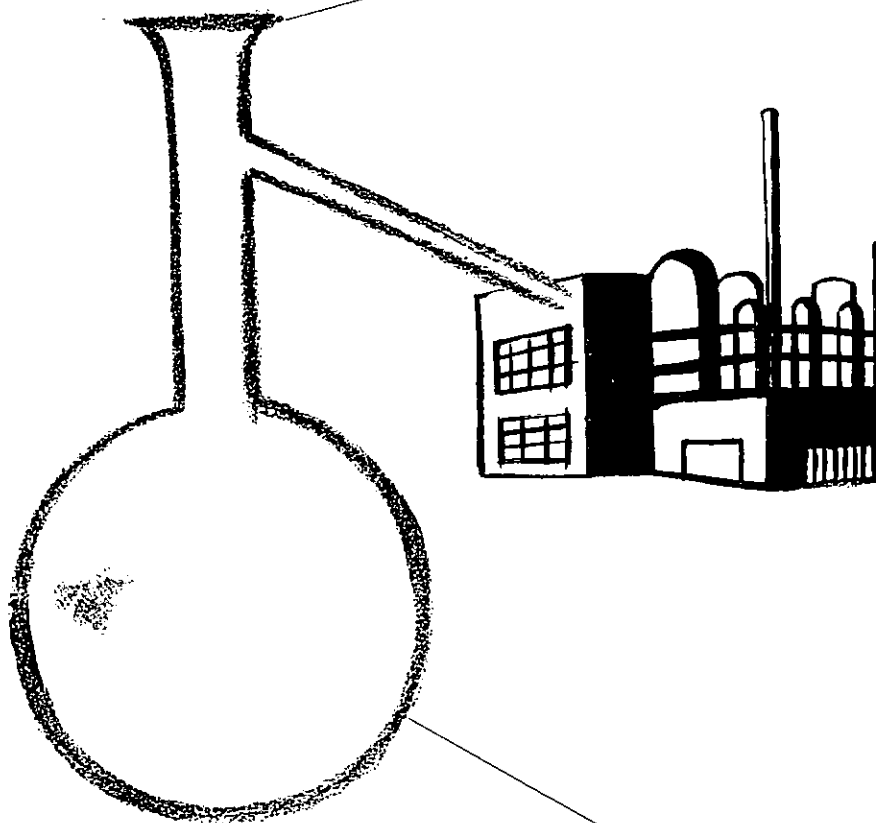
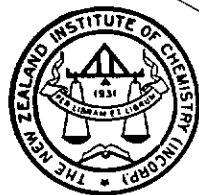


# Chemistry in Action



1959



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*President.*

# THEORY AND EXPERIMENT IN CHEMISTRY

H. N. PARTON

Professor of Chemistry, University of Otago, Dunedin.

In a book on the logic of scientific discovery sent to me recently by a philosopher friend, one chapter begins "Science is a system of theories". About the time I read this remark, with which I agree, I read another one in the *Journal of Chemical Education*: "Chemistry is an experimental science; its teaching deserves to be". How can we have "an experimental system of theories"? I am going to try to explain why I do not think these statements are contradictory; why, for example, the philosopher would not say that chemistry is not a science, though I, as a chemist, am inclined to say that a lot of it is still an art. I want to illustrate the way in which theory and practice interact; to show how dependent we are in the great chemical industries, which are indeed the most characteristic industries of the twentieth century, on well-established theories to guide our practice, and shorten the time and reduce the effort needed to make, on a vast scale, what we want to make. As illustration I propose to take two processes, one probably well known to you, the other not so long removed from the bonds of secrecy, which should have no place in science.

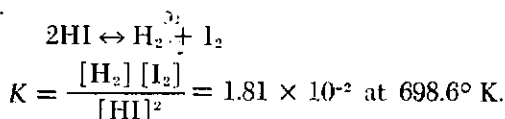
The great German chemist Fritz Haber died in 1934. Three years after in a memorial lecture to the Chemical Society, Professor J. E. Coates said of the synthetic ammonia process which bears Haber's name, that "rarely if ever had a process been brought in an academic laboratory to such an advanced stage of technical development before being handed on to industry". This was justified in 1937 but I think the achievement was matched and perhaps surpassed in my second illustration, the extraction of the synthetic element plutonium in what is now called the atomic energy industry.

Two of the important factors which must be considered for an economic industrial process are the yield of the desired product and the rate at which it is produced; that a high reaction rate often requires a high temperature, but relatively low temperatures may be used if a suitable catalyst is found; that to get a good yield of ammonia the temperature must be kept down to, say, 500° C; that the yield is better at high pressure; and that these last two factors illustrate the principle of Le

Chatelier, which is in fact a theory and one which is not always true.

The story of the process is both more complex and more interesting than that. Like most nineteenth century chemists Haber had started as an organic chemist and then graduated to electrochemistry. His researches on the ammonia equilibrium were begun in 1904 as scientific adviser to the brothers Margulies of Vienna. The idea on which they were working was that continuous synthesis of ammonia from a nitrogen-hydrogen mixture in the presence of a metal, might result from the simultaneous formation and reduction of a nitride by the mixed gases; the metal would react with nitrogen to give the nitride, and the hydrogen would reduce the nitride to produce ammonia and re-form the metal. The latter would thus be a catalyst. Haber knew that whatever the mechanism of the reaction might be the maximum yield must be governed by the equilibrium between nitrogen, hydrogen and ammonia in the gas phase, and he set out to study it.

Gaseous equilibria had been discussed for many years on the basis of the law of mass action. In particular Bodenstein had shown that the law was obeyed by the decomposition of hydrogen iodide.



	Concentration (Mole/ml $\times 10^3$ )		
I <sub>2</sub>	0.1707	0.125	0.0738
H <sub>2</sub>	0.2907	0.356	0.4565
HI	1.648	1.559	1.354
K $\times 10^2$	1.803	1.807	1.812

However, relatively few gas reactions can be studied by the direct experimental method—*e.g.*, allowing H<sub>2</sub>, I<sub>2</sub> and HI to come to equilibrium and analysing the equilibrium mixture, as Bodenstein did. There are however other ways of obtaining the equilibrium constant *K*, and moreover of finding it over a wide range of temperature. All I can say about it in an article of this kind is that theory showed quite clearly that the constant *K* could be obtained for any reaction from the kind of measurements we make in a calorimeter (that is, heat of reaction measurements), if a particular problem could be solved. *K* for a given reaction turns out to be given by an equation involving

the heat effect of the reaction, the specific heats of the substances taking part in the reaction, the temperature and a constant called an integration constant. The problem was the value of the constant. Walter Nernst postulated that the constant should be zero—his so-called Heat Theorem. This is where theory and experiment met, the latter as a test of the former. From heat measurements and the application of his theory, Nernst was able to calculate the equilibrium constant of the ammonia equilibrium. But the value at  $1,000^{\circ}\text{C}$  did not agree with Haber's measurements at that temperature.

The experimental situation was as follows. About 1884 Ramsay and Young, working with an iron catalyst at  $800^{\circ}\text{C}$ , found that ammonia did not decompose completely; that is, there is an equilibrium set up. But they could detect no trace of ammonia from the  $\text{H}_2 + \text{N}_2$  reaction. Haber first worked at  $1,000^{\circ}\text{C}$  and one atmosphere pressure, and unlike Ramsay and Young obtained equilibrium from both directions. But the ammonia concentration was low and hard to reproduce. In fact his values ranged from 0.005% to 0.012% ammonia, and he believed the higher value was correct. Now Nernst's theory gave 0.0045% so he repeated Haber's work, using a pressure of 50 atmospheres to increase the ammonia yield and hence the accuracy of the experiment. Nernst was the first to synthesize ammonia under pressure. His result was 0.0032% when corrected to one atmosphere, a value in reasonable agreement with the theory allowing for the experimental difficulties. Haber and Le Rossignol, still working at one atmosphere, then redetermined the equilibrium, with refinements in the experimental method, and obtained 0.0048%.

%  $\text{NH}_3$  in equilibrium with  $\text{N}_2$  and  $\text{H}_2$  at  $1,000^{\circ}\text{C}$ .

Haber and Le Rossignol	0.0048%
Theory	0.0045%
Nernst (1907)	0.0032%
Haber (1905)	0.0120%

Nernst refused to accept Haber's new figures as accurate because of the low ammonia concentrations at one atmosphere pressure. Haber was very hurt. With Le Rossignol, a specialist in high pressure technique, he began a new determination at 30 atmospheres, and in 1908 they fully confirmed their earlier value, producing, in fact, a whole range of values from  $700^{\circ}\text{C}$  up to  $1,000^{\circ}\text{C}$ . The equation which summed up the results showed that yields large enough to encourage the idea of in-

dustrial development, which had been virtually given up in 1906, could be expected only under conditions regarded as unattainable—*e.g.*, 8% ammonia at 600° C and 200 atmospheres, the upper limit for compressors at that time. But the best catalysts, manganese, nickel and iron, were slow even at 700° C. With Le Rossignol's experimental skill, and the discovery of better catalysts—first osmium and then uranium—the yield of ammonia was so great at 550° C and 150 to 200 atmospheres that the gas could be liquified in a closed system consisting of the reactor, condenser and a circulating pump. When heat interchangers were fitted the apparatus became a small technical plant producing a few hundred millilitres of liquid ammonia per hour. In essentials the problem was solved. Haber's equation for the equilibrium constant  $K$ , as finally published in 1914, took the form

$$\log_{10}K = \frac{9591}{4.571T} - \frac{4.98}{1.985} \log T - \frac{0.0046}{4.571} T + \frac{0.85 \times 10^{-6}}{4.571} T^2 + 2.10$$

From this we can find  $K$  and hence the percentage of ammonia in the equilibrium mixture at any value of  $T$  from about room temperature to 1,000° C.

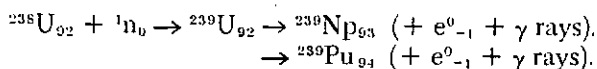
The remainder of the story belongs to the great chemical firm Badische Anilin and Soda Fabrik. They were interested in nitrogen fixation and had launched the Schonherr arc process ( $N_2 + O_2 = 2NO$ ) in Norway. They were sceptical of the synthetic ammonia process. Another distinguished German chemist Wilhelm Ostwald had claimed a good yield of ammonia with an iron catalyst but the company's chemists had shown that it came from nitride in the iron. However, in July, 1909, their engineer Carl Bosch and a chemist Mittasch came to Haber's laboratory at Karlsruhe to see the process. Things went wrong (as they did with Moissan when he first demonstrated fluorine) and late in the day only Mittasch was there to see the ammonia flow. He and Bosch began the task, involving new and formidable problems, of designing a large-scale plant, and three years later it was in regular operation. The credit belongs to Bosch. Haber won a Nobel Prize in 1919. In 1931 Bosch shared one with Bergius, and Haber wrote, with the generosity of a great mind, "it is not sufficiently recognized how little had really been done in the Karlsruhe synthetic ammonia process towards the foundation of a world industry."

The rest of Haber's life work has an epic quality. His work for the German government in 1914 on the production of nitric acid for explosives by the Ostwald process involving the oxidation of ammonia; his role in chemical warfare with the rank only of captain, though for two years he controlled the entire chemical warfare organization, offensive and defensive, with responsibility for research, design, supply and the selection and training of personnel; his attempt from 1920 to 1926 to pay Germany's reparations bill, equivalent to 50,000 tons of gold, by extracting gold from the sea, an investigation which showed, tragically for Haber, that the gold content of sea water is only one thousandth of that claimed by previous investigators; and finally his exile from Hitler's Germany, which perhaps might never have come into its evil existence if there had been more gold in the sea.

Haber was a great chemist and the story of the ammonia synthesis reveals him as contributing to two aspects of the science. On the one hand his experimental results contributed to the testing of Nernst's theoretical work, which has had far reaching effects in the science of thermodynamics. On the other hand it led on to a great chemical industry on which the feeding of increasing populations must lean more and more heavily.

My other example will be less familiar to you. In 1934 the Italian physicist Enrico Fermi bombarded uranium with slow neutrons and interpreted his results as showing that elements heavier than uranium had been formed. But in January, 1939, Otto Hahn and Strassmann discovered barium in the products of the reaction between slow neutrons and uranium. They had the advantage of being chemists, skilled in the analysis of small amounts of radioactive materials. This was something quite new. Uranium has 92 protons and 146 neutrons in its nucleus. All previous experience indicated that when another neutron entered, a small fragment of the uranium nucleus, say an electron, should be emitted, and an element of about the same atomic weight should be formed. Lise Meitner, in Stockholm as a refugee from Hitler's Germany, had a revolutionary idea that the uranium-neutron complex had split into two roughly equal fragments. It is not my purpose to follow the story in detail; how it was found that it was the isotope  $^{235}\text{U}$  which underwent the fission process with the release of an enormous amount of energy, which could be used to make a bomb; and how  $^{235}\text{U}$  was separated from  $^{238}\text{U}$ , at enormous cost in effort, to make the Hiroshima bomb. It is what happens to the atoms of  $^{238}\text{U}$ , which make up 99.3% of natural uranium, that I want to discuss.

$^{235}\text{U}$  absorbs neutrons but does not undergo fission. Instead the reactions are as follows:



An unstable element neptunium (No. 93) is formed, and will lose another electron to give element No. 94, plutonium. Plutonium is stable; it will undergo fission just as  $^{235}\text{U}$  (but not  $^{238}\text{U}$ ) and will be produced in larger amounts than  $^{235}\text{U}$  because most uranium is  $^{238}\text{U}$ . Moreover, it is a chemically different element from uranium and there should be no difficulty in separating it from uranium and purifying it. This was in fact achieved and the second fission bomb, dropped on Nagasaki, was a plutonium bomb. An excellent popular work on atomic energy states, "The details of chemical separation processes make dull reading", and goes on to discuss physical methods of separating  $^{235}\text{U}$ , only one of which was worked on a large scale, and that mainly because economic factors are regarded as unimportant in war time. It is this "dull" process I am going to outline. The intricacy of the problem arises from the following factors. Because of the accumulation of fission products, the conversion of  $^{238}\text{U}$  to  $^{239}\text{Pu}$  cannot be carried very far before the plutonium must be removed. Then the fission products (from the  $^{235}\text{U}$  present) are a large number of highly unstable elements giving off electrons and gamma rays. Thick concrete walls have to be built between the workers and the vats, and the process of taking the irradiated uranium from the "atomic pile", dissolving, precipitating, washing and so on, has to be done by automatic machinery with remote control. The plant built at Hanford in the state of Washington, started in April, 1943, and operating six months later, was designed, and the method of separating the plutonium was selected, at a time when there was only half a milligram of the metal in existence. In fact a small (1,000 kW) plant was built at Oak Ridge, Tennessee, to develop "know how" for the production of plutonium at Hanford. But time was so short that the first production and separation plants at Hanford were far advanced before a single plutonium atom had been made at Oak Ridge. This brilliant achievement of chemical engineering, based on the work of ultra-microchemists, should not be dull.

The plutonium factory is presented with rods of uranium, encased in aluminium, and containing, after the radioactive elements of very short life among the fission products have decayed.

away, ruthenium, zirconium, niobium, some rare earths, and the desired plutonium. Now it is true that plutonium is a different element from uranium, but they are both members of the "actinide" series, which has some likeness to the "lanthanides" or rare earth series. The separation of the rare earths from each other was for long a difficult and tedious operation because in that part of the periodic table the variation in chemical properties with change in atomic number is not great. Would not the same situation exist among the actinide elements? The clue is to be found in the fact that among these elements (as with others) there are greater differences between the properties of the compounds of the same element in different oxidation (valence) states than there are among compounds of different elements in the same oxidation state. Chromium in chromous salts (oxidation state +2) is like iron in ferrous salts, and not like chromium in the chromates, in which it resembles sulphur. While the rare earths (lanthanides) exist mainly in the oxidation state +3 ( $\text{LaCl}_3$  for example), the actinides show much greater variation in their oxidation states. An understanding of the methods developed requires a short digression into the idea of "oxidation potentials".

The displacement series of the metals is familiar. If we take a particular pair — *e.g.*, zinc and copper — we see from the equation  $\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}$  that this is an oxidation-reduction reaction; the cupric ion oxidizes zinc to the zinc ion and is itself reduced to copper. Moreover, as J. F. Daniell found 120 years ago, the system can be set up as a galvanic cell. At the negative pole zinc passes into solution as  $\text{Zn}^{2+}$ —*i.e.*, oxidation occurs. At the positive pole the  $\text{Cu}^{2+}$  ions are discharged as copper by combining with the electrons which have flowed round in the external circuit from the zinc—*i.e.*, reduction occurs. Now if we arrange matters so that no current is drawn from the cell, and hence no reaction is occurring, we can measure the potential difference between the electrodes. The value is 1.100 volts—the so-called reversible e.m.f. This sort of thing can be done with many combinations of "oxidation-reduction couples" ( $\text{Zn}/\text{Zn}^{2+}$  and  $\text{Cu}/\text{Cu}^{2+}$  are both oxidation-reduction couples), not only those in which the reductant is a metal and the oxidant is an ion. With an electrode of an inert metal, usually platinum, the reductant can be a dissolved gas ( $\text{H}_2$ ), or an anion ( $\text{Cl}^-$ ), or a cation in a lower oxidation state

( $\text{Fe}^{2+}$ ), while the corresponding oxidants will be a cation ( $\text{H}^+$ ), a dissolved gas ( $\text{Cl}_2$ ), and a cation in a higher oxidation state ( $\text{Fe}^{3+}$ ) respectively. Instead of listing the e.m.f.s of all the galvanic cells which could be made up by joining all the possible oxidation-reduction couples in pairs, they are listed in the manner of the metal displacement series, taking the  $\text{H}_2/\text{H}^+$  couple as zero. We thus get a table of "oxidation-reduction potential", some couples being positive to hydrogen, some negative. Following the convention which gives a negative sign to the potential of the strongly reducing couples ( $\text{Na}/\text{Na}^+$ ,  $\text{Zn}/\text{Zn}^{2+}$ ), and a positive sign to the strongly oxidizing couples, ( $\text{MnO}_4/\text{Mn}^{2+}$ ) a few values are given below.

Oxidant	Oxidation State	Reductant	Oxidation State	E.
$\text{F}_2$	0	$\text{F}^-$	-1	+2.65
$\text{MnO}_4^-$	+7	$\text{Mn}^{2+}$	+2	+1.53
$\text{PuO}_2^{2+}$	+6	$\text{Pu}^{4+}$	+4	+1.04
$\text{Pu}^{4+}$	+4	$\text{Pu}^{3+}$	+3	+0.97
$\text{UO}_2^{2+}$	+6	$\text{U}^{4+}$	+4	+0.33
$\text{H}^+$	+1	$\text{H}_2$	0	0.00
$\text{U}^{4+}$	+4	$\text{U}^{3+}$	+3	-0.61
$\text{U}^{3+}$	+3	$\text{U}$	0	-1.80
$\text{Pu}^{3+}$	+3	$\text{Pu}$	0	-2.03
$\text{La}^{3+}$	+3	$\text{La}$	0	-2.52
$\text{Na}^+$	+1	$\text{Na}$	0	-2.71

The meaning of this table can be stated quite simply. The oxidant of any couple will oxidize the reductant of any other couple whose standard potential is less positive than its own—*e.g.*, fluorine will oxidize all the rest. The reductant of any couple will reduce the oxidant of any other couple whose standard potential is more positive than its own. The table gives no indication of how rapidly the reactions will occur, and indeed some are very slow; but potentially they may occur. The well-known strong oxidizing agents are at the top, fluorine and the permanganate ion, for example. Strong reducers such as sodium are at the bottom. A reductant such as  $\text{Pu}^{3+}$ , which is part of a couple with a high positive value, is more difficult to oxidize than  $\text{U}^{4+}$  and  $\text{U}^{3+}$ . We note that it is relatively easy to oxidize uranium to its oxidation state +6 (*i.e.*,  $\text{UO}_2^{2+}$ ) but much more difficult to oxidize plutonium to the same state ( $\text{PuO}_2^{2+}$ ). Proper selection of oxidizing agents, on the basis of the theory outlined, will thus allow us to get the two metals into different oxidation states and then separate them.

On the basis of this information, various "unit processes" can be devised. During the war years the object was to get plutonium to make a bomb. Today it is essential to recover the uranium as well for economic production of nuclear power. Some possible processes are as follows; if the irradiated uranium has been dissolved in non-oxidizing agents, the metals are in states  $\text{Pu}^{\text{III}}$  and  $\text{U}^{\text{IV}}$ . If hot  $\text{HNO}_3$  is used, they will be  $\text{Pu}^{\text{IV}}$  and  $\text{U}^{\text{VI}}$ .

A66. Oxidation to  $\text{Pu}^{\text{VI}}$  and  $\text{U}^{\text{VI}}$ .

- (a) 0.1M  $\text{S}_2\text{O}_8^{2-}$ , 1M  $\text{H}^+$ , 20° C,  $\text{Ag}^+$  catalyst, 5 minutes.
- (b) 0.1M  $\text{Cr}_2\text{O}_7^{2-}$ , 1M  $\text{H}^+$ , 90° C,  $\text{Co}^{2+}$  catalyst, 10 minutes.
- (c)  $\text{NaBiO}_3$ , 5M  $\text{H}^+$ , 20° C, 5 minutes.

A46. Transformation to  $\text{Pu}^{\text{IV}}$  and  $\text{U}^{\text{VI}}$ .

- (a) > 8M  $\text{HNO}_3$ , 90° C, 30 minutes.
- (b) > 8M  $\text{HClO}_4$ , 90° C, 30 minutes.

A36. Reduction to  $\text{Pu}^{\text{III}}$  and  $\text{U}^{\text{IV}}$ .

- (a)  $\text{SO}_2$ , 1M  $\text{H}^+$ , 20° C, 15 minutes.
- (b) 0.05M  $\text{N}_2\text{H}_4$ , 2M  $\text{H}^+$ , 20° C,  $\text{Fe}^{2+}$  catalyst, 20 minutes.

A34. Reduction to  $\text{Pu}^{\text{III}}$  and  $\text{U}^{\text{IV}}$ .

- (a) Fe powder, 1M  $\text{HCl}$ , 20° C, 1 minute.
- (b) Zn or Zn-Hg, pH 1, 20° C, 1 minute.

It is generally true that the fission products will keep their normal oxidation states—*e.g.*, +3 for the rare earths (lanthanides), +4 for cerium and zirconium, +6 for molybdenum. But this is not always so.

The next step is separation. The first processes used for the recovery of plutonium were precipitation methods. Although the concentration of plutonium may be too low to exceed the solubility product of even very insoluble compounds, it can be brought down by co-precipitation. For example, lanthanum fluoride is insoluble and will carry down with it plutonium in the +3 or +4 oxidation states, but not in the +6 state ( $\text{PuO}_2^{2+}$ ). Many more such "carriers" are known. Secondly solvent extraction may be used. Plutonium can be extracted from an aqueous solution by one of a number of water-immiscible organic liquids. Solvent extraction is applied mainly to nitrate solutions since anions such as sulphate, phosphate or fluoride form complexes with plutonium which do not extract readily from the aqueous solution. Important solvents are methyl isobutyl ketone (hexone) and tributyl phosphate (TBP). The decisive advantage of solvent extraction over precipitation is that uranium can be recovered and separated from the fission

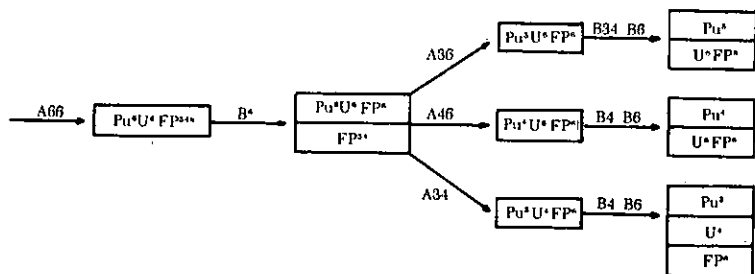
products as well. Thirdly plutonium is readily taken up from dilute aqueous solutions by cation exchange-resins. (These act in the same way as the permutit water softener). The principal use of the method is in the concentration of a desired ion from very dilute solutions and the separation of the actinides from each other and the rare earths (see later).

Some separation processes are as follows:

- B6. Separation of actinides in oxidation state VI.  
 (a) 0.5 M  $\text{HNO}_3$ , 2M  $\text{Mg}(\text{NO}_3)_2$ , extract with ether.  
 (b) 0.1 M  $\text{HNO}_3$ , 2M  $\text{Ca}(\text{NO}_3)_2$ , extract with hexone.  
 (c) Precipitation from acetate buffer,  $\text{U}^{\text{VI}}$  carrier.
- B46. Joint separation of actinides in state IV and VI.  
 (a) 8M  $\text{HNO}_3$ , extract with ether.  
 (b) 1M  $\text{HNO}_3$ , 4M  $\text{Ca}(\text{NO}_3)_2$ , extract with hexone.  
 (c) 2M  $\text{HNO}_3$ , extract with TBP.
- B4. Separation of actinides in state IV.  
 (a) pH 1.0 extraction with 2M acetylacetone in benzene.  
 (b) Precipitation with 0.2M  $\text{IO}_3^-$ , 3M  $\text{H}^+$ ,  $\text{Ce}^{\text{IV}}$  carrier.
- B34. Joint separation of actinides in state III and IV.  
 (a) Precipitation with 1—3 M HF, 1M  $\text{H}^+$ ,  $\text{La}^{\text{III}}$  carrier.  
 (b) Sorption on cation exchange resin; elution with complexing agent.

In each separation process some of the fission products will follow the actinides. Those accompanying the actinides in oxidation states VI, IV and III are indicated below as  $\text{FP}^{\text{VI}}$ ,  $\text{FP}^{\text{IV}}$  and  $\text{FP}^{\text{III}}$ , respectively.

The oxidation reduction processes A, and the subsequent separation processes B, can be combined in many ways. Some are indicated in the following diagram.



In this diagram a single rectangle, with its preceding arrow, indicates the oxidation-reduction A process by which the oxidation states indicated are obtained. Two adjacent rectangles with the preceding arrow indicate a separation process B by which

the elements have been separated into two phases (*e.g.*, aqueous phase, solid precipitate; ion exchanger, organic solvent); any process indicated on the arrow can be used. Three rectangles indicate separation into three phases by two separation processes. Other combinations are, of course, possible.

Much of this information was first released generally at the first International Conference on the Peaceful Uses of Atomic Energy in 1955. It represented, however, a straight-forward application of basic chemistry. The remarkable features are those I have indicated; the way in which the essential chemistry of plutonium was established when the amount available was about a half-milligram; the separation of a small amount of plutonium from a large amount of uranium and the great variety of elements formed by fission, with their unprecedented radioactivity; the purification of plutonium so that its original endowment of fission products is reduced by a factor of  $10^6$  to  $10^7$ ; the designing and building of an enormous factory to produce a product of which so minute a quantity had been previously made.

I will end with a few points about the synthesis of elements heavier than plutonium. At the Second International Conference on the Peaceful Uses of Atomic Energy, held in September, 1958, Glenn Seaborg of the University of California described the preparation of element No. 101, Mendelevium. Einsteinium (Element No. 99) was bombarded with a beam of helium ions containing about  $10^{14}$  ions per second per square centimetre of target. The einsteinium was prepared by irradiating plutonium with neutrons and the target for the helium ions contained only about  $10^9$  atoms of einsteinium. As the atomic weight of the einsteinium isotope used is 253, the weight of the element on the target is  $(10^9 \times 253) \div (6 \times 10^{23})$  grams, *i.e.*,  $4.2 \times 10^{-13}$  grams—below the limit of visibility by many orders of magnitude.

Theory indicated that only about one atom of element 101 could be expected from each experiment. In fact three experiments gave five atoms. The target was prepared by plating the einsteinium on gold foil. The helium beam was sent through the back of the foil so that the atoms of 101 should recoil, owing to the momentum of the projectiles, and be caught on a second gold foil. This was dissolved up and separation performed by the ion exchange method. The latter will now be briefly elaborated. It is, as Seaborg said, the key to the elements above curium (No. 96). The actinides above plutonium are mainly in oxidation state +3 in solution so that oxidation-

reduction cycles are of limited use, as are most conventional chemical separation methods. In addition, in many cases the first isotopes of the heaviest elements to be made are very short-lived and are obtained in very low yield. Highly specific and rapid methods are needed and ion exchange is far and away the best.

The resin mainly used is Dowex 50. It is a network of chains of benzene rings, linked with methylene ( $\text{CH}_2$ ) groups, and carrying hydroxyl (OH) groups, and sulphonic acid ( $\text{SO}_3\text{H}$ ) groups. The latter group is a strong acid and the hydrogen ions from its dissociation are free to diffuse through the resin phase. There is from 30 to 50% of water in the resin, which can be regarded as a "solution" of a high molecular weight sulphonic acid in water. The  $\text{H}^+$  ions on the surface can exchange with cations from an aqueous solution flowing through a bed of resin. The affinity of a cation for the resin increases with increasing valence. For cations of the same valence the affinity increases as the radius of the hydrated ions decreases. The higher the affinity of the cation for the resin, the more difficult it is to elute it, that is, to wash it off. The formation of complex ions plays a large role in elution. For example, the lanthanide (rare earth) cations form complexes readily with citrate anions. The complexes are of variable strength so citrate solutions give selective eluting agents.

In general the method is to adsorb the cations on the resin and separate by the difference in eluting power of suitable solutions for the different cations. For example the transcurium elements (Nos. 97-101) can be adsorbed on Dowex 50 and eluted by ammonium citrate or ammonium lactate solutions at  $87^\circ\text{C}$ . The elements are removed from the resin in the reverse order of their atomic numbers. The elements can be identified in the eluting solution by the characteristics of their radioactivity, and the results of the separation are plotted as radioactivity (proportional to concentration) against the number of drops of eluting solution which have passed out of the column, or against the time of elution (at constant flow). The plots show peaks characteristic of each element. On such plots there is a striking similarity in the spacing of the elution peaks of the actinide series—americium, curium, berkelium, californium—and the corresponding lanthanides—europium, gadolinium, terbium, dysprosium.

It is thus possible to predict the behaviour on an ion exchange column, or rather on elution from such a column, of a

new actinide element. For example einsteinium (No. 99) and fermium (No. 100) were first identified at Los Alamos in the products of the thermonuclear (H-bomb) explosion in 1952 in the Pacific Ocean. The products were dissolved and then adsorbed on Dowex-50 and eluted, and it was the appearance of radioactivity at the expected elution position which indicated the form of einsteinium and fermium. The same method led to the confirmation that mendelevium had been produced in the experiments described above. The einsteinium on the second gold foil (the catcher foil) contained a few atoms which appeared in the elution position of element 101. Later experiments with larger amounts of einsteinium in the target produced several hundred atoms of 101, decomposing by spontaneous fission with a half-life of 3.5 hours. Mendelevium behaves as would be expected for the twelfth member of the actinide series. Its chemical properties so far have been deduced entirely from its behaviour on the ion-exchange column and are in accord with predictions made on the basis of Seaborg's theory, namely, that the elements from actinium (No. 89) onwards form a series parallel to the rare earths (lanthanides).

The search for elements above mendelevium is thus aided by a substantial foundation of theoretical and experimental knowledge. No. 102 has been made, though the original claim for it by an international team at the Nobel Institute in Sweden seems unlikely to be sustained. No. 103 should complete the actinides. The theory is sufficiently established for a prediction to be made that No. 104 will be an analogue of hafnium and zirconium, and Street and Seaborg have even been able to predict how it should be eluted by 6 M HCl from Dowex-50 resin in relation to hafnium and zirconium when it is synthesized. The problem of producing these heavier elements bristles with difficulties. Mendelevium was made from helium ions and the minute amount of einsteinium produced by irradiating plutonium in an atomic pile. The einsteinium was an isotope of mass 253 and half-life 20 days (that is, half of any number of atoms of it disintegrate in 20 days). No. 102 has been made by bombarding californium (No. 98) with ions of carbon (No. 6, with mass 12 units) accelerated in a "linear accelerator" (HILAC) at Berkeley. The Russians may have made it from plutonium and oxygen ions. It seems unlikely that fermium can be used as a target (as einsteinium was for making mendelevium), as the half-lives of the isotopes are in general getting shorter as the atomic number increases, and even less of the heavier element can be made, so far, than the  $10^9$  atoms of einsteinium used in the mendelevium

experiments. By the time Nos. 104 and 105 are reached it may be that the longest lived isotopes that can be prepared will exist barely long enough for chemical identification even by new properties such as the mode of elution from an ion exchange resin. When plutonium was first made from uranium in the Berkeley cyclotron the yield in two days was only 0.5 micrograms from about a kilogram of uranium. Calculations show that it will take about ten years to make one milligram of californium from a kilogram of plutonium using neutron bombardment. No wonder this kind of research is expensive.

Have I made my point? Modern chemistry is not just a matter of "doing experiments". Fruitful experiments are related to a formidable body of well-established theory. Well-equipped chemists have to be masters of the theory, and of the mathematical methods by which it is developed, and skilled in experimental techniques as well. Major advances come more and more from team work under the leadership of the ablest. It should be a matter of great pride to us in New Zealand that the principal architect of the foundations of nuclear science was Ernest Rutherford, who was born at Stoke and educated at Nelson College and what is now the University of Canterbury. We may not produce another Rutherford in this century. But there is no task as important as that of finding and encouraging the few like him upon whose creative work progress in science, will always depend.

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# CHEMISTRY AND THE CROP

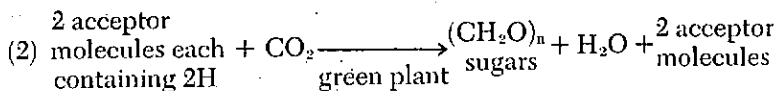
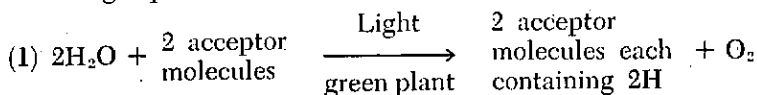
ELSA B. KIDSON

Soil Bureau, Seconded to the Cawthron Institute, Nelson.

How many of us realize our complete dependence on plants? Without plant life, animal life could not exist on this earth. Man with all his cleverness has not found out how to trap, and use, and store, the light energy from the sun, a process carried out by all green plants. Plant material, synthesized with the help of this light energy, supports the grazing animal and so directly or indirectly supplies us with essential foods. Though there is often some mutual benefit, man's relation to the plant is essentially that of a parasite—he destroys. Fortunately, he has learnt how to farm the plant and unlike most other parasites can exercise some measure of control of the plant-man balance, but he is still liable to death by hunger as a result of too many men, and not enough plants. For this reason the study of plant nutrition is a very important one and likely to remain so.

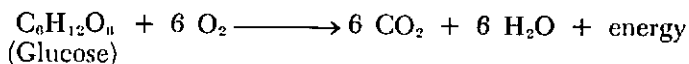
It has been pointed out that plant growth represents the world's most exuberant and extensive chemical activity. Each year some 200,000 million tons of carbon are removed from the air as carbon dioxide and incorporated into the plant material of the earth, fresh water, and ocean, through photosynthesis. Land plants account for roughly 20,000 million tons of this total. Photosynthesis in plants is also the main factor in preventing civilized man from being poisoned by his own activities, reducing the abnormally high carbon dioxide of the air over cities and even over the main steamship routes of the world.

The photosynthetic process is essentially as given in the following equations:



In the first reaction light energy is used to split the water into oxygen and hydrogen, the latter being held by acceptors; that is, by certain compounds which can exist in a reduced or oxidized form by the addition or removal of hydrogen. In the

second reaction these hydrogen atoms are given up and used in the reduction of carbon dioxide to form sugars. This second process is not as simple as it looks and takes place in a number of steps. From the sugars are built up many compounds needed for growth and reproduction. Sugars and sugar derivatives also provide a source of energy for the plant. The energy is liberated by respiration, an oxidation process fundamentally the same as the burning of coal, where oxygen of the air is used up and carbon dioxide liberated.



Some of the released energy takes the form of heat, but much of it is stored in certain energy-rich compounds which will liberate it easily as required, for building up of cell constituents, for the uptake and accumulation of salts, and for the mechanical work of growth.

Such is a very simplified account of organic transformations in the plant, *i.e.*, reactions of carbon-containing compounds. Actually the processes are extremely numerous and complicated and not yet fully understood. A great deal of progress has been made in recent years owing to the development of two new and very important chemical techniques — chromatography, and the use of radioactive and other isotope tracer elements. By the first technique, which relies on the fact that different compounds in a solvent may move at different rates on an absorbent material like filter paper, separation and identification of small quantities of organic materials have become much easier. By the second, the reactions of certain elements can be followed by supplying a small proportion of the element as an identifiable isotope—*e.g.*, the pathway of carbon synthesis can be determined by adding a little radioactive  $\text{C}^{14}\text{O}_2$  to the normal carbon dioxide supply.

But a great deal remains to be discovered. When man's dependence on plants is realized, and the fact that agriculture, depending fundamentally on the plant, is still much the greatest industry on this earth, the importance of plant science becomes obvious. It is of more fundamental importance to man at present than the harnessing of atomic energy.

Plants do not necessarily grow and produce to their full capacity even in their natural surroundings. In addition to the struggle against parasitic diseases, they may not have the most favourable nutritional or environmental conditions. For instance, the weeds growing on clay banks or on the roadside may be small and stunted, but they may flourish in the rich soil of the

home vegetable garden. Wheat may produce 90 bushels per acre in some of the most fertile parts of the Canterbury plains and as little as 10 to 20 bushels in other parts. Apples will grow reasonably well in the unmanured soils of Hawke's Bay but will hardly grow at all in the unmanured soil of Nelson's main apple-growing area.

If we are to make farming more efficient and to increase the world's food supply, it is of great importance to study the crop plants and understand their life processes and requirements. Many scientists are so engaged—botanists, plant physiologists, plant biochemists, crop experimentalists, and so on. Some are studying the fundamental processes in the plant; others study the behaviour of the crop in the field. All these plant scientists need to have some chemical knowledge, and certain branches of the work, for example biochemistry (the chemistry of the plant processes), require a high standard of chemical training.

I propose now to take a brief look at some of these plant sciences, particularly the study of plant environment and the science of mineral nutrition, which is a part of biochemistry.

What are the raw materials a plant needs for growth, and where do they come from? The air supplies the carbon dioxide for the photosynthetic building up of sugars and sugar derivatives, and also supplies oxygen needed for respiration. The soil supplies water which forms a large proportion of the total weight of the plant. It takes part in photosynthesis and it functions as a transport system for raw materials and elaborated compounds. From the soil the plant also gets the mineral elements it requires. By minerals the botanist or plant physiologist means a variety of chemical elements, other than carbon and oxygen, which take part in the plant processes, or form part of the plant structure.

In addition there must be a suitable environment—*i.e.*, conditions of light, temperature and humidity. Plants vary considerably in the type of environment which suits them best. For instance, some plants grow better in dull light than bright light; some will flower only if they have long days, and others if they have short days. Fruiting can be stopped by wrong conditions of light and temperature. Plants have their own particular temperature range outside which they grow abnormally or not at all. For example, apples and pears cannot be grown in the tropics; bananas will grow in Nelson but will not fruit; tomatoes will flower but will not ripen fruit outdoors in some southern parts of New Zealand. But they will ripen fruit in the artificially raised temperature of a glasshouse. Iceland with its cold climate

is a land of glasshouses in which temperate crops are grown in an atmosphere warmed by the water of the thermal springs. Not only day temperatures but also night temperatures have a big effect on plant behaviour.

In recent years there have been developed in many countries methods for studying the effect of environment on plant growth. The plants are grown in glasshouses or rooms or cabinets with methods of controlling light, temperature and humidity. In glasshouses the control is not very easy owing to the influence of weather conditions outside, but in growing rooms or growth chambers, which can be shut off from outside weather, the plants can be subjected to quite a range of carefully controlled environments. By the use of these controlled glasshouses and growth rooms it is possible to study the behaviour of plants in all sorts of climates—hot, temperate or cold, rainy or desert. All sorts of artificial conditions can be tested, such as the effect of the same day and night temperatures or the effect of continuous light. These may lead to an understanding of fundamental plant processes.

So far it has not been possible to provide artificial light as bright as sunlight which is of the order of 5,000 to 10,000 foot candles; but intensities as high as 2,000 foot candles are possible and this is enough for good growth of most plants. Outdoors on a rainy day the light is usually as low as 200 to 500 foot candles.

The problem has been not only to find strong enough artificial light but light of suitable wave-length as many plants respond differently to different colours. Tomatoes under red light alone grow thin and spindly and a little blue light as well is needed to counteract this effect. With blue light alone the tomatoes are stunted. Many growth rooms use fluorescent lights; some use mercury vapour lamps with perhaps tungsten filament lamps as well to boost up the red end of the spectrum. Between the lights and the plants there may be an insulating glass screen with moving air or running water to remove the excess heat.

The required temperature and humidity are usually maintained by controlling the temperature and humidity of the air drawn through the rooms.

It is possible to grow quite normal-looking plants in these growth rooms or cabinets and to make cereals seed and tomatoes ripen fruit. It is strange to see plants growing and thriving under a ceiling of artificial lights as is the case at the Crop Research Division at Lincoln, for example, where there is a walk-in growth room.



*Fig. 1: Water-culture experiment with tomatoes. Plants in polythene buckets supplied with a solution containing essential chemical elements. Air is bubbled through the solution to provide the oxygen required for root respiration without which neither water nor minerals can be taken into the plant.*

The operation of growth rooms and controlled glasshouses requires a great deal of electrical apparatus and so is a costly business. A large set-up of this kind is often called a phytotron. One of the most famous is at the Earheart Laboratories in California. The general servicing of this phytotron requires a regular staff of seven and at times, plumbers, electricians, and refrigeration and air-conditioning specialists. It accommodates research workers from all over the world as well as catering for students. We hope that New Zealand may have one soon.

You may wonder why the phytotron has been included in a discussion on chemistry and the crop. It may seem to be mostly the concern of physicists and botanists. But environment which can have such a great influence on growth can have a great influence on chemical composition also. In fact the two are inter-related. Growth depends on a very complicated system of chemical reactions. Environment can affect not only photosynthesis and respiration but also mineral requirement and absorption, and many studies of plant chemistry are best carried out in a phytotron.

One important branch of plant chemistry is the study of mineral nutrition, and in discussing this aspect I would like to describe water-culture experiments on the tomato being carried out at the Cawthron Institute.

You will see from Fig. 1 that the tomatoes grow very well (up to 8 or 9 ft in height) and produce plenty of fruit. For healthy growth of this kind we have to add to the water some 13 elements—calcium, potassium, nitrogen, magnesium, phosphorus, sulphur, chlorine, iron, manganese, copper, zinc, boron and molybdenum. We add also some sodium and a trace of silicon, which may not really be necessary. But there is no doubt about the others. If any one is left out the plant will suffer. Once by accident we left out calcium and nitrogen from one young plant. Very soon it lagged behind the others and began to turn pale. Even though we soon made good the deficiency, this plant never quite caught up with the others.

Each of the essential elements has its function in the plant and must be present at certain concentrations. There are a number of points to watch: (1) There must be enough of the element present to carry on the growth of the plant; (2) The elements must be present in certain proportions: too much of one may slow down the uptake of another; (3) The total salt concentration of the solution must not be too high or the plant will be stunted or even die because it cannot draw enough water out of a solution of high osmotic pressure.

Different types of plants may have different requirements for minerals. For instance, some plants such as tomatoes, are calcium-lovers while others, including azaleas and rhododendrons, do better with far less.

The following table shows the composition of the culture solution used for tomatoes.

#### CULTURE SOLUTION FOR TOMATOES

(in parts per million)

Calcium .....	335-412	Iron .....	2
Potassium .....	129-229	Boron .....	0.5
Nitrogen .....	150	Manganese .....	0.25
Phosphorus .....	57	Copper .....	0.05
Magnesium .....	53	Zinc .....	0.05
Sulphur .....	114-238	Molybdenum ..	0.05
Chlorine .....	75		

Fresh solution is supplied each week. You will see that the solution contains up to 412 parts per million of calcium and up to 229 p.p.m. of potassium. In the tomato, the leaves have a very high content of calcium, whereas the fruits contain only a small amount. But the fruit needs a lot of potassium. Therefore when leaf growth is heaviest we give the highest level of calcium; and as the fruits begin to develop we have to raise the potassium to its maximum amount of 229 p.p.m.

The first six elements are known as major elements and the last six as minor or trace elements because they are needed in very small amounts. We supply more than 400 p.p.m. of calcium and as little as 0.05 p.p.m. of copper, zinc or molybdenum which is only about one eight thousandth the amount of calcium. If we think, as some home gardeners and even some commercial growers do, that if a thing is good, more of it will be better, we can cause trouble with these trace elements. The plant can adapt itself to a certain range of minerals. It may get along quite well with 300 to 600 p.p.m. of calcium and with 0.01 to 0.05 p.p.m. of zinc. If the zinc is raised to 5 to 10 p.p.m. there will probably be interference with the uptake of iron. In fact abnormally high concentrations of most trace elements can be quite toxic.

The element chlorine has only recently been proved essential to the plant. The amount needed adds chlorine to the list of trace elements but the plants are not so easily poisoned by ex-

cess. For this reason a certain amount of calcium chloride can be used to raise the calcium level without adverse effects: hence the unnecessarily high chlorine content of the culture solution.

If plants are short of any one or more of the essential elements, either major or minor, they develop typical symptoms of the shortage.

Figure 2 shows what happens when too little magnesium and too much potassium is added to the culture solution. This pale leaf with green veins is typical of magnesium deficiency.

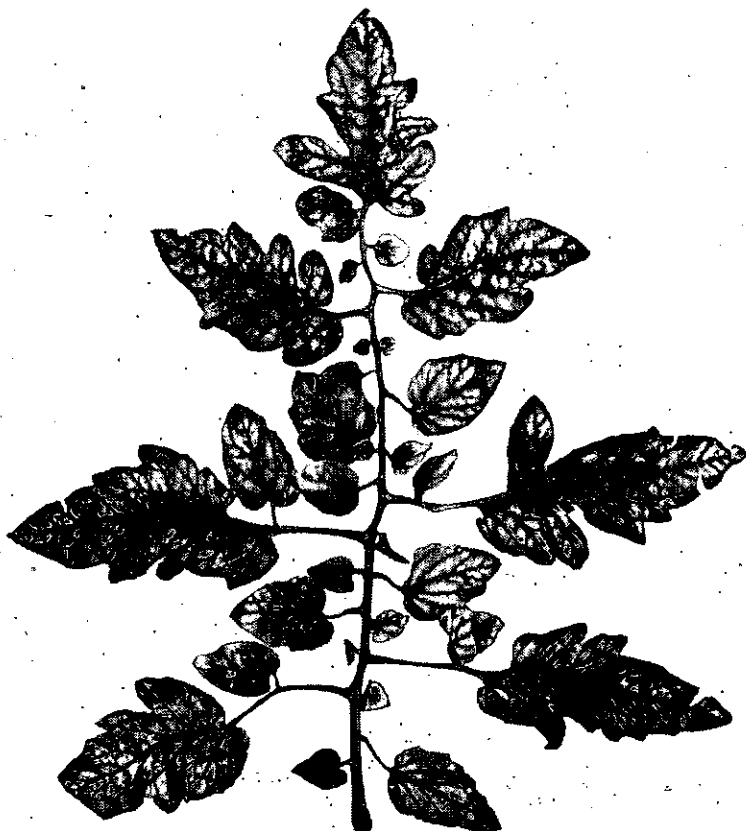


Fig. 2: Magnesium deficiency in the tomato. Leaves yellowed, veins remaining green.



*Fig. 3: Iron deficiency in the tomato. Paling of young leaves and spotting of older leaves produced by depriving well-grown plants of iron.*

Figure 3 shows the very pale leaves produced at the top of the plant when the trace element iron is left out of a previously complete culture solution. Symptoms like this can be easily produced in water cultures because iron sometimes precipitates and becomes less available to the plant. There are certain new compounds recently developed, which keep the iron in solution very well. These are the chelates—organic molecules which bind the iron in a complex form where it is not easily ionized. One of the chelates used is an iron complex of ethylene diamine tetra acetic acid (EDTA).

This iron compound can be taken intact into the plant and it breaks down in the leaves under the influence of sunlight to liberate the iron. Other metals can be chelated by EDTA as well as iron but none of them is as stable as the iron compound. Chelates have many uses in agriculture, particularly in the treatment of trace element deficiencies.

The water-cultures described have been concerned with testing the effect of different levels of minerals on an uneven-ripening disease of glasshouse tomatoes. We know this is worst in wet seasons. If the season is cool and fairly rainy we get the uneven ripening in our standard treatments; but if the season is very hot and sunny we have great difficulty in producing the disease at all and the experiment may be almost wasted. This

is the type of study where a phytotron would be most useful because we could carry out each experiment in the right type of climate—moist, cool, and dull—and need never be at the mercy of the outside weather.

I mentioned that in the present main apple-growing area of the Nelson Province, the Moutere Hills, trees will hardly grow at all unless they are given fertilizer. In the nineteen-twenties the Cawthron Institute did a great deal to establish the industry by finding out how much fertilizer the trees needed and how to supply it. Then in the nineteen-thirties a brown spotting in flesh of the fruit began to appear on the apparently flourishing trees and threatened to ruin the export market. This spotting was not due to an infection but seemed to be some nutritional trouble.

J. D. Atkinson of the D.S.I.R., working in collaboration with the Cawthron Institute, tried injecting into the trunks of the trees a miscellaneous selection of compounds, some of them containing trace elements the importance of which was not fully realized at that time. One of these happened to be boron in the form of boric acid.

When the fruit matured it was found that, whereas the untreated trees had nearly 100% of spotted fruit, the boron-injected trees had none at all. None of the other treatments was effective. It seemed possible, therefore, that the spotting was due to a boron deficiency. This was a very surprising and interesting result because boron deficiency in apples had never been identified before, anywhere in the world, though it has been reported from several countries since. The collecting of evidence to confirm this supposed boron-deficiency was the work of the Cawthron Institute. The chemists analysed many healthy and spotted fruits and showed that the trouble was always associated with low boron. The cure was found to be easy and cheap. Leaves will absorb and use nutrients sprayed on to them in aqueous solution. The spray must be weak enough to avoid burning the leaves and for this reason it is not a very suitable method for supplying major elements where comparatively large quantities are needed. But it is a very effective method of supplying trace elements and has been frequently used for the treatment of boron deficiency of apples. Borax at the rate of 0.1% applied in one or perhaps two of the early routine sprays is all that is needed. Another method of curing the deficiency is to dig in a small amount of borax (about 0.5 lb) round the tree and this remains effective for several years. Boron deficiency is now very rare on the Moutere Hills, and never occurs where borax has been used.

When the boron deficiency problem had been solved, another nutritional disease made its appearance. The leaves began to brown and drop off in early summer so that the fruit was starved, and some varieties like Sturmer stopped sending out new growth. Here again the injection method was used, this time by Cawthron Institute staff. Different major and minor elements were injected into the different branches of affected trees quite early in the season before the browning appeared. By March, only branches which had been injected with mag-

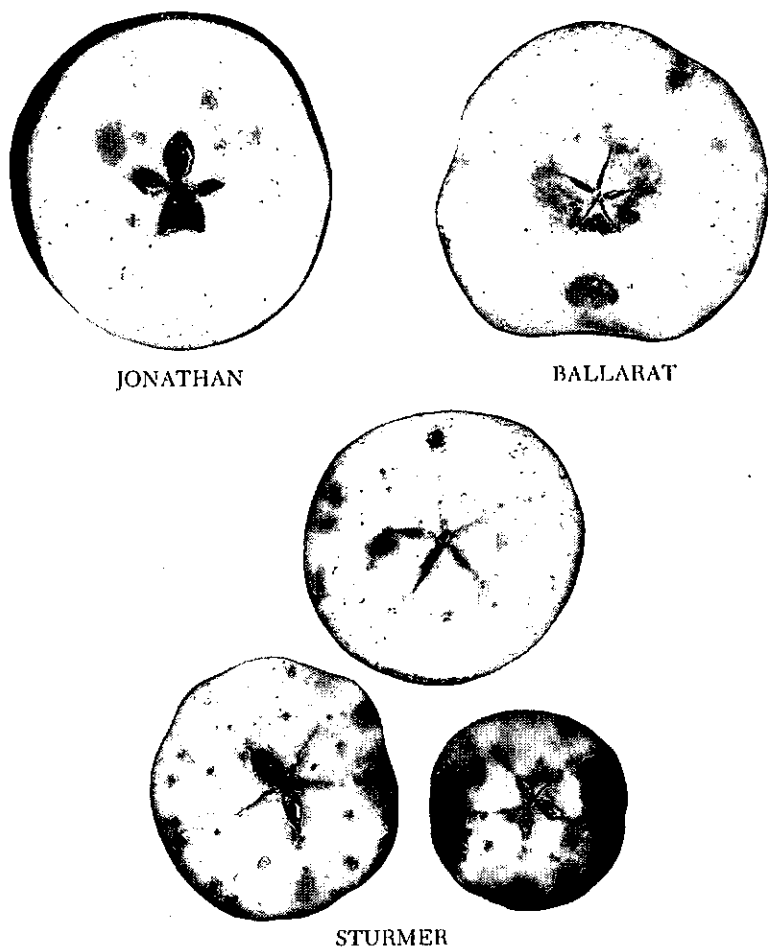


Fig. 4: Internal cork of apples, caused by boron deficiency.

nesium sulphate were still holding their leaves. Analysis showed that the magnesium content of the leaves of the magnesium-injected branches had been raised by the injections. In many orchards examined, wherever the browning was present, the leaves were found to have a low magnesium content. This provided reasonably conclusive evidence of a magnesium deficiency as a cause of the trouble.

The best way of applying magnesium had then to be considered. Quite heavy dressings of magnesium compounds on the soil first gave disappointing results, but gradually, year by year, the trees improved, and with the gradual improvement there was a steady rise in the magnesium content of the leaves. Now, magnesium, formerly the neglected major element, is applied with the other fertilizers, usually in the form of dolomite, a locally occurring magnesium limestone.

I think it is no exaggeration to say that the identification and cure of these two mineral deficiencies saved the Nelson apple industry, which now exports over a million cases each year.

The chemical staff of the Cawthron Institute has since identified other mineral deficiency diseases in the Nelson crops—*e.g.*, boron deficiency in raspberries and boron and molybdenum deficiencies in hops. They have been the first in the world to describe and identify these particular deficiencies.

In many of the universities and research stations of the world and even in New Zealand attention is being focused more and more on the function of minerals in the plant. Why are they needed and what happens when there is a deficiency? The science of the chemistry of the plant is a branch of biochemistry, the chemistry of living things. Knowledge of plant biochemistry has expanded very rapidly during the present century, but much remains to be discovered. Plants, like all living things, are very complicated organisms. Substances are continually being built up, transformed, and broken down.

If we take only one process, such as the respiratory breaking down of sugars into carbon dioxide and water, we find that a long and complicated series of transformations takes place. The sugar is first broken down into a simpler compound, pyruvic acid, which passes through a cycle of changes in which some ten plant acids are involved. During the cycle carbon dioxide is given off and electrons removed. Even the electrons then pass from compound to compound before they finally react with hydrogen ions and the oxygen of the air to form water.

This is only one of many series of reactions in the plant. Nearly all these chemical changes are carried out with the help

of enzymes, which act as catalysts, present in small quantity and speeding up the reaction while remaining essentially unchanged by the overall process. Each reaction, or small group of reactions, has its own specific enzyme so that there are many in the plant. Several hundreds have been recognized and it has been estimated that each cell probably contains something of the order of a thousand different kinds of enzymes. A very small



*Fig. 5: Magnesium deficiency of apples. Browning of leaves and severe defoliation in mid-season.*

amount of enzyme can speed up the reaction of a very large amount of material. A single molecule of the enzyme catalase, which decomposes hydrogen peroxide into water and oxygen, can effect the decomposition of approximately 5 million molecules of  $\text{H}_2\text{O}_2$  per minute. The material being attacked is called the substrate—in the case of catalase, hydrogen peroxide.

The molecular concentration of an enzyme may be very small but the enzyme molecule itself is very large as molecules go. All enzymes so far isolated are proteins, and proteins consist of long chains of linked amino acids—*i.e.*, organic acids containing carbon, hydrogen and oxygen and the  $\text{NH}_2$  group. The molecular weights of the known enzymes fall between 40,000 and 250,000—for comparison cane sugar  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  has a molecular weight of 342 and water, 18.

The enzyme proteins form a large proportion of the total protein of the plant. Leaf protein, which forms some 10 to 30% of the total dry weight, appears to be almost wholly enzyme protein involved in the many reactions of the metabolism of the leaf. It is believed that enzymes can speed up a reaction because a temporary substrate-enzyme compound is formed which requires less energy for the reaction than does the substrate alone. The enzymes are organized in the plant according to their function. For example, the many needed for respiration are all bound up within the cell in small bodies called mitochondria, and those necessary for photosynthesis are located in the chlorophyll-bearing bodies, the chloroplasts.

Certain enzymes consist wholly of proteins. But many others consist of two parts, the protein and another constituent, non-protein in nature, known as the prosthetic group or co-enzyme. In these the protein by itself will not act as an enzyme and must be activated by the co-enzyme. If the co-enzyme is removed, the protein loses its activity. If the co-enzyme is replaced the protein again becomes active. It is known that a number of substances behave as co-enzymes or enzyme activators. Some activators are single elements and some are compounds. It is here, functioning in enzyme activators, that we find not only certain vitamins but also certain trace elements known to be necessary to the plant. These trace elements include iron, copper, manganese, zinc, and molybdenum. We may say that heavy metal trace elements essential to the plant are essential because they form parts of enzyme systems. Copper by itself can act as an enzyme activator and functions in several different enzymes. The action of one of these you have seen

for yourselves. If peaches or apples are bruised, the damaged patches develop a brown colour. If potatoes are peeled and left in the air before cooking, they blacken. These colours are produced by an enzyme called phenolase or polyphenol oxidase which forms coloured oxidation products from phenols in the presence of air.

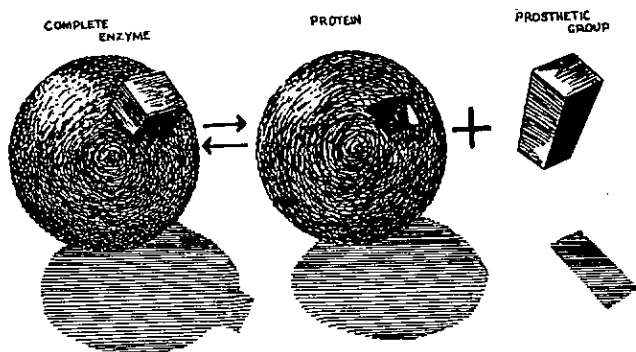


Fig. 6: A complete enzyme molecule is frequently made up of two parts, a protein component and a non-protein prosthetic group. The combination of the two portions is essential for enzymatic activity. (From "Principles of Plant Physiology" by James Bonner & Arthur W. Galston, San Francisco: W. H. Freeman and Company, 1952.)

The simplest phenol is carboic acid and a variety of related phenolic compounds occur in plants. The reaction is essentially the same as the browning of stale photographic developer which takes place of its own accord in an alkaline solution. In damaged fruit and vegetables it can happen under acid conditions provided the enzyme is present.

The very colour of tea is due to this enzyme, which produces phenol oxidation products during the fermentation process. You see the same reaction in the brown rot of stone fruits, in the brown tunnels made in apples by the codlin moth, in brown seeds, and incidentally in brown moles and freckles on the human skin. The function of this enzyme in the plant? Normally it takes part in respiration and does not go to the stage of producing brown oxidized pigments. These are almost invariably the result of injury and abnormal exposure to the oxygen of the air. If this copper enzyme is treated with a chelate or some other compound which can take the copper away it will no longer function.

A recent discovery concerns molybdenum. Nitrogen is usually taken into the plant as nitrate. Before it can be assimilated

lated and built into the plant structure it must be reduced to the ammonium form. The enzyme responsible for the reduction contains molybdenum in its prosthetic group. Hence with molybdenum deficiency the plant can show symptoms of nitrogen starvation.

Magnesium is another element found in the activating groups of certain enzymes. This element is also a constituent of the chlorophyll molecule and of the cell wall.

Nitrogen has received much attention from plant chemists and a great deal is known about the synthesis of nitrogen compounds such as amino acids and proteins and their place in plant metabolism.

Modern techniques in recent years have greatly increased our knowledge of the behaviour of phosphate in the plant. A mechanism of particular interest is the storing of the energy of respiration in energy-rich phosphate compounds which can release it easily as required.

For other mineral elements the information is not so precise. It is known that they are present in certain parts and affect certain reactions though the actual mechanisms may not be fully understood.

In this paper I have touched no more than the fringes of plant chemistry and related sciences. I hope I have been able to convey to you some appreciation of the wonderful organization of the living plant and its importance to man. I also hope I have given the impression that, in spite of the rapid progress of recent years, plant biochemistry is still a comparatively young growth. Perhaps some of my readers are destined to take part in chemical research which will help to bring it to maturity.

## THE CHEMIST AND THE WORLD'S FOOD PROBLEM

N. W. VERE-JONES

Principal Scientific Officer, Dominion Laboratory, D.S.I.R., Wellington.

People considering the choice of chemistry as their life occupation are entitled to the assurance that chemistry is a live and vigorous science, and that the work they will be doing will contribute something towards the general well-being of humanity. In this discussion on "The Chemist and the World's Food Problem", I shall go much further than this, and attempt to show that either the chemist plays a far more important role in this problem of feeding the world than he is doing at present, or the future of mankind is going to be pretty grim.

Consider then Mankind. In Figure 1 is represented his growth since the birth of Christ. I believe that what this not very impressive curve represents is both of great interest and of the utmost importance. Unfortunately its significance is not generally recognized.

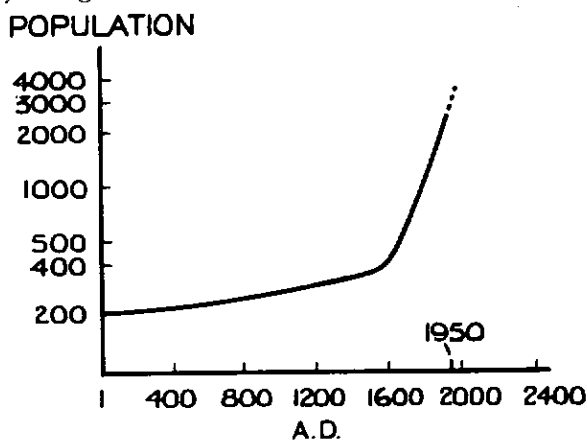


Fig. 1: Growth of world population. (In millions.)

In the first place you will notice that the  $y$ -co-ordinates are logarithmic. Indeed it is a law of all populations; whether of men, microbes, or mice, that they increase exponentially. This is a mathematical way of stating the obvious—namely, that the increase of population in unit time is proportional to the population at that time. Obviously, the annual increase in population of a country with 20 million inhabitants will be, other things

being equal, ten times the increase in the same time of a country with only 2 million inhabitants. As also each year the population becomes larger, the annual increase in the population must also get larger. Hence the population goes shooting ahead at a rate which the mathematicians call exponential and express by the equation  $dN/dt = kN$ . The plot of  $\log N$  against  $t$  is a straight line for such exponential growth.

This law of the exponential growth of a population is a bit like Newton's second law—"every body continues in its state of uniform motion in a straight line, unless acted on by a force". Nobody ever yet saw a body moving like that and similarly populations rarely grow exponentially because outside influences—war or famine or birth control—are always upsetting the growth rate. What is important to remember is that the greater the population, the greater will be the annual increase.

You will see on the graph that from A.D. 1, to about the middle of the seventeenth century, the plot is roughly a straight line—the population was growing nearly exponentially. Then something happened and the graph takes a sharp upward bend and proceeds on a new line of greater slope. What happened? Historians are not very helpful in the matter for rarely, if ever, do they even mention it. However, the historical period when this increase occurred was towards the end of the Renaissance, that burgeoning of men's minds from the Dark Ages of ignorance.

If we put a little circle round the "hinge" of the curve, we should find, if we looked closely enough, that we have included Lavoisier and Dalton, the founders of modern chemistry, Galileo, Newton, and the foundation members of the Royal Society. In fact, we have encircled those men to whom we attribute the birth of modern science.

From their work there developed three revolutions. Firstly the agricultural revolution which increased the supply of food; old methods of strip cultivation under feudal land tenure gave way to more rational farming practices, such as crop rotation. Secondly, a medical revolution which was to increase man's span of life, and, thirdly, the Industrial Revolution with which you are all familiar. Each played its part in raising the standard of living which, I would suggest, caused this dramatic upsurge in the population.

Such a startling increase could hardly have passed without comment. By the end of the eighteenth century, that irascible clergyman, Malthus, pointed out in his essay on Principles of Population, that man's numbers increased exponentially, but that his food supply did not. The result, thundered Malthus,

will be that war, famine, and disaster will overtake mankind (and, reading between the lines, a good thing too, and serve him right). It is popular today to say that Malthus was wrong. Certainly he would never have believed that the world could reach its present population without disaster, but his law of increase of population without a corresponding increase of food supply remains incontrovertible. Nor should we forget the profound influence he had on men's ideas. For example, Darwin himself describes his *Origin of Species* as being but a generalization of Malthusian doctrine. What Malthus did not and could not know was the effect which science was going to have on our productive capacity and our ability to feed ourselves.

For example, just 100 years later the eminent chemist, Sir William Crookes, again warned mankind that disaster threatened him unless food supply could keep pace with population increase. Crookes argued that the known reserves of nitrogenous fertilizers were inadequate to maintain the production of wheat to feed the rapidly increasing population. Only five years later mankind was to be assured for all time of an adequate supply of nitrogenous fertilizers by the discovery of the fixation of atmospheric nitrogen.

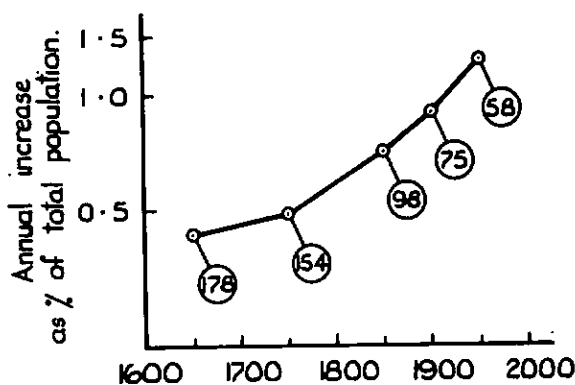


Fig. 2: Growth rate of world population. Figures in circles denote number of years for population to double.

Now let us attempt an extrapolation of the population curve. Figure 2 is an enlargement of Figure 1 from 1650 onwards. It is apparent that it is not a straight line but that there are forces at work still pushing up the rate of growth. If the present trend is continued it is fairly certain that the present world population of about 2,800 million will have doubled before

the year 2000. In my lifetime the population of the world has doubled and has increased by 1,400 million. In a rather shorter period of your lives it is likely to again double, but do not forget that the increase you will see will be 2,800 million against only 1,400 million seen by me.

Those of you who like your figures with a political flavour may find something to argue about in Table I. I will content myself with pointing out that the United Nations' estimate was an underestimate, and that by 1958, according to the Population Reference Bureau, the increase in world population was actually 47 million—more than the population of England and Wales. This year, then, we have to find food for a new country with a population nearly equal to that of the United Kingdom. By the end of the century this increase is likely to be 100 million provided always there is no drastic change in the vital statistics of the world. Is such a change likely?

I emphasized the kink in the curve representing world population that occurred in the seventeenth century. It is possible,

TABLE I: ANNUAL ESTIMATED POPULATION INCREASES BY POLITICAL GROUPINGS

COMMUNIST		<i>millions</i>
China.....	6.5 (12)	
U.S.S.R.....	3	
Eastern Europe.....	1	
	<i>Total</i>	10.5 (16)
UNCOMMITTED		
India.....	5	
Rest of Asia.....	6	
	<i>Total</i>	11
WESTERN POWERS		
United States of America.....	3	
Western Europe.....	2.5	
	<i>Total</i>	5.5
OTHERS		
South America.....	4	
Africa.....	3	
	<i>Total</i>	7
TOTAL		
Estimated.....	34 (39.5)	
Actual, 1958 (Population Reference Bureau, Washington).	47	

even probable, that this century will see another equally dramatic swing in the curve, and for similar reasons. Today we are witnessing a new factor in human history—the industrial revolution of Asia. In China, with a population of 600 million the tempo of this revolution is said to be the fastest that the world has ever known surpassing even that of the Soviet Union. India, Indonesia, and virtually the whole of the Far East have started on the same road. If history is any guide we may expect this industrialization to lead to an improved standard of living, for that is its purpose, and to a new upsurge in population, similar to, but of much greater magnitude than that which occurred in the seventeenth century. The repercussions will be immense and will profoundly affect the economies of the West. I think we inadequately appreciate its significance.

To what extent is the food supply keeping pace with the expanding numbers? Between 1937 and 1957 the world had the largest increase in agricultural production which has ever occurred in any twenty-years' period of man's history. The increase was rather more than 20%—and on what was, in 1937, itself a record. In spite of the slaughter of the second world war there occurred in the same period a population increase of over 500 million. The result was that in spite of the huge leap forward in agriculture, the average daily calorific value of our diet fell from 2,300 to 2,260 calories. Not a big fall, but the figure must be compared with the generally accepted minimum for maintenance of health of 2,800 per day for a sedentary occupation. The figures I have quoted are in fact more disturbing than at first appears because in this period in the United States, Europe and the U.S.S.R. there has been an increase in calorific intake. Today there must be at least 500 million more people in the world than there were in 1937 with not enough food. The plain fact is that agricultural production is failing to keep pace with the enormous growth in mankind's numbers.

That is the problem facing the world. Though agricultural production will, almost certainly, continue to expand, man will have to rely increasingly upon the additional help which the chemist can provide for the increase of his food supply.

Let us, then, consider each of the three major groups of foodstuffs—carbohydrates, proteins and fats—and examine in what way the chemist can supplement (not, of course, replace) agricultural production. Our aim is to look forward rather than backward so that we shall be concerned more with future potentials than past or present achievements.

## CARBOHYDRATES

These are essential for the supply of calories. To increase the calorific value of the world's diet there must be an increase in carbohydrate production. The grains such as wheat and rice and root crops such as potatoes, yams, beet sugar, etc., provide the major sources today. Carbohydrates, *e.g.*, sugar, starch and cellulose, are formed in plants by photosynthesis from carbon dioxide and water. Photosynthesis is thus the essential key to resolving the problem of the world's food supply.

Today, the number of scientists in the world engaged on a fundamental study of photosynthesis might be between fifty and one hundred—judged by the number of scientific papers produced on the subject. I have no idea how many scientists in the world are engaged on the study of nuclear fission but they must considerably exceed 10,000. Though the peaceful uses of atomic energy are many and important the major reason for this tremendous scientific effort was, and still is, the more efficient means of killing ourselves. We may also compare the relative interest taken in space travel and photosynthesis. Judging by the severity of the security measures imposed, one must conclude that the chief object of the former is not knowledge of what the back of the moon looks like.

Photosynthesis can kill nobody but provides us with food, and without it we should be asphyxiated within 24 hours through lack of oxygen. It is thus by far the most important single chemical reaction on this earth and as such you might expect it to hold a special, almost reverential, place amongst chemists. But this is not the case. In fact you may go right through post-primary and university education to a first-class Honours degree in chemistry and yet your knowledge of photosynthesis may be confined to the general ideas you learnt in the General Science course which was compulsory in the third and fourth forms.

Chemically, photosynthesis is of exceptional interest and yet it is totally ignored by chemists in the training of chemists. To me this indicates a serious shortcoming of scientists, including chemists, namely a sublime indifference to the social consequences of our scientific work. We are satisfied, apparently, with the scientific content of our work, and cannot see further to its social or political implications.

I do not want to make any exaggerated claims, but I would assert that if we had attacked the chemistry of photosynthesis with the same effort as has been given to nuclear physics, the world might be better off than it is today, and

when I look at the dandelions flourishing on my lawn, I cannot help thinking that perhaps photosynthesis is a simpler matter than it appears to us at present. Perhaps we do not think right.

Though we know little about its mechanism, the final result of photosynthesis is the formation of starch in the leaves of plants. This starch does not continue to accumulate in the leaf as further photosynthesis occurs. Using the leaves of red clovers it has been shown that the 3 or 4% by weight of starch produced in the leaf in daylight has almost completely disappeared by the end of the night. What happens to it? It is used to provide the plant with the matter for its growth. Probably, for we are also profoundly ignorant of these carbohydrate transformations, the starch is reconverted into soluble sugars which are carried by the sap to the plant cells where it is fixed as cellulose. Cellulose makes up the larger portion of the carbohydrate present in the plant, and forms the main substance of its structure. Later in its life the plant will convert leaf starch into a rather different reserve, starch in the seed or tuber. This is usually the only part of the plant that we eat. The major carbohydrate component, cellulose, we are unable to digest. Of course, the bulk and roughage it provides do aid our digestive processes.

A very different situation obtains with an animal such as a cow, which, as it contentedly stands chewing its cud, is converting cellulose into food. But the cow on its own is no more able to digest cellulose than any other animal. It is the micro-organisms in the cow's rumen which convert cellulose into sugar and other soluble and digestible carbohydrates.

There is no reason why we should not do likewise and in suitable factories convert cellulose, particularly the enormous quantities of waste cellulose lying around, into perfectly good usable carbohydrates. During the last war, Germany was desperately short of food, and did in fact utilize waste wood products for conversion into sugar. Two processes were used—the Schoeller in which cellulose is converted into sugar by cooking it with 5% sulphuric acid under pressure, and the Bergius in which dried wood is hydrolysed with hydrochloric acid vapour. In neither case was the sugar recovered as such, but was used for growing yeast. Dried yeast contains half its weight of protein, and it was protein of which Germany was in most need. The yeast was finally converted into products like "Marmite" by hydrolysis.

New Zealand has a flourishing new industry in the production of wood pulp from her exotic forests. As we have seen,

plant carbohydrates consist of sugar, starch and cellulose. In the manufacture of newsprint from wood pulp, it is the cellulose that is required. In the process the non-cellulose materials are converted into soluble materials which are then separated from the non-soluble cellulose. These materials contain much sugar and in New Zealand are wasted. Nor, as far as I am aware, is there any work being done here on methods for recovering these waste wood sugars. In Sweden, Canada and the United States, however, considerable progress has been made, alcohol, by yeast fermentation, being the usual end product, though food-stuffs are obviously equally possible.

One possible source of carbohydrates is by photosynthesis from the carbon dioxide in coal or oil-fired electrical power plants. A little work is being done, both in the United Kingdom and Germany on this subject. At Poole in England, there is a large power plant burning coal. To avoid air pollution they are required to strip their flue gases of sulphur dioxide which is a fairly expensive process. The resulting gases, containing about 11% of carbon dioxide, are led into sea water tanks containing small quantities of the usual fertilizers and the photosynthetic activity of marine algae is thereby greatly increased to the benefit of oysters also present. At Essen in Germany, purified flue gases are led into greenhouses where, with extra artificial illumination, greatly increased rates of growth and yields of tomatoes have been obtained. Work has also been carried out at Essen on the growth of fresh-water algae, chiefly chlorella, in tanks supplied with dilute solutions of fertilizers into which is bubbled air enriched with carbon dioxide from flue gases. Under these artificial conditions much higher rates of photosynthesis per acre of pond can be obtained than would be possible with any ordinary agricultural crop. Attempts to grow chlorella under these artificial conditions for food production are also being made in Japan and Palestine, both countries desperately short of agricultural land.

### PROTEINS

These are both chemically and nutritionally more complicated than the carbohydrates. They consist of very long chains of amino acids joined together, the simplest known protein, insulin, having 18 different amino acids present, and a total of 107 of them in the molecule. Most proteins are much more complicated and many contain a thousand or more of these amino acid "bricks" of which all proteins are composed.

Excluding water, fat and bone, most of our bodies is protein. Muscles and organs like the heart are nearly wholly so. The activity of every cell in our bodies is carried out with enzymes, and all enzymes are wholly or in part protein. Moreover, our body proteins are in a continual state of flux, their molecules being incessantly broken down and regenerated. In fact, if ever we are able to define life, it will be tied up with protein activity. Hence it is obvious that they play a very important part in our nutrition. If at any time the body is short of a particular protein, it will cannibalize the less essential organs to provide material for the more important.

For our bodies to be able to build up a particular protein molecule there must be present exactly the right variety and proportion of amino acids. Some of these amino acids we are able to manufacture ourselves, others we cannot. These latter are the "essential" amino acids which we must obtain from the digestion of protein in our food—and in the right proportion needed for synthesizing our body proteins. It is convenient that the proteins of all mammals are almost identical in composition with our own, so that animal protein is the ideal food to supply us with just the right mixture of amino acids.

Now there are several catches in this consumption of animal protein. To start with it is very expensive. Meat contains about 75% of water, so at 4s. per lb for steak, this means that we pay 16s. per lb for the protein. Dried skim milk, which is nearly half protein, costs about 9d. per lb. It has a useful sugar content as well, but allowing nothing for this the price of protein works out at only 1s. 6d. per lb. This skim milk protein is nutritionally as good as meat protein but not as nice. Vegetable protein, soya bean for example, is cheaper still.

One result of this high cost of animal protein is that only wealthy countries can afford to obtain most of their supply from this source. This is illustrated in Table 2, which also shows how protein deficiency nearly always accompanies a calorie deficiency.

TABLE 2: RELATIVE PER CAPITA CONSUMPTION OF CALORIES AND ANIMAL PROTEIN

	<i>Calories</i>	<i>Animal Proteins</i>
United States of America .....	100	100
Australasia .....	101	104
Europe .....	89	52
South America .....	77	52
Asia .....	60	10

TABLE 3: EIGHT ESSENTIAL AMINO ACIDS

Amino Acid	Minimum Daily Requirements (grams)	Amount Present in:	
		Myosin, a Typical Animal Protein (%)	Gliadin, a Typical Vegetable Protein (%)
L-tryptophane	0.25	0.8	1.1
L-phenylalanine	1.1	4.3	2.4
L-lysine	0.8	11.9	0.7
L-threonine	0.5	5.1	2.1
L-valine	0.8	2.6	3.3
L-methionine	1.1	3.4	2.0
L-leucine	1.1	15.6	11.9
L-isoleucine	0.7		

Plants also synthesize proteins and, unlike ourselves and animals, can make amino acids direct from inorganic nitrogen, such as ammonia. Seeds of most plants are fairly rich in vegetable protein—*e.g.*, wheat contains about 11%, dried peas 24%, and soya beans as much as 40%. Vegetable and animal proteins differ in their amino acid make-up. The former do not contain the essential amino acids in the correct proportions for our needs. Now if a protein contains a much smaller proportion of one or more of the essential amino acids than the proportion in which we require it, then we have to eat more of the protein to make up this deficient amino acid. Hence, in general, to supply all the essential amino acids in the proportion in which we require them needs more vegetable than animal protein, and the vegetable proteins are therefore often called second-class proteins.

It conveniently happens that the vegetable protein in most seeds, such as wheat, is short in only one essential amino acid. Table 3 sets out first our daily requirements of each of the essential amino acids and then the amounts present in animal and vegetable proteins respectively. It is apparent that lysine is the odd one out. Except for lysine the proportions of amino acids in both animal and vegetable sources are not far from our requirements. Accordingly, by the simple addition of lysine in small quantities to vegetable protein it is possible to upgrade it into a protein comparable with animal protein. By such an addition we can greatly reduce the amount of vegetable protein we must eat to supply all the amino acids we require. Gliadin, after the addition of about 5% of lysine, is actually equivalent to more than twice its weight of unfortified gliadin.

Here then is a first contribution, and it is a major one, that the chemist can make to protein nutrition—the upgrading of

cheap vegetable proteins by the addition of one or other of the essential amino acids. Already lysine is being manufactured in tonnage quantities for this purpose. The process is interesting. It consists of a double fermentation with two organisms in succession. First a synthetic fermentation broth, largely glycerol, is used for the growth of *E. coli*, which in the process of its metabolism produces diaminopimelic acid. Then toluene is added and another organism, *A. aereogenes*, whose enzymes liberate lysine from the diaminopimelic acid. (For the manufacture of these amino acids we shall have to depend upon living processes, such as fermentation.)

You might perhaps expect that lysine so manufactured was being distributed amongst the teeming millions of Asia, but this is not the case. Much of it is used to fortify the diet of chickens reared on the battery system, an exceedingly well fed, if rather dull form of existence. You may also have seen in American "glossies" advertisements for special flour, cake mixes, etc., in which human food is being fortified with lysine. Americans have, with the exception of ourselves, the biggest intake of animal protein of any people in the world. In fact many of them undoubtedly over-indulge their appetite for meat. Great indeed are the powers of advertising!

Referring again to the cow, it consumes only vegetable protein and lacks nothing in consequence. It can, in its rumen, supplement this vegetable protein with micro-biological protein. This can be synthesized, if nothing better is available, from inorganic nitrogen and this suggests another way in which the world's protein requirements could be augmented—namely, by the production of suitable proteins by micro-organisms from waste organic matter. I have mentioned one such development, the growth of yeast on waste wood in Germany during the last war.

The fungi, some poisonous, but many highly nutritious, are also of considerable interest. Many of them have remarkable powers of digesting cellulose and can be used to convert it into a pleasant foodstuff rich in protein. Generally we eat only the reproductive organs of fungi—the sporeheads such as mushrooms—but the threadlike mycelia with which fungi grow by proliferating their environment are also edible, nutritious and tasty. Mushroom mycelia have, in fact, been grown in deep tanks containing organic wastes from citrus factories, concentrated, and used to make mushroom soup. In general, however, no serious attempt has been made to exploit the potentialities of fungi for proteins.

In the transformation of vegetable to animal protein by the normal process of animal husbandry there is very considerable loss of protein. For some years, experimenters at Rothamsted have been trying to develop cheap engineering methods which would enable the protein of grass to be separated from the fibre, without the wasteful interposition of the animal. Reasonable methods are now available which would enable grass protein to be produced at about 1s. per lb dry weight compared with our figure of about 16s. per lb for meat protein. However, I have no knowledge of there being any commercial developments from this work, largely because the food technologists have not yet succeeded in converting this product into an attractive human foodstuff.

Another source of protein not fully exploited is the sea. No attempt has been made as yet to harvest the smaller organisms which occur in much greater quantity than do fish. Photosynthesis and fixation of atmospheric nitrogen are being performed simultaneously by the unicellular marine algae, the phytoplankton. These are, apparently, of limited value for human food. But the phytoplankton nourish the rather larger, but still microscopic zooplankton. Shipwrecked sailors are reputed to have survived for ten to fifteen days by filtering such material with their shirts or other cloth. This is of no great significance because you should, with care and adequate water supply, be able to survive for 30 days on nothing at all. But this zooplankton does satisfy whales. At present we lack the whale's ability to harvest this material economically. Incidentally, this zooplankton has a pleasant shrimplike flavour.

A little work has been done in Scotland on a related subject, namely, adding fertilizers to a contained body of sea water, such as lochs, for the more abundant production of plankton, and thus the increase of the fish population. Fish farms have been used for centuries in Asia, fresh-water fish in China, sea-water fish in Indo-China and other South-east Asian countries. In fact we seem to have rather a blind spot for the Asiatic utilization of fish as a source of protein. We probably know that the Japanese capture and eat more fish than any other people in the world. They fish as far afield as New Zealand. But few people, I think, are aware that Indo-China alone produces nearly as much "nuoc mam"—a fish sauce—as New Zealand does lamb. Nuoc mam is produced by a microbial fermentation of whole fish whereby a liquid rich in amino acids and organic nitrogen is produced, which is used as a sauce of high nutritive value, for

their mainly rice diet. In the fermentation there is no great loss of amino acid as there is, for example, in the transformation of vegetable to animal protein.

### FATS

Fats present probably the least worry of the three major food constituents. Provided people are on an adequate diet with enough calories and enough protein, they are almost certain to collect adequate fat therewith. However, there have been times of a world-wide fat shortage—*e.g.*, at the end of the last war.

Nutritionally, the fats are the least important of the three groups. We are ourselves readily able to convert carbohydrates into fat and the chief function of fat in our diet is actually to make it attractive. Without any fat our food would be inconceivably uninteresting. For this reason they are of considerable importance to the cook and to the food technologist. Moreover, the food technologist has the ability to alter their constitution fairly readily to suit his special purposes. This is impossible, or extremely difficult, with carbohydrates or proteins.

There is no significant nutritional difference between the animal and vegetable fats as there is with protein. The vegetable fats or oils are mostly obtained from the seeds of plants. This is an interesting point because fats appear to play little

TABLE 4: WORLD PRODUCTION OF FATS

	tons
<b>EDIBLE VEGETABLE OILS</b>	
Cottonseed .....	1,491
Groundnut .....	1,481
Coconut .....	1,437
Soya .....	1,201
Other .....	3,005
<i>Total</i>	8,615
<b>ANIMAL FATS</b>	
Butterfat .....	3,304
Lard .....	2,679
Mutton and beef tallow .....	1,295
Ghee .....	850
<i>Total</i>	8,128
<b>MARINE OILS</b>	
Whale .....	522
Fish .....	281
<i>Total</i>	803

part in plant metabolism and the plant produces fat, apparently, to make its seeds attractive to birds and animals and thus ensure their wide dispersal. Table 4 shows the total world production of edible fats. In addition very large quantities of fats, mainly vegetable, are used for making soap.

You will notice that edible vegetable oils now exceed animal and fish oils. Most of these vegetable oils are used in the production of margarine but as obtained from the plant they are unsuitable for this purpose as they are mostly liquid. However, oils can be converted into solid fats by hydrogenation which is carried out by treating the hot liquid fat with hydrogen in the presence of a catalyst, usually nickel. Deodorization is also necessary and this is done by a steam distillation at high vacuum.

Some of you have probably seen or smelt whale oil at Picton. You will know that it is an oil, stinking of fish, which very easily oxidizes and so goes rancid as well. For a really revolting smell whale oil takes a lot of beating. However, by hydrogenation and deodorization it is converted into a hard white substance with no odour and very little taste. The process of hydrogenation can be reasonably controlled to give any required degree of saturation and we can thereby harden the fat or raise its melting point.

World production of margarine now exceeds that of butter, and must, it seems to me, continue to replace butter, and it is right that it should do so. With our present technological processes, butter is an unnecessary luxury. The world can ill afford the extravagant use of our limited land resources which butter-fat production requires.

Perhaps the chief interest of fats is that they are the only foodstuffs which man has as yet succeeded in producing entirely synthetically. Again war was the necessity which drove Germany to accomplish it. A paraffin wax fraction from either the Fischer-Tropsch synthesis of petroleum or the hydrogenation product of brown coal was oxidized with air at  $105^{\circ}\text{C}$  in the presence of small amounts, 0.2 to 0.5%, of potassium permanganate. After 24 hours, about 30% of wax had been oxidized to fatty acid. The mixture was treated with soda to convert the fatty acid to soap and separate it from the residual wax. The soap was reconverted to fatty acid by treating with sulphuric acid and a middle fraction containing acids from  $\text{C}_{10}$  to  $\text{C}_{20}$  was taken and esterified with glycerol which can itself be synthesized. The product was then purified and deodorized and finally emulsified with water to

make margarine with the usual additives of flavour, carotene for colour and as a source of vitamin A, etc.

In conclusion, I want to underline two points.

First, the important role of micro-organisms. Only within the last half century has man come to realize, and as yet but dimly, how they can help him in his struggle for existence. Previously, because of their invasion of his body and resulting disease, they were his major enemies. Today this is rapidly changing. Only those of us who lived before their introduction, can appreciate what antibiotics have meant to mankind. But even more important than these medical benefits is that our eyes are being opened to the immense potentialities of micro-organisms in our continuing struggle, and a struggle not going too well at present, to feed our expanding population. "Bug-food", if that is what it will come to, may not at first sound very attractive but I notice that poets continue to praise, and he-men to relish, those two products of micro-organisms, beer and cheese.

Second, when man has learnt to control photosynthesis and to utilize the thousands of tons of potential food even now produced by it every minute and we are still unable to feed ourselves, then and not till then, will be time to talk of over population. Until then we simply echo Malthus and his cry of despair that War, Famine and Disaster will be the inevitable results of our increasing population. The despair is needless for the remedy is in our hands—chemistry. Theoretical chemistry to explore and comprehend photosynthesis and similar living processes and technological chemistry to formulate the products of these processes into attractive and satisfying foodstuffs.

**BIOGRAPHICAL NOTES**

PROFESSOR H. N. PARTON, M.Sc., Ph.D.(Lond.), F.N.Z.I.C.



Professor Parton was appointed to the chair of Chemistry at the University of Otago in 1954. He graduated from Canterbury University College in 1930 with first class honours in chemistry and shortly after was appointed to the staff of the Chemistry Department. He obtained his Ph.D. degree at King's College, London, in 1934. On his return to Canterbury he assumed increasing responsibility for the teaching of physical chemistry and was appointed Lecturer-in-charge in 1945 and in 1947 was promoted to the newly created status of Associate Professor. His research interests have been in the field of electrolyte solutions. Dr Parton is noted for his stimulating teaching, for his fine appreciation of the relation-

ship between science and society, and for his ready wit. He was recently a member of the New Zealand delegation to the international conference on atomic energy at Geneva.

ELSA B. KIDSON, M.Sc., D.Sc., F.R.I.C., F.N.Z.I.C.

Dr Kidson is one of the foremost women chemists in New Zealand. Born in Christchurch and educated at Nelson Girls' College where she won a Junior University Scholarship, she graduated from the University of Canterbury in 1926 with honours in organic chemistry. After a short time on the staff of the Chemistry Department she joined the chemical staff of the newly formed N.Z. Soil Survey (now the Soil Bureau) which was at that time stationed at the Cawthron Institute. She has remained at this Institute as a seconded officer of the Soil Bureau and has there worked mostly on cobalt in relation to bush sickness, magnesium deficiency of apples,



molybdenum in soils and other trace element nutritional problems. She is at present engaged in the study of "blotchy-ripening" of tomatoes using a water-culture technique. She is a Fellow of the Royal Institute of Chemistry and of the New Zealand Institute of Chemistry and was chairman of the N.Z. Section of the R.I.C. in 1957. Dr Kidson is a member of a distinguished family of chemists and teachers. A brother, J. O. Kidson, holds a senior position in chemistry at the Christchurch Boys' High School.

N. W. VERE-JONES, B.Sc.(Hons.), Dip.Chem.E.(Lond.), A.M.I.Chem.E.,  
A.N.Z.I.C.



Mr Vere-Jones is a Principal Scientific Officer in the Chemical Engineering Section of the Dominion Laboratory, Wellington. He was educated in England where he was production manager for Benges Foods Ltd. After coming to New Zealand and joining the Dominion Laboratory he began an investigation of a process for dehydrating meat which has proved outstandingly successful. Experimental batches of meat, dehydrated by his process, have been used by troops in Malaya, by New Zealand climbers in the Himalayas and in the Antarctic. Mr. Vere-Jones' principal interest has always been the chemical engineering of food processing and he holds very decided opinions on the place of

chemistry in the struggle to keep the world's food supply abreast of the rapidly expanding population.