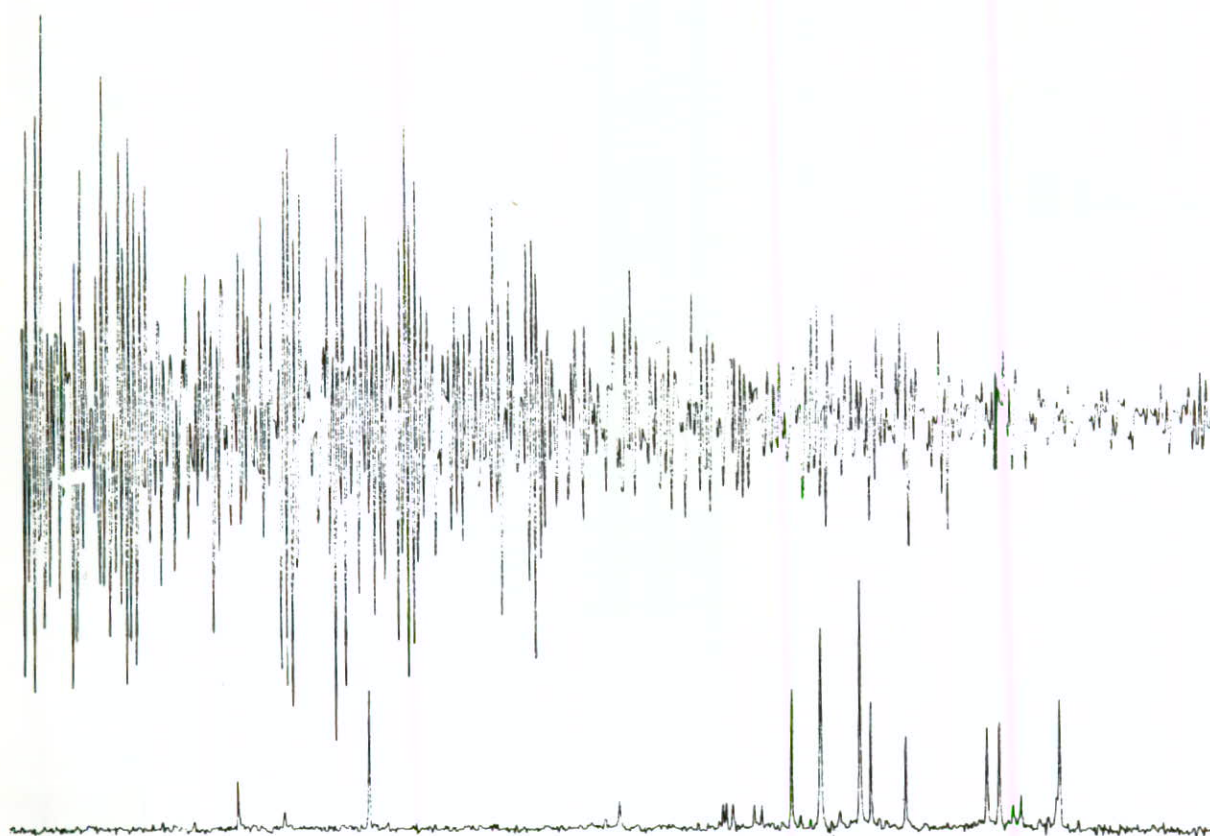


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¹³C NMR

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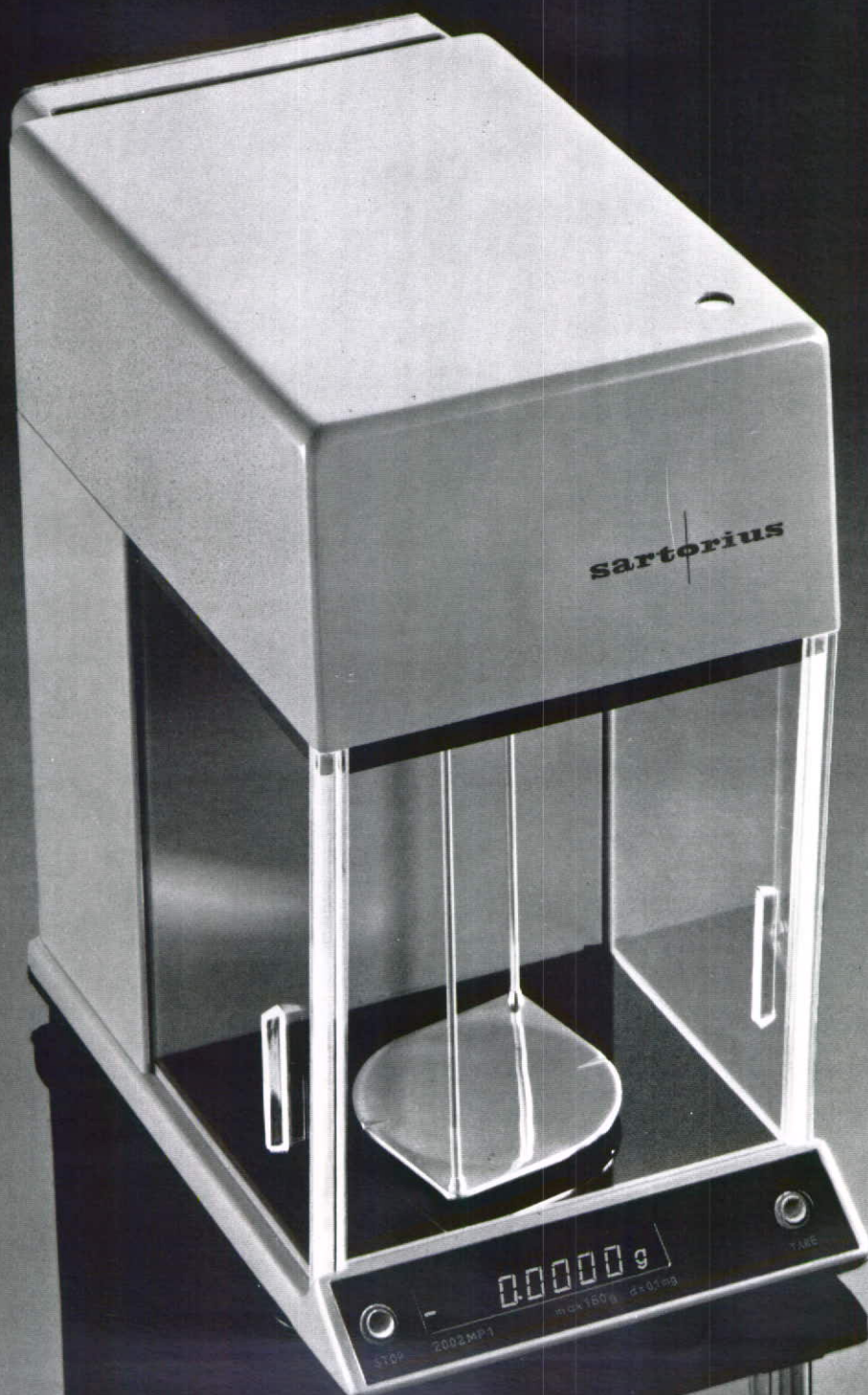
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PREDICTING OUR FUTURE — A CRITICAL VIEWPOINT

Graham A. Wright
President, New Zealand Institute of Chemistry

*"Time present and time past are both
perhaps present in time future, and
time future contained in time past."*

T. S. Eliot.

The future is very much in fashion. Numerous bodies ranging from local authorities and environmentalists to Royal Commissions and Government Departments are producing their forecasts of population, energy, resources and all manner of economic trends in the future [1,2]. Last year Parliament gave a legislative basis for future studies with the establishment of the Planning Council and the Commission for the Future. The National Research Advisory Council plans scientific research objectives for New Zealand based on its appraisal of future technological advances, and the Commission for the Environment attempts to assess the future impact on the environment of major development schemes.

But how reliable are these modern prophets of the future? It is my view that most of these future predictions are likely to be quite unreliable, especially in the medium to long term, and we must be on our guard to avoid taking them too seriously. Most forecasting techniques are obliged to assume a continuation of present trends into the future, and there is no way that they can take into account unpredictable events such as world wars, economic recessions, scientific discoveries and major social changes. There are signs that some types of forecast have become accepted as reasonable guidelines for the future, when the probability is that they will turn out to be quite inaccurate. Let us examine two kinds of forecast which are enjoying some popularity at present: the Limits to Growth model and the Scenario method.

The Limitations of Limited Resource Models

In 1970 the Club of Rome sponsored a computer model of the world's future, which was published as the "Limits to Growth" [3]. The computer was used to simulate population growth and consumption of resources over a period of 200 years, with allowance for capital investment, industrial productivity and pollution, see Fig. 1. The forecasts were alarming and extreme; economic and social collapse, signalled by rising pollution, falling food supplies per person, and increased death rates, was predicted as early as 40 years ahead. Mankind was seen to face a predicament almost impossible to solve. This model of the future caused considerable controversy, and even led to a public disagreement between two D.S.I.R. Divisions [4,5], with the Royal Society of New Zealand striving to offer an impartial judgement [6]. The world dynamics model does appear to predict a catastrophe sooner or later, but it is based on the over-simplified assumption that finite world resources are being consumed by an expanding population. The lesson of history is that economic forces can drastically

control demand, and even produce new resources by intensified exploration, recycling, or substitution of alternative materials. Developments in technology can frequently eliminate the problem of scarcity altogether in certain areas by changing an entire industry [7]. Thus the decline of the hardwood forests in Europe in the 18th Century threatened the building of ships and the smelting of metals with wood charcoal, but these problems disappeared when the industrial base shifted to steel and coal. Until the computer models can be improved to take into account the creativity and adaptability of mankind, it is difficult to take their predictions seriously.

Scenario Futures Which Ignore Surprises

An interesting type of forecast is the scenario technique which allows us the choice of several different futures, depending on how we behave and make our choices [8]. The Maiden Committee has produced energy scenarios for

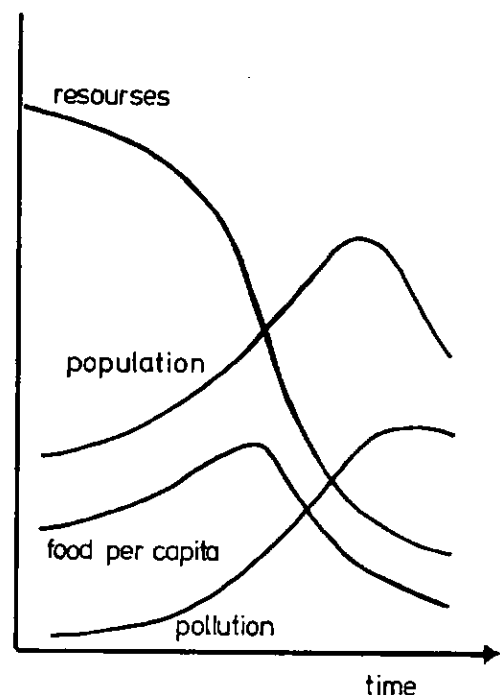


Figure 1. Limits to Growth Predictions

These schematic curves are based on the World Dynamics computer model, which forecasts a catastrophic fall in living standards, as resources are exhausted, and an eventual decline in population. This doomsday is predicted to occur about 40 to 200 years hence, depending on the exact nature of the assumptions made (Reference 3).

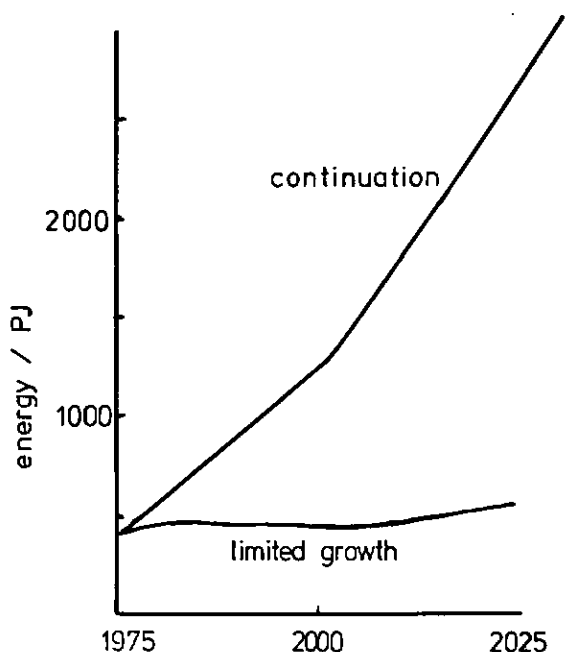


Figure 2. Energy Scenarios for New Zealand

The diagram shows two alternative forecasts of energy consumption, depending on policies adopted. The continuation scenario allows for continued growth of the economy, and as a consequence there will be substantial consumption of fossil fuels with nuclear energy being used after the year 2000. The limited growth scenario would involve severe conservation measures, with reliance on renewable resources such as wood in the future (Reference 9).

New Zealand over the next 50 years (Fig. 2) and these show the energy resources we will need to keep the country running at the level we choose [9]. But these scenarios suffer from the weakness that they have neglected all forms of energy which are not economically viable at present. Solar, tidal, wind, nuclear fusion and photovoltaic energy systems are excluded; but surely a future improvement in the relevant technology may make one of these energy sources (or some other source as yet undiscovered) a major contributor to our future power needs. A more serious criticism of the scenarios is that they are surprise-free. No account is taken of the possibility of future inventions, or unforeseen changes in our economic progress. If the world were to suffer climatic change similar to the little ice-age which occurred about 1500 A.D., there would be dramatic effects on agriculture and energy resources and the scenario predictions would be quite useless [10]. Even short term population trends are difficult to anticipate. The growth rate of Auckland fell from 3½% p.a. in 1970 to ½% p.a. in 1977; this change is difficult to explain and was impossible to predict.

The weakness of the scenario method can be readily appreciated by recalling some of the remarkable changes that have occurred during the last 50 years. In the 1920's coal was the major source of thermal energy and natural gas was burnt off as a waste product. The airship was predicted to be the future mode of air travel, and nuclear energy was a laboratory curiosity. Electronics was in its infancy, and would have been totally ignored by any self-respecting scenario forecaster on the grounds that it was not an established industry. The technological changes of the last half-century have been considerable, and there is no reason to believe that discovery and innovation will not continue at a similar pace in the future.

Chemical Science and The Future

I believe that we can make some contribution to the debate

on the future by examining progress in Chemistry. Three points well understood by pure or applied chemists are worth stating.

- (a) Chemistry has built up an enormous body of empirical knowledge by observation and experimentation. Last December a newly synthesised derivative of cephalosporin was added to the CAS registry of compounds. It became the 4 millionth unique chemical substance known to science. Of this vast number, man uses or comes into contact with about 60,000 substances. The number of combinations of reagents, solvents, catalysts and conditions which cause chemical reactions are immense. It follows that the variety and complexity of chemical phenomena are quite astonishing, and there is ample scope for providing for future needs if sufficient scientific effort is applied to the task.
- (b) The status of scientific theory in Chemistry is still less satisfactory than we would wish. Present theories enable us to interpret our observations, but they are generally not adequate to reliably predict new phenomena. Perhaps Chemists have fallen into the trap of trying to explain chemical behaviour in terms of laws of physics, using the process of reduction into simpler concepts. Thus it is possible to study a single iron atom by spectroscopic techniques and gain a precise knowledge of its structure and energy levels. But this information does not enable us to explain the observation that an iron crystal heated to 910°C changes abruptly from the body-centred alpha phase to the face-centred gamma phase. The whole is greater than the sum of its parts, and in the case of iron, this means that the behaviour of an assembly of iron atoms in the crystal grain can not be predicted from information relating to single iron atoms. The biologists call this the emergence principle: there are higher levels of knowledge which are not derivable from simpler concepts. It is significant that the latest Nobel prize for Chemistry was awarded to the Belgium theoretical chemist Prigogine, who worked on dissipative structures. These are molecular systems far from equilibrium, consuming energy to yield oscillations or cyclic reactions which accurately carry out their appointed tasks, as in the biochemical processes in living cells. Prigogine has attempted to rationalise molecular changes at the level of complexity found in nature, but it is clear that chemical theories still require substantial improvement.

- (c) A striking feature of chemical science is the uncertainty involved in predicting its progress. Many important discoveries have been made by chance, and there are good examples in the field of antibiotics, trace element deficiencies, liquid crystals, crown ligands, and rare gas compounds. There is no reason to suppose that the role of serendipity in scientific advance will diminish in the future. We can be fairly sure that progress will be made by a series of abrupt new insights, rather than gradual development.

Conclusions

Although I have taken a critical view of some current techniques in the field of futurology, I feel that Chemists can also make constructive contributions to the debate on the future and we have a duty to counter some of the less reliable forecasts which are frequently made.

- (a) As scientists we should warn of the limitations of predictions which ignore the possibility of unexpected events. Unfavourable events such as climatic change or international conflict are always possibilities, and any future strategy should take such contingencies into account. The case for conservation should rest not on the need to eke out limited resources but on the wisdom of building up reserves so that mankind can withstand the threats to survival that are bound to arise from time to time. The most predictable fact about the future is its unpredictability – the certainty of uncertainty.
- (b) The capacity for innovation and adaption in the fields of science and technology will continue to produce new inventions and materials in the future, and any forecast which predicts a crisis caused by scarcity of a material is likely to be inaccurate. The possibility of a future shortage, such as liquid fuels, will automatically set in train the research and development to overcome the anticipated shortage before it occurs (if the economic incentives are strong enough).
- (c) It would be unwise to allow ourselves to become pre-occupied with forecasts of doubtful validity, while ignoring the problems that already exist and deserve immediate attention. On a world scale such problems of technology between nations, and the consequential problems of malnutrition and starvation that recur in some regions.
- (d) Within the Institute of Chemistry there may be more we can do to improve the transfer of scientific ideas and information between members. The technique of "brainstorming", defined as creative thinking by imaginative generation of ideas in a group discussion on a defined objective was tested by D.S.I.R. in 1976, when they carried out a review of the applications of molecular biology to agricultural production [11]. It is clear that considerable benefits may be gained from this

method, provided the objectives or topics are carefully defined, and a wide range of informed people participate. Could we not organise brainstorming sessions at our annual conferences, particularly on topics at the interface between industrial and research chemistry where communications is not always as good as desired? Conferences are costly – I estimate about \$100,000 as the cost of the N.Z.I.C. annual conference if we include our subsidy our employers make by paying our salaries while we attend. It could well be that brainstorming sessions (in addition to the set-piece plenary and specialist lectures and social events) may generate useful ideas on the application of science to practical problems in industry. This may be the best contribution we can make as an Institute to the demands of the future.

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LETTER TO THE EDITOR

School of Mathematics and Science
Wellington Polytechnic
Wellington.

Dear Sir,

During the May vacation I attended the South Australian ANZAAS Australian Institute of Science Technology Conference at the ANCL Canberra. During the conference I contributed a paper on the new syllabus for the 5th year of the NZCS Chemistry Syllabus and our experience of teaching it as part of a session on Education and Training.

The actual preparation of the paper itself was a valuable exercise in discussing with colleagues all the five syllabi.

There was general comment on the very comprehensive nature of the syllabus. In discussion it was suggested we are getting into other science disciplines. The point was raised in discussion as to whether in New Zealand the name 'technician' is registered. My information is that it is not, but it is a possibility worth considering.

It was very pleasing to be able to tell another questioner of the good relations technical institutes have with employers in particular over day time release.

In private conversations afterwards I learned that an overall supervisory body for the Colleges of Advanced Education called "The Council for Accrediting of Awards" has been set up on a Federal basis. Australian experience indicates the need for a supervisory body such as the Technicians Certification Authority to set uniform standards. From what I heard in Australia I believe we should not go any further in making Technical Institutes internally examining.

Since the conference I have had some further enquiries from Australia for information on other years of the chemistry course and on bio-chemistry and para-medical courses.

If anyone would like a copy of the paper I would be pleased to supply one.

G. NAISH
Tutor

Carbon-13 NMR

J. W. BLUNT and M. H. G. MUNRO
Chemistry Department, University of Canterbury

For the practising chemist carbon-13 nuclear magnetic resonance spectroscopy ($^{13}\text{Cnmr}$) can now be described as an everyday tool. Yet it is only twenty years since the first nmr observations of the ^{13}C -nucleus [1] were made and less than ten years since $^{13}\text{Cnmr}$ spectroscopy was the realm of those few chemists with sufficient resources to adapt or build suitable spectrometers. Today, dedicated, so-called third-generation $^{13}\text{Cnmr}$ spectrometers are being mass-produced and have been installed in, or planned for, most chemical institutions.

New Zealand now has five $^{13}\text{Cnmr}$ spectrometers. JEOL FT-60's were installed in chemistry departments at the University of Auckland, the University of Otago and Massey University during 1974/1975 while a VARIAN CFT-20 was installed at the University of Canterbury early in 1974, and an FT-80A at the DSIR, Petone in 1978.

One has only to note the increasing frequency of references to $^{13}\text{Cnmr}$ in the literature and the increasing dependence of chemists on the technique to appreciate that the seemingly extravagant claims for the likely impact of $^{13}\text{Cnmr}$ made in the early 1970's were more than justified. Few techniques have been adopted with such enthusiasm and passed so rapidly from the status of a new research area to that of a routine, but extremely powerful option in the methods of probing molecular structure.

$^{13}\text{Cnmr}$ has revolutionised areas such as biosynthesis and molecular dynamics and has already greatly broadened the scope of nmr spectroscopy in determining the structure, stereochemistry and conformation of organic and organometallic compounds.

The aim of this article is to outline both $^{13}\text{Cnmr}$ methodology as well as to illustrate applications of the technique.

The NMR Experiment

All nuclei carry a charge, but some nuclei also possess angular momentum and a magnetic moment, μ . The angular momentum can be described in terms of the quantum spin number, I which has values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$,

The gyromagnetic ratio, Γ , a fundamental nuclear constant, expresses the relationship between I and μ (1)

$$\gamma = \frac{2\pi\mu}{hI}$$

where h is Planck's constant.

It is the spin number I that determines the number of spin states or energy levels for a given nucleus when it is placed in a magnetic field, B_0 . The number of energy levels is given by the relationship $(2I + 1)$, so for $I = \frac{1}{2}$ nuclei, such as ^{13}C or ^1H , there are two possible energy levels. These can be visualised as the nucleus being orientated either parallel with the applied field, B_0 , (lower energy) or antiparallel (higher energy) (see Figure 1).

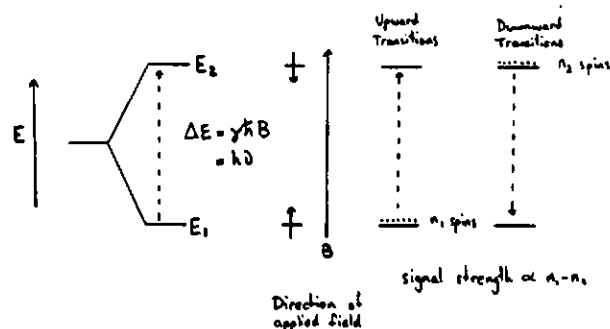
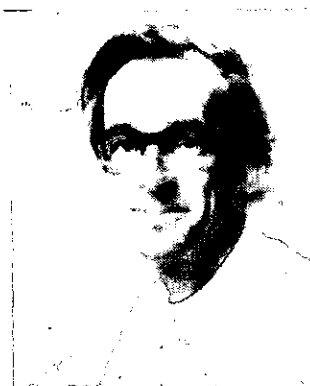


Figure 1 Energy levels for $I = \frac{1}{2}$ nuclei when placed in a magnetic field, B_0 .

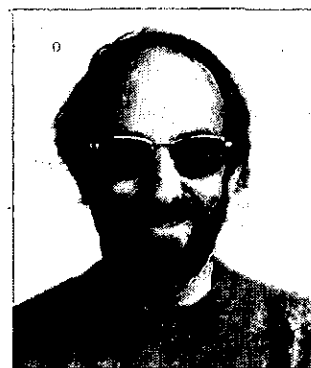
Such nuclei when placed in an external magnetic field, B_0 , will precess about the axis of the applied field (Figure 2). An apt physical analogy for this process is the precession of a gyroscope under the influence of gravity. This precessional frequency, ν , also known as the Larmor frequency, is given by the fundamental nmr equation (2)

$$\nu = \frac{\gamma}{2\pi} B_0 \quad (2)$$



John Blunt obtained his Honours degree in Chemistry at the University of Canterbury in 1963 and his Ph.D. in 1966. He subsequently joined the staff at Canterbury in 1970, where he is now senior Lecturer. His special interests are in the teaching of bio-organic chemistry and in the application of $^{13}\text{Cnmr}$ techniques to structural and analytical problems.

Murray Munro obtained both his B.Sc. (Hons) and Ph.D. at the University of Otago. Following the two years as a Post-doctoral Fellow with Professor A. R. Battersby at the University of Liverpool he was appointed in 1968 to the Chemistry department at the University of Canterbury, where he is now a Senior Lecturer. His research interest lie in areas relating to biologically active compounds and biosynthetic pathways.



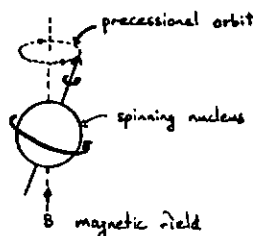


Figure 2 Precision of an $I = \frac{1}{2}$ nucleus about the axis of the applied magnetic field.

The implication of this equation is that if electromagnetic energy of the correct frequency is introduced it will be in resonance with the precessional frequency causing the nucleus to flip to the higher energy level.

As the gyromagnetic ratio differs for each type of nuclei the frequency at which absorption occurs also differs. The nmr frequencies for some commonly observed nuclei are listed in Table 1.

Unfortunately the basic nmr experiment is not very sensitive, even for the more favourable cases such as ^1H . This is because the strength of the signal is dependent upon the difference in population of the two energy levels. This difference is given by the Boltzman equation (3)

$$\frac{N_2}{N_1} = \exp\left(-\frac{\Delta E}{kT}\right) \quad (3)$$

where N_2 and N_1 are the populations of the upper and lower energy states respectively. As this energy difference ΔE (Figure 1) is minute there is only a small excess of nuclei in the lower energy state. It is this small excess that gives rise to the nmr signal, as the probability of an upwards transition is greater than that of a downward transition (induced emission).

Continued absorption of the radiation would tend to equalise the populations, but for the presence of a variety of relaxation processes which effect radiationless transitions returning the upper state E_2 to the lower state, E_1 . Therefore, during irradiation of a nucleus at the appropriate frequency a steady state is achieved in which the original excess population is somewhat decreased, but net absorption is still possible.

The relaxation processes can be divided into two categories, namely spin-lattice and spin-spin relaxation, characterised by the time constants T_1 and T_2 respectively. T_1 is the time constant for the exponential return of the spin populations to their equilibrium values after irradiation. This is achieved by energy exchange between

Table 1: Nmr frequencies for some commonly observed nuclei.

Nucleus	Nmr frequency in MHz for a 2.35 Tesla field	Natural Abundance	Relative Sensitivity for equal number of nuclei
^1H	100.00	99.98	1.000
^{11}B	32.08	81.17	0.165
^{13}C	25.14	1.108	0.016
^{19}F	94.08	100.00	0.834
^{31}P	40.48	100.00	0.67

individual nuclear spins and the surrounding lattice. It takes $\sim 5 T_1$ for a system to be $\sim 100\%$ relaxed after irradiation. Most carbons have T_1 values in the range 0.1 to 20 s.

There are several different mechanisms which contribute to spin-lattice relaxation but the most important of these is dipole-dipole relaxation. In dipole-dipole relaxation it is the interaction of the local magnetic fields of two magnetic nuclei that is responsible. This is a process that is particularly favourable between ^{13}C and ^1H . As dipole-dipole relaxation is proportional to r^{-6} , where r is the separation between the interacting nuclei, it is only protonated carbons that are efficiently relaxed. It is basically for this reason that non-protonated carbons have much greater T_1 values.

^{13}C nmr is confined to the ^{13}C -nucleus as ^{12}C has no magnetic moment, but by comparison with ^1H , ^{13}C has a small magnetic moment, hence lower values for ΔE and an even smaller difference in Boltzman populations. The consequence of this is a very much lower sensitivity for ^{13}C compared with ^1H (see Table 1). Furthermore, the low isotopic concentration of ^{13}C compounds the problem by a further factor of 10^2 . The sensitivity of the ^{13}C experiment at natural abundance is 1.8×10^{-4} that of ^1H . Consequently the development of ^{13}C nmr had to wait for better magnet design, better techniques for spectrometer stabilisation, alternative methods of spectral accumulation such as repetitive pulse Fourier Transform and the development of the experimental technique of wide-band proton-decoupling.

Spectral Accumulation

As magnet design improved, spectrometers were able to work at higher fields and with greater field homogeneity. This resulted in greater sensitivity, but it was the use of an alternative method of spectral accumulation that was primarily responsible for the rapid advance of ^{13}C nmr in recent years. Historically, a continuous wave (CW) method has been used for acquiring spectra. In this method the field or frequency is swept slowly through the spectral range and the spectrum recorded as absorption versus frequency. Of more recent development is the repetitive pulse Fourier Transform (FT) technique. This method is more sensitive than the CW alternative and has made the routine acquisition of ^{13}C -spectra possible.

In the FT method a very short, high-powered pulse of RF radiation is applied to the sample (see Figure 3). This has the effect of simultaneously exciting all nuclei over the frequency range of interest. The decay of the magnetisation induced in the nuclei is then detected and digitised for storage in a mini-computer. The sampling of the decay signal is carried out over about 1 second and the spectrum obtained is known as the free-induction decay (FID) an example of which is shown in Figure 4a. The FID is a complex waveform containing information on all the

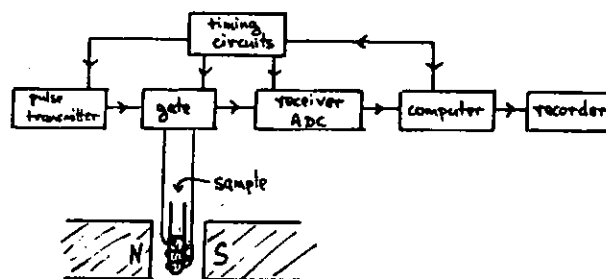
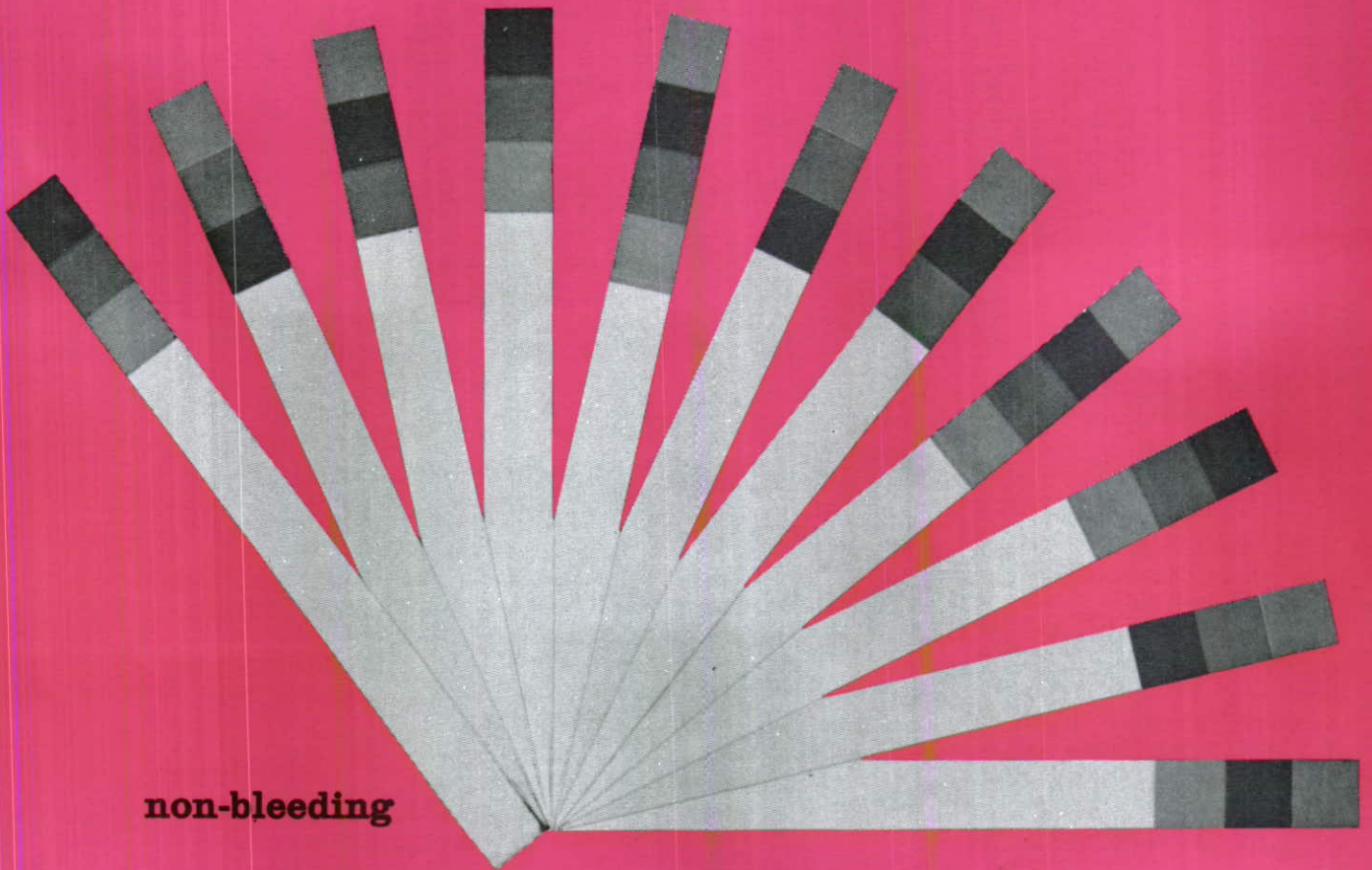


Figure 3 Block layout of an FT nmr spectrometer.

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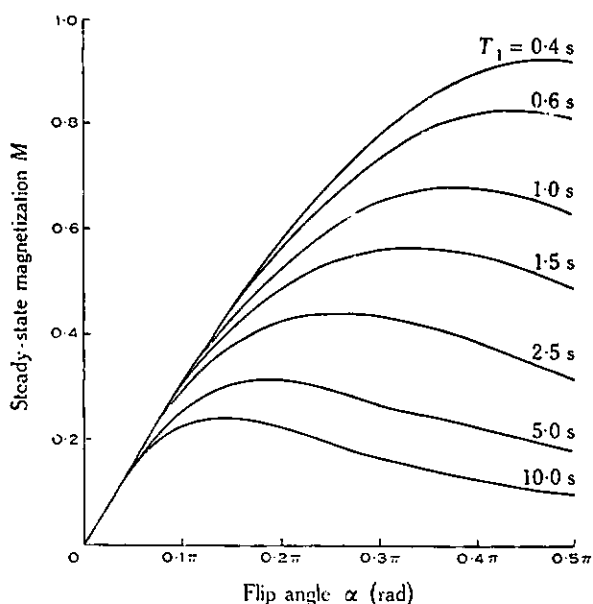


Figure 6 Variation of steady state magnetisation as a function of flip angle (α) and longitudinal relaxation time (T_1) for a pulse interval of 1 s.

of the decoupling is two-fold. Firstly, it is to simplify the spectrum. This has to be done as each ^{13}C -nucleus is spin-coupled to protons up to four bonds distant. The long-range couplings are small ($^4J_{\text{CH}} < 10$ Hz), but the couplings to protons directly attached are large ($^1J_{\text{CH}} \sim 100 - 250$ Hz). The resulting multiplet for a ^{13}C -resonance is complex and would normally overlap with those from other ^{13}C -resonances leading to difficulty in spectral interpretation. Secondly, there is a marked increase in sensitivity as a consequence of the decoupling. This gain is a result of the collapse of the multiplets into singlets, and also from signal enhancement by the Nuclear Overhauser Effect (NOE) (see below).

The areas of each singlet will be non-equivalent if the carbons in the molecule have, as is very likely, differing T_1 values. The influence that T_1 has on the area of a resonance is shown in Figure 6 where the steady-state magnetisation, M (which is proportional to the peak area) is plotted against the flip angle (equivalent to the pulse duration) for a range of T_1 values and at a constant pulse interval (1 s). For a given flip angle, as T_1 increases M decreases and hence the area of the resonance decreases. It is for this reason that non-protonated carbons, which typically have long T_1 values (4 - 20 seconds), give rise to small peaks under normal operating conditions.

The NOE also makes the resonance areas non-equivalent. This effect is a consequence of ^1H -decoupling which causes the population of the ^1H -energy levels to be equal. The ^{13}C -nuclei, which relax principally by dipole-dipole interaction with ^1H , respond to this equalisation of ^1H -energy levels by increasing the relative population of the lower energy level. Experimentally this means an increase in signal strength. The theoretical enhancement by the NOE is 2.99 times, but not all carbons will have the full enhancement, and there will therefore be further variation in the observed areas for each resonance.

Put in practical terms, wide-band ^1H -decoupling simplifies the spectrum and reduces the time necessary for spectral accumulation by at least an order of magnitude. The penalty that has to be paid for this gain is the loss of information inherent in the J_{CH} coupling constants (see later).

For the normal, routine spectrum, wide-band ^1H -decoupling is employed, but an alternative is the use of a single ^1H -decoupling frequency that is off-set from the ^1H absorption frequency range by 500 - 1000 Hz. In this way it is possible to suppress all the long-range couplings ($^{2-4}J_{\text{CH}}$) while still retaining a residual coupling, J_{R} , with the protons directly attached. Under Single Frequency Off-Set Resonance Decoupling (SFORD), conditions the multiplicity of a carbon signal is $(n + 1)$ where n is the number of protons directly attached to the carbon. This procedure aids in the assignment of the carbon resonances.

Also of assistance in assignment is Specific Proton Decoupling (SPD) where ^1H -irradiation is at a frequency corresponding to the shielding of a specific proton. This usually causes the signal for the carbon attached to that proton to collapse to a singlet while all the other carbons retain some residual couplings.

The last type of decoupling normally encountered is that of gated decoupling where the wide-band ^1H -decoupler is turned on during the irradiating pulse and a suitable delay period, but turned off again during acquisition. This gives a fully coupled or high resolution spectrum, which has also retained a substantial degree of enhancement due to the NOE. The values of J_{CH} are of particular importance in making structural and stereochemical assignments.

Application and Techniques

As ^{13}C Nmr spectroscopy has made an impact on most areas of chemistry, especially organic chemistry, no attempt will be made to be comprehensive in the applications, potential or otherwise, of ^{13}C Nmr techniques. Rather, selected examples will be used to illustrate some applications and uses.

Structural Assignments

When interpreting a ^{13}C Nmr spectrum it is usually necessary to have available more than just the ^1H -decoupled spectrum. Take for example the spectrum shown in Figure 7(a). Without much difficulty an alkyl carbon (δ 18.4), a C-O carbon (δ 51.8), two olefinic carbons (δ 125.3 and 137.2) and a carbonyl carbon (δ 167.7) may be identified. Quite probably the structure could be identified from this information only, but the multiplicity of each carbon signal, as revealed by the SFORD spectrum (Figure 7(b)), allows the rapid identification of the carbons as two methyl groups, a methylene double bond and a carbonyl group. With this

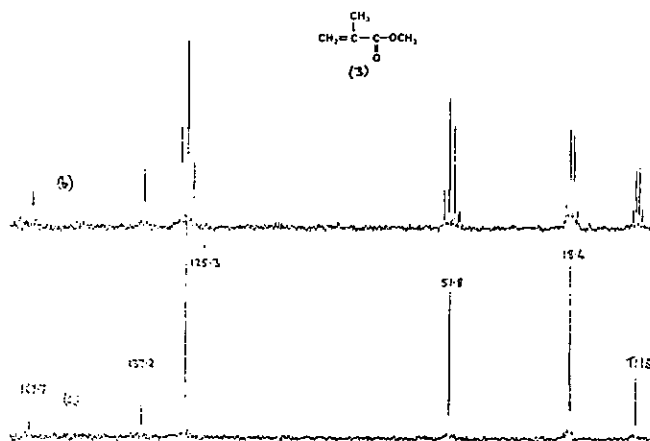


Figure 7 ^{13}C Nmr spectrum of methyl methacrylate (3). (a) H-decoupled (b) SFORD.

additional information the compound may be readily identified as methyl methacrylate (3).

Often when there are a number of methyls, methylenes or methines in a structure which cannot be differentiated, the SFORD spectrum alone is not sufficient and use of the alternative decoupling techniques becomes necessary.

Such was the case with a monoterpene, $C_{10}H_{14}Br_3Cl_3$, isolated from the N.Z. red alga *Plocamium cruciferum* [2]. A combination of the 1H -decoupled and the high resolution ^{13}C nmr spectra (Figure 8(a) and (b)), established that the compound had one trisubstituted double bond, two methyl groups, two methylenes, three methines and one quaternary carbon. From this information and the couplings in the 1H nmr spectrum the carbon skeleton (4) was deduced, but assignments for the methylene and methine carbons were equivocal. To distinguish these, specific proton decoupling was undertaken (Figure 8(c) - (e)).

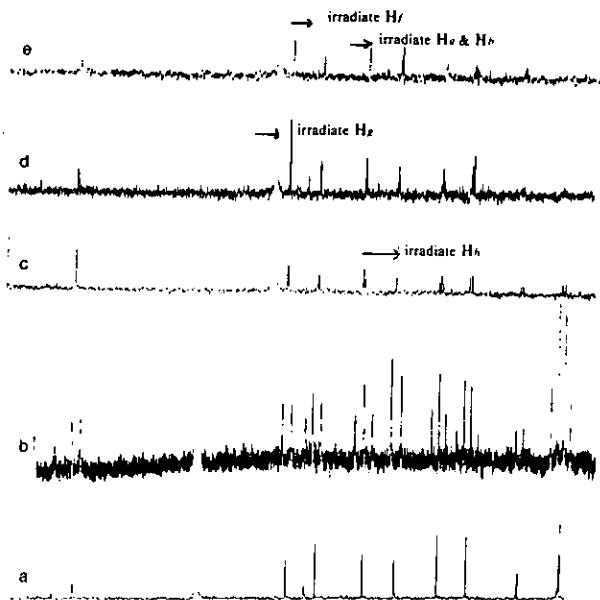
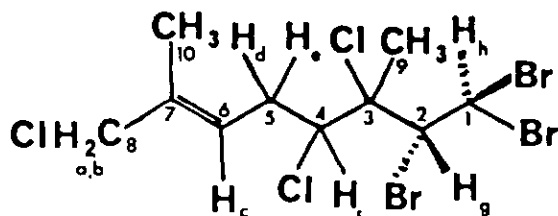


Figure 8 ^{13}C nmr spectra of (*E*)-1,1,2-tribromo-3,4,8-trichloro-3,7-dimethyl-6-octene (4). (a) 1H -decoupled (b) high resolution (c)-(e) specific proton decoupled as indicated.

Table 2: ^{13}C nmr and 1H nmr shieldings for (*E*)-1,1,2-tribromo-3,4,8-trichloro-3,7-dimethyl-6-octene (4).



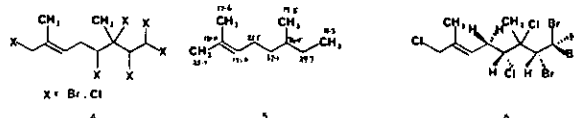
Carbon No.	$\delta(^{13}C)$	$\delta(^1H)$
1	44.2	H_h 5.60
2	64.9	H_g 4.73
3	67.9	—
4	72.8	H_f 4.22
5	32.7	H_d 2.59, H_e 3.03
6	128.7	H_c 5.79
7	134.4	—
8	52.7	H_a, H_b 3.94
9	21.1	CH_3 1.89
10	11.1	CH_3 1.77

Table 3: Additivity values for substitution of halogen in ppm.

Carbon Position	Cl	Br
α	+29.0	+16.2
β	+7.9	+7.6
γ	-4.6	-3.1

As the $^1J_{CH}$ values are markedly increased by substitution of electro-negative substituents [3], the methylene carbons C-5 and C-8 were readily distinguished ($^1J_{CH}$ 127.5 and 155 Hz respectively). Disubstitution increases $^1J_{CH}$ values further and the methine carbon C-1 ($^1J_{CH}$ 179 Hz) were distinct from C-2 and C-4 ($^1J_{CH}$ 155, 156 Hz).

The full assignment was completed by specific proton decoupling Irradiation at δ 4.73 collapsed C-2, and C-4 was collapsed by irradiation at δ 4.22 (Figure 8 and Table 2).



To solve the problem of the isomerism and place the halogens in the structure, derived additivity values [2] for substitution of a halogen (Table 3) were applied to the model hydrocarbon (5). The solution was unique for one isomer (6) (Table 4).

Lanthanide Induced Shifts

Lanthanide shift reagents such as $Eu(dpm)_3$ (7) and $Yb(fod)_3$ (8) became widely used in nmr spectroscopy following the observation in 1970 [4] that lanthanide complexes induced large changes in the shieldings in a wide range of compounds.

The magnitude of the Lanthanide Induced Shift (LIS), ΔS , is a function of the distance r from the lanthanide atom

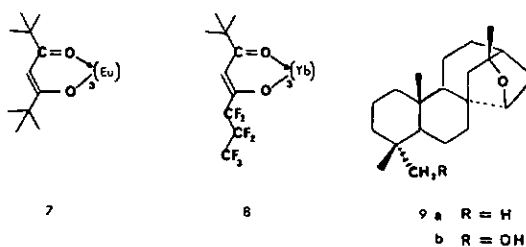


Table 4: Derived Shielding Values for (*E*)-1,1,2-tribromo-3,4,8-trichloro-3,7-dimethyl-6-octene (4).

Carbon	Substituents Added	Calculated Shielding δ	Observed Shielding δ
1	2 α Br, β Br, γ Cl	46.7	44.2
2	α Br, 2 β Br, γ Cl	64.4	64.9
3	α Cl, cBr, β Cl, 2 γ Br	72.8	67.9
4	α Cl, β Cl, γ Br	70.9	72.8
5	β Cl, γ Cl	28.8	32.7
8	α Cl	54.7	52.7
10	γ Cl	13.0	11.1

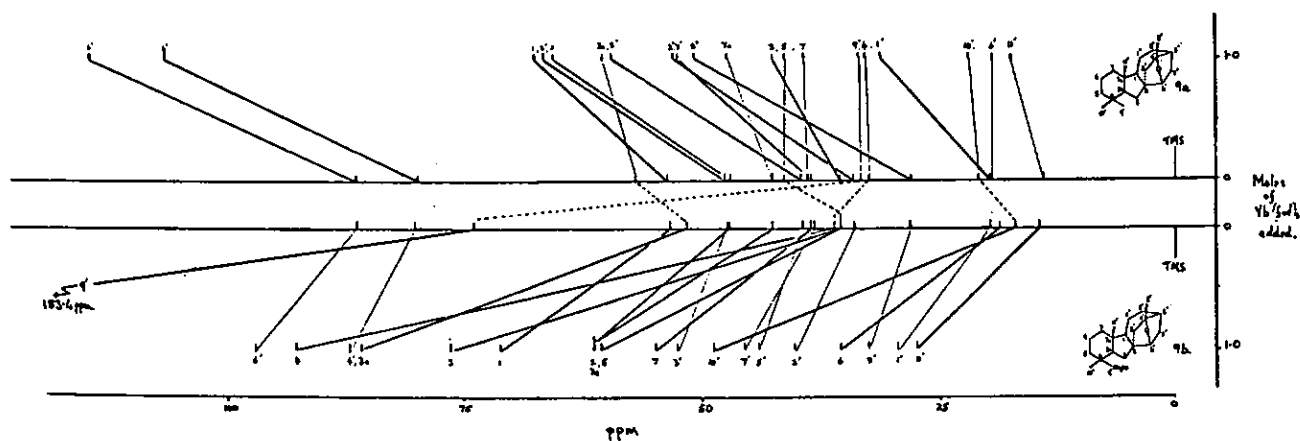


Figure 9. $\text{Yb}(\text{fod})_3$ induced molar shifts in the ether (9a) and hydroxy-ether (9b). Bold lines represent large molar shifts. Dotted lines indicate the major changes on substitution of an -OH group for a -H.

to the nucleus in question and is given by the Robertson-McConnell equation (4)

$$\Delta S = \frac{K(3\cos^2\Theta_i - 1)}{r_i^3} \quad (4)$$

where Θ is the angle between the i th nucleus-lanthanide vector and the magnetic axis of the vector.

By correlating shifts with the expected site of complexation the shift reagents can be used in a qualitative fashion as an aid to structure determination or in assignments of configuration or conformation.

The induced shifts in ^{13}C Nmr can be correlated with the proximity of a carbon to the site of complex formation. This becomes of particular importance when there are no suitable model compounds that can be used in making the assignments.

$\text{Yb}(\text{fod})_3$ is the reagent of choice for downfield shifts which are about three times greater for this reagent than for $\text{Eu}(\text{fod})_3$ and are accompanied by less line broadening.

Spectral assignments for the ethers (9) relied heavily on LIS studies [5]. Initial assignments were made for ring A carbons by correlating δ values with the additivity values upon introduction of an hydroxyl group (α and β downfield, γ upfield) (dotted lines Figure 9). These assignments were confirmed by LIS studies on the hydroxy-ether (9(b)). The site of complexation was selectively at the hydroxyl group which induced large molar shifts in the shieldings for carbons of rings A and B (bold lines Figure 9) particularly those carbons immediately in the vicinity of the hydroxyl group. Lesser shifts were observed for the shieldings of carbons in rings C, D, and E.

For the ether (9(a)) the site of complexation was the ether oxygen and therefore the large shifts were associated with the shieldings of carbons of rings D and E (bold lines Figure 9).

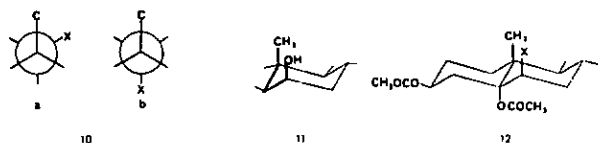
From the molar shift data, the SFORD multiplicities and the shieldings complete spectral assignments were possible.

Stereochemical Assignments

As ^{13}C -shieldings are sensitive to changes in molecular geometry, ^{13}C Nmr spectroscopy is a valuable aid in stereochemical and conformational analysis. Generally speaking the stereochemical assignments are based on the observation that whenever a carbon is *gauche* to another carbon at the γ -position there is an upfield shift (relative to

anti) in the resonance (10(a) and (b); $X=\text{C}$) [6]. This " γ -effect" has been ascribed to steric compression [7].

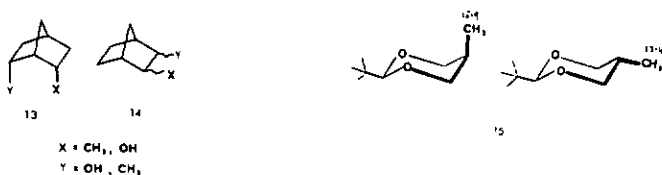
It was also observed that in molecules with *syn*-axial interactions (11), the shifts were downfield. This is the " δ -effect" [8].



In order to define and quantify these effects, we must work with a rigid skeleton of known stereochemistry. One system used to study γ - and δ -effects was a steroid system (12). By changing the nature of the 6- β substituent the interactions between the 19- CH_3 and selected functional groups were studied [9]. Other systems used have been based on the norbornane skeleton [10,11] (13 and 14).

From these studies it was found that if *syn*-axial interaction occurs, those carbons bearing the substituents showed the greatest downfield deviations (6 - 11 ppm) from the shieldings expected on the basis of simple additivity.

Similarly, for γ -*gauche* systems with approximately zero dihedral angle, all carbon nuclei involved have their shieldings shifted from the predicted positions - the shifts now being upfield. It is noteworthy that in γ -*gauche* systems, (10) the upfield shift caused by hetero-atoms ($X=\text{N},\text{O},\text{F},\text{S},\text{Cl}$) is greater than the upfield shift induced by a methyl or methylene group [12] ($X=\text{C}$).



When considering γ -effects on introduction of a hetero-atom into a molecule, caution has to be exercised. Although there are significant upfield shifts when there is a *gauche* relationship (10(a)) with the hetero-atom, the incremental upfield shift for a carbon in an *anti*-relationship (10(b)) with the hetero-atoms N, O or F, is generally greater than that observed for the *gauche*-relationship [12] (see for example 15). Care is also required in *anti*-relationships across two quaternary carbons.

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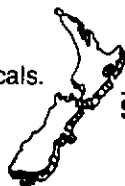
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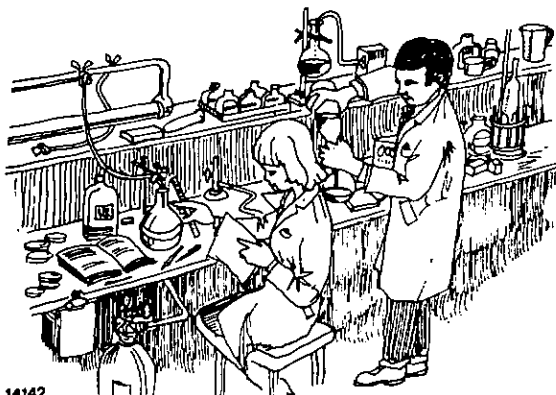


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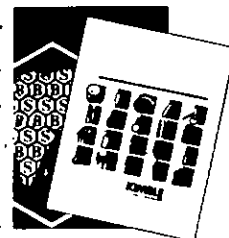
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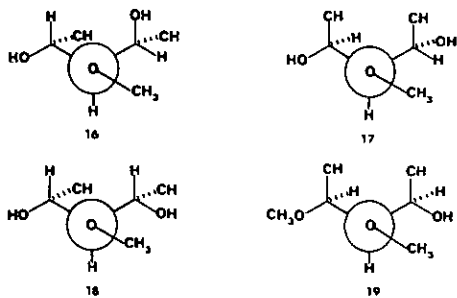
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Although these comments apply strictly to alicyclic systems it is interesting to note that the downfield δ -shift associated with *syn*-axial interactions can still apparently apply to mobile systems. The shieldings of the $-\text{OCH}_3$ group in a series of methylated inositols (16 - 19) were correlated with the δ -atom [13]. The preferred rotamer is shown in each case. On changing the δ -atom from H to O (16 \rightarrow 18) and (17 \rightarrow 19) there was a downfield shift of ~ 3 ppm in the $-\text{OCH}_3$ shielding.

Geometrical Isomerism

It is possible to distinguish (E)/(Z) pairs by ^{13}C nmr spectroscopy. While this has little advantage for 1,2-disubstituted olefins, as the magnitude of the vicinal ^1H - ^1H coupling constant is an accurate guide to stereochemistry, it offers considerable advantages for trisubstituted olefins where ^1H nmr is of relatively little assistance.

Several indicators of stereochemistry are used. Briefly, the sp^2 -carbons of an (E)-olefin have shieldings at slightly lower field (~ 1 ppm) [14,15] and the resonances for carbon α -substituents are shifted upfield in disubstituted (Z)-isomers [14,15,16]. The situation is a little more complex for trisubstituted olefins (see Table 5) [14]. J_{CH} values are also sensitive to the stereochemical environment and $^2J_{\text{CH}}$ and $^3J_{\text{CH}}$ have been correlated with (E)- or (Z)-stereochemistry. The $^2J_{\text{CH}}$ values are consistently more positive for (Z)-isomers [14] and the $^3J_{\text{CH}}$ values are always greater than $^3J_{\text{CH}}$ [16,17].

The magnitude of $^3J_{\text{CH}}$ is reliant on features such as substituent electronegativity, π -bond order, bond angles and especially steric interactions [15]. The relative ratio $^3J_{\text{CH}}^{\text{trans}}/^3J_{\text{CH}}^{\text{cis}}$ varies, as $^3J_{\text{CH}}$ is very sensitive to steric interactions. For an (E)/(Z) pair, whenever there is a large difference in the shielding of the α -carbon (from which the $^3J_{\text{CH}}$ values are taken) the ratio of $^3J_{\text{CH}}^{\text{trans}}/^3J_{\text{CH}}^{\text{cis}}$ is small. This is because steric interactions in the (Z)-isomer decrease $^3J_{\text{CH}}^{\text{trans}}$ and induces an upfield shift in the α -carbon resonance (see table 6).

With both isomers available, the assignment of stereochemistry is straight-forward. With only one isomer

Table 5: Shielding effects of an olefinic bond on the α -carbons.

Olefin Type	α - carbon	
	$-\text{CH}_3$	$-\text{CH}_2-$
1-substituted		+1.8
1,1-distributed	-0.3 to -1.1	-1.0 to -2.4
(Z)-1,2-distributed	-1.5 ± 0.2	-2.6 ± 0.3
(E)-1,2-distributed	$+3.8 \pm 0.3$	$+3.0 \pm 0.2$
trisubstituted ^a	A +1.6 B $\sim +3.4$ C ~ -4.6	+1.1 $\sim +3.4$ ~ -5.2

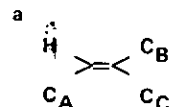
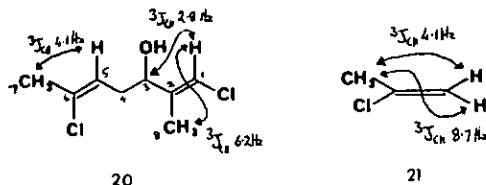


Table 6: Correlation of differential shieldings with the ratio

Structure	$^3J_{\text{CH}}^{\text{trans}} / ^3J_{\text{CH}}^{\text{cis}}$	$\delta_{\text{CH}_3}^{\text{E}} - \delta_{\text{CH}_3}^{\text{Z}}$
		1.75
	1.49	2.6
	1.17	7.2
	1.12	8.1

available, there must be a degree of ambiguity.

Using δ and $^3J_{\text{CH}}$ values the stereochemistry of the diene (20), isolated from a marine source [2], was deduced. $^3J_{\text{C8-H}}$ was measured as 6.3 Hz while $^3J_{\text{C3-H}}$ was only 2.8 Hz allowing an assignment of stereochemistry of the 5, 6 double bond as (E).



The $^3J_{\text{C7-H}}$ coupling was 4.1 Hz. Comparison of this with the model compound (21) suggested that it was the (Z)-isomer. Substitution of an alkyl substituent for Hg increases the magnitude of the couplings; the increase for $^3J_{\text{CH}}^{\text{cis}}$ being greater than $^3J_{\text{CH}}^{\text{trans}}$ [16]. Consequently the 1,2-double bond in the diene was assigned as (Z).

Conformational Equilibrium

Up to this point only compounds existing in one conformation or one isomeric form have been considered. For systems where there is more than one energetically favourable form, variable temperature nmr spectroscopy has been an effective probe to examine these dynamic processes and to provide the basic thermodynamic parameters governing the interconversion [18, 19].

^{13}C nmr has certain advantages over ^1H - and ^{19}F -nmr, not the least being the often large differences in chemical shift of carbons involved in interchanging conformations. The large differences allow measurements to be made over a wider temperature range, with a consequent greater accuracy in the derived thermodynamic parameters.

Dynamic processes such as chemical exchange, tautomeric equilibria, ring inversions, molecular rearrangements have all been studied to advantage by ^{13}C nmr.

The appearance of the nmr spectrum for equilibrating systems is dependent on the rate of interconversion. For two species A and B that are in equilibrium



the ^{13}C nmr spectrum will show two individual sets of superimposed resonances corresponding to the shieldings of A and B, provided that the rate is slow on the nmr time scale. When the interconversion is rapid the observed spectrum is the average of the shieldings for the related carbon pairs, weighted according to their relative population.

At intermediate rates of interconversion, the situation is more complicated. In moving from the slow exchange, the related resonances in A and B, ν_A and ν_B , broaden and then start to move together and finally coalesce to a broad singlet. As the rate increases further this singlet becomes narrower until it reaches the limiting line width.

The rate of equilibration, k , can be calculated in the ranges above and below coalescence from equations (5) and (6)

$$\frac{1}{\tau} = \pi (\nu_B - \nu_A)^2 / (\Delta\nu - \Delta\nu_0) \quad (5)$$

$$\frac{1}{\tau} = 2\pi (\Delta\nu - \Delta\nu_0) \quad (6)$$

where $\Delta\nu$ is the line width of the broadened peak and τ is the mean lifetime of the system. Alternatively, at around coalescence total line-shape analysis may be applied. The

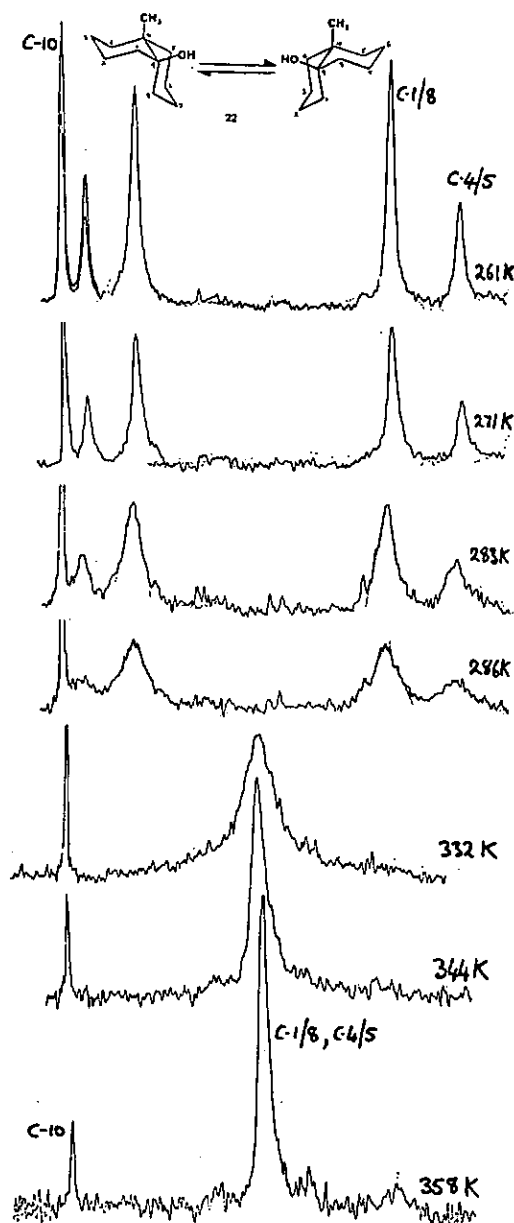


Figure 10 ^{13}C NMR spectra of carbons 1/8, 4/5 and 10 (non-exchanging) of *cis* 10-methyl-9-decalol over a temperature range spanning coalescence for the equilibrating pairs. Temperatures given in Kelvin.

thermodynamic parameters ΔG , ΔH and ΔS can be readily derived if k is measured as a function of T .

At temperatures above ambient the two energetically equivalent chair/chair conformers of *cis*-10-methyl-9-decalol (22) are rapidly interchanging, but on cooling to below coalescence the spectrum increased in multiplicity and the unique shieldings for each conformer could be observed [20] (Figure 10). Carbons 9, 10 and the methyl group were non-exchanging. The rate constants for the conformational inversion were derived by total line-shape analysis of spectra obtained over the range 260 - 352 K, a temperature range which spans coalescence for the various equilibrating pairs (see Figure 10). The derived values of ΔG , ΔH and ΔS allowed important comparisons to be made with related *cis*-decalins.

T_1 and its Applications

Until relatively recently, chemists have concentrated mainly on the determination and application of shielding data and coupling constants to various aspects of structural and stereochemical problems. While the FT ^{13}C NMR spectrometer enables T_1 values to be routinely measured, the application of relaxation studies has trailed other ^{13}C developments [21, 22, 23].

T_1 information relates to areas such as local molecular geometry, internal and overall molecular motion, bonded and non-bonded interactions. This information is often not available by any other technique.

As noted earlier, the spin-lattice relaxation process is normally dominated by ^{13}C - ^1H dipole-dipole relaxation, T_1 DD, although other spin-lattice relaxation processes such as spin-rotation T_1 SR may occur. The relationship between the various types of spin-lattice relaxation is given by equation (7)

$$\frac{1}{T_1 \text{ observed}} = \frac{1}{T_1 \text{ DD}} + \frac{1}{T_1 \text{ SR}} + \dots \quad (7)$$

The relative contributions from the various types of spin-lattice relaxation processes can be measured.

The motional behaviour of medium weight organic molecules is essentially isotropic (motion about each principle axis is the same) and T_1 ,^{obs} is dominated by the contribution from dipole-dipole relaxation.

Under these conditions the relaxation rate is given by equation (8)

$$\frac{1}{T_1 \text{ DD}} = n \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r_{\text{CH}}^6} \tau_c^{\text{eff}} \quad (8)$$

where n is the number of protons directly bonded to the carbon of interest, r_{CH} is the C-H internuclear distance, γ_C and γ_H are gyromagnetic ratios, \hbar is $\frac{h}{2\pi}$, and τ_c^{eff} is the effective molecular correlation time.

A number of procedures are used to measure T_1 values. One sequence, known as inversion-recovery Fourier transform (IRFT), starts with a 180° pulse, which inverts the Boltzman populations. This is followed by a time delay during which the process of spin-lattice relaxation occurs. By varying the time delay between the 180° pulse and the normal acquisition pulse, the rate at which the relaxation of a given carbon is occurring can be monitored. For very short time delays all carbons except those with very small T_1 values will appear as negative peaks. As the delay is increased these negative peaks, depending on their spin-lattice relaxation times, will become more positive (see

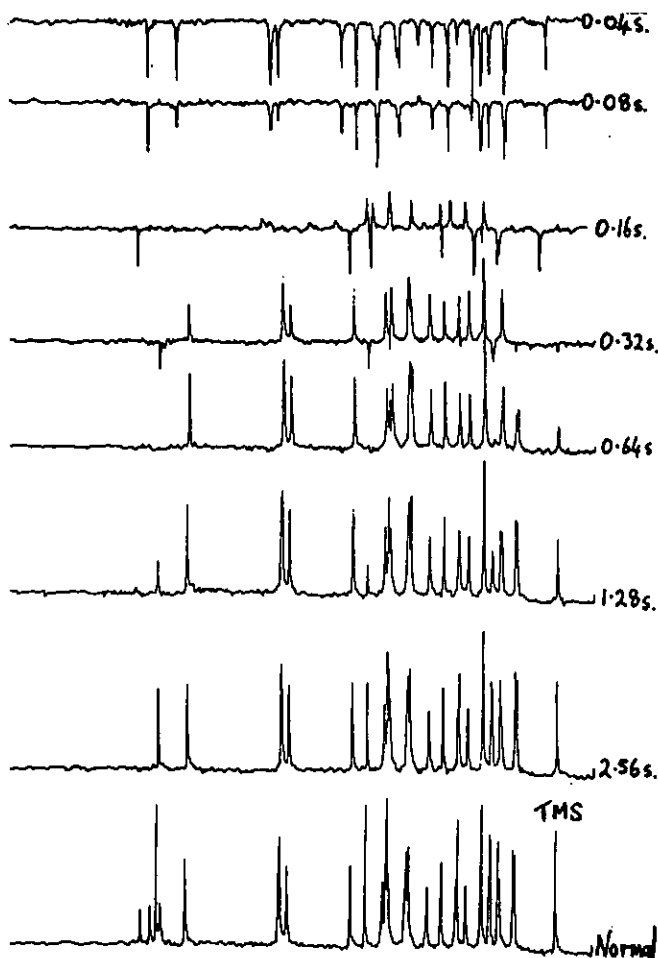


Figure 11 T_1 measurements on 3β 5-diacetoxy-6 β -bromo-5 α -cholestane. Pulse intervals are as noted.

Figure 11) and eventually, when the time delay is sufficiently long, the spectrum will appear similar to that of a normal spectrum.

The relationship between T_1 and molecular motion is, in the main, exploited in a qualitative fashion only. Take for example the ^{13}C NMR spectrum of a mixture of mono- and oligo-saccharides isolated from growing wheat grains (Figure 12(a)). The sharp peaks (longer T_1 's) are associated with the mono- and di-saccharides, while the broad peaks (shorter T_1 's) come from the higher saccharides, which have more restricted overall molecular motion. This complex spectrum can be considerably simplified by obtaining a partially relaxed spectrum (PRFT). With a time delay of .05 s. between the inverting and observing pulses in the IRFT sequence, those carbons with short T_1 values have approximately zero intensity while the carbons with

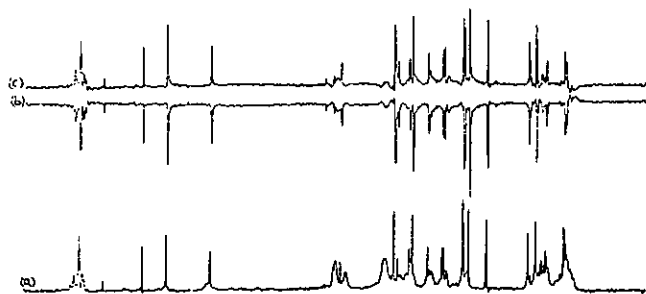
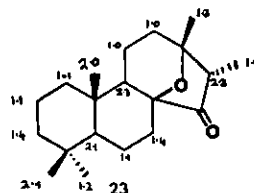


Figure 12 Saccharides from developing wheat grains (a) normal spectrum (b) partially relaxed spectrum with time delay 0.05 s. (c) spectrum (b) inverted for normal presentation.

the longer T_1 values give resonances of good intensity, but are still inverted (Figure 12(b)). Figure 12(c) shows the same spectrum, but with all intensities inverted for normal presentation. Those resonances due to the mono-saccharides glucose and fructose can now be readily identified and estimated (see later).

T_1 data are also useful in the assignment of carbon types (i.e. methylene, methine, etc). In principle the differentiation may be obtained from an SFORD spectrum but for complex molecules this information is not always easily discernible. However, if the molecule is undergoing isotropic motion then T_1 (-CH-) is $\sim 2T_1$ (-CH₂-), while the quaternary carbons, having no directly bonded protons, will relax very much more slowly. The keto-oxide (23) is an



example of a molecule undergoing isotropic motion. All the -CH₂- groups have T_1 values of ~ 1.1 s., the -CH- groups ~ 2.2 s. and the quaternary carbons at least 6 s.; these figures allow a ready identification of the type of each carbon.

The -CH₃ groups have one extra degree of freedom if they are able to rotate. In these circumstances, equation (8) is no longer applicable.

Assuming tetrahedral geometry for the methyl C-C-H angle, the freely rotating methyl group will, in theory [24] have a T_1 value of $3T_1$ (-CH-) and the immobile methyl group a T_1 equal to $1/3T_1$ (-CH-). Relaxation times between these extremes are observed for intermediate rates of rotation. The barrier to free rotation may be calculated from the observed T_1 CH₃ value [25].

There are apparent anomalies however. For example the C-20 methyl group in manool (25) has a T_1 of 1.90 s. while T_1 av. (-CH-) is only 0.49 s. The ratio T_1 CH₃/ T_1 av. (-CH-) is therefore greater than 3. This, and other anomalies were resolved when the dependence of T_1 CH₃ on methyl group geometry was examined. A recent analysis of the problem [27] has demonstrated the sensitivity of the derived rotational barriers to the choice of the methyl C-C-H angle. For example when using $\Theta = 112^\circ$ in the free rotation limit the ratio T_1 CH₃/ T_1 av. (-CH-) becomes 4. In these circumstances an observed ratio of 3 may really indicate a barrier of > 10 kJ mol⁻¹ rather than suggesting "free rotation". Such angles could arise in situations of steric crowding.

The large ratio observed for some methyl groups can often be ascribed to steric crowding which lowers the energy barrier for internal rotation of the methyl group.

Such observations have already been used in a semi-empirical fashion in the assignment of methyl resonances [26]. For a series of diterpenes (24 - 26) it was observed that methyl groups with distinct 1,3-diaxial interactions had significantly greater T_1 CH₃/ T_1 av. (-CH-) ratios than those in equatorial configurations or with lesser 1,3-diaxial interactions.

As well as these applications of T_1 data, significant work is being carried out in applications to segmental motion along a molecular chain especially with respect to biomolecules and polymers.

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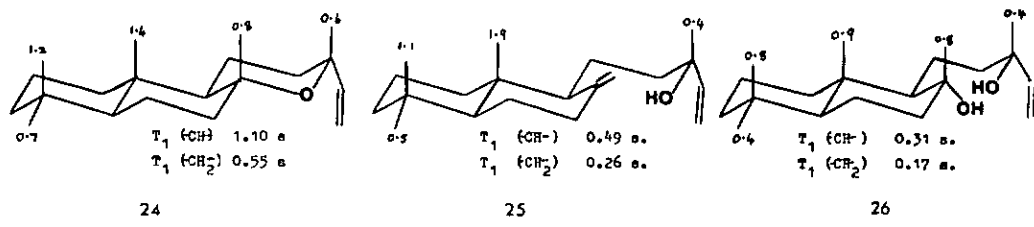
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P3271



Qualitative and Quantitative Analysis

Because of the wide dispersion of shieldings in ¹³Cnmr spectroscopy, even the spectra of mixtures of closely related compounds such as carbohydrates usually have at least one resonance for each component that is unique. For example, in a mixture of six carbohydrates there are more than sixty peaks in the δ 60 - 110 range, but only nine arise from the coincidence of two or more peaks. By matching the shielding values in the mixture against known shieldings for individual carbohydrates the components of the mixture may be identified.

Obtaining quantitative data on the composition of such a mixture is more difficult because of the non-equivalence of peak intensities. One approach to this problem would require both a long delay between pulses (so that all carbons are fully relaxed prior to the application of each pulse) and suppression of the NOE by switching the ¹H-decoupler on during acquisition of the FID, but off during a suitable delay period. This approach, while sound is often not practicable because it may require prohibitively long spectral accumulation times.

An alternative method, which retains the advantage of short pulse repetition times, requires the addition of a paramagnetic relaxation agent such as Cr(acac)₃. The dipole-dipole spin-relaxation is now replaced by an electron-dipole mechanism which effectively suppresses all NOE. Furthermore most carbon T₁ values are decreased markedly. But attractive as it seems, this method is not always reliable [28].

A third approach, developed at the University of Canterbury [29], simply ignores differences in T₁ values and NOE effects and operates with short pulse repetition

times at constant temperature, concentration, pulse width and pulse repetition times. As the T₁ values are viscosity dependent, the maintenance of temperature and concentration conditions ensures constant steady state magnetisations for all nuclei. For spectra obtained under these conditions, the ratio of the intensities of the peaks will be the same even though they do not necessarily reflect the ratios of the numbers of nuclei responsible for the various peaks. By including a known amount of a standard in the mixture, the intensity (area) of the standard peak may be compared with the intensity of each peak in the spectrum, and the concentration of each component may be calculated if the appropriate weighting factors are known. The weighting factors for the peaks of the components are determined independently under identical conditions. Suitable programmes were written that allow the identification and quantitation of the components to be achieved automatically by the spectrometer computer following data collection. Such an analysis is shown in Figure 13.

While a carbohydrate example was used here this method is applicable to the analysis of any type of mixture provided that the operating parameters are correctly selected.

Biosynthetic Applications

Like so many other areas of ¹³Cnmr, biosynthetic applications had to await the impetus provided by the development of the FT nmr technique [30, 31]. Certainly ¹³C biosynthetic experiments had been carried out earlier, but they had suffered from a lack of sensitivity. Indeed, even with the enhanced sensitivity of the FT technique,

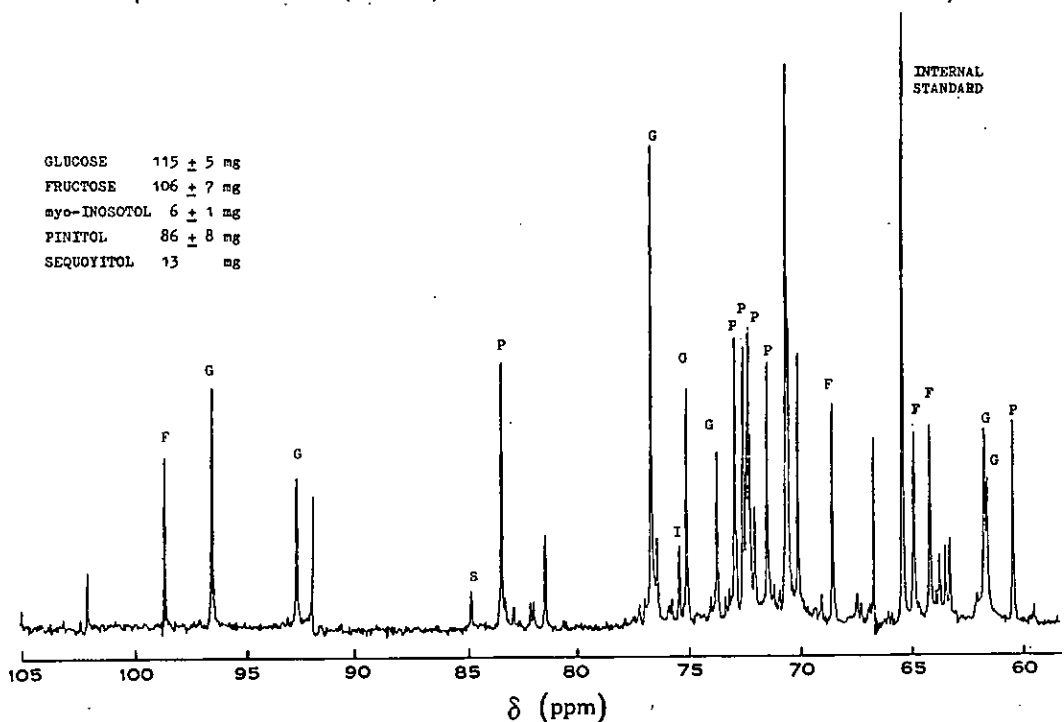


Figure 13. Quantitative analysis of a *P. radiata* wood extract. Those resonances used in the analysis are indicated.

This sequence required a rather remarkable condensation between the polyketide units (route a), or alternatively an alternative pathway involving cleavage, isomerisation and recyclisation (route b). The latter pathway was favoured.

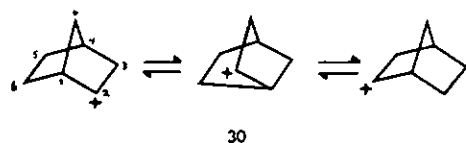
Carbocations

Until the advent of ^{13}C NMR spectroscopy, carbocation could only be observed indirectly by a variety of spectroscopic techniques. The direct observation by ^{13}C NMR spectroscopy has been of considerable advantage and a considerable body of work has been published on carbocation chemistry in the last ten years or so [36, 37].

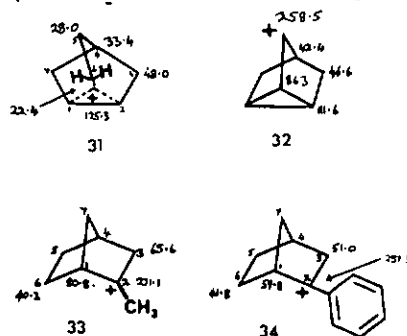
The carbocations are normally generated in super acids, such as $\text{SbF}_5/\text{FSO}_3\text{H}$, from a variety of functionalities such as alcohols, alkyl halides, olefins, cyclopropanes and even alkanes in such an effective proton-abstracting medium.

A carbocation, being electron-deficient, appears at lower field than most other resonances and the increased s-character is reflected in the magnitude of $^1\text{J}_{\text{CH}}$ values. Typically the shieldings are in the range 100 - 330 ppm, with couplings of around 170 Hz. In general those cations that are stabilised by π -bond or σ -bond participation have resonances at higher field than for the simple alkyl carbocations. This observations has been used to considerable effect in studies on the nature of various carbonium ions.

For example, one of the more vexed questions in recent years has been the nature of the 2-norbornyl cation. Is it undergoing rapid equilibration between trivalent carbenium (classical) ion intermediates (30) or is it an alkyl-bridged

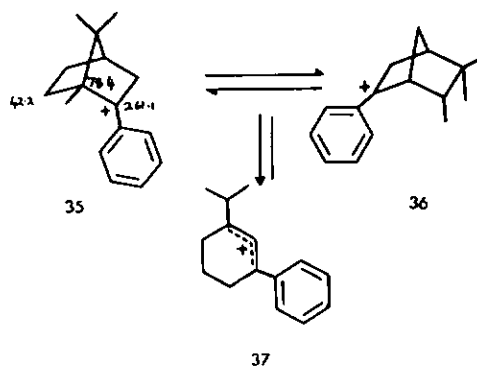


pentavalent carbonium (non-classical) ion (31) formed by σ -bond delocalisation? Recently ^{13}C NMR, and other evidence, was presented [38] that established the 2-norbornyl cation as non-classical (31). The differences between such a pentavalent carbonium ion (31) and a trivalent carbenium ion such as the 3-nor-tricyclyl ion [39] (32) are clearly seen in the different shieldings for the C^+ .



In contrast to the 2-norbornyl cation (31), the 2-methyl-2-norbornyl cation (33) is a partially σ -delocalised carbenium ion with the C-1 - C-6 bond assisting in the delocalisation (note the δ values for C-1 and C-6) [40]. The phenyl group is also effective in delocalising charge, and in the 2-phenyl-2-norbornyl cation (34) there is less evidence of C-1 - C-6 participation [39].

As part of a larger study of the stability and rearrangement of the 1,7,7-trimethyl-bicyclo-[2,2,1]-heptyl system, the carbocation (35) was prepared [41]. At 173 K the carbenium ion (35), Scheme



Scheme 2. Rearrangement of the 1,7,7-trimethyl-2-phenylbicyclo-[2,2,1]-heptyl carbocation (35);

2) is observed with some evidence of C-1 - C-6 participation. As the temperature is raised, the initially formed ion rearranges to the alternative ion (36) in order to relieve the unfavourable C-1-methyl/C-2-phenyl interactions. At higher temperatures the bicyclic skeleton collapses to the allylic ion (37). This probably arises by rupture of the C-1 - C-7 bond in ion (35), thus demonstrating that the transformation between ions (35) and (36) is reversible.

Postscript

As well as the applications referred to, ^{13}C NMR spectroscopy has been applied with singular success to areas such as the conformation of organometallic complexes. There is a rapidly growing literature on ^{13}C NMR of polymers, with information on stereoregularity, composition, and internal mobility being provided. Recent work has included topics such as two-dimensional ^{13}C NMR, solid-state ^{13}C NMR, and the quantitative analysis of mixtures in intact samples such as oil seeds.

Apart from the routine application of ^{13}C NMR to structural problems some of the areas under study in New Zealand at present are the measurement of T_1 values in organometallics, diterpenoids and steroids. These studies in part relate to the application of T_1 data to the assignment of methyl groups and to the calculation of barriers to rotation and related conformational aspects. One ^{13}C NMR application that has proven particularly successful has been the correlation of electron density with shielding in aspects of Hammett equation work. ^{13}C -Enriched steroids are being used in mechanistic studies, and in another area ^{13}C NMR is used as an essential aid in conformational and structural studies on biopolymers.

The future for ^{13}C NMR is assured. Indeed in many areas it is not just the method of choice, it is the only method. Undoubtedly more and more applications are still awaiting exploration.

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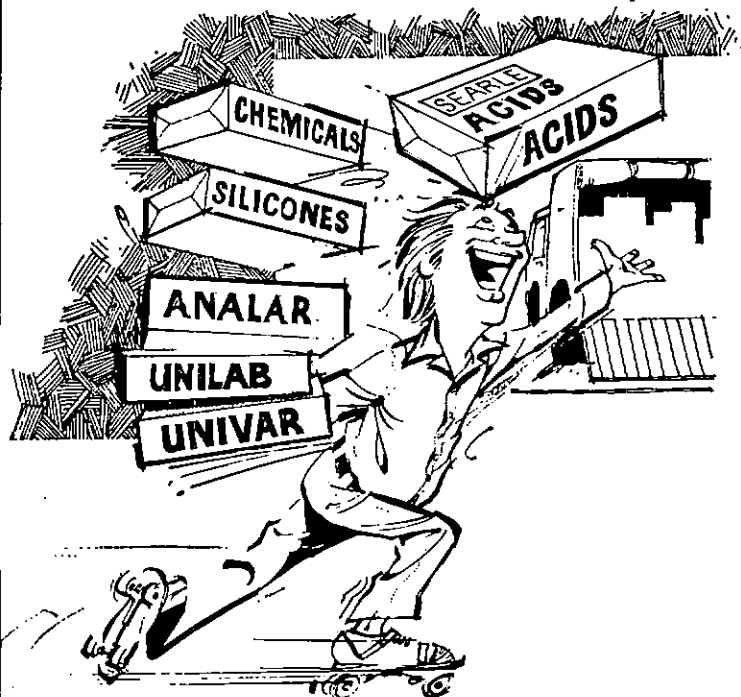
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INTERSTELLAR MOLECULES AND THE ORIGIN OF LIFE

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Historical

Throughout the history of mankind the philosophical questions of the origin of the universe and the origin of life have been a central feature. There is a rich literature of mythologies from ancient and primitive tribes about creation mainly based on supposed creative powers of gods and demons. As just one illustration I point to a famous painting by Tintoretto on the Greek legend of the origin of the Milky Way. This refers to the attempt by the unfaithful Zeus to have immortality conferred on his son Hercules by having him suckled at the breast of his wife Hera. The sleeping Hera was rudely awakened and displeased at having the young Hercules thrust upon her. In the disturbance some of her milk was spilt and became the stars of the Milky Way. The modern account of the origin of the Milky Way is still shrouded in controversy and does not lend itself to such splendid artistry as this!

Legends about the origin of life developed into a widespread belief in various ancient civilizations of India, Babylon and Egypt of spontaneous generations of primitive animal life such as flies, beetles, snakes etc: from inanimate material such as mud or manure. The overthrow of the concept of spontaneous generation of life did not occur until the latter part of the nineteenth century and was contemporaneous with the development of ideas about natural selection and evolution by Darwin and Wallace.

There appears to have been no published scientific thought about the origin of simplest forms of life until early this century when Arrhenius, the famous physical



Figure 1. Tintoretto painting.

chemist, published his ideas of the development of life on Earth from the transportation of simple spores from other parts of the universe. This became known as the Panspermia theory of the origin of life. Some time later, in 1924, the Russian biochemist A. I. Oparin outlined the scheme by which simple molecules, regarded as the precursors of biologically significant molecules such as amino acids and sugars, could be generated by chemical processes in the primitive atmosphere of the young Earth. He envisaged that these prebiological molecules would evolve by chemical processes into an organised system that ultimately would be recognised as a first primitive cell.

Testing the Chemical Approach

Serious attempts to pursue Oparin's ideas by laboratory experiments were not undertaken until the 1950's, culminating in a classical experiment by Stanley Miller in 1953 in which starting with a simple gaseous mixture of methane, ammonia, hydrogen and water, he produced biologically significant compounds such as amino acids by the passage of electric discharges. It is an interesting thought for all chemists that undoubtedly the reason for the long delay in testing Oparin's ideas is that methods of analysing complex mixtures of organic compounds were not available until the development of modern chromatographic methods. This reminds us yet again, if further reminder is needed, that advances in chemistry and kindred sciences often depend crucially on advances in analytical chemistry.

This chemical theory of the origin of life on Earth, pioneered by Oparin, Urey and Miller, is now very widely



After graduating from Melbourne and London Universities, PROFESSOR R. D. BROWN held lecturing posts at University College, London and at Melbourne University. He was appointed Professor of Chemistry at Monash in 1959. He has been awarded the Masson (1948), Rennie (1951)

and Smith (1959) Medals, the David Syme Prize for research (1959) and the Edgeworth-David Medal (1961).

He is a Fellow of the Australian National Academy of Science and is now Secretary of Physical Sciences, as well as the National Committee for Chemistry and Chairman of the Chemical Education Sub-committee.

His current research interests cover theoretical chemistry, spectroscopy, galactochemistry and life in space.

Table 1. The primitive atmosphere and primitive hydrosphere.

Atmosphere	Hydrosphere	Reference
CH ₄ , NH ₃ , H ₂ O, H ₂		Oparin Urey
CH ₄ , CO ₂ , NH ₃ , H ₂ S, H ₂ O, H ₂	CO ₂ , NH ₃ , H ₂ S, H ₂ O	Bernal
CO ₂ , N ₂ , H ₂ S, H ₂ O	CO ₂ , NH ₃ ,	Rubey
CO, CO ₂ , N ₂ , H ₂ S, H ₂ O		Revelle
CO ₂ , CO, N ₂ , H ₂ O		Abelson

accepted as correct and yet there are certain difficulties or doubts associated with it. There are those who find it difficult to believe that, even given a mixture of amino acids, nitrogenous bases, fatty acids and sugars, such "broths" would ever be able to sort themselves into small parcels arranged in the form of primitive cells. Even the problem of going from an aqueous broth of amino acids to a polypeptide, or a corresponding condensation process to produce polynucleotides has proved difficult to demonstrate on the laboratory scale using conditions that could have prevailed on a young planet.

Another possible difficulty with this is that one must assume that the primitive atmosphere of the Earth was in the form of reduced gases, i.e. methane rather than carbon dioxide, ammonia rather than molecular nitrogen. The whole problem of the chemical evolution of the surface of the young Earth and specifically the nature of its hydrosphere and atmosphere has been a point of continued controversy among geochemists (Table 1). At the present time it would seem that a majority of chemists favour the view that by the time the young Earth cooled down to temperatures at which organic compounds can reasonably survive, the atmosphere had already become oxidized to carbon dioxide and nitrogen. Some of the most vigorous protagonists for reduced atmospheres have been geochemists like Urey who might be thought to be influenced by their belief that prebiological chemical evolution depended on reactions in the atmosphere that can occur only if it is reducing. Table 1 illustrates some of the varieties of views held about the early Earth.

Earlier this year Dr M. H. Hart of the Goddard Space Flight Centre reported the results of his computer

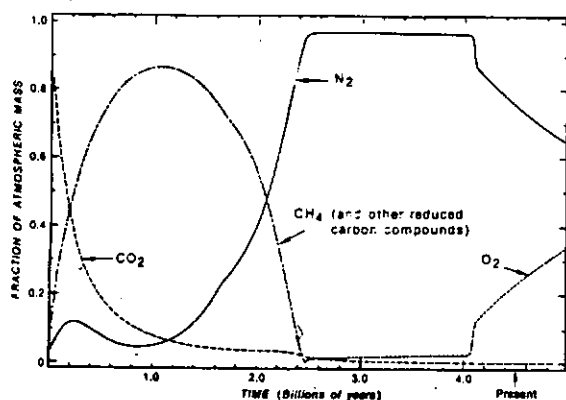


Figure 2. Hart's figure for evolution of Earth's atmosphere.

simulation of the evolution of the Earth's atmosphere over the last 4.5 billion years. Figure 2 shows his curves and they do indeed indicate that in the crucial early period the atmosphere was dominated by methane and other reduced compounds. Dr Hart believes that he can assemble decisive evidence in favour of this but time will tell whether he can persuade the bulk of other scientists of the decisiveness of his calculations.

In view of doubts about the Oparin, Miller and Urey hypothesis of the origin of life it is useful to try and trace the chemical aspects of the formation of the solar system and enquire whether there are any other pathways by which life, or at least the prebiotic chemical precursors of it, could arrive on the surface of the freshly cooled young planet Earth. It is now widely accepted among astronomers that new stars and with them new planetary systems are formed by the gravitational collapse of huge clouds of gas and dust that occur in various places throughout the Milky Way Galaxy and indeed other galaxies that compose the universe. A number of such gigantic clouds of gas and dust are visible to us and still more can be studied with appropriate telescopes. The Coalsack Nebula just at the side of the Southern Cross (Fig. 3) is a spectacular example in the southern skies of one of these dark nebulae. For a long time such objects were neglected by astronomers. Indeed they were treated as irritating objects which obscured

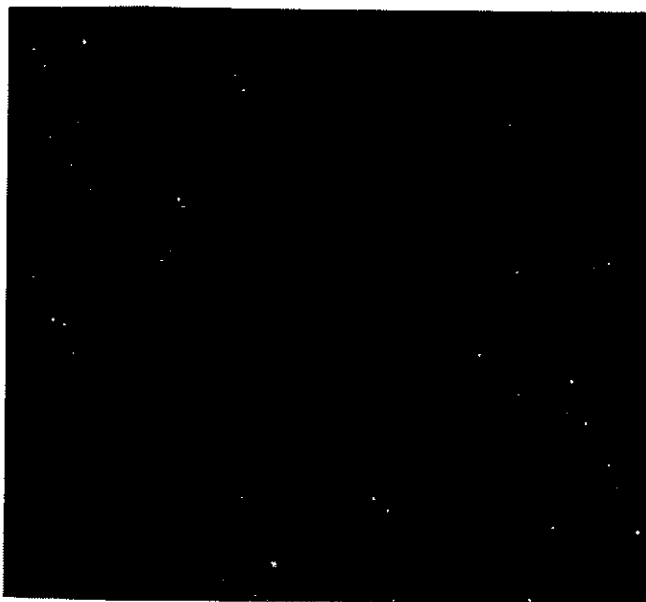


Figure 3. The Coal Sack.

starlight from potentially interesting stars on the far side of them. Again the major part of the problem was that astronomers did not have appropriate tools with which to study such objects thoroughly. It is only in the last decade that we have made rapid strides in understanding the physical and chemical nature of these dark nebulae.

Application of Radioastronomy

The basic technique used is that of radioastronomy. Radio waves, because of their very long wavelengths, penetrate dark nebulae without perceptible attenuation. In contrast, light of visible and nearby wavelengths is rapidly absorbed by the dust clouds so that we are able to see in visible light only dark nebulae that are nearby. Perhaps the most important of all the dark nebulae is a large one near the centre of the Milky Way Galaxy which is completely obscured by clouds of dust and dense accumulations of stars, but with radio-telescopes it is readily available for study.

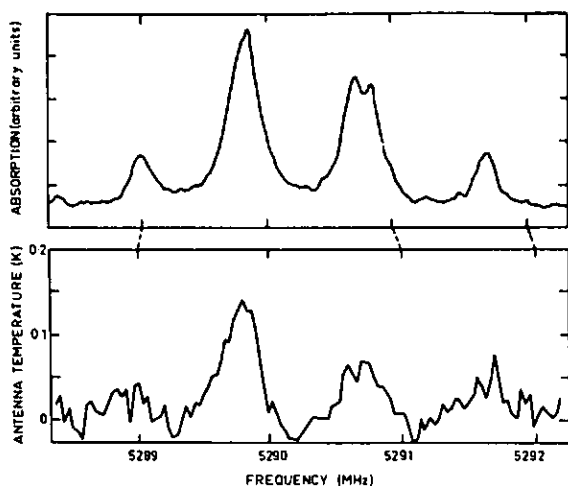


Figure 4 Microwave spectrum of methanimine ($\text{CH}_2 = \text{NH}$) measured in laboratory at Monash University.

Figure 5 Signal of methanimine detected on radiotelescope at Parkes.

The radiotelescope is used together with the technique of molecular spectroscopy for an investigation of the physical and chemical conditions that prevail in these dust clouds. I would remind you that spectroscopy is the crucial tool of astronomers. Astronomy expanded enormously with the development of atomic spectroscopy by Bunsen, Kirchhoff and others. This enabled astronomers to determine the chemical composition of stars and, in addition, by careful study of the intensities of spectral lines, linewidths and shapes, much information about the physical conditions in stars was also revealed. However, atomic spectroscopy is effective for studying only the hottest parts of the universe where atoms are excited into emission. Dark nebulae, which are very cold objects with temperatures generally well below 100 K and sometimes as low as 10 K, are not hot enough for atomic spectral lines in the visible region to be detected. However, it has emerged that these dark nebulae contain vast accumulations of gaseous molecules. The rotational spectra of such molecules fall in the radio or microwave region of the spectrum which is just the region of the electromagnetic spectrum accessible via radiotelescopes. For studying the molecular composition of clouds one first investigates the rotational spectrum of appropriate molecules in the laboratory in order to characterise the molecules by specific spectral lines. These lines are then searched for with radiotelescopes.

Table 2. Interstellar molecules that have been reported.

H_2	NH_3	$\text{HC}\equiv\text{C-CN}$
CH	H_2O	$\text{CH}_3-\text{C}\equiv\text{CH}$
CH^+	H_2CO	CH_3CN
CN	H_2CS	HCONH_2
CO	OCS	CH_3OH
CS	HCN	CH_3CHO
SiO	HNCO	CH_3OCH_3
SiS	H_2S	$\text{C}_2\text{H}_5\text{OH}$
SO	SO_2	$\text{CH}_2=\text{CH-CN}$
NS	HNC	HCO_2CH_3
OH	C_2H	NH_2CN
HCO	HNO	$\text{CH}\equiv\text{C-C}\equiv\text{C-CN}$
HCO^+	HCO_2H	$\text{CH}_3-\text{C}\equiv\text{C-CN}$
N_2H^+	$\text{-CH}_2\text{NH}\cdot$	$\text{H-C}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-CN}$
	CH_2-CH_2	$\text{C}_2\text{H}_5-\text{CN}$
	$\begin{array}{c} \diagdown \\ \text{O} \end{array}$	$\text{CH}_2=\text{C=O}$

By this technique, illustrated in Figures 4 and 5, a considerable number of molecules have been found in the dark nebulae. Table 2 lists molecules so far detected by this means.

These discoveries became something of a sensation in astronomy because the traditional view had been that stars and the interstellar medium were composed of individual atoms or atomic ions and free electrons. It was considered that molecules were too fragile to survive in the presence of ultra violet light. It is now realised that this is not so and the conditions that prevail in dark nebulae are such that molecules can survive very well in them.

The other exciting thing about these discoveries of interstellar molecules can be seen by inspecting the list of compounds so far detected. They are predominantly organic compounds and include a number of reactive species which could readily be used to synthesise a number of significant, biologically important molecules. For this reason, hot on the heels of the initial discoveries, came the speculation that in these interstellar molecules we were seeing the chemical precursors of life already existing in space in the nebulae which had not yet condensed to form new planetary systems. I shall return to this theme later but first I would like to pursue the significance of these discoveries for the understanding of the nature of these cold, dark parts of our universe.

From the intensities of the observed lines and some other assumptions about the nature of the process that excites the molecules into emission, it is possible to deduce the relative concentration of different molecules. One can also, by indirect arguments, derive other properties of the clouds such as the concentration of species within the clouds, the temperature of the clouds, and the way in which various parts of the cloud might be in relative motion. But all of these interpretations and a proper understanding of the manner in which the nebula is collapsing depends on having a clear picture of the processes that lead to the formation of molecules and so forth. This has proved a considerable challenge to chemists and has given rise to the young science of galactochemistry.

Initially one of the great puzzles was that the gas cloud is very cold and, by terrestrial standards, of extraordinarily low density. For example, even the densest clouds have no more than one million molecules per cubic centimetre. A typical cloud might be one hundred times less dense. Such densities of course correspond to the most extreme ultra-high vacua that can be produced in the laboratory. Under such conditions the rate of collision between molecules is exceedingly low and the energy of collision is so low that only processes without activation energy can occur at a reasonable rate.

Various types of chemical processes were contemplated but the most fruitful idea that has been produced so far (by Herst and Klemperer and by Watson) is that the important reactions are those between simple molecules and atomic or molecular ions which occur, without activation energy, at the collision rate. The important overall rate of such processes would be great enough to produce the kind of molecules that have been observed. It has been suggested that in the dark nebulae the process is triggered off by the ionization of hydrogen molecules by cosmic rays. The hydrogen is overwhelmingly in the form of hydrogen molecules, these being formed from hydrogen atoms by heterogeneous catalysis on the surface of the dust grains that are part of the dark nebula. The accompanying diagram (Fig. 6) shows some of the typical reactions that are considered to be involved.

Figure 6: Types of interstellar chemical reactions

IONIZATION	$H_2 + p \rightarrow H_2^+ \text{ (or } H^+)$
	$H_2^+ + H_2 \rightarrow H_3^+ + H$
	$He + p \rightarrow He^+$
ION-MOLECULE	$H_3^+ + C \rightarrow CH^+ + H_2$
	$H_3^+ + O \rightarrow OH^+ + H_2$
	$C^+ + OH \rightarrow CO + H^+$
	$C^+ + NH \rightarrow CN + H^+$
	$O^+ + H_2 \rightarrow OH^+ + H$
	$N^+ + H_2 \rightarrow NH^+ + H$
	$OH^+ + H_2 \rightarrow OH_2^+ + H$
	$CH^+ + O \rightarrow CO + H^+$
	$CH^+ + N \rightarrow CN + H^+$
PHOTO-RECOMBINATION	$C^+ + H_2 \rightarrow (CH_2^+)^* + h\nu$
DIELECTRONIC RECOMBINATION	$CH^+ + e \rightarrow C + H$
	$CH_2^+ + e \rightarrow CH + H$
PHOTO IONIZATION	$CH + h\nu \rightarrow CH^+ + e$
	$CH_2 + h\nu \rightarrow CH_2^+ + e$
NEUTRAL-NEUTRAL	$O + CH \rightarrow CO + H$
	$O + CH_2 \rightarrow OH + CH$
	$N + OH \rightarrow NO + H$
	$C + NO \rightarrow CO + N$

In a classic paper, Herbst and Klemperer attempted an analysis of these processes by using the well-known steady state approximation. Through their calculations they were able to predict concentrations of simple species that were in general agreement with some of the observed amounts of interstellar molecules. In addition they predicted that two molecular ions, HCO^+ and N_2H^+ , essentially protonated forms of two of the molecules expected to be most common, namely CO and N_2 , would occur in detectable concentrations. It was a triumph of their speculations that both of these molecular ions have now been detected and identified by molecular radioastronomy.

The Work at Monash

My own group had also been investigating galactochemistry. We became increasingly worried about the use of the steady state approximation in estimating the progress of chemistry in these nebulae. There is not time here to go into full details but the accompanying diagrams (Figs. 7, 8) illustrate, firstly, results that we have obtained by directly integrating the kinetic equations for the processes that are

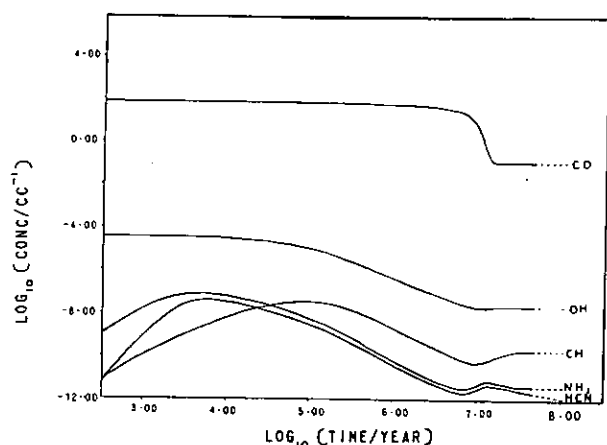


Figure 7 Model calculations of the chemical evolution of a dark nebula (note: carbon assumed to be present initially as CO, hydrogen as H_2 other elements shown).

believed to occur in dark clouds. The results of this very difficult integration show that the concentrations of various simple molecules are expected to fluctuate widely during the lifetime of a dark nebula so that at no stage are the bulk of the constituents of a dark cloud in a steady-state situation. But the second point is perhaps even more interesting. The second diagram (Fig. 6) shows ratios of concentrations of molecular species as a function of time. You will see from this that if one is able to measure ratios of concentrations they can be used as a chemical clock, telling us the age of the cloud from the time the chemical processes commence. This would be a great break-through because hitherto there has been much debate about the ages of dark nebulae but there has been no technique available for any observational test of the various ideas. Incidentally, the work that I am describing is still not sufficiently complete to have been published and so the diagrams referred to are preliminary results.

I must now return to the initial theme of the origin of life. I mentioned earlier that there could be several difficulties with the theory that life can be traced to some initial chemical process occurring in the early atmosphere of the Earth. I now come to an alternative possible mechanism of the origin of life that relates to the interstellar molecules. When the dark nebulae collapse to form clusters of new stars and surrounding planets, there is a considerable amount of debris left in this process which ends up as the smallest parts of the planetary system, objects that we refer to as comets and meteors. The chemical composition of many of these bodies will largely reflect the chemistry of the present dark nebulae since some of them do not experience temperatures greater than $100^\circ C$ throughout their life span. By study of the moon and inner planets we know that there were very heavy falls of meteors on all of these bodies during the first half billion years of the history of the solar system. This corresponds well with the time at which the Earth had cooled down and conditions had been established under which it was possible for prebiotic molecules to survive.

The most common form of meteorite, the one experiencing the least thermal degradation in space, is called a carbonaceous chondrite, the name implying that the meteorite has a substantial content of carbon. Chemical studies of the content of these meteorites, especially one that fell at Murchison in Victoria in 1969, have revealed an interesting array of organic compounds. These include many amino acids and a number of nitrogenous bases including all of those involved in DNA. Moreover, there is a report of some Russian studies in which an organic polymer

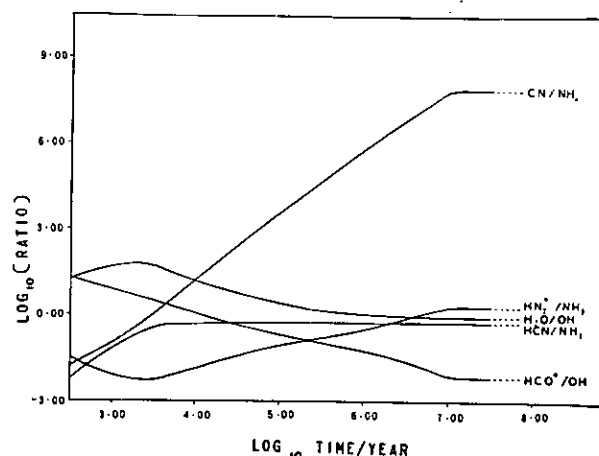


Figure 8 Calculated ratios of molecular concentrations as a function of the age of the dark nebula.

exhibiting a double spiral structure reminiscent of, but not identical with, DNA has been extracted from a carbonaceous chondrite.

Thus the alternative scenario for the early stages of the origin of life is that when the young Earth had freshly cooled down and the first shallow pools of water had formed, there is a heavy fall of meteorites including a number of carbonaceous chondrites. These meteorites are prone to break open readily on falling and are porous enough to soak up some water. If such a meteorite fell into a shallow pool, the conditions may have been favourable for absorbed moisture to promote further reactions among the constituent organic molecules and these might have included condensation reactions that produce biopolymers — at least in primitive form. Some workers have even suggested that they have discerned formations in meteorites that suggest tiny globules reminiscent of a very primitive form of cell structure. Conceivably then prebiotic chemical evolution even up to the stage of formation of somewhat organised packaged chemicals could have occurred following the fall of carbonaceous chondrites. This picture

of the origin of life overcomes difficulties associated with any doubts about whether the early atmosphere was reducing and appears to overcome difficulties in understanding how condensation reactions could have been brought about when the reactants started in relatively dilute aqueous solutions. It traces our ancestry back through carbonaceous chondrites to the chemical precursors in the original dark nebula.

Clearly this is a very speculative theory of the origin of life on Earth, just as is the more widely held theory of atmospheric formation. There is scope for much further research on both of these concepts of the origin of life and I am sure that in the future our views will be steadily refined.

I feel that the present decade has been an exciting one for astronomy, cosmology and for studies of the origin of life. I have got much satisfaction from having had the chance to participate in this stimulating search for the answers to some questions of great importance. I have enjoyed the opportunity to talk to you about them and trust that you have found the story interesting.

CENTENARY: CHEMICAL SOCIETY OF JAPAN

— W. A. McGillivray

I had the honour to represent the New Zealand Institute of Chemistry at the centennial celebrations of The Chemical Society of Japan, which were held in Tokyo at the beginning of April. The centennial was celebrated in a lavish manner, with a series of banquets and receptions which were attended by representatives of The Chemical Society, a number of invited guests from overseas, and representatives of learned societies and other scientific organizations in Japan. The main centennial function was held at the famous Kao University, and at this, messages of goodwill were presented from Chemical Societies and Institutes around the world. Those that had been able to send representatives included The United States of America, Austria, Australia, The Netherlands, New Zealand, Switzerland, the United Kingdom and West Germany. Congratulations were also extended to the Society of representatives of Government Departments and kindred societies in Japan. One of the main features of the centennial ceremony was the conferring of Honorary Membership of the Society on prominent Japanese and overseas chemists who had had some connection with chemistry in Japan. These included Professor Herman F. Mark (USA), Professor Robert S. Mulliken (USA), Professor Tetsuo Nozoe (Japan), Professor Ichiro Sakurada (Japan), Professor Masao Horio (Japan), Professor Vladimir Prelog (Switzerland), Professor Shinjiro Kodama (Japan), Lord Todd (UK), Professor Paul D. Bartlett (USA), Sir Harold Thompson (UK) and Professor Melvin Calvin (USA). Lord Todd provided the star performance of the afternoon when he delivered his speech of thanks in fluent Japanese!

In his centenary address, the President of the Society, Professor Junji Furukawa, made reference to the historic events which surrounded the establishment of the Society in 1878. Although this was long after the time when carbon dioxide was being discovered by Joseph Black, hydrogen by Henry Cavendish, oxygen by Joseph Priestley, it was early in the era of the European upsurge of Chemistry as it was also exemplified by the studies on indigo by Adolf von Baeyer, early in the Meiji era in Japan, which is of course regarded as the start of the modernization of that country. In the early years many famous Japanese chemists were already active, such as Joji Sakurai, who carried out

pioneering work in physical chemistry; Kikunae Ikeda, who discovered aginomoto, the flavour-giving sodium glutamate; Nagayoshi Nagai, the discoverer of ephedrine; Mitsuru Kuhara, who worked on the reaction mechanism of the Beckmann rearrangement; Yoshinao Kozai, who studied mineral poisoning in coal mines; and Jokichi Takamine, who discovered adrenalin. But at that time chemical industry in Japan was still in its infancy, and production of coal was only 60,000 to 70,000 tons, and that of pig-iron about 20,000 tons.

It was not until the end of the Taisho and the beginning of the Showa periods (1920-30) that chemistry and chemical industry really started to develop in Japan. This was marked by the growth of fertilizer, plastics, synthetic fabrics, rubber and dyestuff industries. This progress was, of course, interrupted by the war years, and 1948, when the Societies of Chemistry and Chemical Industry merged to form the Chemical Society of Japan is generally regarded as the birth of present day chemistry in that country. Since that time Japanese chemists have made prominent contributions in instrumental approaches to structural analysis, molecular orbital methods in reaction kinetics, biochemistry, synthetic chemistry, and in natural products, as well as in the phenomenal development of the petrochemical industry, which at peak introduced 6,700,000 tonnes of plastics, 1,300,000 tonnes of synthetic fibre and 880,000 tonnes of synthetic rubber. The reliance of these industries on chemistry and chemical engineering has resulted in The Chemical Society growing to a membership of some 35,000, with a budget of 550 million yen per annum (about 2.3 million).

Chemists in Japan, as in other countries, are now extending their interests to include topics such as environmental pollution, the further development of natural resources, increased food production and energy conservation. Professor Furukawa stressed the importance of these and other problems, not only to the future development of Japan, but to mankind as a whole, and in thanking Chemical Societies around the world for their good wishes on the occasion of the centennial celebrations, issued a plea for greater co-operation in international science for the benefit of all countries.

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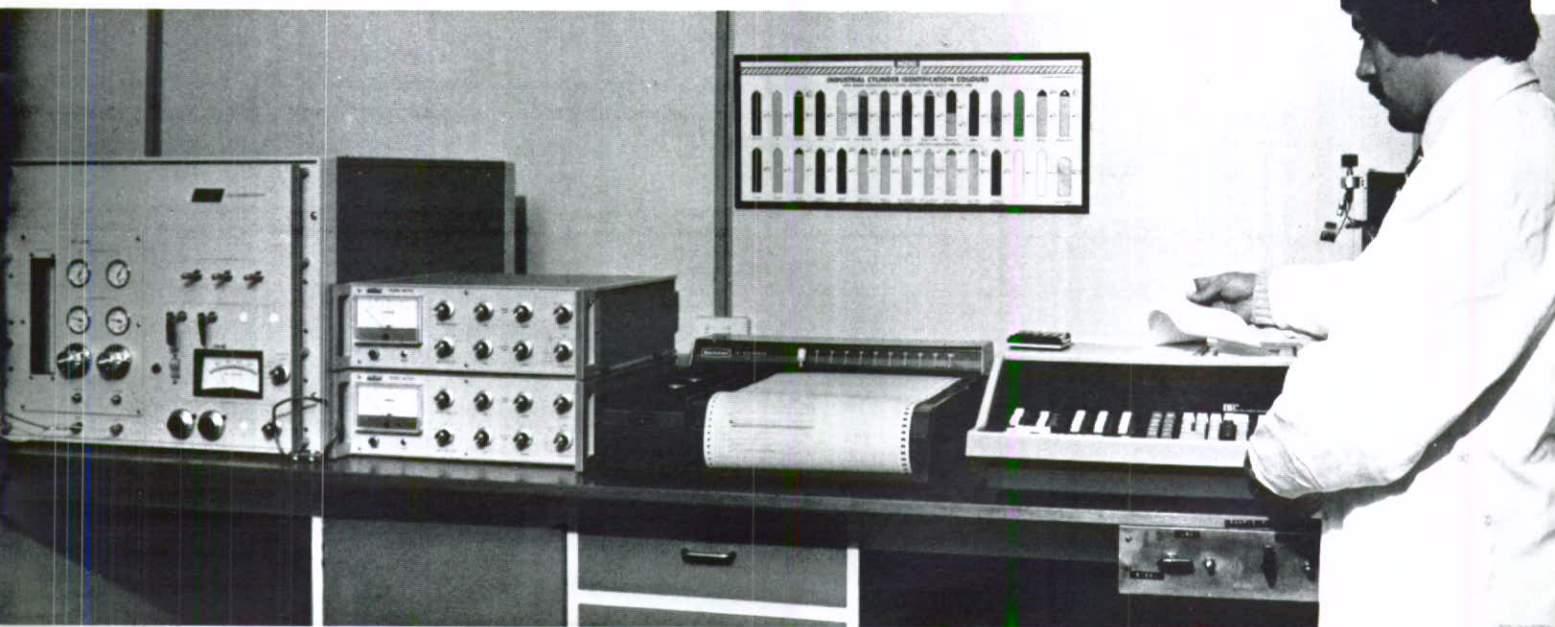
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THE OZONE CONTROVERSY

M.J. McEWAN

University of Canterbury

INTRODUCTION

As a result of possible harmful effects from exhaust gases of aircraft flying in the stratosphere, the chemistry of the mid-atmospheric region has received unprecedented attention in the past 7 years. During the U.S. Congressional debate in July 1970, legislation was introduced directing the U.S. Department of Transport to undertake a research programme (Climatic Impact Assessment Programme or CIAP) to obtain the information necessary for an appraisal of the potential threat to ozone from stratospheric flight. Since the inception of CIAP, a number of investigators in different countries have been encouraged to make new measurements both in the stratosphere and in the laboratory so that a wealth of new information has come to light. New threats to stratospheric ozone have been recognised and new programmes to deal with them have been initiated. A brief review follows some of the important findings of these programmes including appraisals of three potential threats to stratospheric ozone.

THE UNPOLLUTED STRATOSPHERE

Of the different atmospheric regions, it is the STRATOSPHERE that is most sensitive to global pollution because of its physical structure and the vulnerability of O_3 to catalytic destruction. Although the atmospheric pressure decreases as the altitude increases the temperature variation is not uniform. It is the way the temperature varies with altitude that defines the different atmospheric regions [1]. The stratosphere is a region of temperature inversion where the temperature increases with altitude as shown in Figure 1. The temperature minimum of the stratosphere (220K) is called the TROPOPAUSE which varies in elevation from ~10 km in polar regions to ~16 km

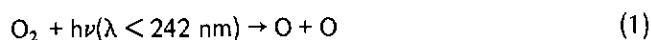


Dr MURRAY McEWAN graduated Ph. D. from Canterbury University in 1965 and after spending 2 years at the Centre for Research in Experimental Space Science at York University in Toronto he re-joined the Chemistry Department at Canterbury University. He spent 1973 at the Laboratory for Atmospheric and Space

Physics, University of Colorado and was an invited participant at a workshop on Halocarbon Monitoring. His interests are in the general area of gas phase chemical reactions.

in tropical regions. At mid-latitudes the stratosphere extends in altitude from ~15 km to ~50 km. The region below the stratosphere is the TROPOSPHERE which is that part of the atmosphere that contains the weather. Rapid mixing by winds and turbulences ensure that air within the troposphere is vigorously mixed whereas vertical mixing is strongly inhibited in the stratosphere because of the temperature inversion.

The chemistry of the stratosphere is quite complex because of the many reactive species that are present. These reactive species are derived ultimately from the action of the UV sunlight on stable molecules such as N_2, O_2, H_2O etc. Solar radiation of wavelength shorter than 190 nm is largely removed above stratospheric altitudes by atomic and molecular nitrogen and oxygen. In the stratosphere, UV radiation below 242 nm dissociates O_2 to produce atomic oxygen.



O_3 is produced by the reaction between atomic and molecular oxygen in the presence of some other molecule M.

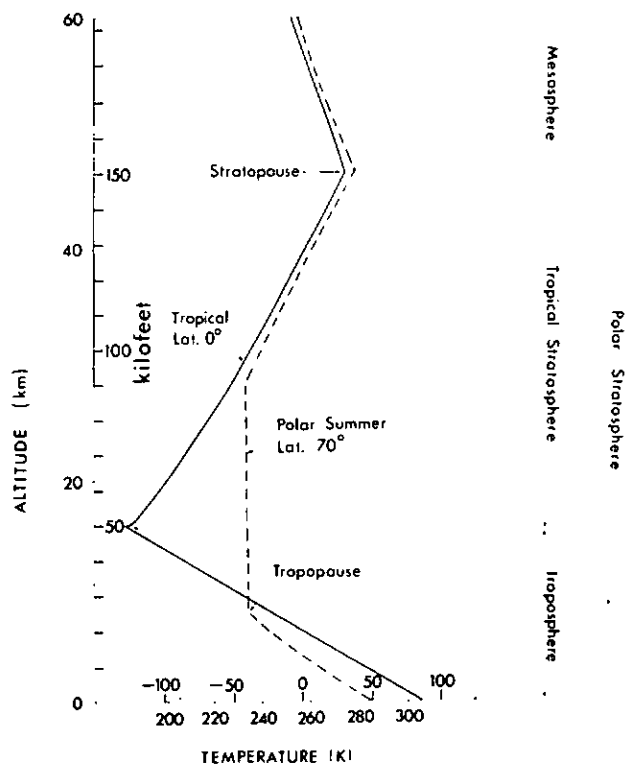
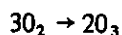


Figure 1. The variation of atmospheric temperature with altitude.

The net result of reaction (1) and 2 times reaction (2) is



Ozone itself strongly absorbs UV radiation below 340 nm and in the process is dissociated to $\text{O}_2 + \text{O}$.

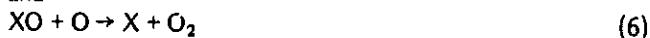


The net effect of reactions (3) and (4) which remove O_3 is $2\text{O}_3 \rightarrow 3\text{O}_2$

Up until early 1960s this simple model (reactions (1) to (4)), called the Chapman mechanism and involving only species derived from O_2 was thought to adequately describe the abundance of O_3 in the stratosphere. Once vertical profiles of O_3 from balloon observation platforms became widely available, it was realised that additional removal processes were necessary to explain the observed O_3 concentrations. These additional processes were subsequently found to be catalytic destruction of O_3 by oxides of nitrogen (NO_x) and hydrogen (HO_x) which are present in the stratosphere. A number of different catalytic cycles for O_3 destruction can all be represented by the general form



and



where X may be H, OH, NO, Cl and Br. The major route for destruction of O_3 in the unpolluted atmosphere is through catalytic removal by HO_x and NO_x .

At high altitudes between 45 to 100 km where H and O concentrations are relatively high the dominant destruction channel is



and



Between 30 and 45 km, OH and HO_2 are thought to be more abundant than H and the destruction channels for O_3 involving HO_x become



and



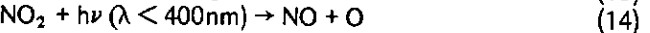
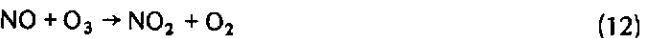
Below 30 km, as $[\text{O}_3] \gg [\text{O}]$, the important destruction channels are



and



To these destruction processes (7) to (11) which all involve 'odd hydrogen' we need to add NO_x catalysed destruction channels:



Before 1973, the concentration of NO in the stratosphere had not been measured. Since then, a number of measurements of both NO and NO_2 have been made [2] which show the predominant pathway for O_3 destruction in the unpolluted stratosphere to be NO_x catalysed destruction (reactions (12) – (14)) [3]. From the measurements of NO_x already reported, it appears likely that NO_x catalysed destruction channels account for 70% of the natural ozone destruction, whereas natural HO_x accounts for only about 10% [4]. The remaining ~20% is removed by the Chapman mechanism (reactions (1) – (4))

and by downward transport of O_3 into the troposphere. In the low stratosphere the chemical lifetime of O_3 is very long – of the order of a year or more – and no chemical removal process controls the O_3 concentration. Instead the distribution of O_3 is controlled by physical processes. Also in the low stratosphere, NO_2 which is an active chemical species higher up, is transported into the troposphere where it is converted into nitric acid and 'rained out'.

Small amounts of gaseous halogen compounds are also present in the atmosphere as a result of sea salt aerosol conversion and volcanic emissions [5]. These very small natural concentrations of gaseous chlorine and bromine compounds are believed to be too small to contribute a pathway for O_3 destruction of more than a few percent. [5] In addition to the chemical reactions already mentioned, the considerable interaction between reactive species means the number of possible reactions included in our model needs to be expanded considerably. Electronically excited atoms (e.g. $\text{O} (^1\text{D})$), electronically and vibrationally excited molecules e.g. $\text{OH}(v)^{\ddagger}$, $\text{O}_2 (^1\Delta)$, often react at different rates and produce different products than their ground state counterparts, when these are included in the scheme, the number of reactions that need to be considered rise to more than 50 (Table 1). It is worth noting from the model in Table 1, the main source of NO_x in the unpolluted stratosphere is reaction (41) and the main loss of O_3 is reaction (12). Other important reactions are between OH and HO_2 (reaction (38)) which is the main removal process for HO_x and reaction (19) which couples HO_x to NO_x and leads to the removal of NO_x from the stratosphere.

Ozone is only a trace constituent of the atmosphere. Yet, even in its small amount, stratospheric ozone absorbs virtually all of the solar UV radiation less than 290 nm in wavelength and most of that in the biologically harmful 290 to 320 nm region. This UV absorption by ozone therefore prevents damaging solar radiation from reaching the earth's surface where it could adversely affect human, plant and animal life. Any process capable of depleting O_3 therefore demands serious consideration. Three of these potential threats are considered in the next section.

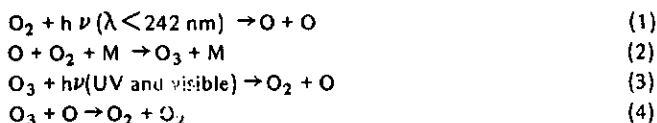
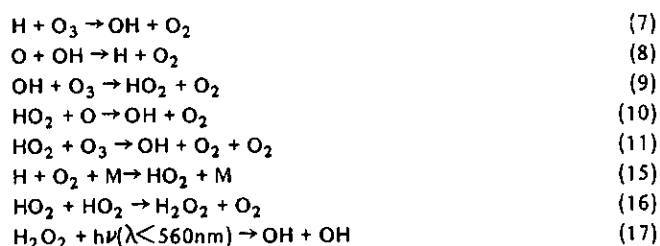
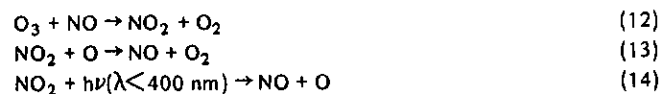
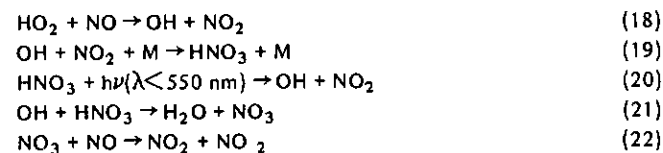
THE POLLUTED STRATOSPHERE

We have noticed that air within the troposphere is vigorously mixed by winds which have horizontal and vertical components and by turbulences which are circular components of motion. Any stable impurity species introduced into the troposphere soon become uniformly distributed. All water-soluble impurities are removed in a few days by rain. Typical time scales in the troposphere are a few weeks for vertical mixing; a few months for east-west mixing and a year or two for exchange between the northern and southern hemispheres. Any species that has no significant removal process in the troposphere gradually accumulates over the years and eventually reaches the stratosphere. The stratosphere in contrast to the troposphere, is virtually stagnant in its vertical dimension as a result of its temperature inversion. Although stratospheric latitudinal winds circle the globe (often in a matter of days and along roughly parallel latitudinal zones) times of the order of a year or more are required for vertical mixing. In addition horizontal eddy diffusion processes mix air from the equator to the poles in a matter of months. Impurities, once they have been introduced to the stratosphere, can remain for periods of 3 years or so even although horizontal dispersion of contaminants is rapid and world wide. Another reason for the long residence times of impurity species in the

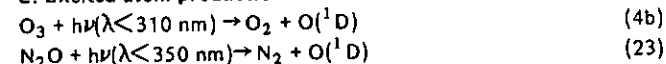
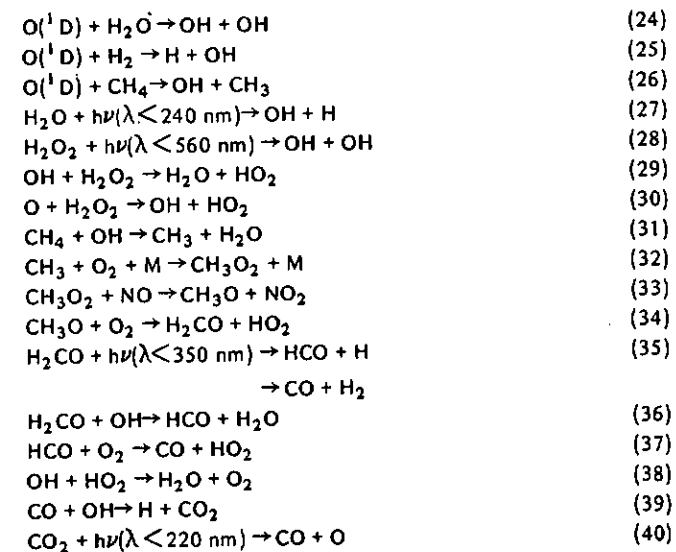
TABLE 1

Chemical reactions in the stratosphere that influence directly, or indirectly, $[O_3]$.

A. Classical 'Chapman Reactions'

B. HO_x catalysed destructionC. NO_x catalysed destructionD. NO_x - HO_x interconversion

E. Excited atom production

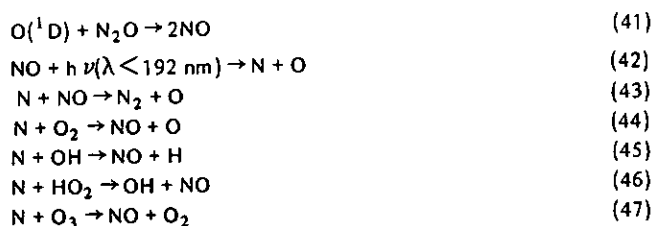
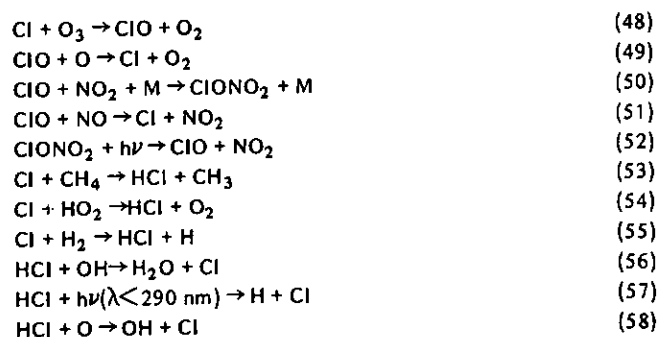
F. Production and loss of HO_x 

stratosphere is the extreme dryness. At ground level the mole fraction of water vapour may be 10^{-2} whereas in the stratosphere it falls to $\sim 3 \times 10^{-6}$. Thus any water-soluble impurities injected into the stratosphere do not have precipitation as an avenue for removal. This sensitivity of the stratosphere to contamination from impurities can be illustrated by likening the stratosphere to a kitchen. When the garbage is collected every day (as in the troposphere) the kitchen stays clean. But if it is collected only after a few years, even a tiny bit generated daily builds up to create a problem [6].

(a) SST Problem

Historically it was the potential threat to stratospheric ozone from the exhaust gases of supersonic transport aircraft (SST's) that initiated the CIAP programme. In 1970, the uncertainties that existed in understanding and knowledge of the stratosphere were so large no adequate basis for judging the pollutant threat from proposed stratospheric flights could be found. During the next few years, as knowledge about the stratosphere increased so the number of reports estimating O_3 loss from SST's grew. It was agreed that the main pollutant threat of SST flights within the stratosphere lay in the NO_x produced in their exhaust emissions. These NO_x species catalytically destroy O_3 by the reaction sequence (12), (13) and (14). (See figure 2). Early estimates of O_3 loss were based on proposed fleets of U.S. Boeing, British-French Concorde and Soviet Tupolev SST's. These estimates ranged from a 70% local reduction in O_3 for a fleet of 1000 Boeing-type SST's, [7] a 23% reduction in O_3 for 500 Boeing-type SST's [8] to a 1% reduction in global O_3 from 250 Concorde flying 11 hours per day. [9]

The cancellation of financial support for the Boeing SST development by the U.S. Congress in 1971 alleviated the possible problem of serious SST pollution. Other types of SST such as the Concorde and Tupolev consume only one third of the fuel of the proposed Boeing and fly at ~ 17 km instead of the 20 km of the Boeing. At present the number of SST aircraft scheduled to enter service and already in

G. Production and loss of NO_x H. Production and loss of ClO_x - Interconversion to HCl

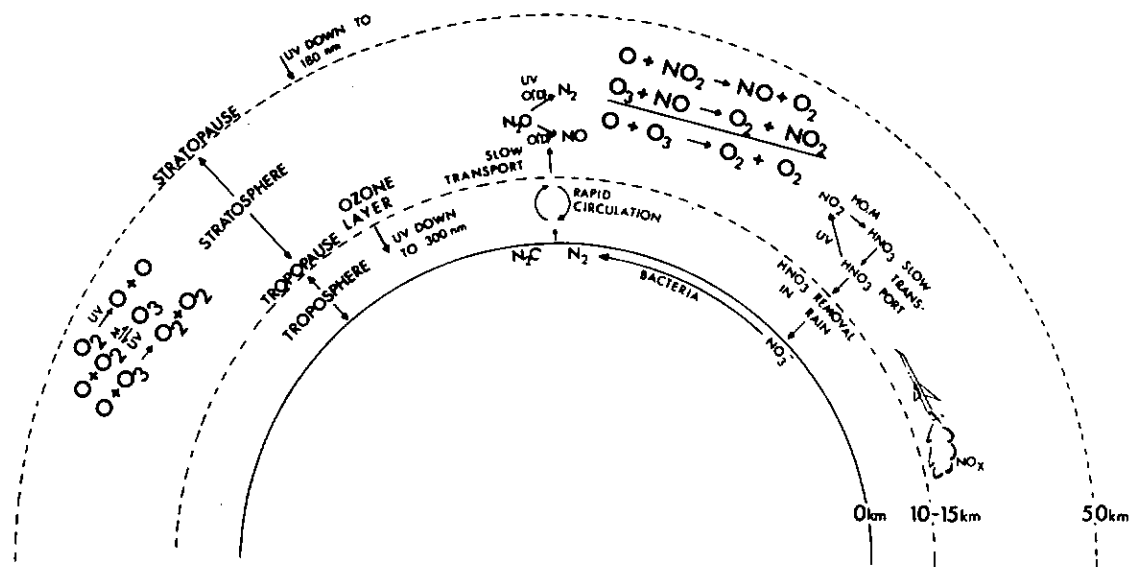


Figure 2. Ozone formation and removal processes from NO_x in the stratosphere.

operation are not sufficient to cause a measurable reduction in global ozone levels. One of the main conclusions of the CIAP programme on the SST problem was that in the future there should be encouragement to develop new low-emission engines and fuels thus permitting greater traffic densities in the stratosphere. In summary, the CIAP investigation did find evidence for O₃ depletion by NO_x in SST exhaust emissions but present-day traffic densities are not sufficient to cause immediate concern.

Although the very long lifetimes of F-11 and F-12 make them prime contenders for entering the stratosphere and eventually depleting O₃ they are by no means the only sources of atmospheric halogens. Other important sources of tropospheric chlorine are methyl chloride (CH₃Cl) which has a mainly natural origin and carbon tetrachloride (CCl₄) which is believed to have both a natural as well as anthropogenic source. Sources of lesser importance are

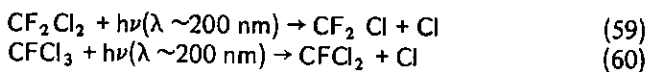
(b) The Halocarbon Problem

General fluorocarbon use began in the 1930s when freon 12 or F-12 (difluorodichloromethane CF₂Cl₂) was introduced as a refrigerant. With the development of the aerosol spray can industry after World War II, (trichlorofluoromethane CFCI₃) became widely used with F-12 as propellants in spray cans. Both F-11 and F-12 appear to have ideal characteristics for their aerosol applications: non flammable, low toxicity and unusual chemical stability. The great stability of these compounds to chemical reaction was further reinforced in 1971 when Lovelock was able to detect their presence in atmospheric samples. [10] Little concern was voiced as the world output of halocarbons rose steadily (see Table 2) until 1974, when Molina and Rowland pointed out that any halocarbon species reaching the stratosphere could be photodissociated by UV sunlight to produce Cl atoms. [12]

TABLE 2

Production and release of F-11 (CFCI₃) and F-12 (CF₂Cl₂) in tonnes/year [11].

Year	F-11		F-12	
	USA	World	USA	World
To 1959		202.2		644.0
1959	27	35.8	71	88.5
1960	33	50.0	75	100.6
1961	41	60.8	79	110.2
1962	56	78.7	94	130.6
1963	64	94.2	99	149.9
1964	67	112.0	104	175.0
1965	77	124.5	123	196.4
1966	77	141.9	130	227.1
1967	83	163.6	141	257.8
1968	93	187.1	148	277.1
1969	109	223.2	167	311.5
1970	111	245.9	170	335.4
1971	117	274.6	177	355.9
1972	136	317.5	200	398.6
1973	148	367.8	221	441.0
1974	158	400.2	231	473.6
1975	121	357.3	178	416.3
TOTAL		3437.3		5089.5
Northern Hemisphere		3326.8		4891.1
Southern Hemisphere		110.5		198.4
Total released to atmosphere		2934.1		4414.1



The presence of Cl atoms in the stratosphere provides a pathway for catalytic destruction of O₃ by the reaction sequence (48) and (49) (See Table 1 and Figure 3).

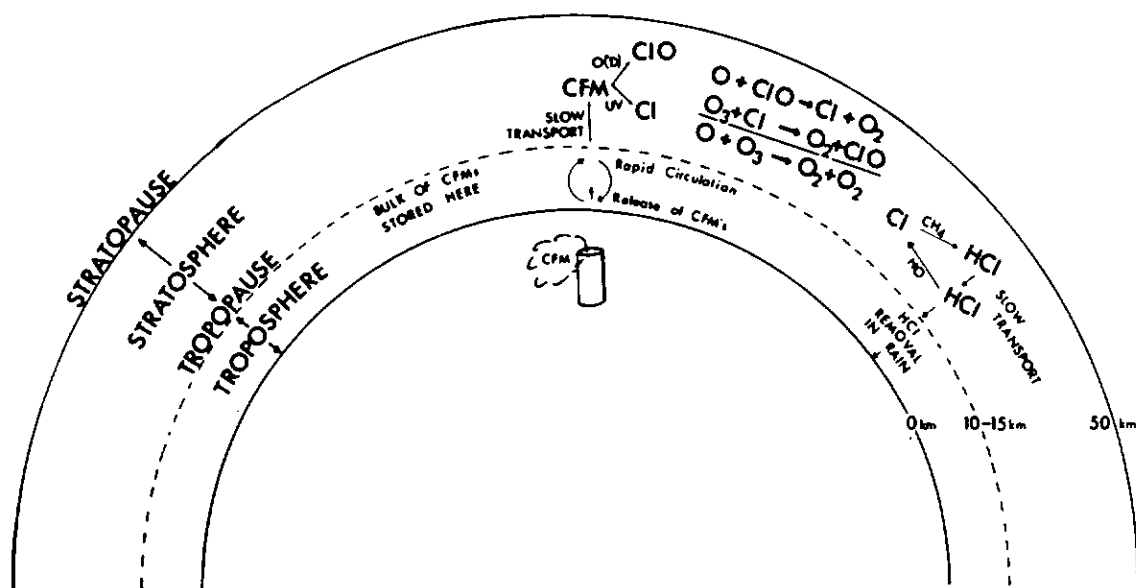
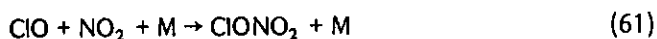


Figure 3. Simplified atmospheric cycle of the chlorofluoromethanes (CFM's).

trichloroethylene (CCl_2CHCl), methyl chloroform (CH_3CCl_3) and F-113 ($\text{CF}_2\text{ClCFCl}_2$) (see Table 3). In addition the U.S. space shuttle will use an ammonium perchlorate-aluminium powder propellant which will release ~100 tonnes per flight of chlorine compounds (mainly HCl) directly into the stratosphere. [13] Volcanic emissions and sea spray are thought to be only minor sources. [11] Not all of these compounds containing chlorine have long lifetimes in the troposphere. Those substances that contain sufficient hydrogen atoms (such as CH_3Cl) and double bonds ($\text{CCl}_2 = \text{CHCl}$) are readily attacked by OH and decomposed to form HCl. Although it can be seen from Table 3 that larger sources of atmospheric chlorine are available, it is mainly the chlorofluoromethanes or CFM's (F-11, F-12, F-113 etc.) that survive long enough to be transported into the stratosphere where photodissociation occurs. It seems likely that almost the entire production of CFM's eventually reaches the atmosphere and is available for O_3 depletion. A recent discovery that chlorine nitrate ClONO_2 may act as a temporary reservoir for active Cl atoms in the stratosphere, [14],



has lowered early predictions of O_3 decreases by about a factor of 1.8 [11]. Regeneration of the halogen from ClONO_2 eventually occurs by photodissociation.



Following the initial report of Molina and Rowland in 1974 of the potential threat of CFM's to stratospheric ozone, [12] a number of attempts were made to estimate the extent of the threat. Rowland and Molina [15] estimated a 1% decrease in $[\text{O}_3]$ had occurred in 1975 and that a 20% decrease could result if CFM release continued at 1973 rates. Other estimates of the 1974 - 1976 period also predicted substantial decreases in ozone by the year 2000. [9,16] The threat to ozone from the ever increasing concentrations of CFM's in the atmosphere was sufficient

to cause a special committee to be established in the U.S.A. whose job was to advise the U.S. National Academy of Sciences on the extent of pollution and on what action should be taken. After 18 months of deliberation the committee reported its findings in September, 1976 [11] and noted that a 0.5% reduction in ozone had already occurred. Further, if the release rate for CFM's continued at 1973 rates the reduction in ozone concentration would rise to 7.5% with uncertainty limits between 2 and 20%. Table 2 indicates a 15% decrease in CFM production took place in 1975. This slowing down in production prompted the committee to advise that a 2 year period could safely be allowed before steps were taken to introduce legislative bans. A 2 year delay would allow time for some areas of uncertainty in the models to be removed. The panel did say, however, that 'selective regulation of CFM uses and

TABLE 3
World production and release of principal halocarbons in 1973 (10^3 tonnes/year) [11].

Halocarbon	Anthropogenic World Production	World Release to atmosphere
CFCl_3	368	314.1 ^a
CF_2Cl_2	441	382.5 ^b
CCl_4	950	41.7
CHCl_3	225	12.4 + (2450) ^d
$\text{C}_2\text{H}_5\text{Cl}$	550	14.6
$\text{CH}_2\text{ClCH}_2\text{Cl}$	12,000	565.2
CH_3Cl	400	7.9 + (6690) ^c
CH_3CCl_3	420	324.2 + (925) ^d
CH_2Cl_2	425	346.4 + (3450) ^d
$\text{CCl}_2 = \text{CCl}_2$	750	609.0 + (1720) ^d
$\text{CCl}_2 = \text{CHCl}$	700	648.3 + (2030) ^d
$\text{CH}_2 = \text{CHCl}$	7100	351.6

a Based on an 85.4% release rate [11].

b Based on an 86.7% release rate [11].

c Estimated emission rate from natural sources, e.g. Marine biological activity and smouldering vegetation.

d Estimated emission rates from unknown sources obtained from the mole fraction in the troposphere divided by the estimated atmospheric residence time.

releases is almost certain to be necessary'. [17] On October 15, 1976, the U.S. Food and Drug administration announced its intention to phase out all non-essential uses of fluorocarbon propellants in products it regulates, which are about 80% of all aerosol products.

(c) The Nitrous Oxide Problem

Molecular nitrogen and nitrous oxide (N_2O) are produced from nitrates and nitrites in the lands and oceans by denitrifying bacteria. Like the CFM's, the chemical stability of N_2O is sufficiently great for N_2O to become uniformly mixed throughout the troposphere with a concentration ~260 parts per billion by volume at ground level. Any N_2O transported into the stratosphere is removed by photodissociation or by reaction with $O(^1D)$ to produce NO. Once converted into NO or N_2 , N_2O cannot be reformed by any known gas phase process at



atmospheric temperatures. We have noticed that in the natural stratosphere, catalytic destruction by NO_x is the main loss process of O_3 . Nitrous oxide produced in the denitrification process therefore becomes the primary reactant responsible for destroying O_3 in the stratosphere. If now some process appeared that was to increase the rate of production of N_2O at the earth's surface then there would ultimately be a corresponding decrease in stratospheric O_3 . A number of investigators believe this increase is already occurring because of an increased application of nitrogenous fertilizers to soils. Also it is estimated that addition of industrial fixed nitrogen is about one-third of that fixed biologically in terrestrial ecosystems. If the current rate of increase in industrial fixation continues, by about 1990 man will be adding more fixed nitrogen to the soil than that fixed biologically [18]. Crutzen in 1972 [19] was the first to recognise the potential danger to O_3 from N_2O and estimated a 20% increase in global production of N_2O would bring about a 4% reduction in O_3 [9]. More recent estimates based on projected increased in fertilizer application show that a 10% reduction in O_3 could result in ~200 years [20] or between 2% and 20% by the year 2025 [21,22].

One of the reasons for the divergence of opinion in these estimates lies in the lifetime of N_2O in the atmosphere, which is not known with any degree of accuracy. Only one major destruction process of N_2O has been established and that is photodissociation in the stratosphere



which leads to a destruction rate of 9×10^6 ton (N) per year. [23] The atmospheric residence time for N_2O produced at the earth's surface on the basis of photodissociation as the only sink, is ~140 years. [20] Other evidence from estimates of denitrification rate and variability in year-to-year measurements suggest the lifetime of N_2O (τ_{N_2O}) to be considerably shorter than 140 years [21]. Current estimates range from 5 to 150 years [20]. If τ_{N_2O} is only of the order of a few years there must either be a large tropospheric sink for N_2O or a ground-based

sink. It is therefore possible that the dominant sink for N_2O has yet to be identified.

Another area of confusion is the importance that oceans play either as a source or sink for N_2O . Hahn [24] estimates the oceans are a net source of N_2O producing 85×10^6 tons (N) per year compared with 15×10^6 tons from soils. Delwiche [25] estimates N_2O source strengths from land are 120×10^6 tons (N) per year and from the oceans are 40×10^6 tons (N) per year. McElroy et al [26] on the other hand postulates the earth's oceans act not as a net source but instead as a net sink for N_2O . A further area of doubt is the value of the ratio of N_2O to N_2 produced in the denitrification process. Empirical evidence suggests the ratio for soils lies somewhere between 0.025 and 0.1 [21]. The ratio for agricultural conditions at high fertilizer application rates is uncertain.

Before any accurate estimate for ozone depletion can be arrived at, these areas of uncertainty must be removed and accurate estimates of the sources and sinks of N_2O established. It will be necessary to include the input of N_2O from thunderstorms and to include the possibility of a substantial increase in atmospheric release of N_2O from the combustion of coal [20].

If regular monitoring of N_2O had been carried out over the past 50 years or so, the effect of a changing rate of N_2O production could be more easily assessed. Unfortunately, until very recently, few regular measurements have been attempted. Early results from 3 stations between 1967 and 1969 show large (30%) variations in N_2O over a period of time [20]. If fluctuations of this magnitude are to prove a feature of N_2O measurement it will take some years of regular monitoring before trends can be established.

(d) Summary

There is general consensus of opinion that stratospheric ozone is under attack from a number of activities of man. Although the chemistry of the stratosphere has been the subject of a great deal of speculation only very recently have some of the fundamental measurements of trace species been accomplished at stratospheric altitudes. Altitude profiles of the important NO_x species have been obtained only within the past 3-4 years. Also within the past 3-4 years a few measurements have been made of HNO_3 , N_2O , CH_4 , H_2 , H_2O , CO, F-11, F-12, HCl and SF_6 . Only one or two measurements of $O(^3P)$ and OH have been reported and species such as HO_2 , ClO, Cl and $ClONO_2$ remain unmeasured. Clearly one of the primary objectives of investigators in the next few years will be in this area of atmospheric measurement and the establishing of a world network of stations to carry out regular monitoring of all potential species capable of destroying ozone.

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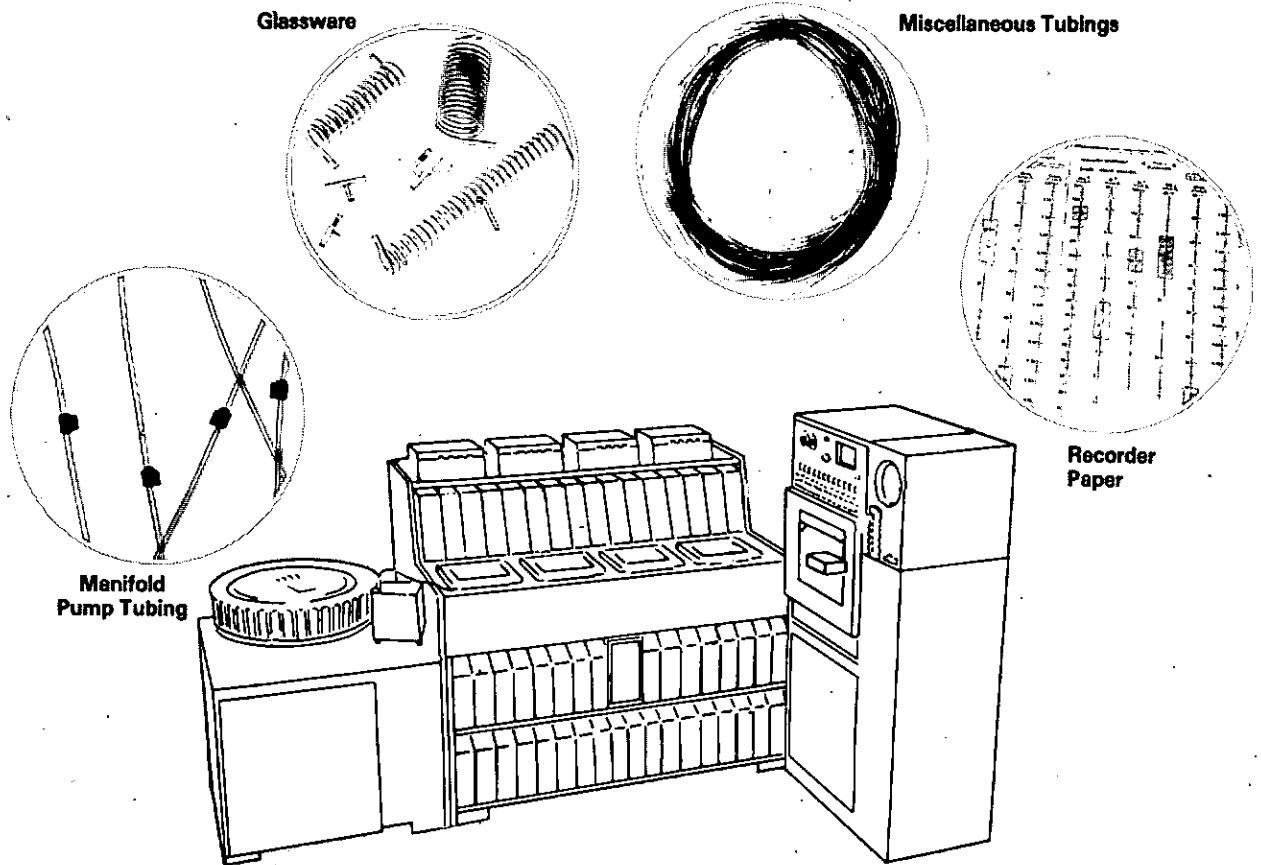
NEW PRODUCT

The NZ Wool Board and Mosgiel Ltd announce the production of a new woollen fabric; 'Flamesafe'. The development is based on the IWS Zirpro process in which wool is impregnated with titanium and zirconium salts. There are numerous applications for the superior insulating and flame-proof properties of the fabric.



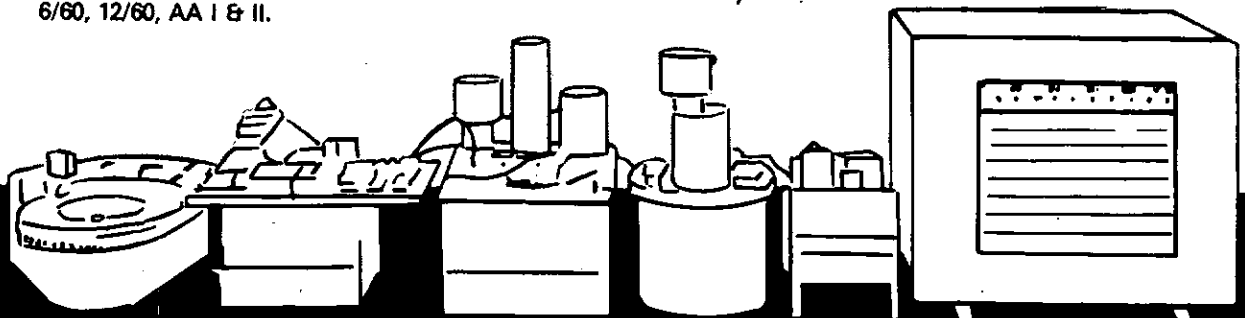
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THE INSTITUTE OF CHEMISTRY AND SOCIETY

by M. Kingsford (Convenor), D. M. Bibby, D. H. Buisson,
J. D. B. Featherstone, B. Halton and L. J. Porter.

INTRODUCTION

This is the report of a working party on "Possible Contributions of N.Z.I.C. to Society", established by Council in response to a resolution of the Annual General Meeting in August 1977. The full report was approved for publication to members by Council in May 1978, with some amendments and abbreviation. The report consists of 18 recommendations, falling into four groups as set out below. The report will be considered by the 1978 Annual General Meeting and by Council. Opinions and comments from members are invited, and should be addressed to the General Secretary or Branch delegates to Council. It should be stressed that none of the recommendations have yet been formally adopted, and there are likely to be differing viewpoints which must be reconciled before any action taken.

A. INSTITUTE POLICY AND COMMENT

The membership of the Institute is such that a wide range of expertise is available in many diverse areas. In order for the Institute to contribute in an effective and informed manner to society at large, it is essential that any opinion expressed, or any comment made, is based upon sound up-to-date scientific advice. However, comments made in the name of the Institute all too often appear long after the specific issues of concern have been made topical by the media. It is essential, therefore, that NZIC streamlines its efforts in these directions by recognising and involving those key members whose expertise might be required and by attempting to assess areas of potential concern before they become topical.

1. Public Affairs Committee

Council should establish a "Public Affairs" committee to be concerned with, among many possibilities, government policies, safety, the environment, energy and education. It should have power to issue statements on behalf of Council.

2. Register of Experts

Council should establish a register of experts who are experienced and active in their fields, and are willing to devote some time to aiding the Institute in formulating policy and/or informed statements. Industrial experts should be included in the register (as a matter of prestige).

When policy matters requiring comment become known, they should be referred to the Branch Chairman who may arrange comment at the local level using Branch experts, or otherwise refer the matter to the Public Affairs Committee. The committee will then make use of experts on the register, conference telephone links and other means of rapid communication, and develop an informed statement.

Members should be encouraged to bring matters to the attention of their Branch chairman or council, if possible well before they become topical.

B. POSSIBLE CONTRIBUTIONS TO SOCIETY

3. Legislation

The Institute should play a more active role in commenting on legislation, both draft and existing, particularly in relation to the policies underlying such legislation.

Until government departments send relevant drafts to the Institute as a matter of course, knowledge of the existence of pending legislation of interest could be provided by those members of the Institute in the civil service who are sent drafts for comment, so that the Institute can request copies of any legislation of interest. Although the technical details of draft legislation should be handled competently within government and by the industry concerned, government policy is a different matter and the Institute may well wish to comment through the Public Relations Committee.

4. Energy Policy

The Energy and Materials Resources Committee of NZIC should continue to examine proposed government energy policies in the light of recent reports, with a view to making analytical comments to the media.

5. Education

A working party should be formed, consisting both of chemists directly involved in education and of chemists representing groups who employ the products of the local education system (e.g. graduates, technicians), to (i) study the findings of the N. Z. I. C. Education Group and establish a consensus for future action; (ii) discuss chemical education with students, teachers (especially those with limited chemical knowledge), and technical institute and university staff; (iii) prepare recommendations for action in a concise document for Council; (iv) approach the appropriate agencies on behalf of the Institute to urge and assist them to implement the policy of the Institute.

Education at secondary and tertiary level is vital to the future of both New Zealand and the Institute. The N. Z. I. C. currently has a chemical education group, whose members have already put much

effort into discussing chemical education (e.g. the publication "Proceedings of a Symposium on Chemical Education", Canterbury University, August, 1976). Unfortunately, this symposium reveals a wide disparity of views at a time when there is considerable dissatisfaction with the products of our education system. There are complaints about the sparse knowledge of both basic facts and basic language. If the "product" is not up to standard, the "production methods" must be adjusted, and it is urgent that remedial action be taken. The N. Z. I. C. has the opportunity to take definitive action, to assess and to implement the suggestions that have been made and to determine any further necessary changes, not only in the teaching of chemistry but also in the teaching of mathematics and English. Possibly a return to a core of basic manipulative skills is necessary. If so, the Institute must press for this.

6. The Future.

Council should examine further ways in which the Institute might co-operate with the Commission for the Future. One important area concerns manpower requirements for science.

7. Research Funds.

The President should make a public statement about the low level of research expenditure and the limited sources of funds for developing ideas, at a time when New Zealand is needing marketable innovations.

8. Major Research Facilities

Council should initiate an investigation into the possible rationalisation of the purchasing of major research instruments and the needless duplication of such purchases. When funds are limited it may be better to establish a single major facility and transport people to it rather than establish several minor facilities.

9. Public Health and Research

A small working group should be established both to investigate how chemists can make a more effective contribution to public health research, and to publicise contributions that have been, or could be, made.

C PUBLIC IMAGE OF SCIENCE

10. Public Information About Science

To aid the general image of science in the community, the president should encourage scientific institutions to create or continue active public relations programmes involving open days, visiting days, and reports of news-worthy scientific achievements.

11. Public Participation in N. Z. I. C. Meetings

The public should be brought into better contact with the Institute by (a) a continuation of the "open" meetings and symposia held by branches and consideration of expanding such programmes; (b) inviting a speaker to deliver an annual N. Z. I. C. public lecture on a topical subject in each of the branch main centres.

12. Press Officer

Council should appoint a part-time journalist to act as Press Officer for the Institute, to liaise with, and be recognised by, the media.

13. Contact with Government

A delegation of Council should hold an annual meeting with the Minister of Science and the Director-General of D. S. I. R. to discuss current problems and trends in science.

14. The Media

Council should encourage branches to cajole the media with a view to involvement on a regular basis.

15. Publicity About N. Z. I. C.

Council should establish a central compilation of publicity about the Institute.

D. STRENGTHENING MEMBERSHIP OF N. Z. I. C.

16. Membership Services

Efforts should be made to make the Institute more attractive to its existing and potential membership by: (a) improving still further the image created by "Chemistry in New Zealand"; (b) publicising more effectively the activities of the Institute; (c) publicising the liaison and special arrangements which exist with overseas societies, and seeking to expand the number of societies involved; (d) creating benefits available only to members.

17. Recruitment

A vigorous campaign should be continued to enrol chemists in the Institute. All heads of organisations employing chemists should be asked to suggest Institute membership to their staff. A possible incentive might be a reduced subscription for the first year of membership. At the same time, efforts should be made not to compete with other professional organisations. Possibly a system of joint subscriptions could be developed.

18. Sister Bodies

Branch chairmen should ask their counterparts in other organisations to make the members of those organisations aware of the membership grades of the Institute open to them, and make the availability of local membership better known to the general public.



THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)
INCOME AND EXPENDITURE ACCOUNT FOR YEAR ENDED 30th APRIL, 1978

1977	EXPENDITURE		1977	INCOME	
\$			\$		
	ADMINISTRATIVE EXPENSES:		17,979	Subscriptions — Annual	20,948.35
4,875	Honoraria (Less \$390 Charged to Journal)	4,853.41		INTEREST:	
3,061	Printing, Stationery, Postages, Tolls, etc	3,829.67	120	Bank of New Zealand	163.10
2,332	Travelling Expenses	2,585.03	144	Local Body Stock	143.76
900	Branch Expense Allowances	900.00	-	U.D.C. Finance Debenture Stock	134.67
46	Legal Fee	25.00	-	General Finance Debenture Stock	52.89
635	Audit Fee	600.00	-	Post Office Savings Bank	2.67
127	Conference Costs paid by Institute	81.00			
77	Donations — S.A.N.Z.	85.00	(264)		497.09
155	—Auckland Institute Museum				
	— 'Rutherfords Den'	200.00			
(192)	Cost of Submission — Industrial Relation Bill	285.00			
50	Interest — Bank of New Zealand	-			
3	Depreciation — Per Attached Schedule	70.00			
43	Royal Society of New Zealand Fee	20.00			
40					
(12,304)		13,249.11			
	PUBLICATIONS:				
6,506	Journal and Bulletin (including \$390 Honoraria)	8,940.59			
73	Environment and Industry Code of Ethics and Commentary on Rules	731.00			
	List of Members	671.38			
	Sundry Publications	1,517.37			
(6,655)		11,860.34			
	Less: Revenue From —				
3,465	Journal Advertising & Subscriptions	5,658.72			
338	Sundry Publication Subscriptions And Sales	1,509.79			
(3,803) Cr.		7,168.51			
(2,852)		4,691.83			
3,087	Excess of Income Over Expenditure	3,504.50			
\$18,243		\$21,445.44	\$18,243		\$21,445.44
=====		=====	=====		=====

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)
OVERSEAS VISITORS TRAVELLING FUND

Payments Made	1,129.10	Balance 1.5.77	521.65
Balance 30.4.78	1,183.04	Education Fund Transferred	140.00
		Contributions Ex Branches	665.00
		Conference Surplus	985.49
	\$2,312.14		\$2,312.14
	=====		=====

We have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended 30th April 1978, and have received all the information and explanations we have required. In our opinion, according to the best of our information and the explanations given to us as shown by the books of account, the Balance Sheet, Income and Expenditure Account, and Trust Fund Account are properly drawn up so as to give a true and fair view of the state of the Institute's affairs as at 30th April, 1978.

SHANAHAN AND WINDER

Chartered Accountants

M. P. Winder

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)
FORTY-EIGHTH ANNUAL REPORT
For the Year Ending 31 July 1978

Elected Officers

President:	Dr G. A. Wright
First Vice President:	Dr W. E. Harvey
Second Vice President:	Prof A. D. Campbell
General Secretary:	Mr J. G. Fletcher

Branch Delegates to Council

Auckland:	Dr L. Eyres
Waikato:	Dr E. Payne
Manawatu:	Dr W. B. Sanderson
Wellington:	Dr B. Halton
Canterbury:	Dr R. F. C. Claridge
Otago:	Dr G. W. Emerson

Officers Appointed By Council

(These appointments continue until the date shown, but are renewable. Appointments are made at the November meeting of Council.)

Registrar:	Mr D. J. Hogan	(31.12.78)
Administrative Secretary:	Mrs N. E. Wignall	(31.12.78)
Journal and Bulletin Editor:	Dr L. K. Creamer	(31.12.78)
Journal Business Manager:	Mr T. R. Johnson	(31.12.78)
Hon. Librarian:	Mr S. G. Booker	(31.12.78)

Committees Appointed By Council

Membership Committee:	Dr P. K. Foster	(31.12.78)
	Mr J. S. Pollard	(31.12.78)
	Prof A. D. Campbell	(31.12.78)
Publications Committee:	Dr A. M. Brodie	(31.12.78)
	Dr R. F. C. Claridge	(31.12.79)
	Dr L. Eyres	(31.12.80)
	Editor (ex-officio)	

Energy and Chemical Materials Resources Committee:	Dr I. D. Watson	(31.12.78)
	Prof A. G. Williamson	(31.12.79)
	Dr G. J. Wright	(31.12.80)

Hazardous Chemicals Committee:	A. C. Kennett
	R. H. Hopgood
	D. J. Ogilvie

Representatives on Other Bodies

Technician Certification Authority Committee for Science:	Dr W. E. Harvey	(31.3.81)
Standards Assn of NZ:	Mr J. A. Gilmour	(31.3.80)
	Dr P. K. Foster (resigned)	
	Mr J. G. Fletcher	(31.3.79)
UNESCO in NZ:	Dr G. R. Burns	(31.12.78)
Royal Society Member Bodies Committee:	Dr I. D. Watson	(31.12.78)

MEMBERSHIP

During the year the following changes in membership have taken place:

New Fellows:	1
Members elected to Fellowship:	17
New Members:	46
Reinstated:	1
Graduate Members elected to Membership:	13
Associate Member elected to Membership:	1
New Associate Members:	7

Technician Member elected as

Associate Member:	1
New Graduate Members:	37
New Technician Members:	5
Resignations (includes one for approval at August Meeting):	16
Deaths	4
Deleted	9

Consolidated membership figures for the last four years are as follows:

	1975	1976	1977	1978
Auckland:	335	343	339	367
Waikato:	97	97	94	110
Manawatu:	131	128	124	123
Wellington:	299	310	306	313
Canterbury:	182	180	174	176
Otago:	105	104	105	109
Overseas:	146	140	138	150
Total:	295	1302	1280	1348

Distribution of Branch membership in 1978 is as follows:

	Hon.F.	Fellow	Mem.	Assoc.	Grad.	Tech.	Total
Auckland:	5	56	262	6	35	3	367
Waikato:	2	12	85	3	8	-	110
Manawatu:	-	18	93	-	12	-	122
Wellington:	10	49	234	3	16	1	313
Canterbury:	4	38	125	1	5	3	176
Otago:	2	23	80	1	3	-	109
Overseas:	-	24	119	-	7	-	150
	23	220	998	14	86	7	1348

OBITUARY:

We record with regret the deaths during the year of the following members: H. O. Askew, J. J. Cornes, A. K. McDowell, D. H. McLean and C. G. W. Mason.

PRIZES:

The I.C.I. Prize for 1977 was awarded to Dr G. P. Glasby. Student Paper Prize: Mr A. G. Bosanquet, Lincoln College.

HONOURS:

Four Honorary Fellows have been elected. They are: Dr A. T. Johns, Dr I. K. Walker, Mr A. W. Mackney and Dr T. A. Rafter.

The Polar Medal was awarded to Prof A. T. Wilson.

The Hector Medal (RSNZ) was awarded to Prof R. E. F. Matthews.

SPECIALIST GROUPS:

Group	Organiser	Membership ¹
analytical	D. J. Hogan	*
Biochemistry	M. G. Smith	*
Chemical Education	D. T. Howarth	325
Chemical Engineers	E. R. Palmer	*
Chromatography	J. Zabkiewicz	152
Electrochemistry	A. J. Easteal	70
Geochemistry	J. A. Ritchie	129
Organic	K. E. Richards	94
Polymer	N. E. Edmonds	72
Thermodynamics	D. V. Fenby	*
Crystallography	W. T. Robinson	*
Trace Elements & Health	T. E. Kjellstrom	*

* Total not available

CONFERENCES

The annual conference for 1977 was held at Waikato University in Hamilton, 22-25 August, in conjunction with related conferences on Clinical Biochemistry, Trace Elements, Wine Institute and a Teachers Course. Enrolments totalled 261, and 163 papers were presented (some in poster sessions). Guest speakers included Prof R. D. Brown, Dr J. R. E. Wells, Prof R. F. Mason, Prof Melvin Calvin, Prof Lloyd Smythe and Prof Ribereau Gayor. The conference was an outstanding success and the Waikato Branch were generous hosts and excellent organisers.

OVERSEAS VISITORS

Prof K. G. Grjotheim (Oslo) and Prof M. Swarz (Syracuse) visited Branches during 1977.

RELATIONS WITH OTHER BODIES

NZIC representatives have been active in the affairs of UNESCO and the Royal Society of NZ. Full support for IUPAC activities has been maintained, especially through the good offices of Dr T. A. Rafter, Chairman of the National Committee for Chemistry. NZIC was represented by Dr W. A. McGillivray at the Centennial of the Chemical Society of Japan in April 1978. There has also been close contact with the American Chemical Society on a number of matters, including the forthcoming CSJ/ACS Congress at Honolulu in April 1979, with NZIC as an official participating body.

PUBLIC AFFAIRS

- (a) **Hazardous Chemicals** There is considerable activity in the area of Dangerous Goods, including safety, labelling, packaging and listing of hazardous chemicals. NZIC has made representation to Government on a number of matters of principle, including the need to unify responsibility for these substances in one Ministry (not four as at present). NZIC has won representation on Standards Association working committees which are drafting standards on labelling and packaging.
- (b) **The Levich Affair** Support for the plight of the Russian chemist V. G. Levich has been confirmed, and this stand has been supported by RSNZ and the Minister of Foreign Affairs.
- (c) **Rutherford's Den** A donation of \$200 to assist the resoration project was made by Council.
- (d) **Working Party** A working party convened by Dr M. Kingsford has produced a stimulating report on the Insitute of Chemistry and Society. The 16 recommendations are currently being studied with a view to adoption where possible.
- (e) **Planning Perspectives 1978-83** A comment has been made on this document from the Planning Council, particularly its neglect of science and technology.
- (f) **Environmental Impact Report** A supporting comment and assessment was made to the Commission for the Environment on the Runciman Fertilizer Works proposal.

PUBLIC RELATIONS

Press statements have been made on School Science; the Levich Affair; Chemical Hazards; Planning Perspectives and

Science; the Royal Commission on Nuclear Power; Forecasting of Future Trends in Energy and Related Matters; Insitute Officers; Awards and Prize-winners.

Sympathetic coverage has been given by newspapers, and the Auckland Star (7.3.78) ran an editorial supporting NZIC in its stand on hazardous chemicals. The President has given three radio interviews.

Media coverage is quite satisfactory, provided NZIC officers are prepared to issue suitable press statements on matters of concern. There is no doubt that Government Departments, politicians and other interested parties take note of publicly stated viewpoints expressed by NZIC spokesmen. This is one area where NZIC officers can promote the science and practice of Chemistry in the public arena.

PROFESSIONAL WELFARE

The Institute has a firm commitment to the professional welfare of all its members. Members should not hesitate to approach Council officers for support or advice on professional matters.

- (a) **A Number of Members** have been advised on matters of concern relating to union membership and employment conditions.
- (b) **The 1977 Membership List** has been issued to members. It is based on a new computer file of NZIC members designed and developed by Dr R. Maclagan.
- (c) **Salary Survey** Dr G. J. Gainsford and W. A. Singer conducted a survey in August 1977 and their analysis has been published in the journal. The survey is a difficult task, and NZIC is grateful for the expert work of the authors. It is hoped to further streamline the procedures for the next survey.
- (d) **Taxation Advice** circulars have been issued to members.
- (e) **The Guidelines to Professional Employment** document (see Journal 41 p.66, July 1977) has been reprinted for issue to all new members.
- (f) **Remission of Subscriptions** is possible under the discretionary powers of Council according to Rules 6.2 and 13.2.2. Council has issued an information sheet indicating present subscription concessions available to members on retirement, overseas service, or temporary unemployment due to ill health, family responsibilities, etc. The Registrar will advise on these matters.
- (g) **Registrar's Visit to RACI.** Mr Hogan visited officers of the Royal Australian Chemical Insitute in March 1978 and useful exchange of information resulted.

PUBLICATIONS

The Journl and the Bulletin continued under the excellent editorship of Dr L. K. Creamer. A high standard of content and presentation was maintained, three journal issues and six bulletins being published in the calendar year. The Publications Committee has been active on future policy on publications.

FINANCE

The Balance Sheet again shows a substantial operating surplus, this year amounting to \$3504.50. Council has held expenditure as low as possible over the last two years and reserves have been brought to a level similar to that of two years ago. During the year Council invested \$5000 in two guaranteed debenture stocks for different terms at favourable interest rates. Possibly a level of investment

reserve should be agreed to by Council and the budget adjusted to achieve this. What level is desirable and how it should be invested are matters for discussion.

Expenditure has been close to budget forecasts but the disappointing aspect of the Balance Sheet is a further increase in subs in arrears which now amount to \$3499.00. This sum represents about 16% of the Institute's income. The Overseas Visitors Fund remains in healthy credit owing to the transfer of the handsome profit from the 1977 conference in Hamilton.

APPRECIATION

A large number of members have contributed to the work of NZIC in many different capacities. This report follows the practice of the last two years in setting out the names

of all the committee members and appointees, so that the range of involvement can be properly judged by the members. The Institute operates on the principle of maximum delegation of responsibility and initiative and there is no doubt that Council is highly appreciative of the efforts and concern for the interests of NZIC shown by all those involved.

A special word of thanks is due to the Registrar and Administrative Secretary who handle an increasing work load with good humour and commendable efficiency.

On behalf of Council —

G. A. Wright President
J. G. Fletcher General Secretary

Visit by the Registrar to the Royal Australian Chemical Institute

While in Australia in March this year I called on the Royal Australian Chemical Institute headquarters in Melbourne. Some of my observations may be of interest to members.

I was made welcome by Mr Peter Woodhouse, Executive Secretary and Mr Keith Ryan, Registrar. They showed a real interest in N.Z.I.C. affairs and I would hope that more interchange between Institutes could be arranged. R.A.C.I. have their quarters in Clunies Ross House, a fine building owned by a number of scientific bodies. It is similar in concept to Royal Society Science Centre in Wellington although considerably bigger. It includes lecture theatres, display space and a science club with restaurant and bar facilities as well as offices. It was obvious that the principal difference between R.A.C.I. and N.Z.I.C. was of size. With over 6,000 members R.A.C.I. can provide facilities and activities for members that N.Z.I.C. is just beginning to reach for. Their thriving specialist groups and their monthly journal are cases in point. Their annual subscription is \$44 having been raised to this level in a series of small increments following a period of financial difficulty. Their 'Proceedings' is as much a touchstone of their finances as 'Chemistry in N.Z.' is of ours. Its monthly publication makes for good communication with the membership. In addition branches individually issue quite extensive newsletters. I would like to express my thanks for the opportunity to visit R.A.C.I. and to Mr Woodhouse and Mr Ryan for their hospitality and to express the hope that official R.A.C.I. party will be able to come to New Zealand for the 50th Jubilee Conference.

D. J. Hogan
REGISTRAR

Chromatography Group

A successful Workshop on High Pressure Liquid Chromatography (HPLC) was held in the Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North on 25 and 26 May. Formal lectures were introduced by the coordinator of the Workshop, Dr J. A. Zabkiewicz (Forest Research Institute, Rotorua) who compared HPLC with other forms of chromatography. Dr N. J. Eggers (DSIR, Chemistry Division, Gracefield) described the various types of column packings that are available and then Mr K. D. Steele (Forest Research Institute, Rotorua) described a method for packing columns.

Dr W. S. Hancock (Department of Chemistry, Biochemistry and Biophysics, Massey University) described his work on the analysis of amino acids using ion-pairing reagents with reverse phase chromatography. The analysis of peptides, proteins and glycoproteins was described by Dr M. T. W. Hearn (Medical School, Otago University, Dunedin) and Mr B. D. Wills (Ivon Watkins-Dow Ltd, New Plymouth) discussed quantitative ion-exchange chromatography of phenolics (chlorophenoxy esters) by chemical plant operators.

HPLC apparatus associated equipment and chemicals were displayed by nine manufacturers. On the second day of the Workshop, participants had an opportunity to discuss various problems with the manufacturing representatives and see the methods and equipment in action.

Dr C. B. Johnson,
Branch Editor,
Manawatu

FELLOWSHIP FOR A. W. MACKNEY

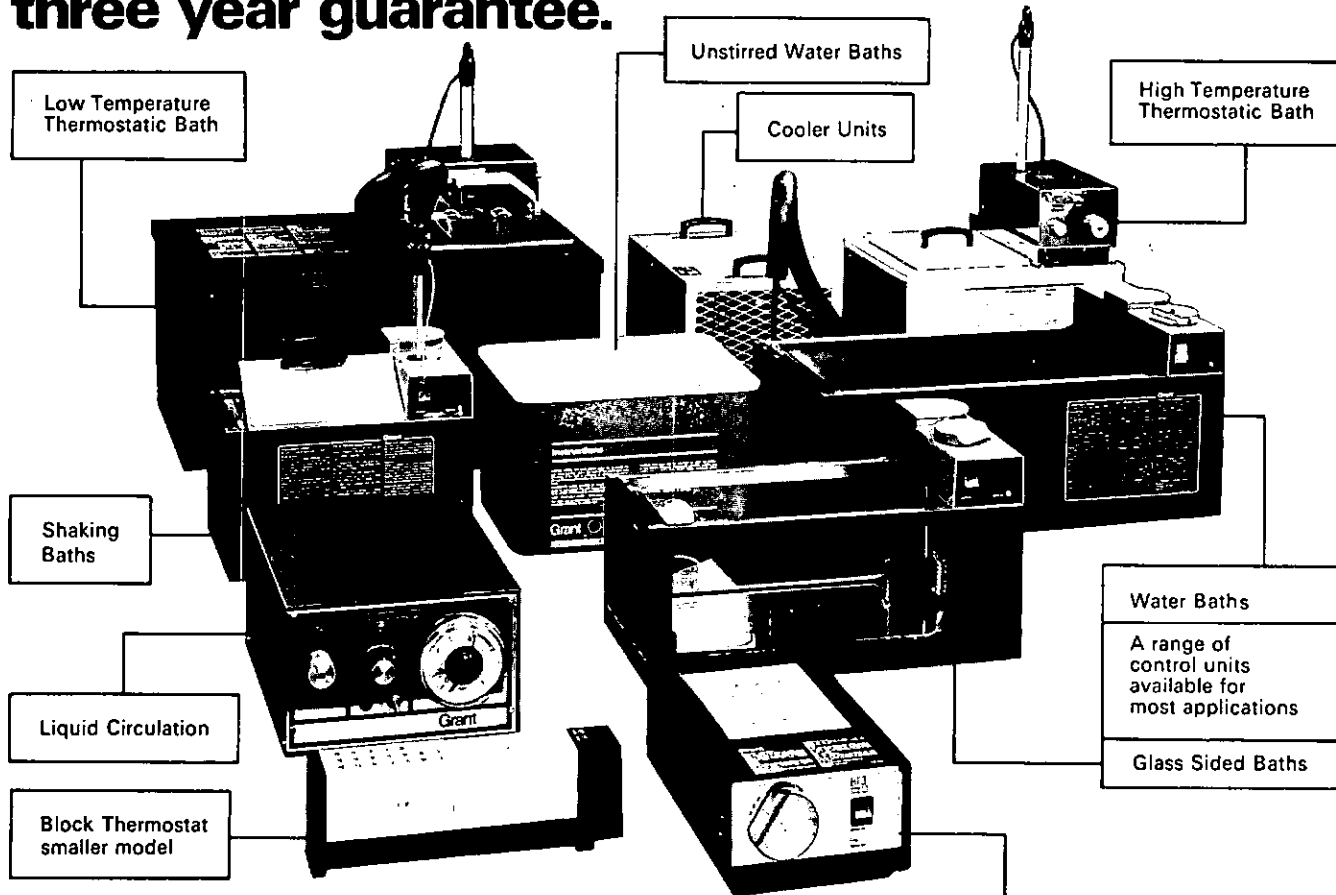
Alan William Mackney was born in Australia, graduated M.Sc. 1st Class Honours from the University of Sydney in 1934 and in 1935 began work with the Division of Forest Products, C.S.I.R.O., Melbourne. Mr Mackney later joined the Australian Newsprint Mills at Boyer, Tasmania and in 1944 took the position of Chief Chemist for New Zealand Forest Products Limited. In his years with the company, Mr Mackney has been General Manager of the Penrose Industries, Deputy Managing Director from 1966 and Managing Director from 1973.

In the early 1960's, Mr Mackney became a foundation member of the Forest Products Research Advisory Committee, and joined the Board of New Zealand Forest

Products in 1961. From 1961 to 1964 he served as a member of the New Zealand Atomic Energy Commission and was a foundation member of the National Research Advisory Council, on which he served from 1964 to 1969. He has served on the UN FAO Advisory Committee on pulp and paper since 1972. In 1973, Mr Mackney was awarded the L. R. Benjamin Medal by Appita, the technical association of the Australian and New Zealand pulp and paper industry, for his outstanding contribution to the technical progress of the industry. Mr Mackney, retiring this year, has been elected an Honorary Fellow of the N. Z. I. C. for outstanding achievement in his professional career, as an Industrial Chemist.

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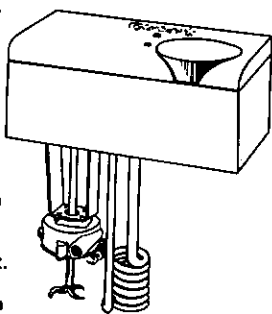


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BOOK REVIEW

Neighbouring Group Participation.
Volume 1. B. Capon and S. P. McManus,
Plenum Press, New York, 1976. Pp 280.
Price \$35.40.

Neighbouring group participation is a term coined in 1942 by the late Saul Winstein to describe how an atom or group not directly bonded to a reaction centre nonetheless influences the reaction rate (anchimeric assistance) or products, or both. The phenomenon is clearly exemplified in intramolecular organic cyclizations, but hidden participation, in which no new rings are formed, can have an important bearing on rates and on product stereochemistry. Examples of interest to the synthetic and mechanistic organic chemist are scattered throughout the literature, and thus the present authoritative volume is timely.

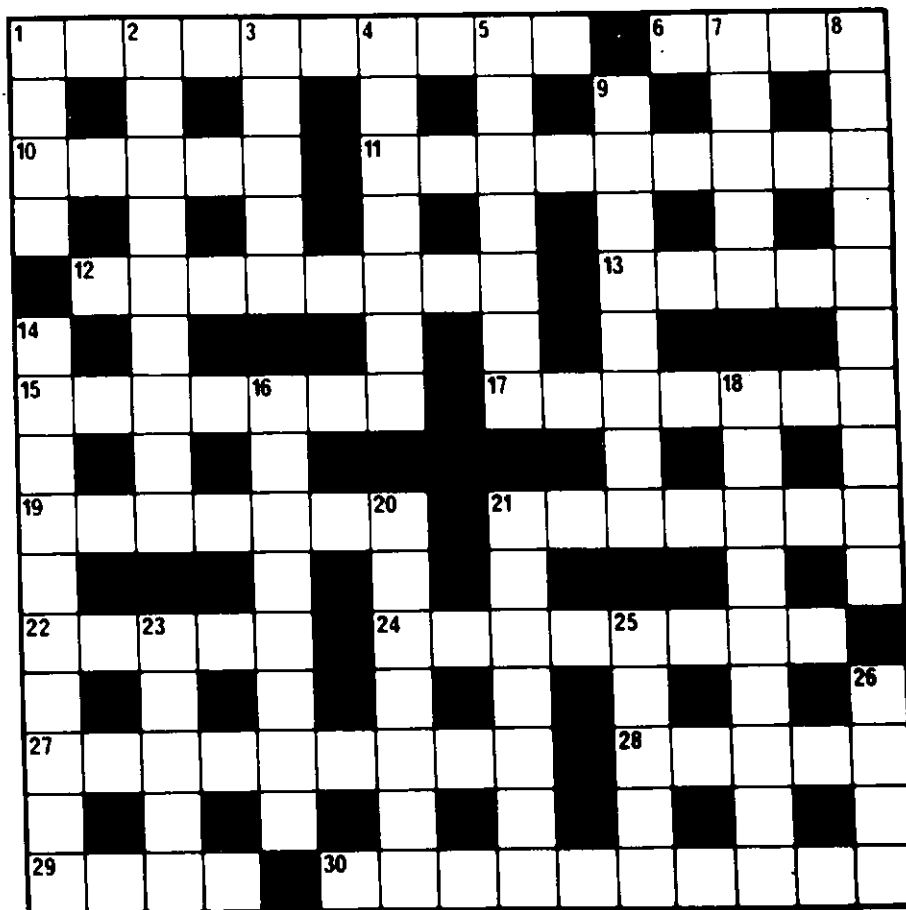
In the first part of this book we find an exposition of the basic physical-organic principles involved and a discussion of relevant experimental methods. Emphasis is on nucleophilic participation in reactions involving carbocations. This section will be heavy reading for the uninitiated, and the terse review of MO calculations concerned with the question of bridging in carbocations tends to bring out the fact that the theoretical approach has yet generated more heat than light. Part 2 marks the start of a systematic survey arranged according to the participating atom or group. Treated here are neighbouring oxygen (ether, hydroxyl, hydroperoxide, oxime), sulphur (thioether, thiol), and nitrogen (amino, nitrile, and hydrazone). The preface promises that Volume 2 will continue the systematic survey in covering neighbouring halogen, carbon (presumably the norbornyl cation controversy yet again), hydrogen, amide, ester, and organometallics; and will feature a survey arranged according to reaction type.

If the present high standard is maintained, the set should be of value to mechanistically and synthetically inclined organic chemists and, as a discussion of basic principles, to biochemists. It should be required by institutional libraries, but the price should keep it out of too many individual hands. The only other drawbacks are minor but irritating errors or omissions in a few structural diagrams.

D. J. McLennan



CHEMICAL CROSSWORD – By Mike



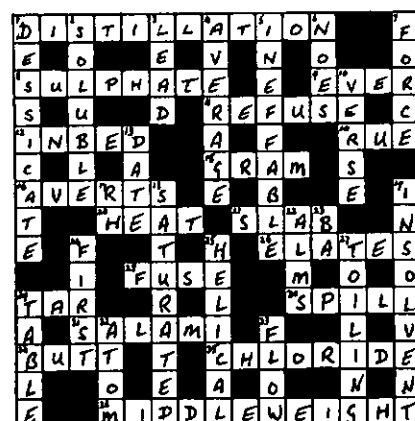
ACROSS:

- pH-pH-[H] is going forwards, not backwards – it comes out in the fire – or so we thought (10).
- 6,10. Sounds like an old tar (4,5).
10. See 6.
- Vulgar tongue about t' obtain confused freedom (7,2).
- 12,6. Useful in all seasons if taken with caution (1,5,2,4).
13. Complaint of constabulary losing 100 points ten times (5).
15. Little 15 plus 29 = 15 later in the year (7).
17. Writing about a nice pair (4,3).
19. Two peaks on the Main Divide (7).
21. Six and fifty about three for burning oil (7).
- 22,28. Heads against the wind, basically (5,5).
24. South African horse about, if producing 6 (8).
27. Fr. scientist relative to water? (9).
28. See 22.
29. Going into Berlin – or above (4).
30. About a vessel sees point badly and takes a new view of the situation (10).
3. Confused black takes a point, gives nothing away and changes colour (5).
4. Pretty yellow flowers? (7).
5. None left, no longer included (3,2,2).
7. Leg up to article, dancing on 9 (5).
8. But with a Fr. airport they do it properly (10).
9. Make a stab, but very accurately (8).
14. See 1.
16. Sounds like a fancy hat, but is less common in public (4,4).
18. Has another go to fit screen, perhaps (9).
20. What London had before (or so Dick believed) – now its less fancy (7).
21. Gases causing faintness (7).
23. A goddess of entertainment? (5)
25. T'is used up in Irish Republic as 6,10 (5).
26. Help destroy street but leave it unchanged (2,2).

DOWN:

- 1,14. Whistle for wind? or smoke?? (4,3,7).
- Parent of an orphan? (4,5).

Answer to the last Crossword



Carl Wilhelm Scheele

a sad tale if ever there was one



CARL WILHELM SCHEELÉ
1742-1786

It is said of Scheele that his record as a discoverer of new chemical substances is probably unequalled. Besides discovering chlorine and ten important acids including citric, he prepared oxygen a couple of years before Priestley.

Unfortunately for Scheele, he forgot to tell anyone about the oxygen and must have got quite inflamed when Priestley took all the limelight. Therein lies a moral: if you come across something big, don't let the news hang fire—tell as many people about it as you can. Which is why we're now going to say that 'Pronalys' analytical reagents are exceptionally pure chemicals ideal for use in the most exacting analytical procedures.

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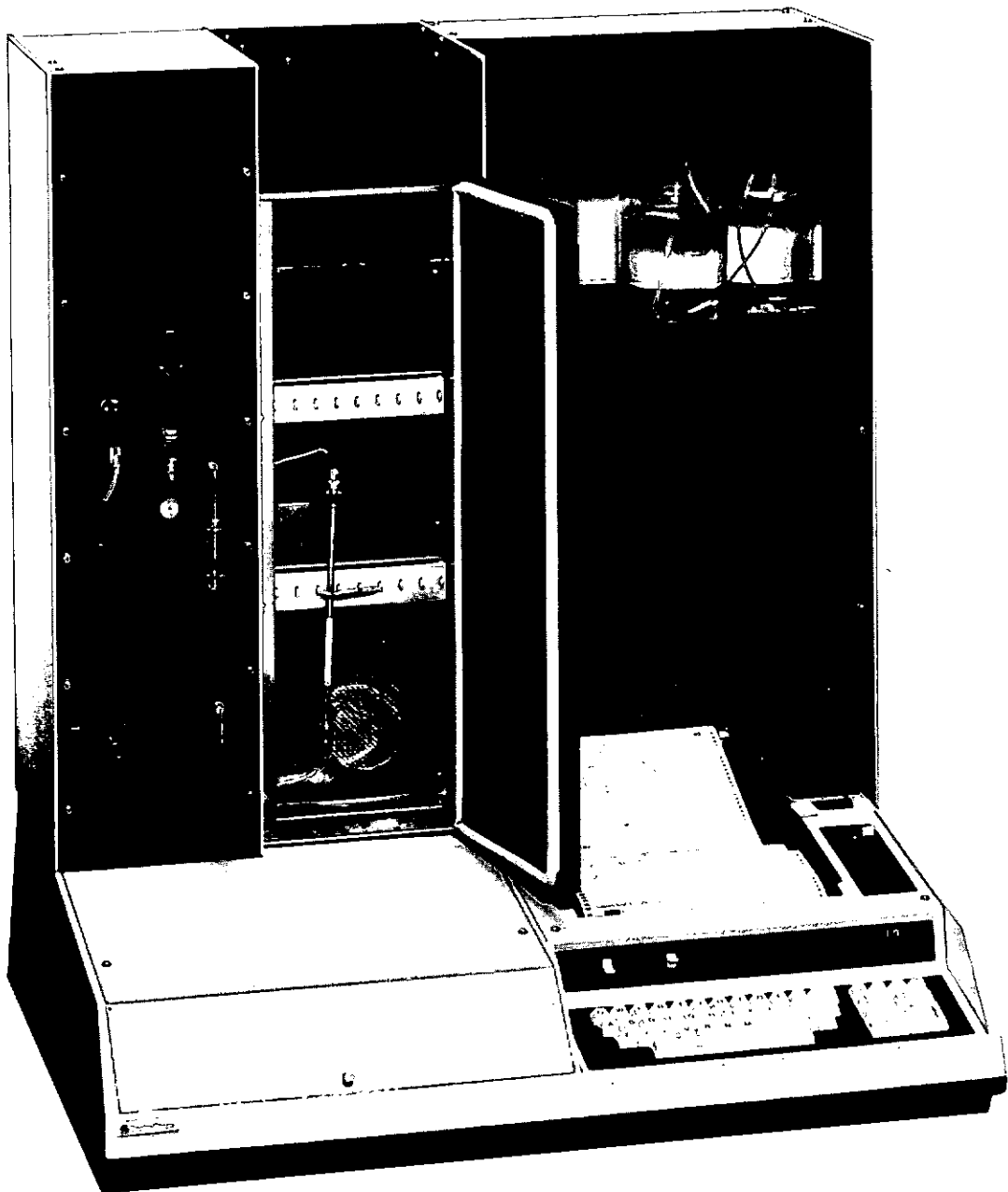
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