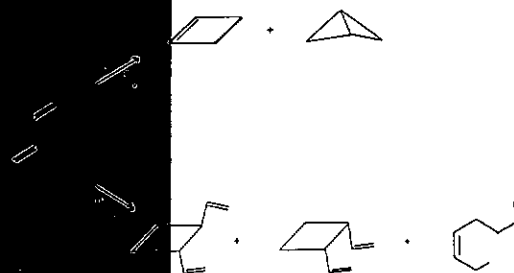


# CHEMISTRY IN NEW ZEALAND

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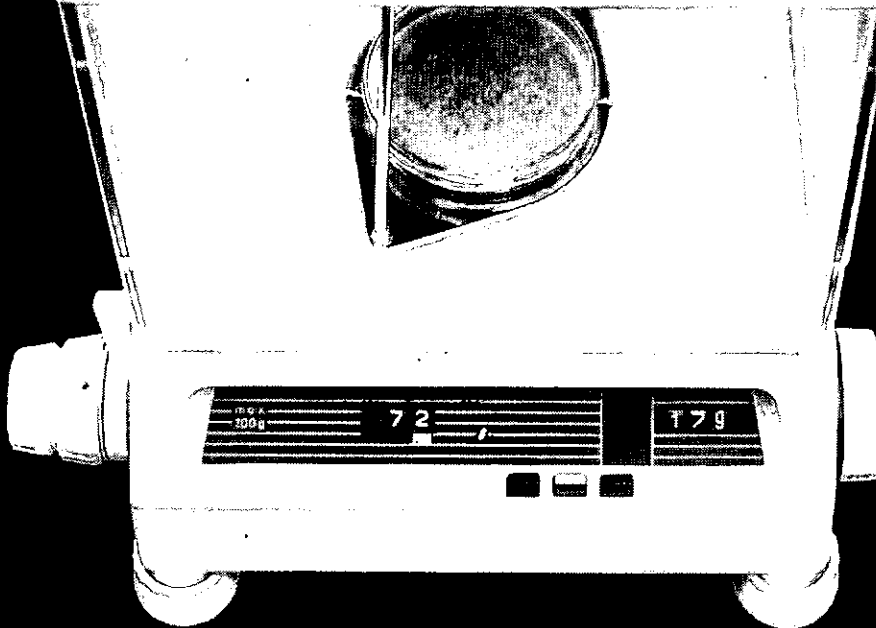
Vol. 35, No. 5, October, 1971

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# CHEMISTRY IN NEW ZEALAND

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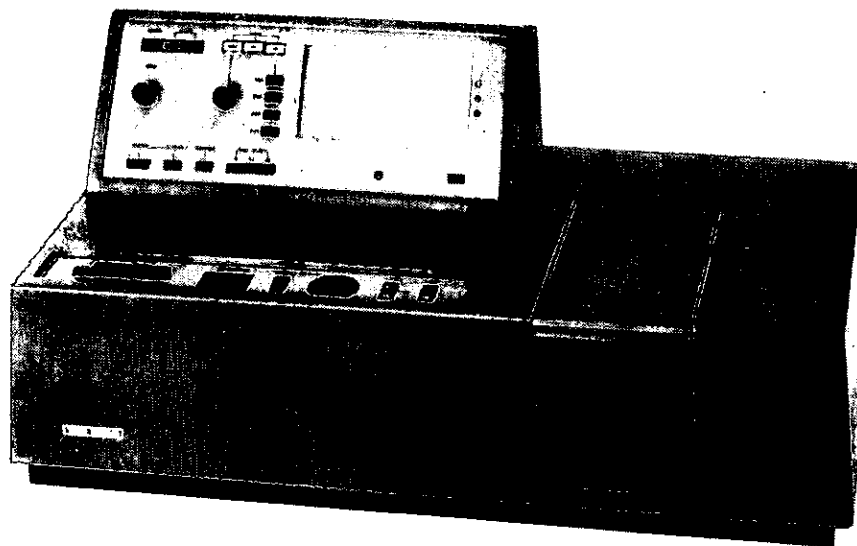
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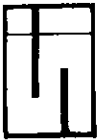
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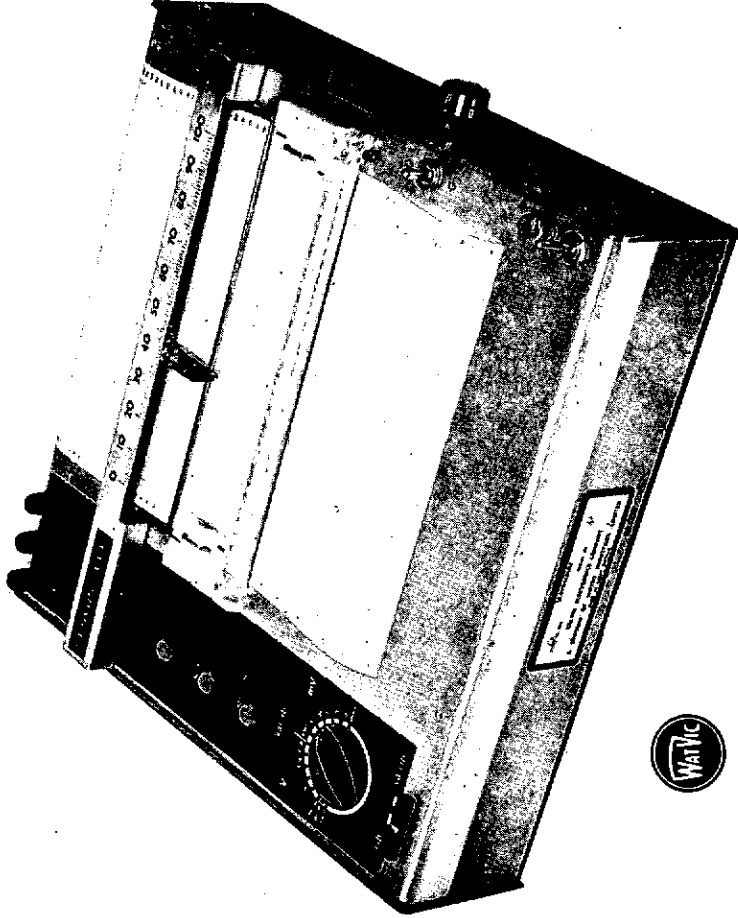
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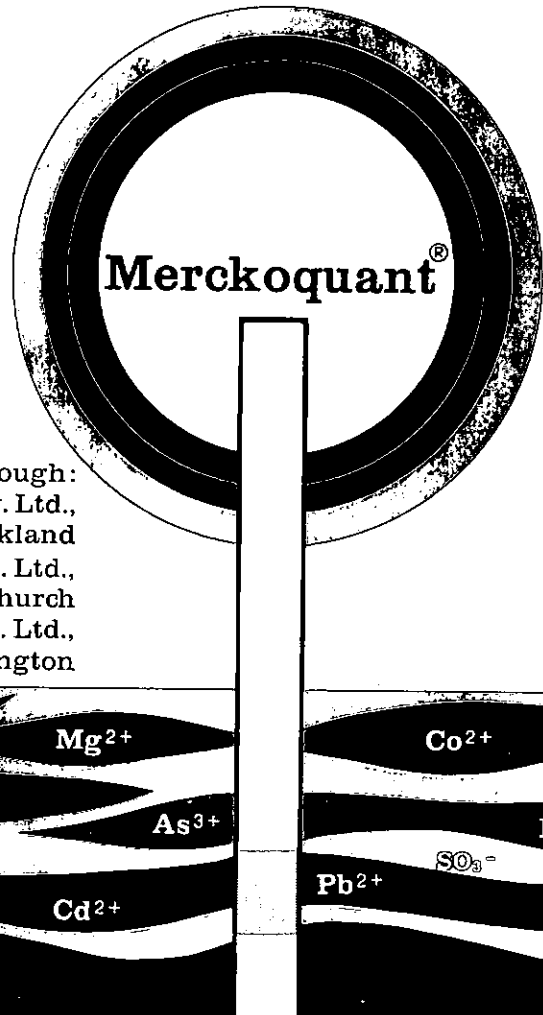
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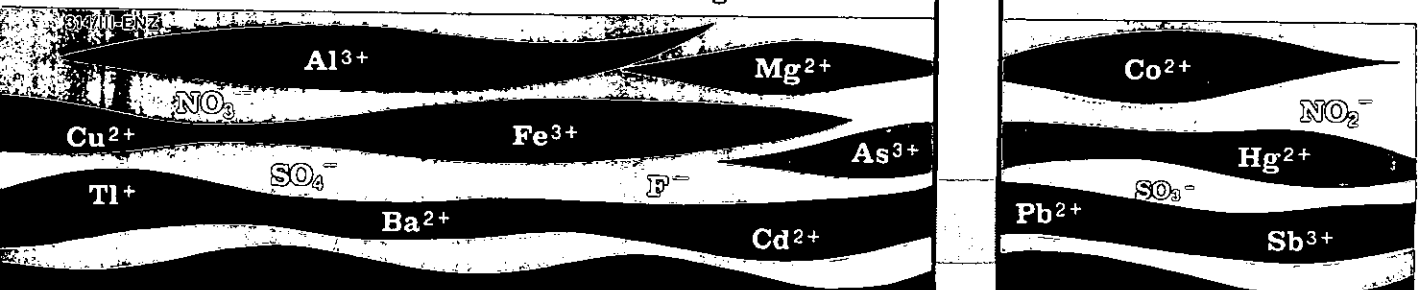
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## THE TRIPLET STATE

by B. Halton, B.Sc., Ph.D., A.N.Z.I.C. and Margaret P. Halton, M.Sc., Ph.D.,  
Department of Chemistry, Victoria University of Wellington, Wellington.

The absorption of radiation by a molecule in the ultraviolet or visible regions of the electromagnetic spectrum leads to electronic excitation and the formation of excited singlet and triplet species high in energy. Interest in these excited states first arose from the interpretation of the phenomena of fluorescence and phosphorescence where deactivation to the ground state occurs, but with the increased activity in the field of organic photochemistry<sup>1</sup>—chemical reactions proceeding from an excited state—a more detailed study of the triplet species has been necessary.

### The Nature of the Triplet State

In general, a molecule in its ground state has all of its electrons spin-paired with two in each molecular orbital.<sup>2</sup> On absorption of electromagnetic radiation, electronic excitation results in one electron being promoted from the highest occupied molecular orbital to the lowest unoccupied antibonding orbital.<sup>3</sup> Two possible electron spin arrangements may then result, that with the electron spins parallel being termed the triplet excited state, and that with the electron spins antiparallel (paired) being termed the

singlet excited state (Figure 1). The names singlet and triplet result from the multiplicity  $M$ , observed in atomic absorption or emission spectra where  $M = 2S + 1$ ,  $S$  being the total electron spin of the system. Thus in the excited state with parallel electron spins,  $S = 1$  and hence  $M = 3$  (triplet), and for the species with antiparallel electron spins,  $S = 0$  and  $M = 1$  (singlet). The first excited singlet and triplet states are denoted by  $S_1$  and  $T_1$  respectively, and the ground state singlet by  $S_0$ . Higher excited states,  $S_2$ ,  $T_2$  etc., would result from the promotion of an electron to a higher molecular orbital as is observed in flash photolysis. Not all molecules exist in their ground states as singlet species  $S_0$  and, although a ground state triplet is unusual, oxygen and nitric oxide provide the most noted examples.

The potential energy curves of a typical organic molecule are shown in Figure 2 where the excited triplet state is of lower energy than the corresponding singlet. This is supported by both theoretical and experimental data and results from the maximum multiplicity (parallel spins) of the triplet state being preferred, in accord with Hund's rule. Furthermore, the geometries of the ground state singlet, excited singlet, and excited triplet state differ at their energy minima as a result of the differing electron distributions. Because a spin inversion is required for  $T_1$  to collapse to  $S_0$ , with loss of excitation energy, the lifetime of the excited triplet state is longer than that of the corresponding singlet state ( $10^{-5}$ — $10^{-8}$  sec. and  $10^{-9}$ — $10^{-6}$  sec. respectively) where no such spin barrier to deactivation exists.

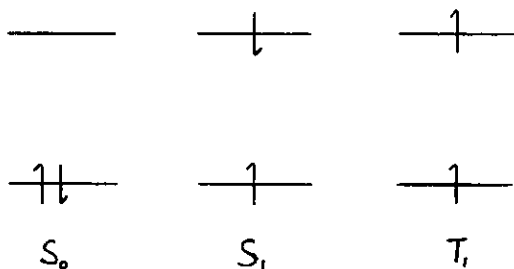


Figure 1  
Molecular Orbital Spin States

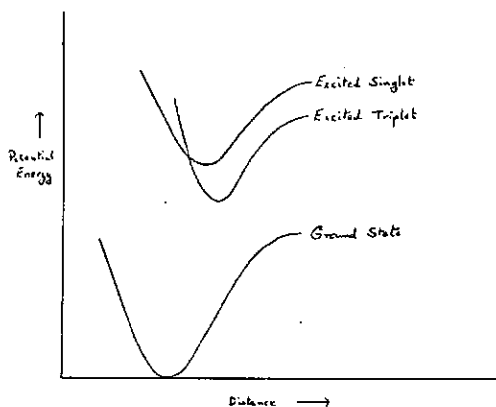


Figure 2  
Potential Energy Diagram

### Population of the Triplet State

A high triplet state population cannot be obtained by direct irradiation of a molecule, since singlet to triplet ( $S_0 \rightarrow T_1$ ) excitation is spin forbidden by quantum mechanics. Theory predicts that there should be no  $S_0 \rightarrow T_1$  absorption, whereas in practice weak bands for this transition are observed in the ultraviolet spectra of a variety of molecules, together with strong bands due to the allowed  $S_0 \rightarrow S_1$  transitions. The intensity of a given ultraviolet absorption band, measured by the extinction coefficient  $\epsilon$ , corresponds to the probability of the transition occurring. Thus for  $S_0 \rightarrow S_1$  transitions  $\epsilon$  is *ca.*  $10^5$  while for  $S_0 \rightarrow T_1$  transitions  $\epsilon$  is *ca.*  $10^{-2}$ . The reason that very weak absorption occurs at all is because the true nature of a given state, singlet or triplet, includes some mixing with other states. Thus the first excited triplet state  $T_1$ , is more accurately described as being largely  $T_1$  with small components due to  $S_0$ ,  $S_1$ ,  $T_2$ , and perhaps other excited states. A complete theoretical description of the  $S_0 \rightarrow T_1$  transition must therefore incorporate such mixing, and the outcome of this is a correct prediction of weak absorption due to the three components (a—c):

- (a) Interaction between the electron spin vector and the orbital angular momentum vector (spin-orbital coupling) occurs between  $S_1$  and  $T_1$  and some  $S_1$  character must be included in the description of  $T_1$ . Thus weak absorption will arise from the  $S_0 \rightarrow S_1$  character of the transition.
- (b) Further spin-orbital coupling, between  $S_0$  and the triplets  $T_1 \dots T_k$ , must also be included and thus there will be a contribution from the allowed  $T_1 \rightarrow T_k$  transitions.
- (c) The mixing between  $S_0$  and  $T_1$  results in contributions to the absorption band intensity by the  $S_0$  and the  $T_1$  dipole moments.

The  $S_0 \rightarrow T_1$  absorption band intensity can be further enhanced by the presence of heavy atoms in the molecule which characteristically have greater spin-orbital coupling. For example, 9,10-dibromoanthracene has more intense  $S_0 \rightarrow T_1$  absorption bands than anthracene itself.

While the direct  $S_0 \rightarrow T_1$  transition can be rationalised, the low intensities of the absorption maxima observed preclude this from being an effective method of obtaining a high triplet state population.

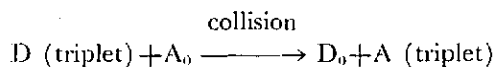
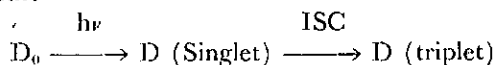
Transitions from ground state singlet to excited singlet occur with spin conservation and are therefore allowed, occurring with high extinction coefficients. Consequently, absorption of radiation by a chromophore will give rise to a high excited singlet state population. For a molecule whose excited singlet and triplet states are of comparable energy, a transfer from  $S_1$  to  $T_1$  can occur when the energies of the two states are identical, corresponding to the point where the singlet and triplet energy curves cross (Figure 2). Such a process is termed *intersystem crossing* and is a radiationless transfer. The excited triplet so formed is in a high vibrational level and rapidly passes to the lowest level, with the evolution of heat. Con-

sequently, the excited triplet once formed cannot readily revert to the parent singlet state. Successive transfers from  $S_1$  to  $T_1$  in this manner result in a significant triplet state population. The efficiency of intersystem crossing can be described by the quantum yield  $\Phi_{st}$  which is defined as:

$$\Phi_{st} = \frac{\text{number of triplets formed}}{\text{number of photons absorbed}}$$

Carbonyl compounds provide the most noted examples of this process with high quantum yield.

Not all molecules possess efficient intersystem crossing, and for these systems an alternative route to the triplet state must be used. This involves the transfer of excitation energy on collision and is known as *sensitisation*. Collision between a ground state molecule, an acceptor  $A_0$ , and an excited triplet state species, a donor  $D$ , can result in the transfer of excitation energy and formation of triplet state acceptor and ground state donor, with conservation of spin:



D = donor (e.g. carbonyl compound);

A = acceptor (e.g. olefin).

ISC = intersystem crossing.

For sensitisation to be effective, the donor molecule must have an efficient intersystem crossing process to the first excited triplet, which must be sufficiently long lived to allow

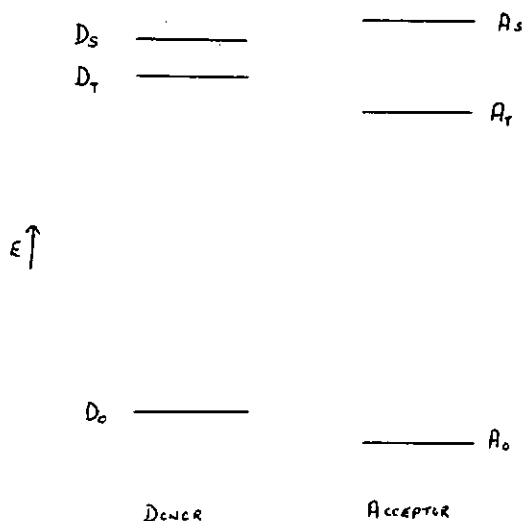


Figure 3

Energy Level Diagram for Sensitisation

collision to occur (*ca.*  $10^{-9}$  sec.). Furthermore, it is important that the energy of the donor triplet be greater than that of the acceptor triplet state while, at the same time, the donor singlet state should be lower in energy than the acceptor singlet state (Figure 3) to prevent singlet excitation of the acceptor by singlet donor.

Sensitisation is well illustrated by the naphthalene-benzophenone system. The criteria outlined above for the donor species (sensitiser) are satisfied by benzophenone, and triplet excited naphthalene is formed quantitatively when a benzene solution 0.1 M in benzophenone and naphthalene is irradiated at 370 nm where only benzophenone absorbs (Table 1). Sensitisation is therefore

TABLE I  
Excited State Properties

Species	$E_1$ , $10^{-5}$ J mole $^{-1}$	$\lambda$ nm	$E_3$ , $10^{-5}$ J mole $^{-1}$	$\tau$ sec	$\Phi$ st
Benzophenone	3.75	320	2.55	$10^{-9}$	0.4
Naphthalene	3.27	367	2.87	$10^{-5}$	1.0

the method of choice for populating the triplet state when intersystem crossing is inefficient.

### Characteristics of the Triplet State

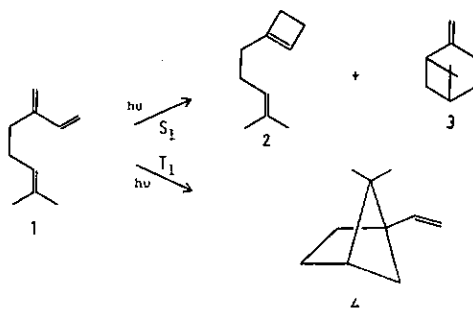
Deactivation of a triplet species by the emission of radiation and conversion to the singlet ground state gives rise to the phenomenon of phosphorescence which is characteristic of the radiative interconversion of states with dissimilar spin. Both fluorescence (radiative interconversion of states with the same spin) and phosphorescence have been known for a considerable time, but it was only in 1944 that Lewis and Kasha established that phosphorescence was characteristic of the  $T_1 \rightarrow S_0$  conversion. The presence of a weak absorption band in the ultraviolet spectrum of a molecule is further evidence for the existence of a triplet species, and was first shown to be due to a  $S_0 \rightarrow T_1$  transition by Sklar from the weak absorption at 340 nm in the benzene spectrum.

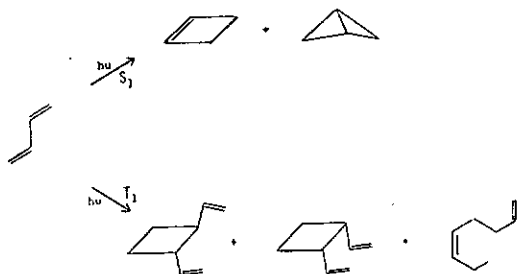
A molecule in its triplet state has two unpaired spin-parallel electrons and is therefore paramagnetic. However, paramagnetism alone does not characterise the triplet state since a diradical can also exhibit the same magnetic properties. By far the best diagnostic tool for identifying a triplet species is electron spin resonance (esr).<sup>4</sup> A triplet species consists of a set of three sublevels which arise from the magnetic quantum numbers,  $M_s = \pm 1$  or  $0$ , since the total spin  $S = 1$ . In an external magnetic field these sublevels are split and the esr technique observes transitions between them. Even in the absence of an external magnetic field, splitting can occur due to the total electron environment and this is known as "zero field splitting". Initially applied to an examination of the naphthalene triplet, the esr technique has become increasingly important in both diagnosis and examination of the triplet state. Triplet state lifetimes can be determined from the decay of the esr signal and information about  $\pi$ -electron delocalisa-

tion is obtained from variations in the zero field splitting with substitution. The zero field splitting is also characteristic of the mode of formation of the triplet state species such that  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  triplet excitation can be distinguished. Furthermore, the electron densities at different positions in the molecule can be obtained from the observed hyperfine splittings. Thus the applications of electron spin resonance are numerous,<sup>5</sup> and by this technique will be of value in understanding the energy transfer processes in protein molecules.

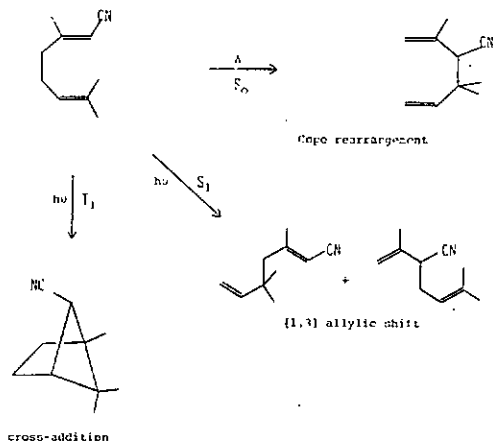
### The Triplet State in Photochemistry

The deactivation of an excited state species can occur by loss of excitation energy on collision with a ground state molecule (sensitisation or quenching); by emission of radiation (fluorescence or phosphorescence); by conversion to a high vibrational level of the ground state with subsequent loss of vibrational energy; or by chemical reaction. It is this last process that forms the vast field of photochemistry where reactions proceed from the excited singlet and excited triplet states.<sup>1</sup> In many instances the reaction products formed from the excited singlet and triplet states differ. Thus direct irradiation ( $S_1$ ) of myrcene (1) leads to the cyclobutane derivative (2) and  $\alpha$ -pinene (3), whereas the sensitised irradiation ( $T_1$ ) affords (4) as the sole product.



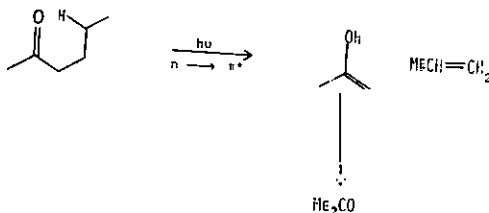
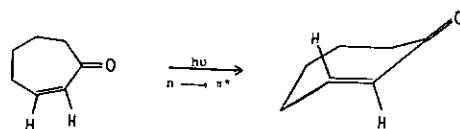
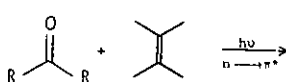


In like manner singlet butadiene gives the valence bond isomers cyclobutene and bicyclobutane, whereas the triplet state reaction results in dimeric products. The course of the reaction of a 1,5-diene is completely dependent on the electron state from which the reaction proceeds. The triplet state reaction results in cross-addition, the excited singlet state reaction leads to [1,3] migra-



tion across the allyl system, and in the ground state a Cope rearrangement is observed. The majority of the photochemical reactions of carbonyl compounds proceed

from the triplet state because of their efficient intersystem crossing.



Thus the rapidly developing field of photochemistry has led to renewed interest in the nature of the excited states involved, and because of its longer lifetime the triplet species is of prime importance.

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## OBITUARY

**Thomas Hagyard B.Sc., Ph.D.(Lond.), M.I.Chem.Eng., F.N.Z.I.C., M.N.Z.I.E.,  
Reader in Chemical Engineering, University of Canterbury.**

Tom Hagyard received his early education in Stockton-on-Tees. He graduated B.Sc. and Ph.D. from London University. After working for many years in industry in Great Britain he came to New Zealand in 1950 to take up an appointment as Senior Lecturer in Applied Chemistry at Canterbury University College.

In the twentyone years that followed, Hagyard played a major role in the growth of Chemical Engineering from a minor activity within the Chemistry Department to a full department with an academic staff of 11 members. He, more than anyone else, was responsible for the development of both breadth and depth in teaching and research in Chemical Engineering at Canterbury. He encouraged post-graduate research before it was generally recognised that this was an essential activity of an engineering department, and was himself one of the most active research workers in the Faculty of Engineering. His research activities revealed both his wide range of interests and his concern with the development of chemical industry in this country. Fundamental studies of electrode kinetics, work which received international recognition, was carried out alongside research on the production of chemicals from turpentine, studies of the production of plastics from indigenous raw materials, and investigations of the use of fluidisation for preventing the formation of sand bars at rivermouths and harbour entrances. It is a sad comment on the timidity of both industry and government that so many of Hagyard's efforts to arouse interest in development of New Zealand chemical industry were not followed up. His work, started almost ten years ago, on the manu-

facture of anode carbon from West Coast coal has recently, with the construction of the aluminium smelter at Bluff, begun to receive the recognition and support from government sources which it should have had much earlier. His efforts to promote chemical industry in this country did not stop at his own research. He provided encouragement and stimulus to his colleagues and was a constant goad to both industry and government.

In his teaching Hagyard set high standards. There are many of his former students who, though they perhaps did not appreciate his methods at the time they were undergraduates, now remember with warmth and respect the demands he made of them.

The esteem in which Hagyard was held by his former students was shown at a symposium held in May of this year. Almost half of all graduates from the department returned from all parts of the world to help celebrate his twenty-one years at Canterbury, and to honour him in the year of his impending retirement. The record of this symposium is a lasting tribute to the man and to his work.

His sudden death on 9 August came as a shock to his friends and colleagues, and brought to an untimely close a major chapter in the growth of the University of Canterbury.

Tom Hagyard's influence, through the men he trained and through his research, will however, be felt for many years to come and many developments in New Zealand chemical industry yet to take place will trace their origin back to him.

—A.G.W.

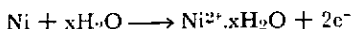
## THE ANODIC DISSOLUTION OF NICKEL\*

G. T. Burstein

(Chemistry Department, University of Auckland, Auckland, New Zealand)

For some decades now, the mechanisms by which metals anodically corrode have been the subject of investigation. My own work is a mechanistic study of the anodic dissolution of nickel, and its relationship to those of iron and cobalt. Owing to its extensive industrial use, iron has been studied widely; cobalt and nickel less so. Even so, strong disagreement still exists for all three metals despite the fact that the mechanisms seem to resemble one another closely.

Let us examine first a potential-pH diagram for nickel. Figure 1 is a so-called Pourbaix Diagram. This is a plot of equilibrium potential vs. pH for the nickel-water system. It can be seen that up to a pH of about 6, nickel is in equilibrium with its aqueous species. Thus if nickel is anodised in this region, aqueous nickel 2+ ions should be formed.



There should be no solid film, and the metal should dissolve freely and continuously. This is so-called active dissolution. As the potential increases further, a solid phase can be formed. This phase which is stable, compact and adherent to

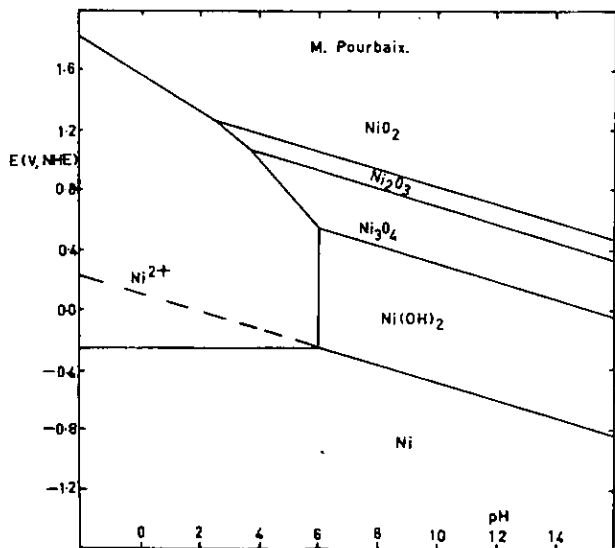
POTENTIAL-pH DIAGRAM FOR Ni-H<sub>2</sub>O SYSTEM AT 25°C

Fig. 1

\*This paper was awarded the Institute Prize in the Students' Papers Session at the N.Z.I.C. Conference, 1970.

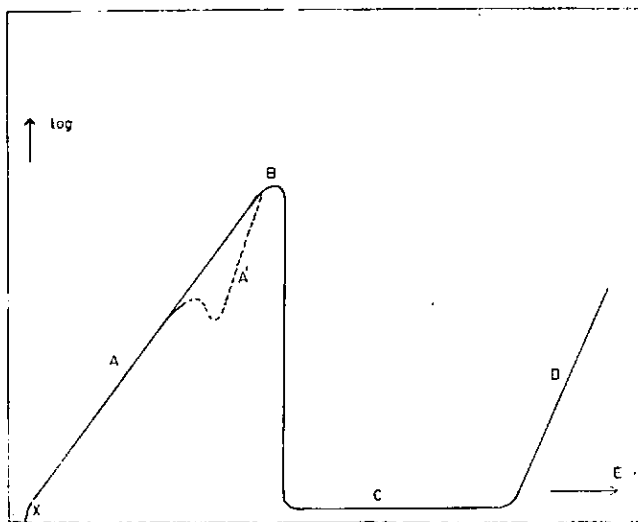


FIGURE 2—General Anodic Polarisation Curve for Nickel

- A — Active dissolution of nickel  
 $\text{Ni} \rightarrow \text{Ni}^{2+}(\text{aq}) + 2e^-$
- A' — Pre-passive film present on metal surface
- B — Flade Potential. Passivation occurs  
 $\text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + 2\text{H}^+ + 2e^-$   
or  $\text{Ni} + 2\text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2 + 2\text{H}^+ + 2e^-$
- C — Passive nickel
- D — Transpassive nickel  
 $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$
- X — Cathodic reaction becoming important.

the electrode surface, blocks the passage of a current, and the metal is said to be passivated. At  $\text{pH} > 6$  no soluble ion is formed, and a thick film of the oxide or hydroxide predominates.

It will be shown that the metal-oxide line may be extrapolated back into the active region, where it represents formation of a meta-stable film of some molecular layers in thickness. Both iron and cobalt exhibit similar characteristics in the potential-pH diagram, but on different scales.

Consider next the general characteristics of an anodic polarisation curve for nickel in acid solution as shown in Figure 2. As the potential  $E$  is increased, active dissolution occurs to give aquated  $\text{Ni}^{2+}$ . For this region the current density  $i$  follows the plot  $\log i \propto E$ . This is the particular region

I am studying. As the potential rises the current reaches a maximum and then suddenly drops, almost to zero. At this potential, known as the Flade potential, a film of metal oxide has been formed over the electrode surface and passivation occurs. The electrical resistance of the film causes the current to drop. As the potential increases, the film grows slightly with the current barely increasing. Finally the so-called transpassive region is reached and the potential once again becomes proportional to  $\log i$ . At this stage the film itself may be oxidised to some soluble species, or as it occurs on nickel,  $O_2$  may be evolved.

The region I am studying is therefore the active region where  $E \propto \log i$ . The Tafel equation, which dates back to 1905, is more accurately

$$E = a + b \log i$$

$$b = \text{Tafel slope} = \frac{2.3RT}{\beta nF} = \frac{\partial E}{\partial \log i}$$

$$a = \frac{2.3RT}{\beta nF} \log i_0$$

where  $R$  = gas constant,  $T$  = absolute temperature,  $F$  = Faraday =  $96,500 \text{ C mol}^{-1}$ ,  $n$  = number of electrons lost in the rate determining step of the electrode reaction, and  $\beta$  is the transfer coefficient, which in general terms gives a measure of the symmetry of the energy barrier in the reaction, where  $0 < \beta < 1$ . In practice  $\beta = \frac{1}{2}$  approximately.

Finally, the exchange current density  $i_0$  is equal to the individual anodic and cathodic densities  $i_a$  and  $i_c$  respectively, at the equilibrium potential. No net current flows, so  $i_a = i_c = i_0$ . Thus by plotting  $E$  vs.  $\log i$ ,  $a$  and  $b$  may be obtained and hence  $\beta$  and  $n$ .

Experimentally the potentiostatic sweep technique was used. Figure 3 shows a block diagram of the circuit. A selected ramp potential is fed from the wave generator into a potentiostat which in turn gives out a similar ramp with respect to a reference electrode. The potentiostat also produces the requisite current to flow through the nickel electrode and a platinum counter electrode. The current is measured as the voltage across a standard resistor, and the potential is measured between the nickel and reference electrodes. These are recorded on an X-Y recorder or an oscilloscope. The nickel electrode is in the form of a rotating disc electrode encased in glass. Rotation is carried out to minimise diffusion control.

Consider now a set of results obtained by anodising nickel in 1M perchloric acid. A set of consecutive readings is shown in Table 1. Good linearity occurs over a limited region giving an average slope  $b$  of 90 mV per decade of current. The scatter however is fairly wide. This scatter is also shown by inspecting values of the current density taken at a particular potential. As can be seen,

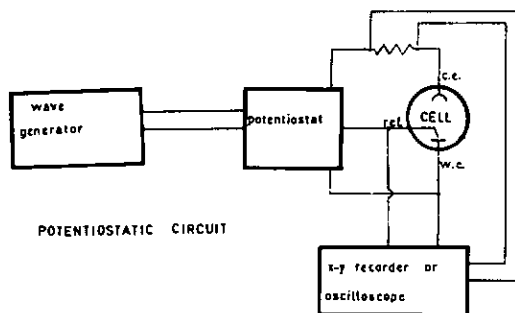


Figure 3

w.e. — nickel working electrode  
c.e. — platinum counter electrode  
ref. — saturated calomel reference electrode

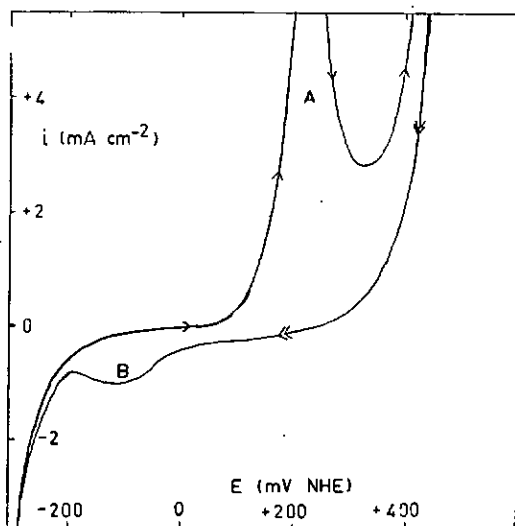


Figure 4

Anodic dissolution of nickel, showing pre-passive film formation peak (A), and film reduction peak (B).

Electrolyte 1M  $HClO_4$

Forward sweep rate  $33 \text{ mV s}^{-1}$  ———→

Reverse sweep rate  $333 \text{ mV s}^{-1}$  — — —

hysteresis almost always occurs between the forward and backward sweeps. The hysteresis has been the cause of much difficulty in the interpretation of the results. It appears to be irregular and exhibits a slow drift with time.

The lower part of Table 1 shows some results obtained by other workers under slightly differing conditions, and showing enormous variation. For a Tafel slope of 120 mV, the rate-determining step is a one-electron loss ( $n = 1$ ,  $\beta = 0.5$ ). For a slope of 60 mV the slow step can be a simultaneous 2-electron loss ( $n = 2$ ,  $\beta = 0.5$ ) or a single electron loss. A typical Tafel line takes the form shown in Figure 2. When forward and reverse sweeps are included, hysteresis is encountered with the reverse sweep lower than the forward sweep. Hysteresis also occasionally occurs with the forward sweep at lower current than the reverse sweep. It is found that well before complete passivation occurs, a hump appears in the polarisation curve (shown dotted in Figure 2) where the current drops briefly, and then continues to rise. This hump is an all-important factor for it indicates the presence of a "pre-passive" film on the metal surface—a film which passivates the metal partially, and then permits further active dissolution.

This pre-passive film, if indeed it does occur, should be able to be reduced and its reduction observed. However, the film is only meta-stable, since it is directly soluble in the strongly acid electrolyte. Once it is formed it undergoes continuous formation at the metal-film interface, but also undergoes continuous dissolution at the film-electrolyte interface. Thus, to establish its presence a forward sweep must be made to enable the film to form initially, and then a high-speed reversed sweep may record a film-reduction peak, provided the sweep is sufficiently rapid to allow some oxide to remain by the time the reduction potential is reached. Such a sweep is shown in Figure 4. The forward sweep was made at 33 mV sec<sup>-1</sup> and although the sweep has gone off scale, a large film formation hump (A) was observed. The reverse sweep made at 333 mV sec<sup>-1</sup> shows a cathodic hump (B) at a potential slightly more positive than that for cathodic hydrogen evolution. Calculation shows that peak B corresponds to the reduction of 2 molecular layers of oxide film over the entire electrode area. Notice that the cathodic peak B is considerably smaller than the anodic peak A, implying that the film had partially dissolved in the electrolyte before the reduction potential was reached.

TABLE 1. Anodic Dissolution of Nickel

G. T. Burstein, 1969  
25°C 860 r.p.m. 1.00M HClO<sub>4</sub>  
Potential Sweeps

$\frac{dE}{dt}$ mV sec <sup>-1</sup>	Sweep Direction	b mV	i (240 mV) mA cm <sup>-2</sup>
3	+	96	4.4
3	—	96	4.4
3	+	97	3.3
3	—	88	4.6
8	+	91	4.0
8	—	91	4.0
8	+	90	3.7
8	—	78	4.0
17	+	92	3.7
17	—	81	3.7
1.7	—	91	2.2 +
1.7	+	80	4.6 —
3	+	93	2.8
3	—	85	8.5
3	+	95	5.9
3	—	92	8.4

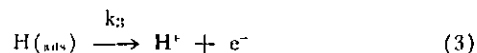
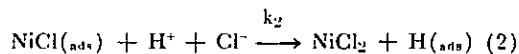
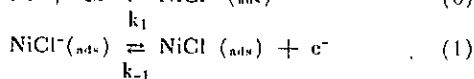
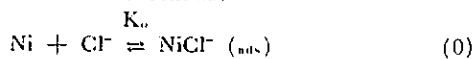
Mean i (240 mV) = 4.5 ± 1.2 mA cm<sup>-2</sup>

Mean b = 90 ± 5 mV

In order to deduce a mechanism for the purely active dissolution process, sweeps were made in concentrated perchloric acid, and also in another electrolyte consisting of fluoride ions in an acetate buffer at pH 5. Both of these failed to eliminate film formation, although some interference with passivation was shown by  $F^-$ .

However, runs done in the presence of chloride ions shows that chloride accelerated the reaction to such an extent that the active region lay well below the metastability line in the Pourbaix diagram (shown as dotted line in Figure 1). These results, together with some others, are shown in Table 2.

From these results a mechanism can be postulated, although this is far from proven. The mechanism is as follows:



Coverages of adsorbed species:

$$\begin{aligned} NiCl^-(ads) & \theta_1 \\ NiCl(ads) & \theta_2 \\ H(ads) & \theta_3 \\ Ni & (1-\theta_1-\theta_2-\theta_3) \end{aligned}$$

where  $0 < \theta < 1$

Assumptions (a)  $\theta_2 \ll \theta_1$ ,  $\theta_3 \ll \theta_1$

(b) The Langmuir isotherm holds for reaction (0), i.e.,  $\theta_1 < 0.2$  or  $\theta_1 > 0.8$ .

(c)  $NiCl(ads)$  is in a steady state,

$$\text{i.e. } \frac{d\theta_2}{dt} = 0$$

TABLE 2. Anodic Dissolution of Nickel

Electrolyte	pH (*H <sup>+</sup> activity)	Results		Comments
		25°C;		
Rotating Disc Electrode;		Potential Sweep Method		
		Average Tafel Slopes (mV)		
		+ve sweep	-ve sweep	
1M HClO <sub>4</sub>	0	93	86	severe hysteresis; pre-passive film formed on metal surface
conc. HClO <sub>4</sub> (11.5N)	* very large	123	91	hysteresis; pre-passive film formed on metal surface
1M HOAc, 1M NaOAc NaF up to 0.46M	4.75	104	severely curved	severe hysteresis; pre-passive film formed on metal surface
HCl, HClO <sub>4</sub> such that [HCl] + [HClO <sub>4</sub> ] = 5M	* 13 to 23	$b = 117 \text{ mV}$ maximum $\frac{\partial \log i}{\partial \log [Cl^-]} = 1$		very little hysteresis; no film formed
HCl + HClO <sub>4</sub> such that [HCl] + [HClO <sub>4</sub> ] = 1M	0	$b = 60 \text{ mV}$ minimum $\frac{\partial \log i}{\partial \log [Cl^-]} = 2$		very little hysteresis; no film formed
HCl + NaCl such that [HCl] + [NaCl] = 1M	3 to 0	$b = 60 \text{ mV}$ minimum $\frac{\partial \log i}{\partial \log [H^+]} = 1$		very little hysteresis; no film formed

$$K_0 = \frac{\theta_1}{(1-\theta_1)[Cl^-]}$$

$$v_1 = k_1\theta_1 \exp\left\{\frac{\beta FE}{RT}\right\}$$

$$v_{-1} = k_{-1}\theta_2 \exp\left\{\frac{(\beta^{-1})FE}{RT}\right\}$$

$$v_2 = k_2\theta_2 [Cl^-][H^+]$$

$$v_3 = k_3\theta_3 \exp\left\{\frac{\beta FE}{RT}\right\}$$

Also  $i = 2Fv_2$

By employing the above assumptions,

$$i = \frac{2FK_0k_1k_2[Cl^-]^2[H^+] \exp\left\{\frac{\beta FE}{RT}\right\}}{(1 + K_0[Cl^-])\left(k_{-1} \exp\left\{\frac{(\beta^{-1})FE}{RT}\right\} + k_2[Cl^-][H^+]\right)}$$

Assume

$K_0$  to be sufficiently small that  $K_0[Cl^-] \ll 1$

$$\text{Then } i = \frac{2FK_0k_1k_2[Cl^-]^2[H^+] \exp\left\{\frac{\beta FE}{RT}\right\}}{k_{-1} \exp\left\{\frac{(\beta^{-1})FE}{RT}\right\} + k_2[Cl^-][H^+]}$$

Case (a) For high E or high  $[Cl^-][H^+]$

$$k_2[Cl^-][H^+] \gg k_{-1} \exp\left\{\frac{(\beta^{-1})FE}{RT}\right\}$$

$$i = 2FK_0k_1[Cl^-] \exp\left\{\frac{\beta FE}{RT}\right\}$$

Predicts:

$$\text{For } \beta = 0.5, \quad b = 120 \text{ mV}$$

$$\frac{\partial \log i}{\partial \log [Cl^-]} = 1$$

Reaction (1) is rate determining

Case (b) For low E or low  $[Cl^-][H^+]$

$$k_2[Cl^-][H^+] \ll k_{-1} \exp\left\{\frac{(\beta^{-1})FE}{RT}\right\}$$

$$i = 2FK_0k_1k_2[Cl^-]^2[H^+] \exp\left\{\frac{\beta FE}{RT}\right\}$$

where  $K_1 = k_1/k_{-1}$

Predicts:

$$b = 60 \text{ mV, and independent of } \beta.$$

$$\frac{\partial \log i}{\partial \log [Cl^-]} = 2, \quad \frac{\partial \log i}{\partial \log [H^+]} = 1$$

Reaction (1) is in rapid equilibrium compared with reaction (2), which becomes rate limiting.

These results are in agreement with the observed values.

The chloride acceleration means that the whole Tafel line is shifted to more negative potentials. The metastability line is not reached and the dissolution process is purely active. Free nickel atoms here refer to those atoms not covered by  $Cl^-$ , and these may be covered by  $H_2O$ . However, because of the lowered potential, dissolution proceeds only through the chloride path, and adsorbed water would merely serve to block some of the surface from dissolution.

In 1M  $HClO_4$ , the mechanism seems to be of a similar nature, except that it is complicated by a film formation. The perchlorate ion itself is assumed to play no role in the mechanism and is merely a spectator ion. Adsorbed hydrogen atoms may or may not be formed, but the mechanism appears to involve two consecutive electron transfer reactions.

The biggest practical problem in this work has been the slow drift characteristics and the related hysteresis. It seems that the drift characteristics of a metal under these conditions are directly related to its physical hardness. Studies similar to the type just described made on soft metals such as bismuth, thallium, lead, and mercury show almost no hysteresis or drift. These are non-transition metals whose valence electrons are in s and p orbitals, and which have filled d orbitals. The transition metals such as iron, cobalt and nickel are physically much harder and show steady drift and large hysteresis. Because of their hardness, which is related to the stronger metal-metal bonds formed by d-orbitals, these metals require large overvoltages to get them to dissolve at all. The atoms of transition metals are difficult to withdraw from the surface. It is probable that the atoms at corners and kink sites on the surface dissolve more readily than the others and the number of kink sites changes continuously. On a macroscopic level these kink sites are shown as crystal edges. Figure 5 shows the surface of nickel after anodisation in 5M  $HCl$ . The surface has become rough and deeply pitted, with the appearance of a random crystal face structure. This provides a large number of corners and edges from which dissolution may proceed. On a microscopic level these can be imagined as corners and edges of atomic dimensions. As kink sites are lost, more are generated and drift occurs.

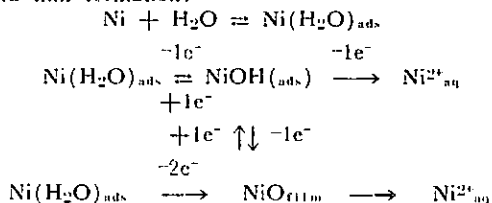


Figure 5

Nickel electrode surface after anodising in 5M HCl. The electrode shows deep pitting (dark patches) and appearance of etched crystal faces (paler patches).

Electrode diameter—0.5 cm. Encased in glass and sealed with epoxy-resin.

Using all the data this far, a mechanism may be postulated, including both active dissolution and film formation:



It must be realised, however, that this mechanism is as yet tentative, pending further investigation.

The process of this mechanism is shown in Figure 6. A nickel atom loses one electron and breaks off from a kink site to form a Ni(I) intermediate which then loses the second electron to form either a film of NiO or an aqueous species ejected into the electrolyte. The film also dissolves in the acid to produce the aqueous species.

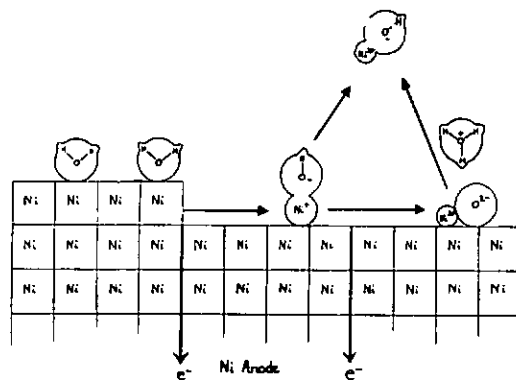


Figure 6

Schematic diagram of electrode surface showing the anodic dissolution mechanism in perchloric acid. (see text).

Further studies will include very high speed sweeps, and relaxation studies, firstly in an attempt to eliminate film formation and obtain a purely active process, and secondly to study the film formation itself.

**Acknowledgement.** I extend my sincere thanks to Associate Professor G. A. Wright for his help throughout this work, and to Mr. P. T. Wilson for many valuable discussions.

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2. R. R. Sayano and K. Nobe *Corrosion* (1966), 22, 81.
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5. K. E. Heusler and L. Gaiser *Electrochim. Acta* (1968), 13, 59.
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#### Ref.

#### Some Tafel Slopes Extracted from the Literature

1.	Hollnagel and Landsberg	87	0.2N H <sub>2</sub> SO <sub>4</sub> , 0.01N NiSO <sub>4</sub>
2.	Sayano and Nobe	48	1N H <sub>2</sub> SO <sub>4</sub>
3.	Sato and Okamoto	92	0.5M SO <sub>4</sub> <sup>2-</sup> , pH = 1.10
4.	Kronenberg, Banter, Yeager and Hovorka	120	ClO <sub>4</sub> <sup>-</sup> , pH = 2.5
5.	Heusler and Gaiser	66	HClO <sub>4</sub> , Ba(ClO <sub>4</sub> ) <sub>2</sub>
6.	Voigt	72	0.005M NiSO <sub>4</sub> , 0.1M HClO <sub>4</sub>

## UNDERSTANDING THE LIQUID STATE — THE DEVELOPMENT OF THE HARD SPHERE APPROACH

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It has been the custom for textbooks in chemistry to discuss at length the behaviour of gases and solids, and to devote but few lines to the behaviour of liquids. The explanation is simple. Until recently, discussions of the liquid state were confined mainly to the discipline of mathematical physics, and the results predicted from the obtuse theories contained therein were in bad disagreement with observed behaviour. In the past five years however, much progress in the study of liquids has been made, and the more concrete models now put forward give results in much better agreement with experiment. Here it is proposed to outline the development and success of one such model—the notion that the liquid state can be represented by the perturbed behaviour of hard spheres.

### Perfect States of Matter

The main problem in liquid state studies has been the absence of a concept of a perfect liquid. This is in contrast to the gaseous and solid states, where the concept not only exists, but is realised experimentally at room temperatures and pressures. For instance the equation of state of a perfect gas

$$pV = nRT \quad (1)$$

gives a very good account of real gas behaviour at room temperature and pressures up to 1 atmosphere. Similarly the equation which accounts for X-ray diffraction by perfect solids

$$N\lambda = 2d\sin\theta \quad (2)$$

is extremely useful in interpreting real crystal structures.

The perfect state for both phases can be understood in terms of the behaviour of hard spheres under certain conditions. For the gaseous phase we assume that the particles are at sufficiently low densities to allow random movement within the confines of the container, and to allow neglect of collisions between the particles, and particle size. For the solid phase we assume that the density of particles is high, and that they are stationary and arranged in an ordered array.

Unfortunately these appear to be the only cases in which at reasonably accessible temperatures and pressures matter does approach hard sphere behaviour. At pressures up to about 10 atmospheres, the experimental compressibility behaviour of gases can be represented by the virial equation

$$pV/nRT = 1 + B \left[ \frac{n}{V} \right] + C \left[ \frac{n^2}{V} \right] \quad (3)$$

B and C are known respectively as the second and third virial coefficients, and are both temperature dependent. They can both be calculated using statistical thermodynamics, provided some assumptions are made about the shape of the molecules and the function and range of the intermolecular potentials.

In the case of spherical particles where only forces between any pair of molecules need be considered, the second virial coefficient takes the form

$$B(T) = 2\pi N \int_0^{\infty} (1 - \exp(-\mu(r)/kT)) r^2 dr. \quad (4)$$

Here  $\mu(r)$  is the intermolecular pair potential, and N is the number of molecules. It has been found that there are several forms of the intermolecular potential which will reproduce experimental data, but these do not include the hard-sphere potential. It gives a value of B which is badly in error numerically, and which is temperature independent.

### Liquid State as a Very Imperfect Gas

The virial equation of state can be regarded as an extension of perfect gas behaviour into denser regions. Its success for moderately dense gases led to the hope that further extension of the series might lead to useful results for the liquid state. Unfortunately it has been shown that the series diverges well before liquid densities are reached. A similar result is obtained if the liquid is treated as a slightly disordered solid. Thus, neither of our perfect states will serve as a reference for liquids.

### p-V-T Behaviour of Hard Spheres

Are there other conditions of temperature and pressure in which matter approaches hard sphere behaviour? To answer this we need to know the p-V-T behaviour of hard spheres. It is now possible to simulate such behaviour using Molecular Dynamic and Monte Carlo techniques with high speed computers. In the Monte Carlo method a small number of particles (32) are given a large number of random configurations (10,000). For each configuration interactions between pairs of molecules are calculated using some predetermined

intermolecular potential, and the appropriate property of matter is obtained by averaging over all the configurations.

The result of such calculations done to obtain the compressibility factor,  $\frac{pV}{nRT}$  for hard spheres is

shown in Figure 1. The most remarkable feature of this graph is the discontinuity at a reduced density  $s_r$ , [ given by  $s_r = \frac{s}{s \text{ close packed solid}}$  ]

of about 0.7. It is at this density that the melting of real substances occurs, and hence this discontinuity is taken as unambiguous evidence for a phase transition. Therefore, if matter was made up of hard spheres there would exist but 2 phases, a solid phase and a fluid phase. The fact that three phases, two of them fluid, are found must be due to the presence of attractive forces.

#### Behaviour of Real Systems at High Temperatures and Densities

The phase diagrams for hard spheres and for a simple substance such as argon are shown in Figure 2. It can be seen that at pressures and at

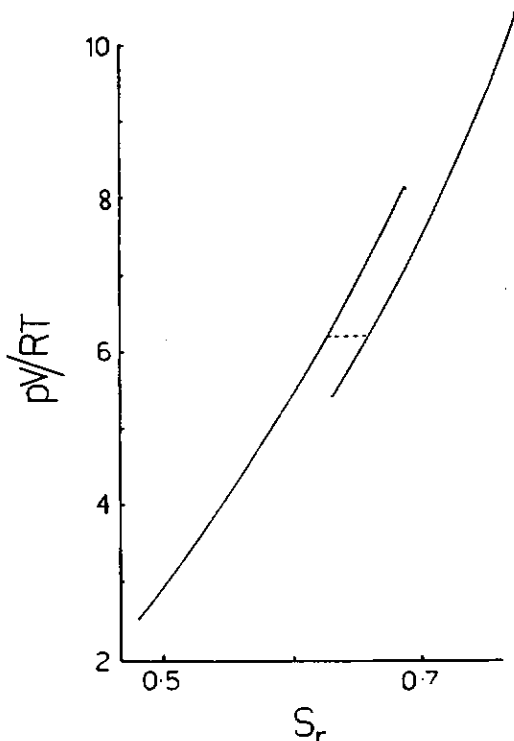


Figure 1. Equation of state of Hard Spheres as calculated on computers. The broken line represents the probable position of first order transition.

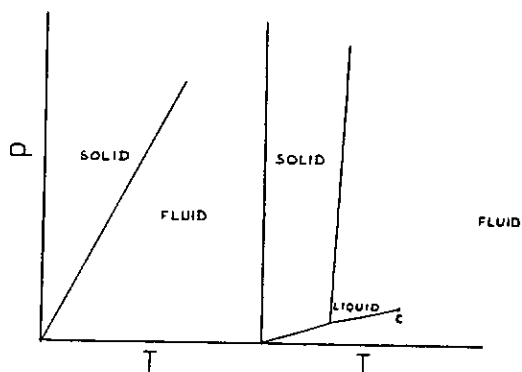


Figure 2. Phase diagrams of an assembly of hard spheres (on left) and a simple substance such as argon (on right). The critical point is designated C.

temperatures above the critical point the phase diagram of real substances is similar to the hard sphere one. This can be accounted for if we examine the form of the intermolecular potential. The most widely used, that of Leonard-Jones, can be written

$$\mu(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (5)$$

where  $\sigma$  is the value of  $r$  when  $\mu(r) = 0$ , and  $\epsilon$  is the maximum attractive value of  $\mu(r)$ . It can be seen to be made up of a steep repulsive part

$\frac{\sigma^{12}}{r^{12}}$ , which may in the limit be idealised as a hard sphere potential  $\left( \frac{\sigma}{r} \right)^\infty$ , and an attractive

interaction which at high temperatures may be counteracted by the thermal energies of the molecules.

Recent experimental evidence on the structure of liquids suggests that the arrangements of molecules in that state is determined by the repulsive part of the intermolecular potential. The structure is discussed in terms of the radial distribution function  $g(r)$  which is a measure of the probability that two molecules occupying the same region of space, and which can be obtained from X-ray and neutron diffraction measurements. The results show that at constant density  $g(r)$  is virtually temperature independent, and independent of the kind of attractive interactions present. It is the same, for instance, in ionic substances as in covalent ones.

### A Hard Sphere Model for the Liquid State

From these results it has been suggested that the perfect state of liquids should be taken as the high density, high temperature behaviour of hard spheres, and that real liquids be regarded as hard spheres in a weakly attractive environment. This leads to an equation of state of the form

$$\frac{pV}{nRT} = f(y) - \frac{4ay}{RT}$$

where  $y$  is a reduced volume,  $f(y)$  is an integration constant identified with the hard sphere contribution, and  $a$  is a temperature and density independent constant.

Now this result is implicit in the equation of state first put forward by van der Waals in 1873! His equation can be written

$$\frac{pV}{nRT} = (1-4y)^{-1} - \frac{4ay}{bRT}$$

$$y = b/4V$$

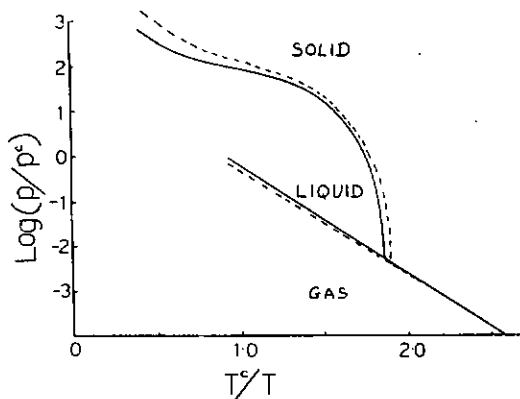


Figure 3. The phase diagram of argon. The full curve is the experimental results. The dashed curve represents the results of Barker and Henderson.

The first term of this equation has been shown to be a very inaccurate account of hard sphere behaviour. When it is replaced with either the "experimental" hard sphere results from computer calculations, or with a better theoretical approach such as that put forward by Frisch

$$\left(\frac{pV}{nRT}\right)_{\text{Hard sphere}} = \frac{1+y+y^2}{(1-y)^3}$$

it is found to give a qualitatively correct account of liquid behaviour. It is extremely good near the melting point, but poor near the gas-critical point. More sophisticated perturbation methods give better results. In Figure 3 the phase diagram of argon is compared with that calculated by Barker and Henderson using a double perturbation approach. They firstly obtained a repulsive potential, then perturbed this using a more realistic attractive potential. Their result is very encouraging.

### Application to Fluid Mixtures

This model for liquid behaviour has had greater success in accounting for the behaviour of fluid mixtures. Here we have the additional complication of the interactions between unlike molecules. It has been shown that in the idealised case of soft spheres the fluid mixture can be treated as a hypothetical pure fluid whose parameters  $a$  and  $b$  are quadratic functions of composition

$$a_{\text{mixture}} = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}$$

$$b_{\text{mixture}} = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22}$$

For the pure components  $a$  and  $b$  are related to the critical temperature and volume,  $T_c V_c$  by the proportionalities

$$\begin{aligned} a &\propto T_c V_c \\ b &\propto V_c \end{aligned}$$

The cross terms  $T_{c12}$  and  $V_{c12}$  can be obtained using the Lorentz-Berthollet Rules

TABLE 1

Prediction of Excess Thermodynamic Functions at  $x = 0.5$  using Van der Waals Equation of State

System	T/K	$H^E/[\text{Jmol}^{-1}]$		$V^E/\text{cm}^3\text{mol}^{-1}$	
		calc	obs	calc	obs
A + N <sub>2</sub>	84	37	51	-0.29	0.18
A + O <sub>2</sub>	84	49	60	0.11	+0.14
A + CH <sub>4</sub>	91	85	103	0.00	+0.17
CCl <sub>4</sub> + (CH <sub>3</sub> ) <sub>4</sub> C	273	353	314	-0.43	-0.5
CCl <sub>4</sub> + C <sub>6</sub> H <sub>6</sub>	298	103	110	0.17	.01
C <sub>6</sub> H <sub>14</sub> + C <sub>6</sub> F <sub>14</sub>	308	2415	2703	22.04	5.38

$$T_{c12} = (T_{c11}T_{c22})^{1/2}$$

$$V_{c12} = \left\{ \frac{(V_{c11})^{1/3} + (V_{c22})^{1/3}}{2} \right\}^3$$

These approximations together with the van der Waals equation of state have been used to calculate the p-V-T behaviour of fluid mixtures, and the thermodynamic mixing functions,  $G^E$ ,  $H^E$  and  $V^E$ . In the first case a very good qualitative account is given, even for long chain hydrocarbons, where assumptions of spherical symmetry is a very crude approach. The results of the calculation of mixing functions are given in Table 1. Here the unlike term  $a_{12}$  has been adjusted to fit the value of  $G^E$  at equimolar concentration, and the fitted value has been used in obtaining  $H^E$  and  $V^E$ . The agreement is very good in the case of simple fluids, and qualitatively so in more complicated cases. The agreement there is improved if better approximations to hard sphere behaviour are used.

Despite the progress made, we still have a long way to go before we can claim to have complete understanding of the behaviour of liquid and liquid mixtures. The problems look much less intractable now, however, than they did 10 years ago.

#### References:

- J. S. Rowlinson, Ch.8 *Liquid and Liquid Mixtures*, 2nd ed. Butterworth & Co., London, 1969.  
 J. S. Rowlinson, *Disc. Faraday Soc.*, 49, 30, 1970.  
 B. J. Alder and W. G. Hoover, in. *Physics of Simple Liquids*. North-Holland. Amsterdam. 1968.

#### Extract from a Letter to the Editor

" I have just returned from a brief visit to the University of the South Pacific. Having recently become chairman of the local CORSO committee, I have been concerned with looking at ways in which CORSO can more effectively increase its aid, particularly in the Pacific area. A first desperate need I found at the school of Natural Resources is for at least ten years of back numbers of "Chemical Abstracts". The school has only just been started, and in a country with virtually no scientific journals, it is rather an uphill job trying to do any chemical teaching or research without access to Abstracts running back at least a few years. . . . I had thought of ten years as a satisfactory period. If we could locate such a set I will try to persuade CORSO to finance its purchase."

Anyone having such a set to donate or to sell, please contact:

Dr. W. Whittlestone,  
 Ruakura Animal Research Station,  
 Private Bag, Hamilton.

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Members of the Institute are reminded that the Proceedings of the Royal Society are available free, on application to the General Secretary, Royal Society of N.Z., P.O. Box 12249 Wellington. Remember to state your membership of the New Zealand Institute of Chemistry.

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## BRANCH NOTES

### Auckland

#### *Branch Meetings*

Three well-attended branch meetings have been held recently. Professor A. R. Katritzky, University of East Anglia, Norwich, spoke on "Seven Years of Chemistry at a New University". The President Dr. W. A. McGillivray visited the Branch on 11th August and was entertained at dinner by the committee. Dr. McGillivray addressed the Branch on "Coronary Heart Disease". Dr. B. F. G. Johnson, Cambridge University and Mellor Fellow at Otago University, gave a lecture to the Branch on "Olefin Rotation" on 30th August.

#### *Dominion Breweries Ltd*

Mr. D. I. C. Willox has been appointed Technical Manager. Mr. A. Muir, formerly Chief Chemist of Inver House Distillers Ltd. (U.K.) has been appointed Chief Chemist at the Waitemata Brewery laboratory.

#### *University*

Professor Saul Patai, Hebrew University, Jerusalem, is spending several months at Auckland as Visiting Professor.

Professor P. B. D. de la Mare is spending two months overseas on leave. He will visit England, U.S.A. and a number of other countries. Professor D. Hall is acting Head of Department.

On 12th August, the Annual Research Dinner was held in the Chemistry Department. Over 100 students and staff attended. Professor de la Mare addressed the gathering.

#### *Visitors*

Recent visitors to Auckland included Professor R. D. Brown, Monash University; Professor J. M. Bobbitt, University of Connecticut; Professor J. Robinson, University of Otago.

#### *Personal*

Mr. M. A. Anderson is engaged in geological exploration for gold, copper and bismuth in the Tennant Creek in Australia. He reports that a nugget of pure bismuth is displayed at the Tennant Creek Post Office.

Dr. I. C. Dean graduated Ph.D. recently, and is now a lecturer at the University of the South Pacific, Fiji.

Dr. T. J. Fullerton has taken up a post-doctoral research fellowship at the University of Wisconsin, Madison.

Mr. A. C. Kennett, Chemistry Division, D.S.I.R. has been re-elected President of the N.Z. Branch of the Australasian Corrosion Association.

Dr. J. B. Macaskill is now in England and has been appointed to a Research Fellowship at the University of Reading.

Mr. H. A. R. Martin is now Exploration Manager for Delta Exploration Corp., which has responsibilities for oil prospecting and geophysical surveys in Indonesia and South-East Asia.

Mr. D. A. Morrison, who visited Auckland recently, is Course Supervisor in Chemistry at Algonquin College of Technology, Ottawa.

Mr. G. R. White was a delegate to the annual meeting of the National Council of Churches, held at Nelson this year. He also attended the Symposium on "Education in Science, with Special Reference to the Use of Television" held in Wellington by the Chemical Society (London).

### Wellington

#### *The P. W. Robertson Club*

The first Annual General Meeting of the P. W. Robertson Club (V.U.W. Chemistry and Biochemistry Departments' Old Members' Society) was held on July 8 in the Conference Room of the Easterfield Building, with an attendance of 30, following

the dinner which commenced at 7.30 p.m. in the Students Union. At the meeting Dr C. R. Barnicoat, the recently retired director of the Cawthorn Institute at Nelson, gave the first Robertson Memorial Lecture entitled "Some Recollections of P. W. Robertson and his Contemporaries".

The Committee and Officers for the coming year are as follows:

President: Dr F. B. Shorland, O.B.E.

Honorary Secretary-Treasurer: Mr W. Freitag.

Committee: Messrs W. E. Dasent, B. E. Jackson, R. J. Work, D. W. Richardson.

Hon. Auditor: Dr R. J. Furkert.

#### *Biochemistry Department, V.U.W.*

Professor J. N. Smith, Head of the Department of Biochemistry, at Victoria University of Wellington, has been elected a Fellow of the Royal Society of New Zealand. Professor Smith came from St. Mary's Hospital Medical School in 1964 as the first Professor of Biochemistry at Victoria University. His research interests have centered on the detoxication mechanisms in invertebrates, and he is regarded as a world authority in this field. The Royal Society of New Zealand award was made in recognition of Professor Smith's research contributions to the field of drug metabolism and insecticide metabolism.

#### *Chemistry Department, V.U.W.*

We extend our congratulations to Professor N. F. Curtis on his appointment to a Personal Chair in Chemistry. Professor Curtis has active research interests in coordination chemistry, including complexes of cyclic and linear polyamines, isomerism associated with asymmetric coordinated secondary amines and conformation of polychelates. He investigates the structures of coordination compounds using infrared, electronic and N.M.R. spectroscopy, magnetic susceptibility and X-ray crystallography.

Professor F. Jakob, of the Sacramento State College, California, will spend a period of his sabbatical leave in the Chemistry

Department. Professor Jakob's research interests are in electrochemistry and chemical instrumentation, including the use of digital computers, and he has conducted a variety of special courses and seminars on these subjects. He trained at the City College of New York and Rutgers University, and has been on the staff of Sacramento State College since 1961, including a period as Chairman of the Chemistry Department from 1965 to 1968.

Visitors to the Department included Dr G. J. Wright of the Chemistry Department, University of Canterbury, who discussed "The Mechanism of a Non-Existent Reaction", Dr. R. D. Gillard (University of Kent at Canterbury, England) who spoke on "The Origins of Asymmetry" and "Biological Effects of Platinum Metal Complexes", and Professor P. L. Speeding, Department of Chemical and Materials Engineering, University of Auckland.

#### *Chemistry Division*

Chemistry Division staff have recently been addressed by Dr G. J. Wright, University of Canterbury, on "Some Aspects of Mass Spectrometry", and Professor R. D. Gillard, University of Sussex, on "Metabolism of some Cobalt and Rhodium Coordination Complexes by Bacteria".

Dr S. J. Dickson has been appointed to the Toxicology Section. Dr Dickson took his Ph.D. at the University of Calgary after graduating M.Sc. at the University of Canterbury. He recently completed post doctoral studies on Enzyme Kinetics, at the University of Santa Barbara, under the supervision of Professor C. A. Bunton.

Mr S. K. Fellows, who has recently joined the Geochemistry Section, will be studying some aspects of mineral extraction. Mr Fellows is at present writing a Ph.D thesis on the conductance of aqueous solutions at elevated temperatures, which he will submit to Victoria University.

Mr P. G. Sims, an M.Sc. graduate of the University of Auckland, has joined the spectrographic section.

Mr W. C. Tennant recently rejoined the

Physical Chemistry section. He has returned from leave spent at the University of New South Wales studying for his Ph.D. under the supervision of Professor R. M. Golding.

#### *Institute of Nuclear Sciences*

The Hudson Memorial Lecture to the Royal Society of New Zealand was delivered in June this year by Dr T. A. Rafter. He discussed the role of isotopes of sulphur in geochemical studies.

Dr G. L. Lyon attended the 23rd ANZAAS Conference at Brisbane, and lectured on his geothermal temperature studies based on isotope measurements.

Dr P. Blattner, Dr J. R. Hulston, Mr W. J. McCabe and Dr N. E. Whitehead attended a Geochemical Symposium at Wairakei on 27 to 29 May, and lectured on recent work. Dr C. J. Adams also attended.

An afternoon geochemical symposium was held at the Institute on 2 April during Professor W. S. Fyfe's visit to New Zealand.

#### *Chemical Society (London) Meeting*

An official meeting of the Chemical Society, arranged by the Chemical Society Local Representative, Professor S. N. Slater, was held at Victoria University recently when the President, Professor G. Porter, F.R.S., visited Wellington. Professor Porter is Director and Fullerian Professor at the Royal Institution, and Director of the Davy Faraday Research Laboratory. After a welcome by Professor J. F. Duncan and the formal admission of Fellows, Professor Porter presented his Presidential Address, "Chemistry in Microtime", in which he dealt with the development of the flash photolysis technique for which he shared the Nobel Prize for Chemistry in 1967.

Earlier in the day Professor Porter addressed a Symposium on "Education in Science", and showed the first two of a new series of four films on "The Laws of Disorder", made by I.C.I. Ltd. in collaboration with the Royal Institution.

#### *Soil Bureau*

Dr Cyril Childs has recently joined the Physical Chemistry section at Soil Bureau from the Canada Centre for Inland Waters, Burlington, Ontario, where he worked on metal complex equilibria in solutions and the thermodynamics of brines. Dr Childs graduated Ph.D. in Physical Chemistry at Otago University and subsequently worked with Dr D. D. Perrin, Department of Medical Chemistry, A.N.U., on metal complex equilibria in solutions.

#### *Canterbury*

Dr G. J. Wright recently attended the First Australian Conference on Mass Spectrometry held at McQuarrie University, N.S.W.

Dr R. Cole, who has been a visiting lecturer in the Chemistry Department for a year, has returned to U.K. to take up a Post-Doctoral Fellowship with Professor Cookson at the University of Southampton.

Professor L. F. Philips, Drs M. J. McEwen and A. Metcalfe presented papers at the symposium in Hamilton organised in conjunction with the visit of Professor C. Porter.

The N.Z. Endocrinology Society recently held a meeting at the University of Canterbury, which was attended by staff and students from the Chemistry Department and the School of Engineering. S. W. Metcalf chaired one of the sessions.

Mr H. G. Way has transferred from Hastings to become Development Manager for General Foods Corporation of Christchurch.

#### *Otago*

Recent Branch activities included a very successful social evening at which Rev. Dr. I. Breward, Professor of Church History at Knox College, gave an address entitled "Scientific Imagination and the Future". The Branch also visited the new "Phase I" Chemistry Department Building of the University of Otago last month.

### *Electron Microprobe Analyser*

Of interest to all chemists, and an essential tool for solid state chemistry these days, is the \$80,000 electron microprobe analyser recently installed in the Geology Department of Otago University. The instrument is the first three-spectrometer microprobe analyser in New Zealand, and was manufactured by the Japan Electric and Optical Laboratory (JEOL). In the analyser an electron beam of diameter as low as one micron produces X-radiation from a polished, irradiated surface. Thus one can analyse the elements present in virtually any solid phase — minerals, metals, tooth enamels, etc. Operating the University instrument is Dr. Y. Nakamura, Scientific Officer in the Geology Department, who is on leave for two years from the Geological Institute, Tokyo University.

### *Industry News*

It is now over a year since the Technical Consultant Service of the University of Otago was established; the purpose of this service is to make available to industry the technical skills and facilities available within the Science Faculty. The recent report from the Service shows activity in the mineral industry nationally, and in general industry locally. Work includes raw material evaluation, process design and product evaluation. The director of the service is Mr. A. G. Fricker, a chemistry graduate from Imperial College, University of London, who has chemical engineering experience in the lead and china clay industry in the U.K., and in geochemical exploration in Australia.

Considerable interest has been generated among local chemists on the subject of Montan wax, a valuable industrial wax which occurs in low grade lignite deposits of Otago and Southland. Investigations on wax yield and quality are underway, and a pilot plant extractor is to be designed in the Chemistry Department, Otago University.

Renovation now being carried out at the Pharmaceutical Laboratories of Kempthorne Prosser and Co. Ltd., include extensive

re-designing of the "Galenical" department, where creams and sirups are prepared. The modifications are aimed at making operations more functional, and also at keeping ahead of the ever tightening hygiene standards of the pharmaceutical industry.

### *Chemistry Department, O.U.*

The University Council has announced the promotion of Dr. A. D. Campbell to a personal chair in the Department of Chemistry.

Dr. P. J. Gardner arrived early in September to take up a post-doctoral teaching fellowship for one year. Dr Gardner is from the Chemistry Department, Royal Holloway College, University of London, and his research interests are in the field of inorganic thermochemistry.

Mellor Visiting Professor B. F. G. Johnson, from Cambridge University, is at present giving a series of Mellor Lectures within the Chemistry Department on the "Reactivity of Coordinated Organic Groups". Subjects covered in these lectures include "Electrophilic addition and substitution to cyclooctatetrene", "Heptafulvene complexes", "Olefin rotation" and "Coordinated carbonium ions".

Dr. G. S. Bailey has been appointed to a lectureship in the Department of Biochemistry. Dr. Bailey is at present a post doctoral fellow in the Department of Biochemistry of the University of British Columbia, Vancouver. His work there is with Professor G. Dixon on histone structure.

Progress on the new Biochemistry Building was mentioned in the June Branch notes. The first stages of moving into the new building begin next month.

### *Visitors*

Recent visitors to Dunedin included Professor E. Reich of the Rockefeller University, New York, U.S.A. Dr. Reich gave a seminar in the Biochemistry Department describing his studies with nucleotide analogues.

continued on page 176

**12th ROYAL SOCIETY SCIENCE  
CONGRESS, MASSEY UNIVERSITY**

31 JAN.-4 FEB. 1972

**PRE-ENROLMENT**

If you plan to attend the above Congress, you are advised that it is important that you fill in a pre-enrolment form in order to receive the final programme and other details of the Congress.

Pre-enrolment forms are available from:

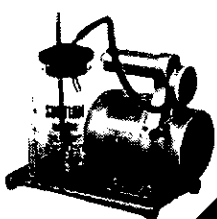
- (a) The secretary of your professional organisation or society;
- (b) The local head of your appropriate government department or DSIR division, if you are a government employee;
- (c) Your departmental head if you are a university employee;
- (d) Dr. T. J. Brown, Dept. of Microbiology and Genetics, Massey University, Palmerston North.

The 12th Science Congress has been built around the following themes:

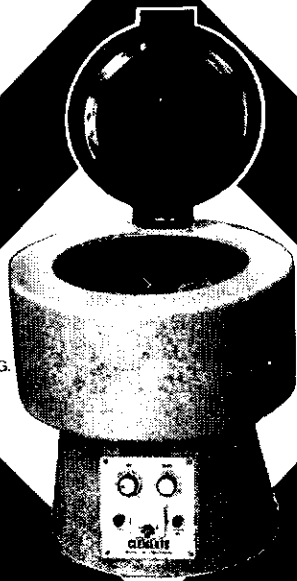
- (a) The Growth and Development of Science in New Zealand;
- (b) Growth and the Use of Natural Resources;
- (c) The Impact of Growth on Society.

There will be interdisciplinary symposia, intradisciplinary sessions, and public meetings. Eminent local and overseas speakers will include: Professor W. D. Borrie (Aust. Nat. Univ., Canberra), Professor A. W. Linane (Monash Univ., Australia), The Rt. Hon. R. D. Muldoon M.P., and Mr. T. E. Clark (Managing Director of Crown Lynn Potteries).

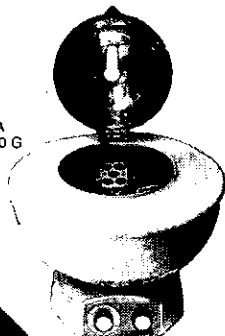
Please send in your pre-enrolment forms as soon as possible to Dr. T. J. Brown, Department of Microbiology and Genetics, Massey University. The original closing date of 30 September has been extended.



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## BOOK REVIEW

"Safety in Chemical Laboratories and in the use of Chemicals." By College Safety Committee, Imperial College of Science and Technology (University of London), 1971, iv + 46 pp, 15 × 21 cm, 15p (post free).

Safe practice in the laboratory should be a concern of all chemists.

A booklet has been prepared by the College Safety Committee of the Imperial College of Science and Technology, London. It comprises 42 pages covering general rules for safe practice in laboratories.

A large section deals with hazards associated with certain chemicals that need special care. They are divided into 4 classes—

1. Unstable chemicals, e.g. azides, chlorates and perchlorates, peroxides.
2. Highly reactive chemicals, e.g. strong acids and bases, halogens, strong oxidizing agents.
3. Flammable chemicals, e.g. solvents, alkali metals, metal hydrides, phosphorus.
4. Toxic chemicals, e.g. benzene, halogens, hydrogen sulphide, mercury, thallium.

General precautions to be taken with each class are mentioned, and more specific dangers associated with individual substances are discussed.

There are sections on General Laboratory Practice, Precautions and Protection, Compressed and Liquefied Gases, Use of Fume Cupboards, Storage of Chemicals, Disposal of Chemicals, Handling of Chemicals by Vacuum Techniques, and First Aid.

A bibliography lists twelve text-books related to the subject.

This booklet provides a very good general code of practice for safety in chemical laboratories and is sufficiently condensed to be read completely by all who work therein.

The Imperial College is prepared to send a complimentary copy to any individual who asks for it. If additional copies are requested, it is expected that they be paid for at the price of 15p per copy (post free) while stocks last.

This well produced, clearly written little booklet is strongly recommended.

Enquiries should directed to—

The Secretary  
College Safety Committee  
Imperial College  
London, SW7

J. L. Mandeno

## DETERGENTS AND THE ENVIRONMENT

The fate of the household detergent after it has done its job in the home and goes down the drain has been the subject of intensive study overseas for many years. In Western Europe the rapidly increasing use of synthetic detergents in the years following the war led to public concern over the obvious pollution of rivers—obvious because even small concentrations of detergent resulted in a build-up of foam at places such as waterfalls where greater aeration occurred.

It was discovered that the type of synthetic detergent most widely used by the householder—alkyl benzene sulphonate—was not easily broken down by the action of the oxidising bacteria upon which sewage purification processes depend. Consequently, much of the detergent in the sewage entering the treatment plant passed through into the effluent discharged to the river. Further investigation showed that this was because the bacteria could not easily oxidise the heavily branched structure of the alkyl chain introduced into the alkyl benzene molecule. However, replacement of the branched alkyl chain by a more linear structure gave a molecule which was more easily degraded.

Developments in the Shell laboratories at Amsterdam resulted in the first linear alkyl benzene, "Dobane" JN. An alternative detergent was thus made available which was biodegradable (often simply termed "soft") yet could replace the "hard" material in household detergent formulations with only minor modifications to production methods. Many liquid detergents sold in New Zealand are based on Shell "Dobane" JNX, a subsequent development to "Dobane" JN.

Although much of the problem of river pollution by detergents was overcome by using these "soft" alkyl benzenes for household detergents (which continue to form the major part of the total detergent consumption), there remained the question of non-ionic detergents (ethoxylates).

Most common nonionic detergents, widely used in the textile industry as scouring agents, are alkyl phenol ethoxylates containing a highly branched alkyl chain (normally octyl or nonyl). By analogy with the branched "hard" alkyl benzenes as used in liquid and powder household detergents, (i.e. anionic detergents) it would be expected that these nonionic detergents were also "hard". However, opinions based mostly on the conflicting results of laboratory-scale tests were divided on this issue.

Trials from mid-1966 to the beginning of 1969 were carried out at the village of Preston, Hertfordshire, U.K., where a group of 31 houses was served by a small sewage works using a trickling filter purification plant. Shell Research Ltd., together with the Water Pollution Research Laboratory (WPRL) of the U.K. Ministry of Technology, set out to obtain further information about biodegradation of various anionic detergents in the practical scale. These Preston trials provided a good opportunity to study also biodegradation of nonionic detergents using various types of nonionics as a component of the dishwashing liquid supplied to the villagers. Initial results on the Shell alkyl phenol ethoxylate "Nonident" P40 were so surprising that the trials were continued for an extra year so



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Christchurch and Dunedin.  
South Island Chemicals Ltd., Christchurch.

that the matter could be resolved in greater detail. Eventually it was established that the biodegradation of "Nonidet" P40 and similar products depended very markedly on the time of the year. In the winter and spring only about 26 percent degradation was achieved in the Preston sewage works. The level increased to about 80 percent by September-October. During November and December biodegradation decreased dramatically to 20-25 percent. It was concluded that bacteria capable of degrading the alkyl phenol ethoxylates were active during the summer but became dormant in the colder weather. This explained the conflicting evidence from the laboratory-scale tests. On the other hand, ethoxylates of straight chain or primary alcohols were shown to be highly biodegradable even in winter. There is thus good reason to replace progressively alkyl phenol ethoxylates by alcohol ethoxylates as nonionic surfactants. Shell companies are now doing this.

Below is the preliminary information sheet on a research and development product designated RD482 which, following the successful completion of product development and initial field trials, is now entering a full market development programme. RD482 is a primary alcohol ethylene oxide derivative which, as can be seen from the general information, is highly biodegradable.

RD482 is still in the market development stage but limited quantities are immediately available from the U.K. for any trials here.

The current development price for RD482 is slightly more than "Nonidet" P40, but in due course with increased production it is expected to be fully comparable.

Further information can be obtained from W. R. Strang, Industrial Chemicals Development Officer, Shell Oil New Zealand Limited.

**RD 482 BIODEGRADABLE  
NONIONIC DETERGENT  
A Primary Alcohol Ethylene Oxide  
Derivative**

**PRELIMINARY DATA**

Property	Test Method	Typical Test Method
Active matter % wt.		Nominal 100
Appearance at 20°C		Pale straw coloured liquid, mini-settlings.
Density g/ml at 20°C	ASTM D1298	0.99
Water % wt.	ASTM D1364	0.4
Ash % wt.	SMS 1663	0.2
pH of 0.5% wt. aqueous solution	ASTM D1172	7
Pour point °C	ASTM D97	9
Cloud point of 5% wt. aqueous solution	SMS 1664	56
Kinematic viscosity at	ASTM 445	
10°C cSt		90
20°C cSt		50
30°C cSt		30

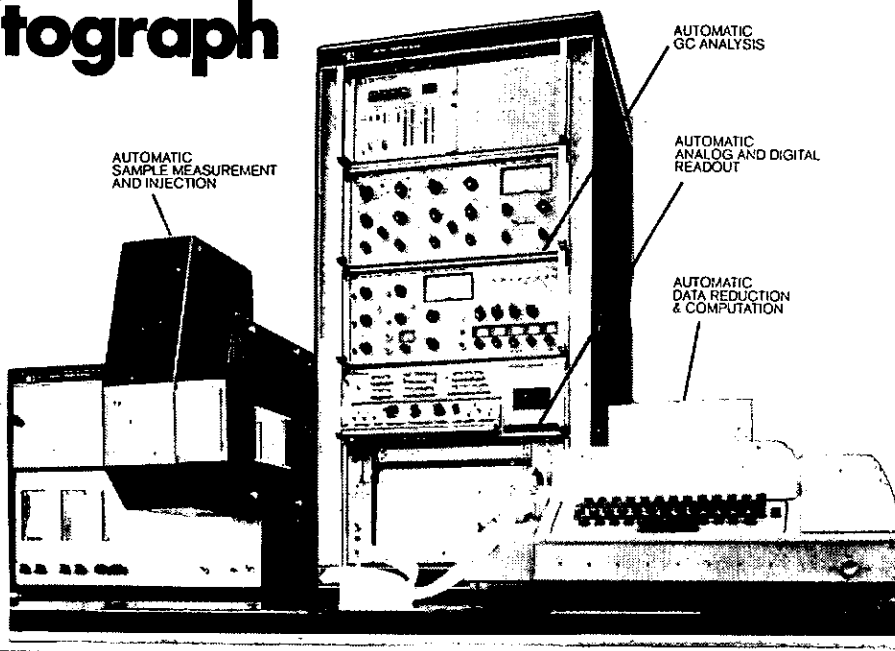
(continued from page 172)

Professor B. J. F. Ralph, Professor of Biological Technology and Dean of the Faculty of Biological Sciences at the University of New South Wales, visited the Chemistry and Biochemistry Departments of the University in August. He gave an address on research activities in the Department of Biotechnology and Biochemical Engineering at New South Wales, with particular reference to his more recent work on continuous fermentation.

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## BOOK REVIEW

*An Introduction to Physical Organic Chemistry*, by E. M. Kosower. Published by J. Wiley, 1968, 480 pp. Price: \$15.00.

This book is organised in a very different way from the classic texts of Ingold and Hine who discuss the mechanisms of various reaction classes, and Wiberg who examines methods and technique in organic quantum chemistry, thermochemistry and kinetics. Under the headings of "Substituent Effects", "Medium Effects", and "Intermediates and Unusual Molecules", Kosower classifies mechanistic processes according to the nature of the transition states involved, either ionic (carbanions or carbonium ions), free radical or charge transfer complex, and isopolar (cycloaddition and electrocyclic) reactions. Quantum organic chemistry is introduced indirectly in the fragmented discussion of the Woodward-Hoffman rules. Spectroscopy is also covered indirectly via discussion of the Kosower Z-values (solvent polarity parameters). As expected, the section on medium effects is outstanding.

The setting-out of the material does not lend itself well to the use of this book as a reference

source. A chemist interested in the reactions of free radicals in solvent cages for instance, would find this section mixed in with discussions of Winstein's special salt effect, the behaviour of radical anion ion-pairs and Cram's carbanion studies. While this may be an excellent way to view physical organic chemistry as a whole (the above four topics are grouped under the heading "Reaction Partners"), it does not make the book a suitable graduate teaching text either, unless time for an American-type one-semester course is available, which is generally not the case in New Zealand universities. The chief value of the book is in its provision of high-grade and reasonably up-to-date (1967) background material that will be of interest to any chemist who, commencing mechanistic studies, wishes to obtain an overall view of the field.

The book is well-produced and is attractively priced. Minor irritating points are: (i) that the bibliography (793 references) is grouped on 24 pages before the indices and (ii) that the familiar  $S_N1$ ,  $S_N2$  etc. mechanistic labels become  $S_1N$  and  $S_0N$  etc. Such a reclassification makes some sense in the context of the book, but it has found no wider usage than this.

D. J. McLENNAN.

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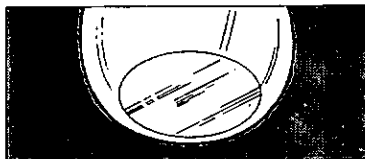
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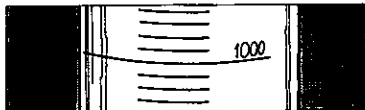
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**CHEMICAL INSPECTOR**

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Staff Clerk

Department of Health

P.O. Box 5013, WELLINGTON

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**Potassium Bromide**  
"AnalAR" Standards for Laboratory Chemicals

Description		KBr Mol. wt. 119.01	
Colourless crystals.		Not less than 99.5 per cent KBr.	
<b>Insoluble Matter</b>			
Free Alkali		0.003 per cent.	
Bromide (Br <sub>2</sub> )		0.1 mg N/1 per cent.	
Chloride (Cl)		0.004 per cent.	
Iodide (I)		0.2 per cent.	
Nitrogen Compounds (N)		0.54 per cent.	
Sulphate (SO <sub>4</sub> )		0.001 per cent.	
Calcium Group and Magnesium (Ca)		0.006 per cent.	
Iron (Fe)		0.002 per cent.	
Heavy Metals (Pb)		0.0003 per cent.	
Sodium (Na)		0.0005 per cent.	
Loss on Drying		0.25 per cent.	
		0.2 per cent.	

**Methods of Test**  
**Insoluble Matter:**  
Dissolve 50 g in water to produce 500 ml. The solution is colourless. Filter through a weighed filtering crucible, wash with water and dry at 105°. The residue weighs not more than 1.5 mg.

**Free Alkali:**  
Dissolve 10 g in 100 ml of carbon dioxide-free water and titrate with 1/50 hydrochloric acid to pH 7.0. Not more than 0.5 ml of 1/100 hydrochloric acid is required.

**Starch Solution:**  
Dissolve 1 g in 10 ml of freshly boiled and cooled water. Add 2 drops of potassium iodide solution, 1 ml of starch solution and 1 drop of dilute sulphuric acid. No blue or violet colour is produced.

**Loss on Drying:**  
Dissolve 4 g in a mixture of 75 ml of water and 25 ml of nitric acid in a 500-ml distillation flask with a rubber stopper carrying a thermometer and tapered air-inlet tube, both of which extend to the bottom of the flask. Heat the solution and, when it boils, commence passing a gentle stream of air and continue boiling (105° to 106°) for 5 minutes. Remove the source of heat and pass a brisk stream of air for 20 minutes to complete the removal of bromine. Then transfer to a stoppered vessel, add 10 ml of 1/10 silver nitrate and 5 drops of nitrobenzene vigorously for 1 minute. Titrate the excess silver nitrate with 1/10 ammonium thiocyanate. Potassium tetrathionate sulphate as indicator.

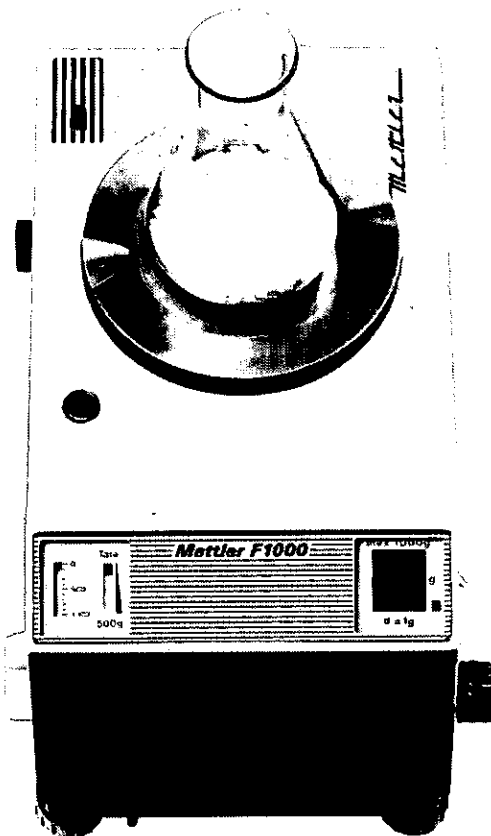
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**ANALAR**  
STANDARDS FOR  
LABORATORY  
CHEMICALS

SIXTH EDITION

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3. **Weighs Rapidly:** The balance beam comes to rest in less than 1.5 seconds.

4. **Accurate Results:** Accuracy is  $\pm 0.25g$ . Fulfills soon-to-be-introduced calibration standards.

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