S isotope but no ^{36}S rich meteorites could be found. This means that the material from which meteorites are formed had been thoroughly mixed within the solar system before solidification.

As the meteorite is orbiting around the sun, it is hit by cosmic-ray particles that can transmute iron (the major constituents of iron meteorites) to elements of lower atomic weight. One of these elements is chlorine-36 with a half-life of 308,000 years. ^{36}Cl decays to the inert gas ^{36}A. By measuring the radioactivity from the ^{36}Cl and the quantity of ^{36}A gas formed, it is possible to tell how long the meteorite has been around the solar system before hitting the earth.

We have done a considerable amount of work on the sulphur isotopes of New Zealand's volcanic and hydrothermal regions; of the rich sulphide mineral deposits of Australia; of sulphur from the volcanoes of the Pacific; and of the sulphate falling in rains and snows. When a bacterium utilizes sulphur in its metabolism, it fractionates the sulphur isotopes and this indicates whether substances have been through the biological processes. No matter what we do on earth because of our atmosphere, and the living and non-living processes that have been going on for millions of years, indelible imprints have been left on earth which scientists are now endeavouring to read.

Because of present knowledge we are today in a much better position to study the moon. A few years ago, we could not even measure the isotopic variations of the elements, let alone attempt to understand them. If we had had a sample of the moon we could have made a chemical

analysis and found the elements we already know to exist on earth, but we could have learned little else.

Finally, a few comments on some of the planning behind the Apollo Programme which is concerned with the geochemistry of the moon. The central questions about the moon have to do with its origin and history and the light that the answers can shed on the origin and history of the solar system.

The moon may have originated at a distance from the earth and later may have been captured by it; it may have grown along with the earth as a double planet system; it may have been torn out of the earth after its formation. In later history, the moon may have been and remained a cold rigid body, modified only by occasional meteorite impact and minor local heating. Or it may have had an extensive history of melting, vulcanism and crustal evolution like the earth.

The Apollo Mission hopes to bring back 80 lb of lunar surface matter. If it is obtained, it will surely become the most valuable possession on earth. The problems associated with the collection of the sample are enormous. The surface conditions of the moon are not even known. There will be problems of trying to collect a sample in a vacuum. Even the simple task of knocking off a piece of moon surface becomes a major undertaking. The eye will probably be of less service on the moon than on the earth, because solar radiation and particle bombardment may well have darkened all rocks to a similar shade. The astronauts have to undergo a special training programme in geological methods. When they return to earth astronauts and samples will have to go into quarantine. At some central organization the moon sample will be opened for mineralogical and chemical examination. A special measurement which must be made immediately is the gamma-ray spectrum, for this contains important information concerning the cosmic ray and particle bombardment of the lunar surface, some of which will disappear with the decay of short-lived radioactive species. The concentration of K, U and Th will be made as soon as possible. Isotopic and chemical composition of a few samples may make it possible to place the moon in a sort of planetary chemical context. The Rb/Sr ratio, U and Th ratios will be measured.

From existing knowledge of the meteorites it is already known that earth has a much lower abundance of Rb relative to Sr than found in the so-called chondritic meteorites, as well as much higher abundance of K relative

to U and Th. If the moon is, on the average, earthlike or achondritic, the $^{87}Sr/^{86}Sr$ ratios should not exceed 0.725. If it is chondritic, the ratio should be 0.750.

The rare gas abundances in lunar materials, particularly helium and argon, would when coupled with U, Th and K content yield a gas retention age which will be another indication of whether or not rock-forming events have taken place in the recent history of the moon. The abundance of the other rare gases Ne, Xe and Kr in the rocks may be the most sensitive indicator of how important solar wind accretion is to the lunar surface. Important chemical isotope effects are expected for H, C, N, O, Si and S. If the lunar matter had a different history of proton bombardment in the young solar system, the concentration of D, ^{13}C, ^{15}N and ^{17}O and the isotopes of Li, Be and B may differ from terrestrial values. The great hope is that cosmic ray-produced ^{40}K of half-life 1.25×10^9 years will be measurable in some K-poor phase and that this will tell something definite about the cosmic ray intensity on a billion year time-scale. Bombardment by solar particles and photons of all energies may have profoundly altered the exposed moon surface material.

This short address has attempted to indicate something of the past, the present and the hopes of the future. It may stimulate some to think about a career in science. It is a career that does not concern itself solely with petty local problems, its scope is the Universe, its platform the earth, its creed breaches all political opinions. Its facts are interpreted only in the light of present knowledge; in the physical universe it is all powerful; of the spiritual it should lead the student along the path of humility for he would walk in the steps of a Great Master — the Creator.

FORCES BETWEEN MOLECULES

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Current theory attributes the bonding of atoms to the interactions of electrically charged particles. Charged bodies attract or repel each other according to Coulomb's law. This law states that the force F operating between two bodies each with charge $+q$ (or each with charge $-q$) and r cm apart is given by $F=+q^2/r^2$, where the + sign indicates repulsion. If one body has charge $+q$ and the other $-q$, the force is $F=-q^2/r^2$, the − sign indicating attraction. Thus in atoms and molecules the nuclei repel each other, as do the electrons, while nuclei and electrons attract each other. In discussing bonding, the "energy" concept is more useful than the force concept. The "potential energy" V involved in the Coulomb's attraction and repulsion is given by $V=+q^2/r$ for particles repelling each other and $V=-q^2/r$ for particles attracting each other. All particles in motion have kinetic energy, given by $T=\frac{1}{2}mv^2$ (m=mass, v=velocity) and the total energy of a system of charged particles (atom, ion or molecule) is $E=T+V$. The important principle to remember is that, as the total energy of a system is lowered (*i.e.*, becomes more negative), the system becomes more stable. Two or more atoms will remain in close contact, if, and only if, they are more stable (*i.e.*, have lower energy) when they are together than when they are apart. Usually systems of particles (*e.g.*, molecules) in the gas phase have appreciable kinetic energy corresponding to their thermal motion; the constituent atoms of a molecule are vibrating and the whole molecule is rotating. The atoms will only stay together long enough for the combination to behave as a molecule if its stability is sufficient for it to withstand molecular collisions.

We must focus attention on the energy changes which result when atoms or ions are brought together. It is in this way that we must look for a theory of bonding. What processes can occur when atoms or molecules are brought together which will produce a lowering of their energy? Let us consider first the formation of one molecule of an ionic substance, sodium fluoride NaF, from its constituent atoms. Energy must be expended to remove an electron from the sodium atom, and energy is gained when it is added to the fluorine atom. With energies expressed in

electron-volts (one electron volt per atom is equivalent to 23.06 kcal per mole of atoms), we find

$$\mathrm{Na} = \mathrm{Na}^+ + e \qquad E_1 = +5.14 \text{ eV}$$
$$\mathrm{F} + e = \mathrm{F}^- \qquad E_2 = -3.50 \text{ eV}$$

Hence the energy which must be supplied to form Na^+ and F^- is $E_t = E_1 + E_2 = 5.14 - 3.50 = +1.60$ eV. We can now calculate from Coulomb's law the distance to which the two ions must approach in order that the fall in their mutual potential energy will just provide the net 1.60 eV required to allow the reaction

$$\mathrm{Na} + \mathrm{F} = \mathrm{Na}^+ + \mathrm{F}^-$$

to occur.

By Coulomb's law, $q_+ q_- / r = e^2/r$ where e is the charge on the electron and hence on the two ions.

$$-e^2/r = -1.60 \text{ eV} = -1.60 \times 1.602 \times 10^{-12} \text{ ergs.}$$

Since $e = 4.80 \times 10^{-10}$ e.s.u.

$$r = \frac{(4.80 \times 10^{-10})^2}{2.56 \times 10^{-12}} \text{ cm} = 9 \times 10^{-8} \text{ cm} = 9 \text{ A}$$

Provided the ions can approach closer than 9 A the overall process of forming ions and bringing them together gives a decrease in the total energy of the system — *i.e.*, the energy of formation becomes negative — and NaF can be formed. In fact the equilibrium separation of Na^+ and F^- ions in an isolated unit is only 1.88 A. The Coulomb potential energy at this distance is 7.65 eV, so that the overall energy decrease when the NaF unit is formed is 6.05 eV (7.65 − 1.60). It is consequently a very stable unit.

Crystalline sodium fluoride consists of an array in three dimensions of Na^+ and F^- ions, and it can be shown, by a more complex calculation, that such a "lattice" has a total energy still lower, in the ratio 1.748: 1, than the same number of ions in the form of separate NaF units (or molecules). This is why we find NaF as an ionic crystalline solid.

If we could now destroy the charges on the sodium and fluoride ions, we would have an array, in effect, of neon atoms. Neon is normally a gas, but by lowering the temperature, we can convert it into a solid. This is one of the pieces of evidence which show that attractive forces exist between such particles, even though they have no net electric charge. How are such forces produced?

This question was not answered till 1930, though the fact that weak forces of attraction between molecules must

exist was understood in the 18th century — *e.g.*, by Boscovich. In the 19th century precise measurements on gases revealed that they do not behave exactly in accordance with the laws of Boyle and Charles. Van der Waals emphasized the role of attractive forces in explaining these deviations from "ideal" behaviour, and they are called Van der Waals forces in consequence.

In some molecules — *e.g.*, hydrogen chloride — the pair of valence electrons wihch constitute the covalent bond are not equally shared between the bonded atoms. The chlorine nucleus has more than its fair share of the electron pair. Consequently the hydrogen atom has, on the average, a fractional + charge and the chlorine atom a fractional − charge. The molecule behalves as an "electrostatic dipole" and may be represented $H\delta^{(+)}$ —— $Cl\delta^{(-)}$. Such a molecule is called a polar molecule. One of the properties of electrostatic dipoles is that, like ions, they attract one another, provided they are free to assume an anti-parallel configuration

$$(+)\text{——————}(-)$$
$$(-)\text{——————}(+).$$

This can occur provided the energy of rotation is less than the energy of interaction, and the potential energy V is given by

$$V \propto \frac{\mu_1\mu_2}{r^3}$$

where μ_1, μ_2 are the dipole moments. (If a dipole is made up of two charges $+e$ and $-e$, a distance r apart, the dipole moment is $\mu = er$). These attractive forces are fairly strong, and compounds made up of polar molecules are fairly readily liquefied. However, at sufficiently high temperatures, negative to positive orientation is opposed by the high thermal energy, and the potential of the attractive force is much less, being given by $V \propto \mu_1^2\mu_2^2/kTr^6$ where k (Boltzmann's constant) is the gas constant R per molecule — *i.e.*, $k = R/N$ where N is Avogadro's number.

Non-polar molecules, such as N_2 O_2, H_2 and the rare gas atoms, cannot exercise such attractive forces. F. London realized, however, that attractive forces between such apparently dipole-free molecules can arise from "induction of dipoles". The rare gas atoms, for example, appear to be spherical particles with positive nuclei and negative electrons, with the centres of positive and negative charges coinciding (at the nuclei). This is an essentially static

picture. A more dynamic picture suggests that, as two rare gas atoms (or other atoms or molecules) approach one another, the nuclei and electrons can form configurations over finite periods of time which are dipoles, so that attraction occurs. The attractive force becomes particularly large when the outermost electron shell is occupied by many electrons, and its influence is increased by induction (deformation of the electron cloud). This kind of dipole interaction is closely related to the phenomenon of dispersion of light — the resolution of multicoloured light into a spectrum. The attractive forces are called dispersion, or London, forces. The potential V is given by $V \propto n^3\ \alpha^{3/2}/r^6$ where n is the number of electrons in the valence shell and α is the polarisability of the molecule (which will not be discussed).

All particles, atoms, ions and molecules have a value for n and α and the London force is a universal attractive force. It always exists; between negative and positive ions; between negative and negative ions; between positive and positive ions; between dipoles; and so on. In these cases it is superimposed on other attractive forces — Coulomb, dipole, etc. It is small, but still far stronger than the other well-known universal attractive force, that of gravitation: in fact of the order of 10^{38} times stronger.

It will be useful now to consider the relative magnitude of these forces.

TABLE 1

Interacting Pair	*Type of Attraction*	*Dependence on r*	*Distance Equilibrium*	*Interaction Energy kilocal. mole^{-1}*
Na^+ F^-	Coulomb	$1/r$	1.88	157
Na^+ H_2O	Ion-dipole	$1/r^2$	2.14	21.6
H_2O H_2O	Dipole dipole	$1/r^3$	2.37	4.84
Ne Ne	London	$1/r^6$	3.30	0.0613

In Table 1, in addition to pairs whose attractive forces have been considered, data are also given for the hydrated ion $Na^+ - H_2O$, for which the potential of the attractive force is given by $V \propto e\mu/r^2$. As the depence of V on r changes to higher powers (representing attractive forces of increasingly shorter range), we pass from a typical ionic solid NaF, through a polar liquid H_2O, to a non-polar gas Ne. (the $Na^+ - H_2O$ interaction occurs in hydrated sodium salts and in aqueous solutions).

In Table 2, the contribution of the London forces to the "lattice energy" of certain salts is shown.

TABLE 2

Compound	Outer Electrons on Cation	Lattice Energy kcal mole^{-1}	% from London Forces
NaF	8	219	0
NaCl	8	187	0
CuCl	10	222	6.8
AgF	10	218	10.9
AgCl	10	206	14.2
TlCl	12	170	16.5

The lattice energy is the energy required to carry out reactions of the type

$$Na^+F^-(\text{crystal}) \rightarrow Na^+(g) + F^-(g)$$

and is a measure of the attractive forces which hold the crystal together. Table 2 shows how the contribution of the London forces to the total attraction (Coulomb+ London forces) increases with the number of electrons in the valence shell of the cation.

Nothing has been said so far about repulsive forces, except those between ions of like sign. Universal repulsive forces must exist, because when any atom (or ion or molecule) approaches sufficiently closely to another, the outermost electron clouds will tend to overlap and will repel each other strongly. If it is assumed that such forces of repulsion obey an inverse power law with respect to distance, and it is by no means certain that they do, the net potential energy of a pair of particles can be written in a general way, in the form suggested by Mie,

$$V = -(A/r^m) + (B/r^n)$$

It is certain that $n > m$, that is the repulsive forces fall off with distance more rapidly than the attractive forces. For ions, values of n from 6 to 14 varying with the ion size have been used, and for molecules, $n = 12$ is commonly assumed.

LIQUIDS AND LIQUID MIXTURES

What has been considered above are the forces which operate between particles in pairs. Extension to systems of enormously large numbers of particles (1 mole of any substance contains 6×10^{23} particles), is difficult. For crystalline solids, where the simple and beautiful patterns of arrangement of ions, atoms and molecules have been revealed by X-ray analysis, much progress has been made. For gases at low pressure, the intermolecular forces, being short range, do not affect the properties very much and such simple laws as those of Boyle and Charles hold reasonably

well. For gases at other than low pressures, and for liquids, the situation is otherwise, and these states of matter are of major importance in chemistry.

Some aspects of the relationship between the states of matter are listed in Table 3.

TABLE 3

State	*Intermolecular Forces*	*Ratio l/d*	*Molecular Arrangement*
Gas	weak	$>>1$	chaotic
Solid	strong	$<<1$	orderly
Liquid	medium	~ 1	partially ordered

l = mean free path d = molecular diameter.

It has already been mentioned that deviations of gases from the ideal gas laws (*e.g.*, Boyle's) were attributed by van der Waals to intermolecular forces. The study of such deviations is one experimental approach to testing the theories of such forces. Chemists have always been concerned with the liquid state — a frequent first step in a chemical investigation is to get the substance into solution. The theory of the liquid state is difficult. As Table 3 shows, the forces are strong and the arrangement partially ordered. Considerable progress has been made by studying mixtures of liquids — in fact, physical chemistry originated in the study of solutions and they are still one of its major concerns.

Let us consider forming a mixture of a liquid of molecules A and another of molecules B. While we have scant knowledge of the interactions A-A of the molecules in pure liquid A, and of the B-B interactions in pure liquid B, the mixing of A and B merely introduces new interactions A-B which are not very different from those already existing. We can study the deviations from complex behaviour more readily than the complex behaviour itself. To put it another way, we can try to predict the properties of the solution from those of its components, even if we cannot explain the properties of the components.

Two experimental methods have contributed largely to progress in the study of solutions. On is calorimetry — the measurements of the heat of formation of a liquid mixture from its pure components; the other is the measurement of the partial pressure exerted by a component in the vapour which is in equilibrium with a liquid mixture. Some results of such measurements will be considered in turn.

Vapour Pressure

If we have a mixture of two volatile liquids A and B whose molecules are similar in size and shape and in the magnitude of intermolecular forces operating between them, we might expect to find a fairly simple situation. If we think of the saturated vapour pressure of a liquid as a measure of the "escaping tendency" of its molecules from the liquid environment to the vapour, then we might expect the addition of B to A merely to lower the vapour pressure of the latter in direct proportion to the fraction of B in the mixture. This was, in fact, the original form of Raoult's law, discovered experimentally,

$$(P_A - P_A)/P_A = N_B/(N_A + N_B) = X_B.$$

In this equation, P^0_A is the vapour pressure of pure A, and P_A its vapour pressure over a mixture containing N_A moles of A and N_B of B. The fraction $N_B/(N_A+N_B)$ is the mole fraction of B in the mixture, designated X_B.

This law will also hold for component B, and can be more compactly written

$$P_A = P^0_A X_A \text{ and } P_B = P^0_B X_B$$

where the additional symbols have similar definitions to those given. Mixtures obeying Raoult's law are termed "ideal mixtures" (or solutions), and it can be shown that the law can be deduced theoretically if the following conditions hold: (1) That the ratio of the diameters of A and B is not greater than 1.26: 1 and (2) the force A-B between molecules A and B is close to the arithmetic mean of the forces A-A and B-B, — *i.e.*,

$$f_{A-B} = \tfrac{1}{2}(f_{A-A} + f_{B-B})$$

For a mixture obeying Raoult's law, a plot of the vapour pressure of a component against its mole fraction is a straight line as shown in Fig. 1. A few systems of chemically similar substances obey the law — *e.g.*, ethylene dibromide and propylene dibromide at 50°C. Figure 1 also shows the data for the methyl iodide-ethylene dichloride system, in which small positive deviations from the law occur — *i.e.*, that vapour pressures of the components, and also the total pressure, are greater than Raoult's law predicts. Clearly these molecules are not quite so comfortable when surrounded by a mixture of their own kind and a foreign kind, as when surrounded only by their own kind, so their escaping tendency is increased.

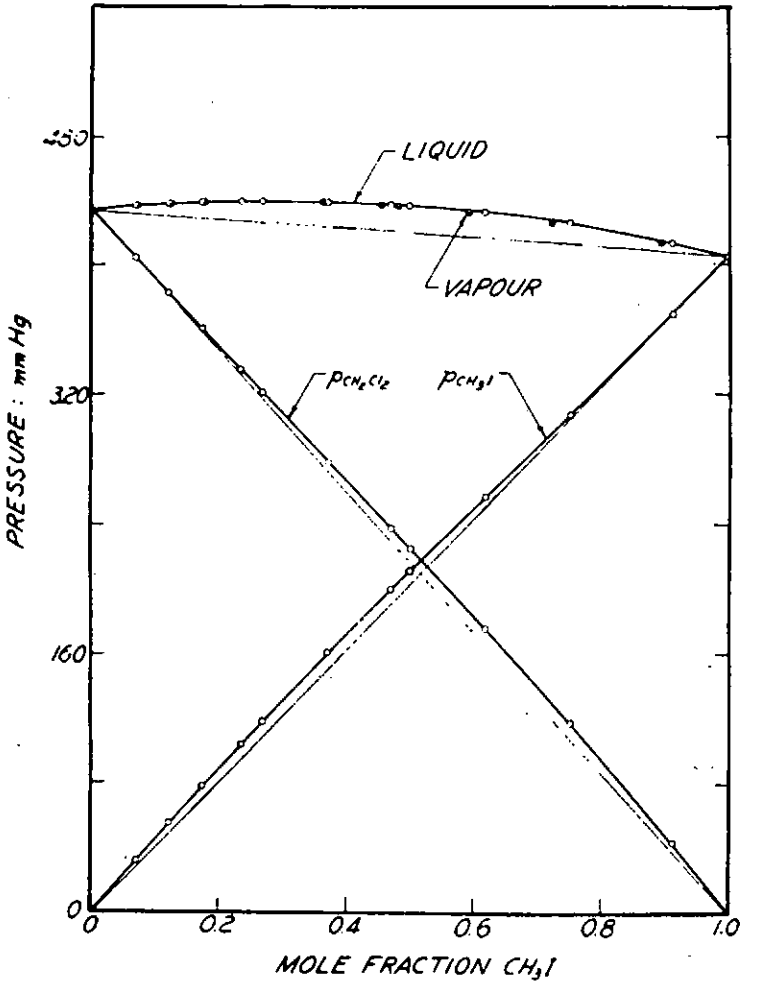

FIG. 1

Experimental work in this field is concerned with studying deviations from the force relationship $f_{A-B} = \frac{1}{2}(f_{A-A} + f_{B-B})$. The accuracy required is better than 0.02%, or 1 part in 5,000. For a vapour pressure of 500 mm Hg, it is necessary to be able to measure to better than 0.1 mm. One piece of apparatus*, designed for such measurements is shown in Fig. 2. It had to meet the following specifications:

* I. D. Watson and A. G. Williamson (unpublished).

(1) The volume of liquid was to be small, 1 to 5 ml. One of the components $C_7F_{15}H$ costs $30 per ml.
(2) The volume of vapour must be of the same order to enable its composition to be determined by calculation without the necessity of analysis.
(3) The measurements were to be made at 50°C. The components are immiscible below 35°C.

The last specification required the vapour to be isolated from the atmosphere by a cut-off device which is sensitive to pressure. The spiral gauge in Fig. 2 achieves this. The vapour pressure of the system causes it to expand, and its tip rotates. The gauge tip moves 0.2 degrees of arc per mm change in pressure, so it is necessary to detect 0.01° of rotation for an accuracy of 0.05 mm in pressure. This is impossible with a pointer attached to the fragile gauge. The position of the gauge must be detected without touching it.

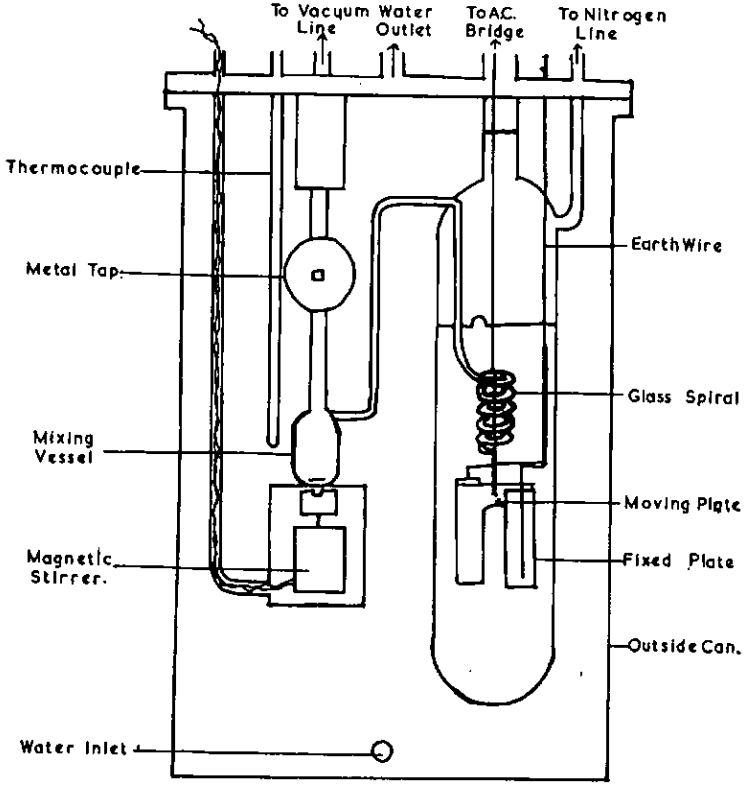

FIG. 2: *Mixing cell and spiral gauge cut-off.*

This is achieved by measuring the capacity of a condenser formed by two metal plates, one of which is attached to the gauge. The pressure of the vapour causes this plate to move from some initial position, changing the capacity of the condenser. Nitrogen is admitted to restore the capacity of its original value by nullifying the effect of the pressure of the vapour. The pressure of nitrogen required is observed on a manometer, and equals that of the vapour.

With this apparatus the effect of hydrogen bonding, another kind of intermolecular force, between $C_7F_{15}H$ and dioxane, is being investigated through the way in which it causes deviations from ideal behaviour.

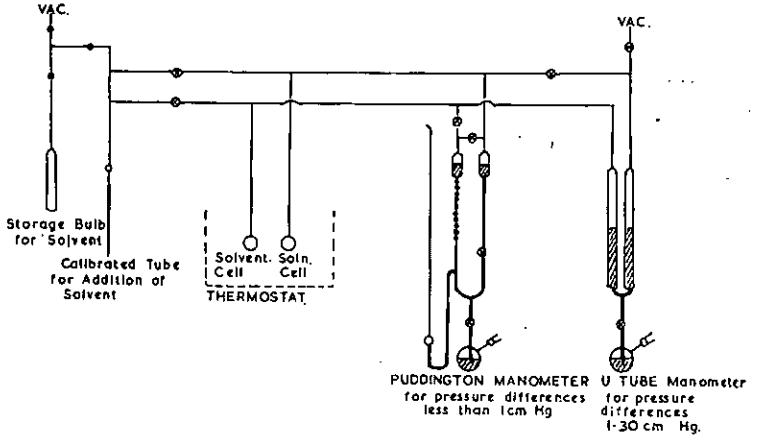

FIG. 3: *Apparatus for measuring vapour pressure differences between solution and solvent.*

In another investigation,* solutions of the polypropylene glycols in carbon tetrachloride are being studied. In this system only one of the components, CCl_4, is volatile, and it is cheap. Large amounts of solution can be used, and large volumes of CCl_4 vapour. On the other hand, at the temperature used, 5°C, the vapour pressure is only 100 mm, and it is necessary to measure it to an accuracy of 0.01 mm in some of the solutions. A differential manometer system is used (Fig. 3).

The two vessels containing pure solvent and solution are connected one to each side of a wide bore mercury manometer, and the difference in the mercury levels gives the vapour pressure difference directly. For vapour pressure

* R. W. Kershaw and G. N. Malcolm (unpublished).

differences of less than 10 mm, the Puddington manometer shown in Fig. 3 is used. Although it is not possible to measure the difference in the levels of mercury, when it is less than 10 mm, to the required accuracy (0.005 mm), it is possible to detect when the levels are equal to that accuracy. In the Puddington manometer, what is measured is the volume change of mercury in a narrow bore tube required to restore the difference in level in the wide bore tubes to zero. In calibrating this manometer, the vapour pressure of water at its triple point (where ice-water and water vapour are in equilibrium) was reproduced to within 0.01 mm of its standard value.

Heats of Mixing

Systems which obey Raoult's law have zero heat of mixing, symbolized $\Delta_m H = 0$. Systems deviating only moderately from the law will have finite heats of mixing which are small, being wholly due to the deviations. They range from ± 1 calorie to ± 100 calories per mole of mixture, compared with heats of vaporization of liquids which range up to 10,000 calories per mole. To achieve a 1% accuracy in measuring $\Delta_m H$ it is necessary to measure temperature differences between 0.0002°C and 0.02°C. The calorimeter

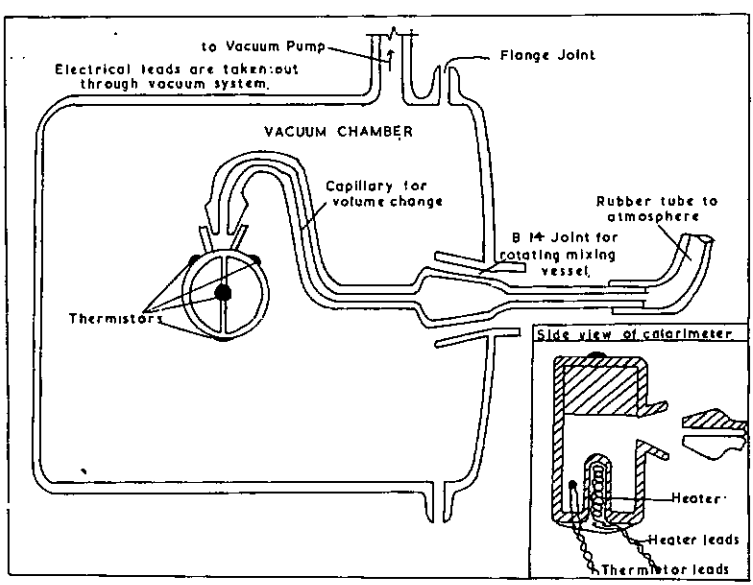

Fig. 4: *Calorimeter and vacuum jacket.*

shown* in Fig. 4 was designed to meet the following specifications:

(1) Small amounts of very pure, and hence expensive, liquids are being studied.
(2) The calorimeter vessel must have no vapour space. If the vapour space is approximately the same volume as that occupied by the liquid, then, on mixing, the vapour pressures of the liquids are changed, and the compounds are either evaporated or condensed, giving a heat of vaporization effect of the same order of magnitude as the heat of mixing which is being measured.
(3) The volatile liquids have to be weighed and inserted into the mixing vessel, and kept apart.
(4) Mixing must be quick and thorough.

The small calorimeter vessel, holding about 2 ml of liquid, is filled with mercury, and known amounts of the liquids to be mixed are inserted by a syringe, one into each half of the upper part of the vessel. Mixing is achieved by inverting the vessel. A change of volume occurs, so expansion or contraction must be allowed for in the capillary side tube. The temperature change is measured by thermistors, consisting of rare-earth oxides whose electrical resistance changes with temperature. A number of these are sealed to the calorimeter vessel. In the experiment the thermistors make one arm of a Wheatstone bridge, by which the change in their resistance is measured. They are calibrated by passing a known current through a heating coil of known resistance, thus producing a known evolution of heat. The calorimeter vessel is suspended in an evacuated chamber, to minimize heat loss to the surroundings.

Notable contributions have been made to measurements of this kind by Dr M. L. McGlashan, a Canterbury graduate currently at the University of Reading, and soon to become Professor of Physical Chemistry at Exeter. Despite the precision of measurement which can be achieved in modern calorimetry, not all its problems are solved, as is shown by the data illustrated in Fig. 5 on the heat of mixing of benzene and carbon tetrachloride. Before the work of Larkin and McGlashan, this system had been studied in several laboratories and, for a 1: 1 mixture, the results scattered over a range of about 10 joules $mole^{-1}$ — *i.e.*, about 10% of the average value of about 110 joules $mole^{-1}$. Larkin and McGlashan "made and tested a new calorimeter for measuring the heats of mixing of liquids and believe it to be capable

* D. Fenby and A. G. Williamson (unpublished).

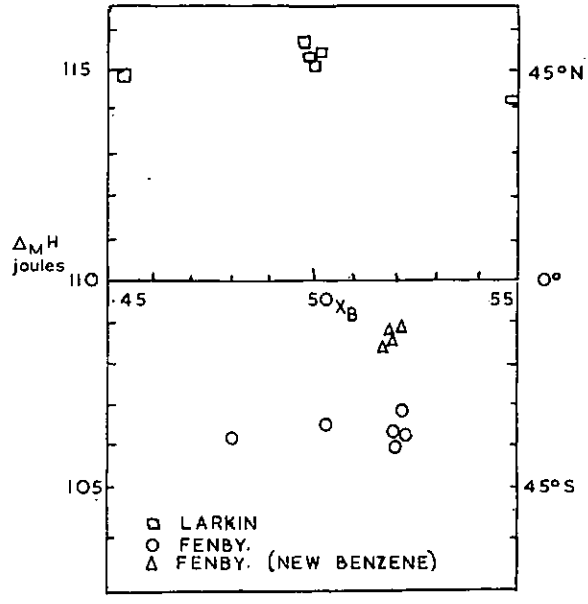

FIG. 5: *Heats of mixing of benzene and carbon tetrachloride at 25°C.*

of higher precision, and to be more convenient, than any previous design". Their result for the 1: 1 mixture is 115 joules mole^{-1}, with a precision of ± 0.3 joules mole^{-1}. This is some 4 joules mole^{-1} higher than was expected from several sets of earlier measurements, and they attribute the difference to incomplete mixing in those measurements. They conclude their paper with the remark, "We hope that benzene and carbon tetrachloride will soon be studied somewhere else in a calorimeter capable of a precision similar to or better than ours and in which it is certain that mixing is complete."

Data of similar precision, and regarded as meeting the specification mentioned are also shown in Fig. 5. These were obtained at the University of Otago by Fenby and Williamson. The lower set, about 106 joules mole^{-1}, was obtained with one sample of benzene, purified by distillation and chemical treatment. The other set, about 108.5 joules mole^{-1}, was obtained with benzene which had been further purified by fractional crystallization. Both were apparently pure by gas chromatographic analysis. Similar care was taken with the carbon tetrachloride.

Both sets of data claim high precision. What is their accuracy? The answer may be found in Los Angeles, where Larkin and Fenby are currently working. It may be found in Otago.

The gap between the present status of the theory of forces between molecules, and the type of experimental work I have been discussing is a large one. Theory can deal reasonably well with gases at low pressures, with ions in very dilute solutions, and with some of the properties of the solid state. With liquids and liquid mixtures we are still groping in a complex and difficult field. Precise experiments have a major contribution to make, but they must be related to whatever theoretical insights have been achieved. The experimental work I have described is simple in principle. The attainment of high precision in it is just as difficult as in any other field.

BRANCH NEWS AND NOTES

AUCKLAND

Dr D. Hall has succeeded Dr D. R. Llewellyn as Head of the Chemistry Department of the University of Auckland. Dr R. C. Cambie has been promoted to Associate Professor. Dr B. A. Grigor and Mr M. A. Long have been appointed to the lecturing staff.

Dr R. N. Seelye has resigned to take a position in cancer research at Greenlane Hospital.

Student numbers in chemistry classes have risen sharply this year. Approximate enrolments are Stage I, 590; Stage II, 140; and Stage III, 80.

The Stage I laboratory and the Stage II inorganic laboratory will be housed in the part of the new chemistry block on the corner of Wellesley Street and Symonds Street.

WAIKATO

Mr J. H. Watkinson has been granted two years' study leave to attend Victoria University of Wellington. While there he will work on some aspects of "surface chemistry of selenium" under Professor A. T. Wilson. Mr Watkinson is well known for his work on the analytical determination of this very important element.

Mr N. T. Clare of the Ruakura Agricultural Research Centre, and past Editor of the *Journal*, has joined the staff of FAO. He will work on a special fund project on sheep diseases. During his two years' absence overseas he will be stationed at the Veterinary Institute at Pendik, 20 miles east of Istanbul, Turkey. His duties include the establishment of a biochemical research laboratory, the training of Turkish personnel, and initiation of research on diseases of a biochemical nature, including trace element deficiencies.

SCIENCE CONGRESS

The 11th New Zealand Science Congress recently held in Auckland (February 11–17) attracted a large group of chemists from throughout the country. The Chemistry Section was organized by the 1964 Committee of the Auckland Branch of the Institute with Mr G. R. White, convener, and Dr F. J. B. Aggett, secretary. In accordance with the wishes of the Executive committee of the Congress that all papers should be invited and be of a general nature, the programme of the chemistry section consisted of review papers by chemists prominent in different fields.

We were pleased to have Dr J. C. Andrews as Chairman of the Chemistry Section and his address on "The Chemist and N.Z. Industry" received considerable publicity in the local newspapers.

One session entitled "Chemistry and the Plant" included a review by Professor L. H. Briggs of the research which has been carried out in the natural products field at various institutions in N.Z. Dr D. S. Letham, well known for his work on the separation and identification of "zeatin", reviewed the roles of the three main types of growth stimulants, auxins, gibberellins, and kinins.

As a gesture to the recently formed metallurgical association, one of the sessions was devoted to metallurgy and was organized by the metallurgists themselves. Mr G. S. Adams (MetLabs Ltd.) and Mr G. Langslow (Auckland Technical Institute) provided the review papers in this field.

Dr E. P. White in a session devoted to "Chemistry and Animal Health" reviewed the work which has been done to isolate and identify the liver-damaging toxin, sporidesmin, cause of facial eczema. A comment that the chemist had still not helped the farmer solve the facial eczema problem was naturally seized by reporters as a heading for a local news item. Dr G. W. Butler reviewed some of the work being carried out at Plant Chemistry Division, D.S.I.R., on the effects of inorganic and organic feed constituents on the ruminant.

Dr P. K. Foster and Mr K. E. Seal discussed aspects of cristobalite research as related to the ceramic industry. It was interesting for members to learn how the Pottery and Ceramics Research Association and the ceramic industry complement each other in tackling their particular problems.

With little doubt the most popular session was one devoted to a discussion of radioactive isotopes. Mr T. A. Rafter gave examples of their applications in industry. One particularly interesting tool developed by Nuclear Sciences is a mobile radiographic camera for examining cable joints. Dr R. O. Farrelly's paper, which dealt with the applications of radioactive isotopes in medicine, was regarded by many as the highlight of the chemistry section. Their use as tracers in diagnosis, in experimental studies and in radiotherapy were reviewed. Perhaps Dr Farrelly's ability to combine so much chemistry with a number of actual case histories accounted for the interest which was created during this session.

The Chemistry sessions concluded with two important papers — Professor C. J. Wilkins reviewed recent advances in inorganic chemistry and Professor J. Vaughan discussed the effect of molecular shape on organic reactions. Both speakers succeeded in giving excellent reviews of these areas of chemistry and held the interest of a large audience which included many non-specialists.

A series of general symposia were held during the afternoons. In one, "Antarctic Research", Professor A. T. Wilson discussed his theory of ice age periodicity. Another general symposium chaired by Dr D. R. Llewellyn included papers by the Hon. B. E. Talboys, Minister of Science, Professor H. N. Parton and Mr W. H. Cooper on the place of science in education.

Some Institute members who delivered papers in other sections of the Congress included Mr E. D. Andrews, Mr P. J. Clark, Dr E. B. Davies, Dr B. W. Doak, Dr R. H. Jackman, Dr M. Kingsford, Dr J. W. Lyttleton, Mr K. J. McNaught, Mrs M. G. Metcalf, Mr A. J. Metson, Mr H. A. L. Morris, Dr G. B. Petersen, Dr L. F. Phillips, Dr R. K. Ralph, Dr L. M. Saunders, Mr C. W. Small, Professor T. W. Walker, and Mr N. Wells.

Although the trades exhibition was not well supported by members, the large number of films shown each morning and afternoon received a great deal of support and were a real feature of the Congress.

Prominent overseas scientists who visited Auckland for the Congress included Sir John C. Eccles, Dr W. H. Pickering and Professor B. J. Bok, all of whom gave public lectures.

Towards the end of the Congress a social evening organized by the local branch of the Institute proved an outstanding success. The main general social function of the Congress was a conversazione held at the Auckland War Memorial Museum. Mr and Mrs S. G. Brooker greeted guests as they arrived.

An excursion to the Chelsea Sugar Works and Crown Lynn Potteries organized by Mr R. W. Olliff, gave visitors an opportunity to see something of local industry.

Thanks must go to the Executive Committee for their excellent work in organizing one of the best Congresses held in this country. Dr H. C. Holland as Chairman of the Organizing Committee, and Dr G. A. Wright, Programme Organizer, are to be congratulated on the efficiency which they displayed.

G.R.W.

CONFERENCE 1965

Note date. Conference will be held in Dunedin from Tuesday evening, August 17, to Friday evening, August 20. Hostel accommodation is being arranged for about 100 people, and hotel and motel accommodation for a further 50 to 60.

Conference committee: Dr J. Rogers (*Chairman*). Dr G. N. Malcolm (*Secretary*, Chemistry Department, University of Otago, Box 56, Dunedin). Dr A. Campbell, Dr A. M. Kennedy and Dr A. G. Williamson (*Committee*).

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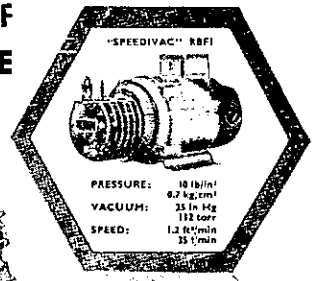

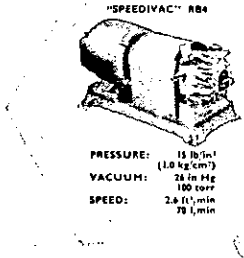

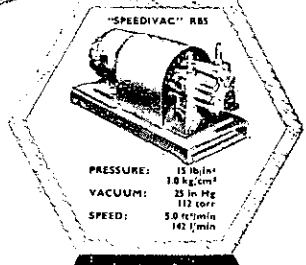

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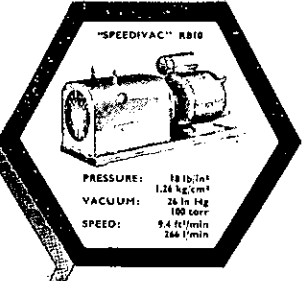

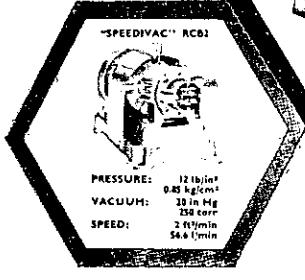

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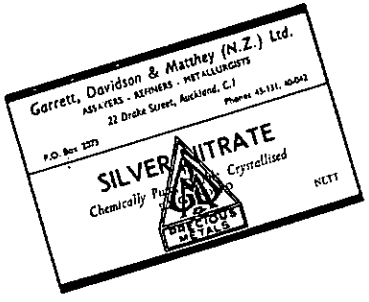

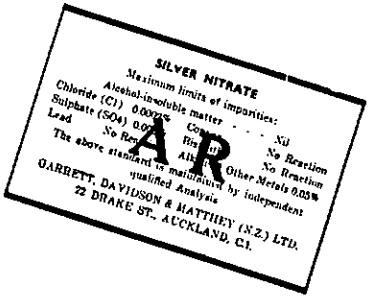

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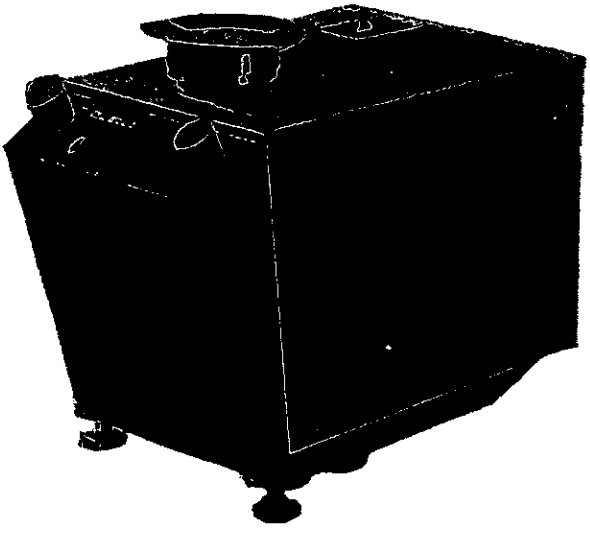

Mettler announce 3 New Precision Balances, designated P1000, P1200 and P3. Details are set out below. P Balances previously announced were: P120, Capacity 120 grams, and the P10, Capacity 10 Kilograms.

Model	P1000	P1200	P3
Weighing range	0 g to 1000 g	0 g to 1200 g	0 g to 3000 g
Taring in optical range	300 g	100 g	2500 g
Capacity	1300 g	1300 g	5500 g
Readability	0,1 g	0,01 g	0,2 g
Precision	±0,05 g	±0,005 g	±0,05 g

We will gladly provide further details with literature, prices and delivery information.

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