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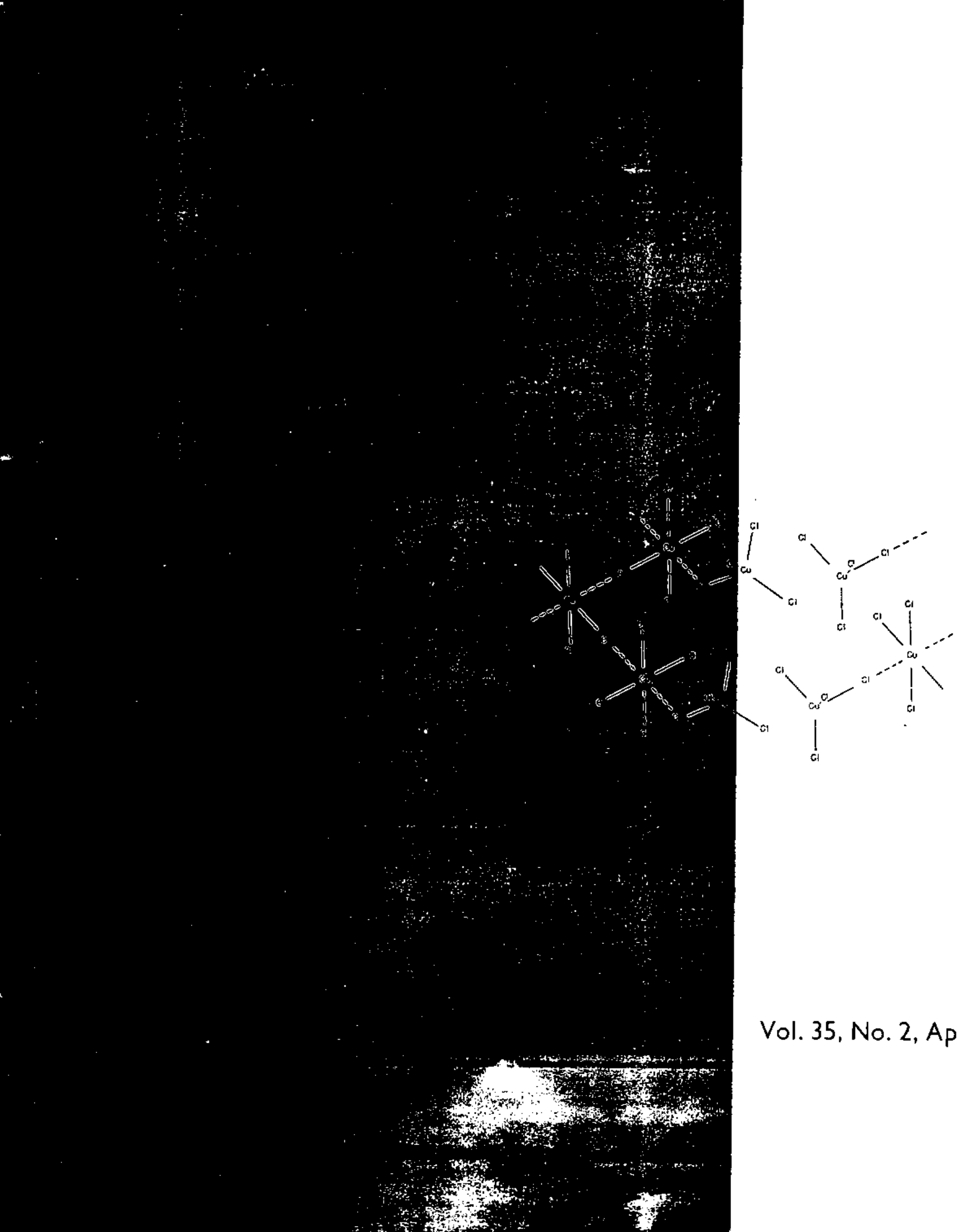

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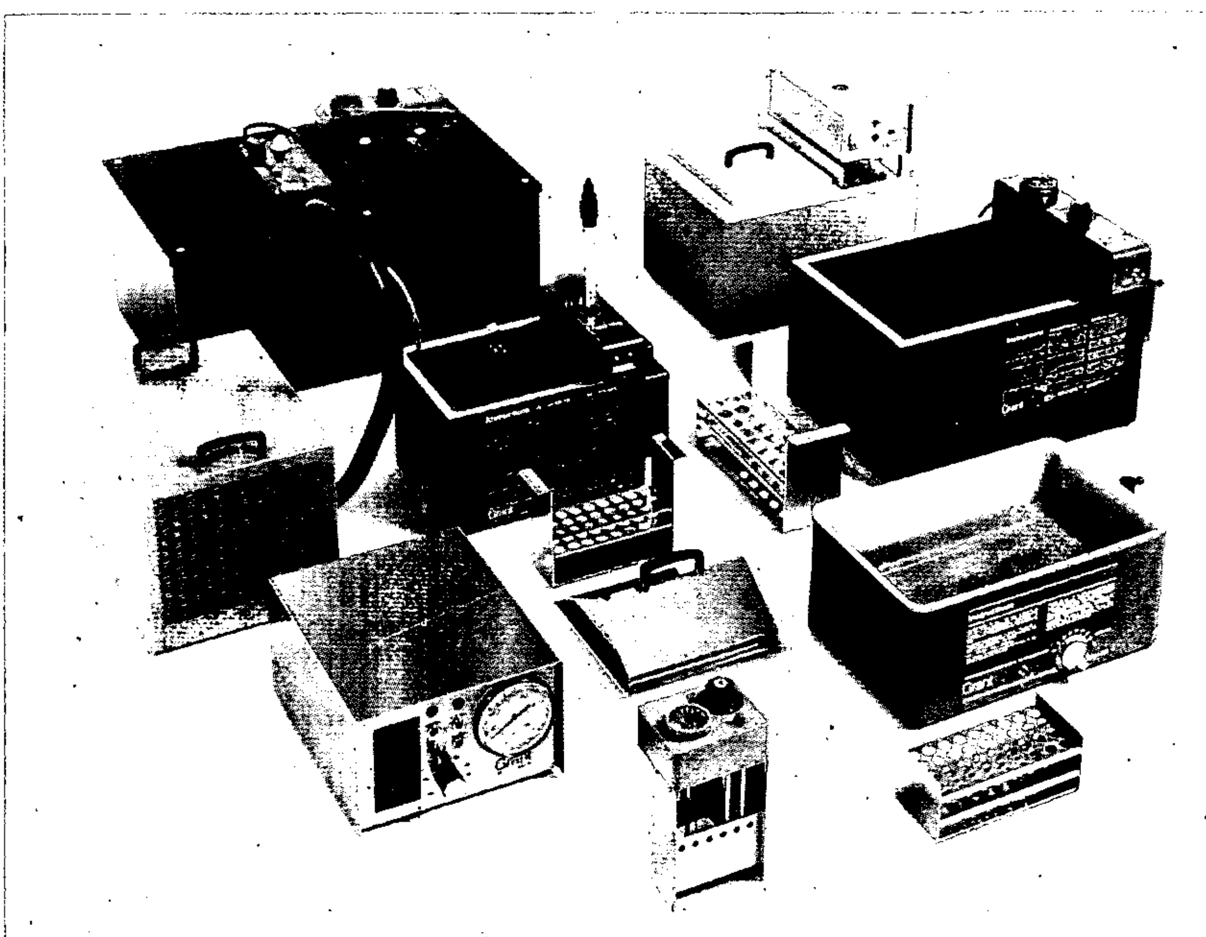

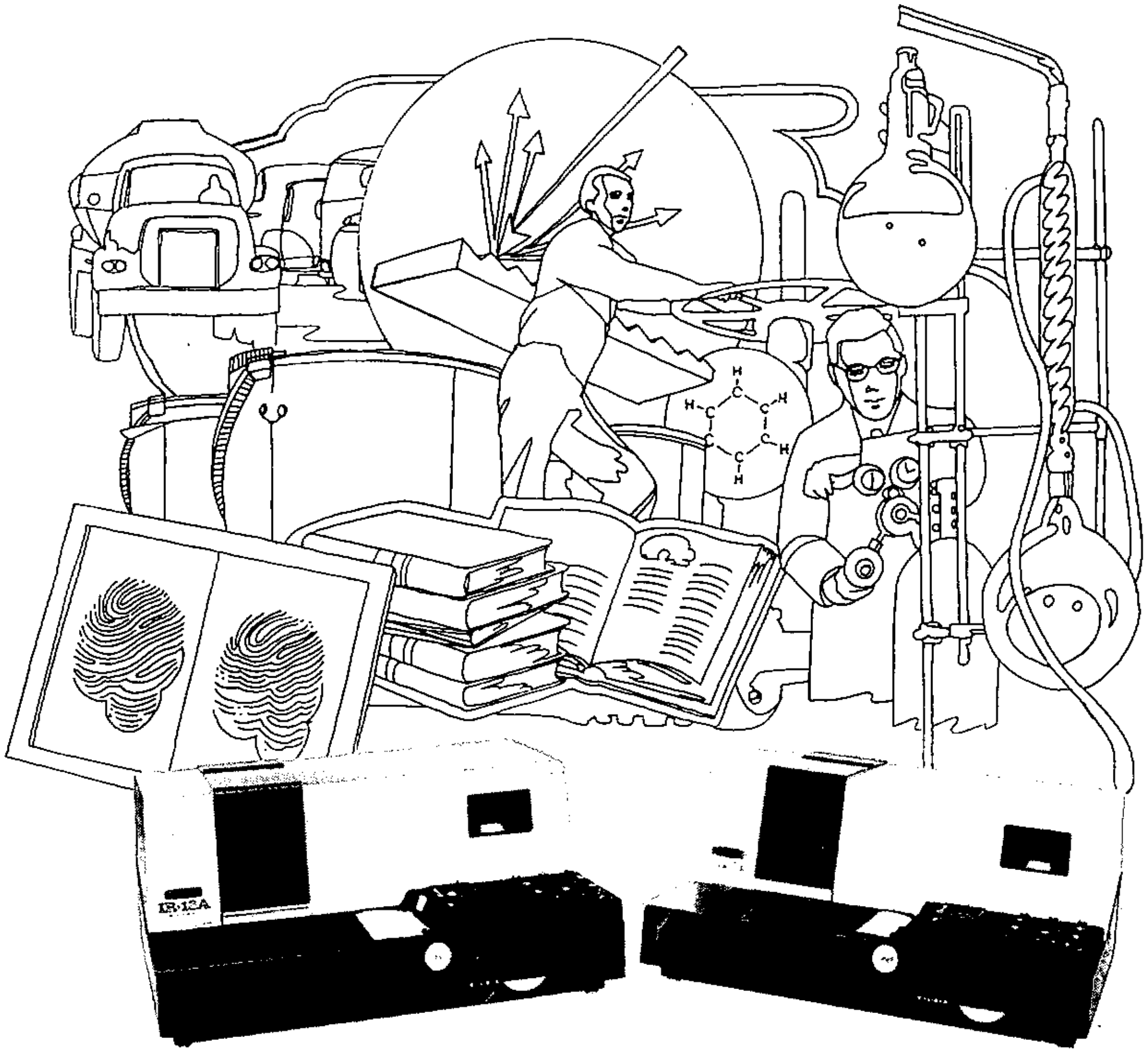

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HETEROGENEOUS CATALYSIS IN SOLUTION*

By M. Spiro

Chemistry Department, Imperial College of Science and Technology, London S.W.7, England; recently Visiting Mellor Professor, Chemistry Department, University of Otago, Dunedin.

Some twelve years ago we were studying the simple oxidation-reduction reaction

$$2\,Fe(CN)_6^{3-} + 3I^- \rightarrow 2Fe(CN)_6^{4-} + I_3^- \quad (1)$$

During these experiments a platinum electrode and a calomel reference electrode were immersed in the reacting mixture. To our surprise the potential of the platinum electrode was virtually constant from the first e.m.f. reading onward although the redox reaction itself took 15-30 minutes to reach equilibrium. The only explanation that fitted all the facts was that the platinum electrode was catalysing the chemical reaction. Around the platinum wire the system had come to equilibrium very rapidly, hence the invariant potential.[1]

Was this catalysis an isolated phenomenon? Textbooks on kinetics discuss at length the heterogeneous catalysis of gas reactions and the homogeneous catalysis of solution reactions but make no mention of the other two permutations. The implication is that they do not exist or are of no importance. Yet many more laboratory experiments, and a careful search of the literature, revealed that numerous redox reactions in solution were strongly catalysed by platinum[2] and by other electronically conducting solids such as charcoal.[3] A mechanistic interpretation had been independently proposed by several workers.[4] The oxidant (e.g., $Fe(CN)_6^{3-}$) and the reductant (e.g., I^-) were thought to sit on the catalyst surface, not necessarily on adjacent sites, with the electron transfer taking place through the solid phase (Fig. 1). It seemed an attractive hypothesis, and one worth testing further.

The catalysis will be marked only if every step in the catalytic process is reasonably fast. Certainly the passage of the electron through the metallic phase will be very rapid indeed. The rate of the electron transfer between reductant and catalyst, however, and between catalyst and oxidant, could be either fast or slow. A measure of this velocity is given by electrode kinetics. Consider a particular redox couple such as

$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-} \quad (2)$$

in equilibrium at a platinum electrode. The equilibrium is a dynamic one: ferricyanide ions continually collide with the electrode and form ferrocyanide ions, and at exactly the same rate ferrocyanide ions hit the platinum surface and are converted to ferricyanide. This rate, in electrochemical terms, is the exchange current density i_0. If i_0 is large, exceeding 10^{-6} A cm^{-2}, the couple is said to be electrochemically reversible; if i_0 is small, the couple is irreversible. Should a small potential η be applied over and above the equilibrium potential, the net current flowing is proportional to i_0. In symbols,

$$\frac{\delta\eta}{\delta i} \propto i_0 \quad (3)$$

Equation (3) is one method by which exchange current densities can be determined and hence the degree of electrochemical reversibility ascertained. It follows from this discussion that the rate of electron transfer between the metal, be it electrode or catalyst,

* Based on a Guest Lecture given to the N.Z.I.C. Conference at Massey University on 27th August, 1970.

and a component of any couple, is large if the couple is electrochemically reversible, small if it is irreversible. (This statement requires modification if the standard potentials of the two couples are far apart.[2])

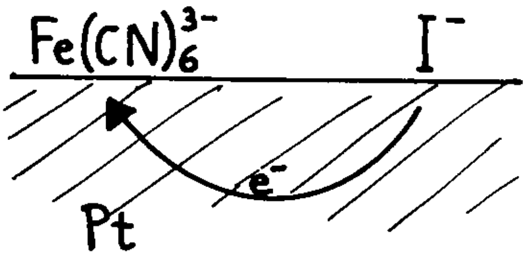

Fig. 1. Diagrammatic illustration of the mechanism by which platinum metal catalyses reaction (1).

The catalytic mechanism depicted in Fig. 1 can now be tested. Table 1 lists several typical redox reactions and the effect platinum has on them, and Table 2 gives the reversibility characteristics of the couples involved. The first 6 reactions in Table 1 are all between reversible couples and, as the mechanism would lead us to expect, platinum strongly catalyses every one. The last 5 reactions in Table 1 involve one reversible and one irreversible couple, and the transfer of an

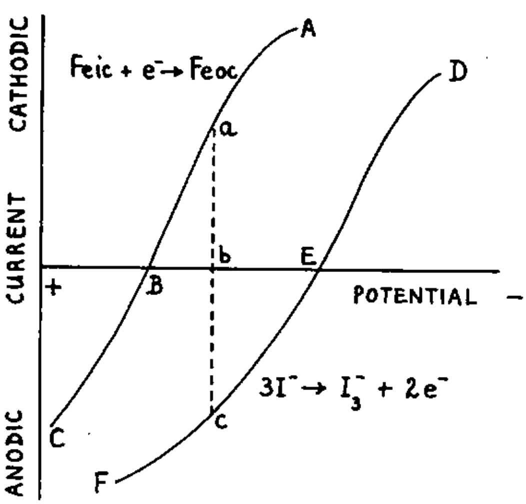

Fig. 2. Schematic current-voltage curves.

electron between the reactants through the metal phase thus involves a slow stage. Catalaysis is therefore not anticipated and, with one exception, is not found. This exception, the only definite one encountered in some 80 reactions,[2] is the ferricyanide-thiosulphate reaction. The mechanism of its catalysis by platinum must be a different one and presumably depends on interaction between adjacently adsorbed species as is commonly the case in heterogeneously catalysed gas reactions. Overall then, there is a good qualitative agreement between the predictions of the postulated mechanism and the experimental findings on catalytic behaviour.

For a quantitative test we must examine the mechanism in more detail. Take reaction (1) catalysed by platinum. The Feic/Feoc couple alone would tend to impose a certain potential on the metal, and the I_3^-/I^- couple another potential. Nature opts for a compromise, and in practice the metal takes up an intermediate "mixture potential". The catalyst then acts simultaneously as an anode to the reductant I^- and as a cathode to the oxidant Feic. The electrochemical situation is sketched in Fig. 2. B represents the Nernst equilibrium potential of the Feic/Feoc couple, and ABC is its current-voltage curve at platinum. The slope at B is high because the exchange current density of the couple is large (equation (3)). The point E, and the steep curve DEF, are the corresponding properties of the couple I_3^-/I^-. When both couples are present together an additivity rule applies[5]: at any given potential, the current of the mixture equals the algebraic sum of the currents of the individual couples. At one point, b in Fig. 2, the current-voltage curve of the mixture crosses the zero-current axis. This is the mixture potential of the system where the cathodic current ab of one couple (Feic/Feoc) equals the anodic current bc of the other (I_3^-/I^-). If the electrochemical mechanism of heterogeneous catalysis were valid, b would be the potential adopted by the platinum catalyst and the catalytic rate—the velocity at which Feic is reduced and at which I^- is oxidised—would be equivalent to the current ab (or bc). It therefore seemed possible to test the proposed mechanism by comparing the results of kinetic and electrochemical experiments.

As a catalytic tool a large horizontal platinum disc was employed,[6] rotating at a constant speed of 200 r.p.m. and immersed in 300 cm^3 solution at 0°c. In a particular ferricyanide-iodide mixture, the rate of iodine formation determined spectrophotometrically was $6.7_8 \times 10^{-9}$ mol l^{-1} sec^{-1} with the disc spinning in the solution and $0.5_1 \times 10^{-9}$ in the absence of the disc. The velocity of the heterogeneous reaction was therefore $6.2_7 \times 10^{-9}$, or rather $6.2_3 \times 10^{-9}$ mol l^{-1} sec^{-1} after the application of a small sampling correction. The potential of the catalysing disc was found to be 293 mV relative to a saturated calomel electrode. In a completely separate set of purely electrochemical experiments, the current-voltage curves of the Feic–Feoc solution alone, and again of the $I_3^- - I^-$ solution alone, were determined with the same rotating platinum disc. The two curves were plotted on paper as in Fig. 2 and the mixture potential was found to be 295 mV (S.C.E.). At this potential the anodic and cathodic currents were each 354 μA which, by Faraday's laws, corresponds to a rate of iodine production in 300 cm^3 solution of $6.1_1 \times 10^{-9}$ mol l^{-1} sec^{-1}. Thus the kinetically and the electrochemically determined potentials were only 2 mV apart and the rates agreed to within 2%. The hypothesis that platinum catalyses reaction (1) by a mechanism of electron transfer through the metal is thereby confirmed, and it seems highly likely that this mechanism is a general one for catalysis of redox reactions by electronic conductors. If so, we are now in a position to predict the extent of such catalysis solely from the electrochemical properties of the reacting couples.

Isolated observations in the literature suggested that another important class of solution reactions, substitution processes, may be subject to heterogeneous catalysis. No systematic work had been done in this field and it appeared to merit more detailed investigation. In one project we chose a simple inorganic aquation reaction

$$Co(NH_3)_5Br^{2+} + H_2O \rightarrow Co(NH_3)_5(H_2O)^{3+} + Br^- \quad (4)$$

which could be conveniently followed spectrophotometrically. Conductometric and potentiometric methods were ruled out because the electrodes might have acted catalytically. Several solids—silver and mercurous halides, mercuric sulphide, gold, platinum and palladium—were found to be catalysts, and three of these (HgS, AgBr, and Pt) were selected for more intensive kinetic study.[7] The results were unexpected. In every case, the lower the concentration c of the substrate RBr^{2+} (R here stands for $Co(NH_3)_5$), the greater was the apparent first-order heterogeneous rate constant k_{het} given by

$$-\,dc/dt = k_{het}c \quad (5)$$

Some typical data are shown in Fig. 3. The reason for this behaviour soon became apparent: the catalytic reaction is truly first-order

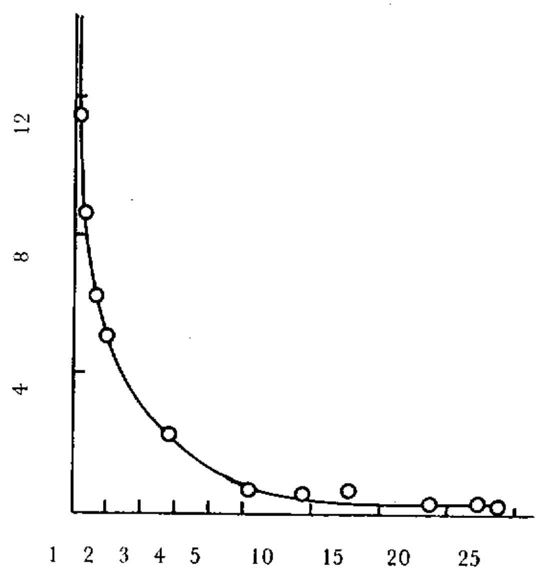

Fig. 3. Variation of the heterogeneous rate constant with the concentration of bromopentaamminecobalt (III) ion, the catalyst being mercuric sulphide.

with respect to the concentration of adsorbed ions, c_{ads} (in mol m^{-2}), and not with respect to the bulk concentration c. Accordingly, a more significant equation than (5) is

$$- d(cV)/dt = k_s c_{ads} A \qquad (6)$$

where V is the volume of solution and A the area of catalyst. A relationship between c_{ads} and c is provided by Langmuir's isotherm

$$c_{ads} = c_{mono} \ \sigma c/(1 + \sigma c) \qquad (7)$$

in which c_{mono} is the value of c_{ads} at monolayer coverage and σ is the Langmuir adsorption coefficient. Combination of the last three equations leads to

$$-\frac{d\ln c}{dt} = k_{het} = \frac{k_s A}{V} \cdot \frac{c_{mono}\sigma}{1 + \sigma c} \qquad (8)$$

The decrease of k_{het} with increasing concentration is thus explained. The experimental results fitted the predicted linear variation of $1/k_{het}$ with c; from the intercepts and slopes, and certain ancillary data, the surface rate constants k_s were evaluated.

Platinum proved to be by far the most powerful of the three catalysts that were studied in detail. It also displayed a most curious property—it catalysed reaction (4) better when some of the products of the equation, $R(H_2O)^{3+}$ and Br^-, were added to the solution. Surely, it was reasoned, these added ions would partly adsorb on the platinum surface in competition with RBr^{2+} ions and so decrease the catalytic action, and indeed such a decrease was found when HgS or AgBr was the catalyst. It was clear that in the case of platinum the product ions must have not only occupied sites on the surface but played another role as well—an electrical role, it would appear. By a fortunate coincidence the catalytic experiments with platinum had been carried out with a rotating platinum disc, and it had been easy to monitor the electrical potential of the disc. The potential was found to jump whenever the reagent RBr^{2+} was added to the solution, thereafter drifting slowly as the reaction proceeded. It seemed possible that the heterogeneous rate might be altered at will by imposing a different potential on the disc, and so it proved. In one particular run the observed value of k_{het} was 7.8×10^{-4} min^{-1} while the mean potential on the disc was 596 mV (S.C.E.); on raising the latter to 630 mV the rate fell to 2.4×10^{-4} min^{-1} and on lowering the potential to 560 mV the rate increased to 9.2×10^{-4} min^{-1}. The catalytic effectiveness was therefore greater the more negative the potential, and a likely explanation is that the cation RBr^{2+} was then more strongly adsorbed. The addition of product ions increased the catalytic rate by altering the structure of the ionic double layer and so indirectly lowering the platinum potential. That a substitution reaction whose normal pathway involves no electron transfer should have its heterogeneous catalysis controlled by electrochemical factors is intriguing, and further research is needed on this point.

Organic substitution reactions, too, are heterogeneously catalysed,[8] and various other processes such as ester hydrolyses and isomerizations are being currently studied. Nor must we forget in this context the catalytic efficacy of certain large molecules and agglomerates like enzymes, polyelectrolytes, and micelles.[9] Although this type of catalysis is not heterogeneous in the strict phase rule sense, reacting ions and molecules would view the interface between such catalysts and the solution in much the same way as the interface between the solution and a genuine solid. It is no mere coincidence that the famous Michaelis-Menten enzyme equation bears a striking resemblance to equation (8), a relation derived from the Langmuir adsorption isotherm. In another respect, too, there is a close connection between homogeneous and heterogeneous catalysis, for ions that act as catalysts in solution will often continue to do so when immobilized on the surface of an added solid.[7] The ease with which the solid can be physically removed from the solution when the reaction is complete is one of the intrinsic advantages of heterogeneous catalysis. It is all the more astonishing that the field has lain fallow for so long, and the results that are now beginning to appear promise to have considerable application in preparative work, in industry, and in biochemistry.

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TABLE 1 — Catalytic Effect of Platinum on Various Aqueous Oxidation-Reduction Reactions

Reaction	*Medium*	*Temp.*	*Catalysis*
$2Ce(IV) + 2Br^- \rightarrow 2Ce(III) + Br_2$	1M H_2SO_4	20°	marked
$Ce(IV) + Hg(I) \rightarrow Ce(III) + Hg(II)$	2M $HClO_4$	15°	marked
$2Fe(III) + 3I^- \rightarrow 2Fe(II) + I_3^-$	0.5M KNO_3	0°	marked
$Q^* + 2Fe(II) + 2H^+ \rightarrow H_2Q + 2Fe(III)$	0.38M $HClO_4$	20°	marked
$I_3^- + 2Ti(III) \rightarrow 3I^- + 2Ti(IV)$	0.13M HCl	20°	marked
2Feic† + $3I^- \rightarrow$ 2Feoc + I_3^-	1M KNO_3	25°	positive
		0°	marked
2Feic + $2S_2O_3^{2-} \rightarrow$ 2Feoc + $S_4O_6^{2-}$	1M KCl	20°	marked
$Cr_2O_7^{2-} + 14H^+ + 9I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_3^-$	0.4M NaCl	5°	slight
$S_2O_8^{2-} + 3I^- \rightarrow 2SO_4^{2-} + I_3^-$		room	none
$2Fe(III) + Sn(II) \rightarrow 2Fe(II) + Sn(IV)$	0.1M HCl	0°	none
$2Fe(III) + 2S_2O_3^{2-} \rightarrow 2Fe(II) + S_4O_6^{2-}$	0.25M KNO_3	0°	none

* Q stands for p-quinone, H_2Q for p-hydroquinone.
† Feic stands for ferricyanide, Feoc for ferrocyanide.

TABLE 2 — Electrochemical Reversibility at Platinum Electrodes of Various Couples in Aqueous Solution at 25°C.

Couple	*Rev'ty*	*E°*
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	rev.	1.70
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	rev.	1.09
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	rev.	0.91
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	rev.	0.77
$Q + 2H^+ + 2e^- \rightleftharpoons H_2Q$	rev.	0.70
$I_3^- + 2e^- \rightleftharpoons 3I^-$	rev.	0.54
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	rev.	0.36
$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$	rev.	0.1
$S_2O_8^{2-} \rightleftharpoons 2SO_4^{2-}$	irrev.	2.01
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	irrev.	1.36
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	irrev.	0.15
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	irrev.	0.1

STRUCTURAL PROBLEMS IN A SERIES OF IONIC TETRACHLORMETALLATES

**Kenneth Emerson*

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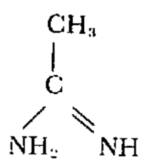
In the fall of 1963 Leo Bares was at work on a Masters degree at Montana State University trying to make a coordination compound of copper with acetamidine(I). The amidine was most readily available as the hydrochloride salt, and one night in one of those fits of irrationality by which science



(I)

often progresses, he dissolved copper chloride and acetamidine hydrochloride in alcohol and mixed the two solutions on a watchglass. As the alcohol evaporated a bright yellow crystalline compound formed. We were surprised by two things: the colour, which we were naive enough to think was unusual for a copper compound, and the fact that any new compound formed at all under the conditions of the experiment. We subsequently found that neither of these things should have surprised us a bit, and so in its way the result was very illuminating; but the time lag between the experiment and the resulting illumination was long. Perhaps that was just as well, because during the lag we studied our bright yellow copper compound which in the end proved to have some quite unique properties of its own.

The compound had the formula $(CH_3C(NH_2)_2)_2CuCl_4$; if the organic group is regarded as just an accidentally complicated cation and the copper as a representative metal, then this compound can be formulated as a representative of a very large class of compounds C_2MCl_4 where C is a univalent cation and M is a divalent metal ion. Many of these compounds are known as double salts, especially when C is an alkali metal, and have been known since the very early days of chemistry. Because M is usually a transition metal and at least some of the chloride must be coordinated, many of these compounds have been used as models of tetrahedral or square planar four coordination—sometimes ill-advisedly. The salts of this group form a very colourful study: manganese salts are pink or green, cobalt salts are all bright blue and copper salts are yellow, orange or green.

At the time we first prepared $(CH_3C(NH_2)_2)_2CuCl_4$ quite a lot of structural work on copper compounds of this type had just been done by Willett and his coworkers at Washington State University. Two distinct structural types appear to occur for crystalline compounds. In the first type the copper ions are surrounded by four chlorides in a distorted tetrahedral array to give a $CuCl_4^{=}$ anion. When the cations are large, like triphenylmethylarsonium ion, the anions are far part; when the cations are small, like cesium ions, the anions can be very close together. In the second type of structure the $CuCl_4$ unit is square planar, but by sharing alternate chlorides each copper achieves a distorted octahedral configuration. In this

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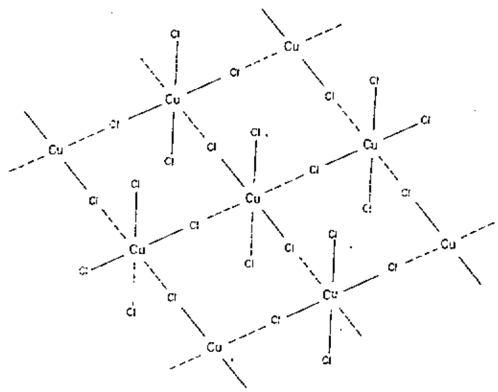

Figure 1: Structure of the $(CuCl_4)_n$ layer in alkylammonium tetrachlorocuprates.

way a layer of stoichiometry $(CuCl_4)_n$ is formed; these layers are similar in structure to the mineral perovskite. A diagram of such a $(CuCl_4)_n$ sheet is shown in Figure 1. Each sheet is separated from neighbouring layers by a layer of cations. The structure is characteristic of the monoalkylammonium salts in this series.

Those salts which contained tetrahedral copper were orange in colour, and remained so down to liquid nitrogen temperatures. Those with the perovskite-like structure were yellow, and transformed on cooling to a green form. This property of changing colour with temperature is called thermochromism. In a few cases the green form was stable at room temperature, and transformed on warming to a yellow modification: $(i\text{-}Pr)_2CuCl_4$ is green at room temperature and transforms at about 40°c to the yellow form. The nature and cause of this transition are not as yet understood. Several laboratories in addition to ours at Montana State University have been interested in this problem, and some critical experiments which we hope will shed more light on the matter are underway. For purposes of this discussion the thermochromism is simply a diagnostic tool for detecting a perovskite-like $CuCl_4$ layer as distinguished from an isolated $CuCl_4^{=}$ ion of roughly tetrahedral symmetry.*

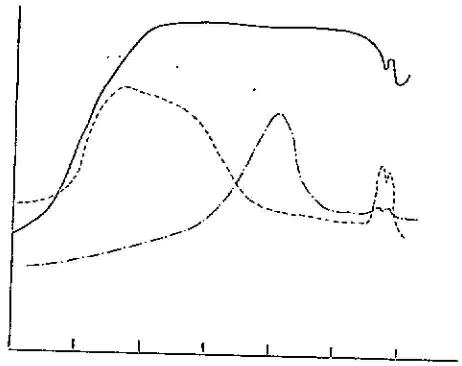

Figure 2: d-d spectra of some solid tetrachlorocuprates. ———, acetamidinium tetrachlorocuprate; - - - - - -, methylammonium tetrachlorocuprate (layer structure); -.-.-.-.-.-, tetraethylammonium tetrachlorocuprate (tetrahedral anion). The bands near 5000 cm^{-1} are vibrational combination bands.

Crystal spectra of solids exhibiting each of the two types of structure had also been taken and reported in the literature: these spectra were not startingly different, but they looked distinguishable (see Figure 2). Magnetic susceptibility measurements on each type of structure had also been done and again small but measurable differences between them were apparent. There was thus a wealth of data on compounds of this type in the literature, and we felt that it would be an easy matter to determine the structure of $(CH_3C(NH_2)_2)_2CuCl_4$ by a few simple spectral and magnetic experiments.

* For compounds with the general formula C_2MCl_4 this seems to be a safe tool for the moment. For compounds of other stoichiometries it is not so safe. The compound tri(dimethylammonium) pentachlorocuprate(II) is not so safe. The compound tri(dimethylammonium) pentachlorocuprate(II) is thermochromic but contains tetrahedral $CuCl_4^{=}$ units and not a perovskite layer. No explanation for this has yet been proposed.

Let me finish the story of "our" compound—let me call it Bares' compound for brevity!—and then return to some more general structural problems involving this series of compounds. The thermochromism of Bares' compound was tested: it was indeed thermochromic, changing from yellow to green as did compounds having a perovskite-like layer structure. However, the transition was less startling than for a compound like methylammonium tetrachlorocuprate. The latter changed from a bright yellow to a very bright green, while Bares' compound changed to a rather yellow green. The difference was subtle, and while reasonable men could agree that it was there, they also could—and did—argue about whether it was significant. The magnetic moment was measured, and gave a value of 1.95 Bohr Magnetons. Octahedral copper complexes generally have moments around 1.9 B.M., while tetrahedral complexes are generally a little higher, about 2.0 or even 2.1 B.M. Finally the d-d spectra in the near infra-red region was measured and compared with spectra observed for the two types of structure. The results are shown in Figure 2. Obviously Bares' compound does not conform very well to either spectrum of a known structure.

The system began to seem much more interesting and a bit puzzling at this stage of the study. The thermochromism should, we felt, have settled the question of structure if there were, as we hypothesized, only two choices. But there was this subtle difference in colour change which made us a bit dubious. The magnetic moment is of no diagnostic value since it lies in the grey area between the tetrahedral and octahedral values. And finally the spectra, which should have been definitive, seemed to indicate a structure different from either of our chosen possibilities.

One more property of the tetrahedral and the perovskite-like systems had been studied in detail—the Electron Paramagnetic Resonance. The obvious difference between the EPR spectra of the two types of structure was in the breadth of the observed resonance. Tetrahedral $CuCl_4^{=}$ ions gave a very broad resonance because of dipole broadening; the perovskite-like structure, because it contained chloride ions shared between two copper atoms, gave a much narrower line because of electron exchange between copper atoms. We decided to try to observe the EPR spectrum of Bares' compound and see if it would resolve our questions about the structure. Large crystals of the yellow form at room temperature were readily obtainable, and the EPR spectrum was easy to obtain. To our great surprise, the spectrum showed two bands at room temperature, one of which was broad and the other narrow. This had to mean that there were two very different kinds of copper ions in the lattice, and one possible explanation for this would be that half the copper atoms were in tetrahedral sites and half were in a perovskite-like site. The earlier data on spectra and magnetic properties tended to reinforce this suggestion, and we feel that at the moment it is as well supported as can be without X-ray diffraction data. The crystallographic study is in progress, but not yet far enough along to confirm or deny this hypothesis. There are probably several models which would fit the data available at present. One of these has been discussed in some detail in a recent paper of ours.[1] A diagram of the $CuCl_4$ layer

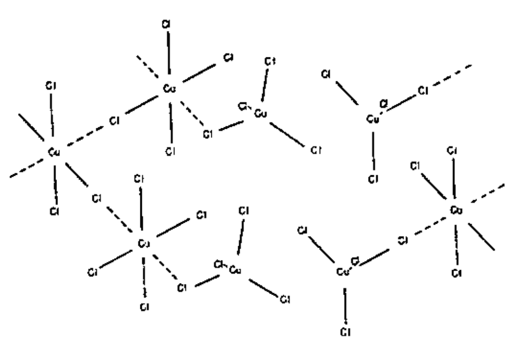

Figure 3: Proposed layer structure for $(CuCl_4)_n$ layer in acetamidinium tetrachlorocuprate.

proposed to account for the properties of Bares' compound is shown in Figure 3, but until further crystal data are available this can only be regarded as a working hypothesis.

So much for the special case which developed our interest in this field. What explanation can be given for the variety of structures which occur in this related series of compounds? An examination of the available data showed that all the compounds which were known to display the perovskite structure were primary amine salts or simple ammonium salts: those which were known to contain tetrahedral $CuCl_4^=$ ions were quaternary salts or alkali metal salts. The difference is that the primary amine cation can hydrogen bond to the chlorides, and crystal structure studies have indeed shown that this sort of bonding does occur. This must be necessary to stabilize the perovskite-like lattice, since when no hydrogen bonding can occur, the salts always contain tetrahedral $CuCl_4^=$.

This raises a whole series of interesting questions for which we have no answers at present. Let us consider a few of these. First, how much hydrogen bonding is necessary to stabilize the perovskite-like structures, and are there geometrical restrictions on its distribution? To answer this question we need to know the structures of dimethylammonium- and trimethyl-ammonium tetrachlorocuprate. Both these compounds are known and both are thermochromic, but there have been no spectral, magnetic or X-ray studies on either of them. The question about geometrical requirements arises from the study of Bares' compound. There we have four hydrogens capable of hydrogen bonding, but they are distributed between two nitrogens attached to the same carbon atom (see Figure 1). This seems to disturb the perovskite-like lattice in some way, because the structure is much more complex. It would be very interesting to see if hydrazinium tetrachlorocuprate or hydroxyl-ammonium tetrachlorocuprate could be prepared and what structures they would exhibit. Methyl phosphonium tetrachlorocuprate would also be an interesting study, since hydrogen attached to phosphorus is a far weaker H-bonder than when attached to nitrogen.

A second question is whether all this interesting structural variation occurs only for copper, or whether tetrachloro derivatives of other transition metals exhibit the same pattern. We know a part of the answer to this question already, because Dr. N. S. Gill of ANU has recently made a spectral study of a series of tetrachloromanganates and found a very similar pattern. The methylammonium salt has the perovskite-like structure and a pink colour; dimethyl-, trimethyl-, and tetramethylammonium salts all have tetrahedral anions and are green in colour.

What about other transition metals? Similar series of compounds can easily be made for cobalt and for zinc; the anions in all these compounds have been widely assumed to be tetrahedral. There is no obvious reason why this should be true when copper and manganese show an entirely different pattern. We are currently studying the zinc series by a variety of means to see if it shows the same pattern of structural types that we have found in the copper series.

Tetrachloronickelates are more difficult to prepare because the trichloronickelate salts are very stable and usually precipitate preferentially. Tetrachloroferrates of divalent iron are very difficult to work with because they are so readily oxidized. A few examples are known and have been studied for these two metals, but no broad series has been prepared.

A third question is whether the thermochromic transition of the copper series, or some other transformation related to it, can be observed in other compounds with the same structure, but containing a different metal ion. We have not been able to observe any changes in colour on cooling methylammonium tetrachloromangate to liquid nitrogen temperatures, but since we do not know the nature of the transition which occurs in the copper series, we do not even know whether it would give rise to a colour change if it occurred in the manganese compound! We hope to find out a bit more about the nature of the transition in the copper series by using differential thermal analysis to study the thermochromic transition in copper, and then perhaps by applying what we learn to a study of the related manganese systems.

Finally one can ask whether the layered perovskite-like structures exhibit any unusual properties because of their structure. One would expect them to be highly anisotropic and to exhibit strong cooperative effects within the layers at very low temperatures. Conductances might well be very large parallel to the layers, but they should be very low perpendicular to the layers. No measurements of this sort have been done. The few measurements which have been done at helium temperatures suggest that these compounds exhibit a variety of antiferromagnetic effects. They may possibly be very interesting as models to test certain physical theories of cooperative phenomena; in some ways these perovskite-like structures are "two-dimensional crystals", and two-dimensional models are always easier to treat mathematically then three-dimensional ones.

Additional Reading

Since this is not a technical research article no attempt has been made to give complete references, although credit has been given to other contributors. For those who wish to read further the following articles may prove useful.

1. Bares, L. A., Emerson, K. and Drumheller, J. E., *Inorg. Chem.*, (1969), **8**, 131.
2. Foster, J. J., and Gill, N. S., *J. Chem. Soc.*, (1968), (A), 2625.
3. Willett, R. D., *J. Chem. Phys.*, (1964), 41, 2243.
4. Willett, R. D., Liles, O. L. and Michelson, C., *Inorg. Chem.*, (1967), **6**, 1885.

NOTICES

Symposium on Atomic Absorption

April 26 and 27, 1971

Danish Hall, Parnell Road, Auckland

The Auckland branch has arranged a symposium on atomic absorption. The emphasis will be on practical and industrial applications rather than on the theory.

Topics to be discussed include:
Analysis of ferrous metals, aluminium alloys, minerals; techniques e.g. carbons, filaments, choice of flame, flameless atomic absorption.

Companies representing atomic absorption manufacturers will be taking part and providing working displays of equipment.

On the evening of Monday 26 April, Mr. J. E. Allan of Ruakura Soil Research Station will address the members of the Auckland Branch and the Symposium on atomic absorption.

Anyone wanting to attend or give a paper, or needing further information, contact:

Dr. I. Devereux (Chairman),
Rocklabs,
215 Parnell Road, Auckland.
Telephone 75-854.

CHEMISTRY TODAY

A Refresher Course for Secondary School Teachers

10th - 14th May 1971
at the University of Auckland

A 5-day full-time course will be held in the first week of the May vacation 1971 at the Department of Chemistry, University of Auckland. There will be a series of lectures, seminars and laboratory sessions.

Modern developments in the major branches of chemistry will be covered, with emphasis on the subject matter of the sixth and seventh form curricula.

A brochure is obtainable from Department of University Extension, University of Auckland, P.O. Box 2175, Auckland.

BRANCH NOTES

CORRECTION

Auckland Branch Officers 1970/71

Chairman: Mr. J. C. Hawthorn.

Immediate Past Chairman: Dr. J. Rogers.

Hon. Secretary: Mr. G. McSweeny.

Hon. Treasurer: Mr. D. B. Rands.

Committee: Dr. I. Devereux, Mr. J. G. Fletcher, Mr. A. C. Kennett, Dr. M. S. White.

Branch Editor: Dr. G. A. Wright.

Hon. Auditor: Mr. L. S. Spackman.

Auckland

Fibremakers N.Z. Ltd.

On 24th February thirty members of the Branch visited the Wiri factory of Fibremakers where nylon spinning operations were inspected.

Australasian Institute of Mining and Metallurgy

The Annual Conference of this body was held in New Zealand during March with sessions at Auckland, Wellington and Dunedin, and extensive tours to localities of interest to the delegates. Dr. John Rogers, New Zealand Chairman of A.I.M.M., was responsible for the local arrangements. Papers were presented by the following N.Z.I.C. members: Dr. M. S. White, Mr. J. E. Rouse, Dr. J. Rogers, Dr. H. P. Rothbaum, Dr. R. R. Brooks and Dr. G. A. Wright.

University

Dr. P. D. Woodgate has returned to Auckland to take up a lectureship in chemistry. Dr. Woodgate is an organic chemist, and has had post-doctoral experience at Oxford University and Stanford University, where he specialised in mass spectroscopy. His wife, Dr. Shiela D. Woodgate, who received her Ph.D. from Stanford University, has held research fellowships at Vermont University and ETH, Zurich. She is at present Graduate Research Assistant in the Department of Biochemistry, Auckland University.

Dr. R. Geddes has been appointed Lecturer in Biochemistry. He is a graduate of Edinburgh University, and is a specialist in protein reactions and conformations.

Personal

Mr. R. J. Sims has been appointed Science Reporter to the New Zealand Herald.

Wellington

Chemistry Department, V.U.W.

A Siemens X-ray fluorescence spectrometer was installed recently in the Chemistry Department. This instrument, which forms part of the University Analytical Services Laboratory, is capable of quantitative elemental analysis of elements above Atomic Number nine.

Apart from its analytical applications, the instrument will be used by Dr. A. G. Freeman and co-workers for valence and coordination studies in which chemical shifts of characteristic emission lines are utilised.

Recent appointments are as follows:

Mr. W. E. Dasent returns to the Chemistry Department as Reader with responsibility for Stage I teaching, after a period as Bursar and Assistant to Vice-Chancellor.

Dr. H. Keyzer, at present Associate Professor in the California State College at Los Angeles, has been appointed Reader in Applied Chemistry. He will join the Department in December.

Dr. A. F. M. Barton has been promoted to a Senior Lectureship in Physical Chemistry, and Dr. S. I. Smedley, a V.U.W. graduate, will join the Department in August as Lecturer in Physical Chemistry. Dr. Smedley obtained his Ph.D. degree at the University of Southampton where he worked on high pressure molten salt chemistry. At present he is a Post-Doctoral Fellow at Case Western Reserve University, Ohio.

The push-button activates your balance operation

The new Sartorius "Auto-Arrest" Analytical Balances are additions to the popular Series 2400 models. They are distinctive because they offer the most important feature since the introduction of the Sartorius Preweighing System:

"Auto - Arrest" - push-button operation of the beam arrest and beam release mechanism. Automation of these functions through a motor-driven system not only further simplifies analytical weighing, but substantially prolongs the life-expectancy of knife edges and provides the permanent accuracy of the balance. Smooth weighing technique is no longer a function of operator skill, and accidential "jarring", which can lead to chipped knife edges, is impossible.

Green button:	*Preweighing Balance*
Grey button:	*Arrest position*
Red button:	*Analytical Balance*

Other design features of these new models are identical to Series 2400 balances and include TABLE-LEVEL-CONTROLS providing pan, optical scale and controls in a single field-of-view.

Fully automatic arrest and beam-release mechanism

Available for macro and semi-micro balances

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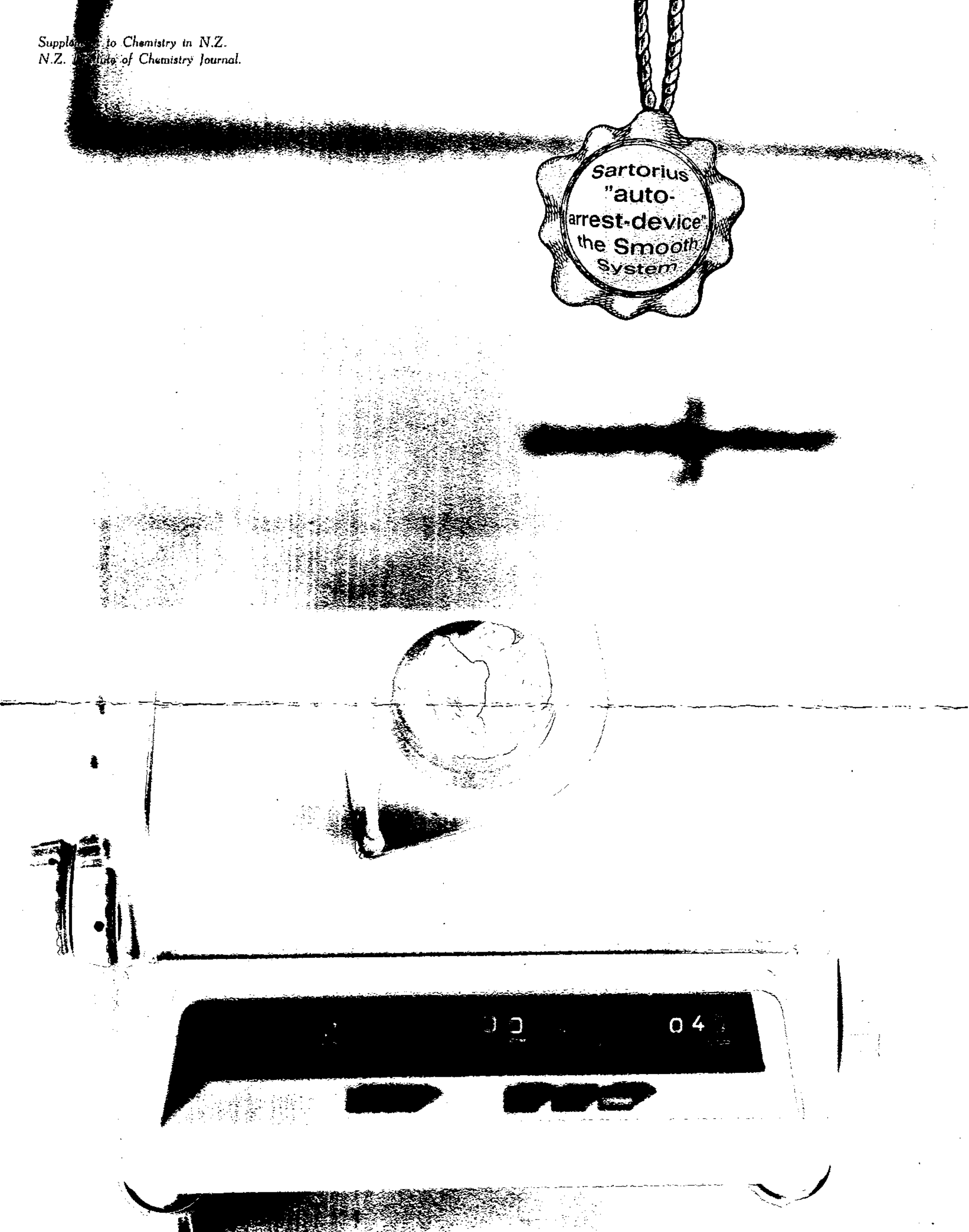
Supplement to Chemistry in N.Z.
N.Z. Institute of Chemistry Journal.



For further information, for a practical demonstration, or a free-trial of any balance type, please contact a dealer in your vicinity or your Sartorius representative.

The "Auto-Arrest"-System is available in the following models:

	2472 Macro Balance with Sartorius Preweighing, Optical Tare and Auto-Arrest	2492 Macro Balance with Preweighing, Optical and Mechanical Tare and Auto-Arrest	2474 Semi-Micro Balance with Sartorius Preweighing, Optical Tare and Auto-Arrest
Weighing Range	**200 g**	**200 g**	**160 g**
Readability	0.1 mg	0.1 mg	0.01 mg
Precision (Standard deviation)	0.05 mg	0.05 mg	0.01 mg
Built-in Weights	1—199 g	1—199 g	0.1—159.9 g
Accuracy	± 0.1 mg	± 0.1 mg	± 0.1 mg
Optical Range	1 g	1 g	0.1 g
Accuracy	± 0.1 mg	± 0.1 mg	± 0.01 mg
Distance between Scale Divisions	5.4 mm	5.4 mm	5.4 mm
Taring in Optical Range	1 g	1 g	0,1 g
Mechanical Tare (Separate tare weight indication)	—	199 g	—

Specifications are not binding in detail and may be changed without notice to further improve our products.

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Chemistry Division

Dr. I. K. Walker, Director of Chemistry Division since 1960, has been appointed Asssitant Director General of the D.S.I.R. and has taken up his new position at the head office of D.S.I.R. in Wellington.

Dr. A. J. Ellis is the new Director of Chemistry Division.

Dr. I. E. Maxwell resigned from Chemistry Division in November in order to accept an appointment at the Shell Research Laboratory in Amsterdam.

Dr. I. J. Miller has joined the Organic Chemistry Section and will be studying the chemistry of lignin and lignin precursors. He recently completed a post-doctoral fellowship at the University of New England, Armidale, where he worked under the supervision of Professor N. V. Riggs on the stability of stereoisomers of various lactones.

Dr. L. J. Porter has returned to Chemistry Division after completing a post-doctoral fellowship at Flinders University, Adelaide. At Adelaide, Dr. Porter studied the chemistry of a number of polyphenols under the supervision of Professor Clark-Lewis.

Dr. M. Zobel has been appointed to the Pesticides Section of Chemistry Division. He will be studying environmental pollution. Dr. Zobel recently completed a Ph.D. at the University of Bristol.

Dr. K. McKenzie has joined the Physical Chemistry Section where he will be studying the spontaneous ignition of coal and cellulosic materials. Dr. McKenzie, a Ph.D. graduate of Victoria, has recently returned from a post-doctoral fellowship at the University of Sheffield.

Mr. L. Aldridge, who recently submitted his Ph.D. thesis to the University of Otago has joined the Concrete Section. At Otago he studied the properties of some synthetic Faujasites under the supervision of Dr. Pope.

Dr. A. Truesdell of Geological Survey, Menlo Park, California, is working for nine months in the Geochemical Section of Chemistry Division.

Dr. N. A. Miller recently resigned from the Metals Section in order to accept a managerial position at the Auckland branch of New Zealand Industrial Gases.

Mr. R. Armstrong, a recent B.Sc. (Hons.) graduate from Canterbury, where he investigated some chemical syntheses of Vitamin D, has joined the Toxicology Section.

Miss J. Murrow, a chemical engineering graduate of Canterbury who recently worked at the Wool Research Organisation, has joined the Chemical Engineering Section.

Mrs. H. Passl, a graduate of the University of Warsaw has also been recently appointed to the Chemical Engineering Section.

Mrs. W. Singers is a recent addition to the Physical Chemistry Section. A B.Sc. graduate of Otago University, she was previously a Biometrician with the Applied Maths branch of DSIR at Palmerston North.

Dr. B. V. Walker, a member of the Chemical Engineering Section, has recently returned from England. At Cambridge University he studied for his Ph.D. investigating some aspects of fluidisation under the supervision of Dr. J. F. Davidson.

Mrs. A. Goldman who has an M.Sc. in Food Science from the University of Leeds has joined the Food Section. For the last two years she has worked at Bovril in London on product development.

Mr. W. Edgerley, a B.Sc. graduate from Victoria, has transferred from the Information Section, Head Office, D.S.I.R., to the Food Section at Chemistry Division.

Mr. D. E. Rodgers has commenced work with the Concrete Section. He recently submitted his M.Sc. thesis on zinc complexes of macrocyclic tetramines to Victoria University.

Mr. L. Sibley, who recently completed his B.Sc. at the University of Auckland, is now working in the Physical Chemistry Section.

Mr. D. McGavin, a recent M.Sc. graduate of Victoria, has joined the Physical Chemistry Section. At Victoria he carried out a theoretical study on the normal modes and force field of spiropentane.

Institute of Nuclear Sciences

Dr. B. J. O'Brien is spending two months at the United Nations headquarters in New York to upgrade a report on the effects of nuclear fallout.

Dr. H. Melhuish attended the 5th A.I.N.S.E. conference on Radiation Chemistry at Lucas Heights in Australia at the end of October and read a paper on his studies on radiation mechanisms in plastics.

Dr. C. B. Taylor and Dr. G. L. Lyon visited Antarctica in December to collect samples of snow and of salts from dry valleys for isotopic studies. One of our vacation students, Mr. A. Bates, joined the staff of the Scripps Oceanographic Institution research vessel "Thomas Washington" during its recent voyage near Antarctica to collect samples of deep water for ^{14}C and ^{3}T analyses.

A new member of the Radiochemistry group is Dr. N. E. Whitehead who has studied at Victoria and Massey Universities. He is applying nuclear techniques to geochemical problems.

Distinguished visitors in this period have included Professor V. P. Guinn from the University of California, Irvine, who is on his way to the Far East to discuss nuclear techniques. His lectures on neutron activation analysis and its uses were greatly appreciated. Sir Philip Baxter and Dr. R. K. Warner of the Australian Atomic Energy Commission also visited to exchange information on nuclear matters.

Canterbury

The first meeting for 1971 was held at Kempthorne Prosser & Company's Hornby works. The meeting, to which wives were invited, was preceded by a light meal and took the form of an inspection of the firm's contact sulphuric acid and superphosphate manufacturing plants. Despite the wet night there was a very good attendance.

Dr. B. R. Mann delivered his chairman's address to the March meeting on "The Leather Industry in New Zealand" on his home ground, the meeting being held on the premises of C. L. Bowron & Company's Tannery, Woolston.

The Junior Chemical Society began its year with a lecture-demonstration on active nitrogen by Professor C. A. Winkler of McGill University, Montreal, who is spending a sabattical leave at Canterbury University.

Mr. N. P. Alcorn retired recently from Chemistry Division, D.S.I.R., Christchurch, after 24 years as Government Analyst, Christchurch. He has been succeeded as Government Analyst by Mr. L. Wilkinson.

Mr. W. S. Peddie has returned from a year's voluntary service in New Guinea to a teaching appointment at Wellesley College, Auckland.

Mr. P. R. Richards has transferred from Cashmere High School to become Head of Science at Riccarton High School.

Dr. Christine Winterbourn has returned from Canada and has joined the staff of the Biochemistry Section, Pathology Department, Christchurch Hospital.

THE REGISTRY

The following were elected Fellows at the Council meeting of 2/12/70:

EARLE, William Brian, B.Sc., B.E.(Chem.) (Hons.) (N.Z.), Ph.D.(Cantua.), C.Eng., A.M.I. Chem.E., M.N.Z.I.E., Department of Chemical Engineering, University of Canterbury, Christchurch.

WOOFF, Alan Herbert, B.Sc., Dip.Ind.Chem., Christchurch Boys' High School, Christchurch.

REMINDER

THE CHEMICAL ESSAY PRIZE REGULATIONS

1. The New Zealand Institute of Chemistry shall offer annually a prize for an essay or review on a chemical topic.
2. The prize shall be open to anyone who has not attained the age of 25 years before 30 April in the year of the contest, whether a member of the Institute or not.
   (Note: Entries from students will be welcomed).
3. The entry shall be not longer than 5,000 words.
4. The entry shall be in a form suitable for publication, and the Institute shall have the right to publish the winning entry.
5. Applications, in completed form, must be received by the General Secretary, P.O. Box 250, Wellington, not later than 30 April in the year of the contest.
6. The entries shall be judged by a Committee of examiners set up by Council for the purpose. The President of the Institute and the Editor of the Journal shall be ex-officio members of this Committee.
7. The award shall be made by the Council after consideration of the report of the Committee of examiners, and the presentation of the prize shall be made, whenever possible, at the annual conference of the Institute.
8. No award shall be made if, in the opinion of the Committee of examiners, there is no entry of a sufficiently high standard of merit.
9. The value of the prize shall be such sum as the Council may from time to time determine, and the prize shall be spent on books or instruments to the satisfaction of the Council.
   (Note: The value of the prize is at present $50).

MR. KEITH E. KELLY

People associated with science throughout New Zealand will learn with regret of the sudden death on March 1st of Mr. Keith E. Kelly, General Manager of Watson Victor Limited.

Keith Kelly's association with the scientific field commenced in 1948 when he joined Watson Victor Limited as Manager of their Scientific Division. He travelled extensively throughout the country in the course of his duties and made many friends who will remember him as much for his cheerful friendliness as for his wide knowledge of scientific equipment. He had been several times overseas, and shared widely the wealth of knowledge and experience that he had gained. His passing will leave a real gap in the whole field of applied science in New Zealand.

We extend our deepest sympathy to his wife and two daughters.

Professor J. Packer

We record with regret the sudden death recently of Professor J. Packer. An obituary will be published in the next issue.

BOOK REVIEWS

Steroid Reaction Mechanisms, by D. W. Kirk and M. P. Hartshorn, Elsevier Printing Co., Amsterdam, 1968, xi 476 pp., 14 22 cm U.K. 200/-.

This book maintains the high standard set by other titles in this series (Reaction Mechanisms in Organic Chemistry). It gives a most comprehensive coverage of steroid chemistry and will undoubtedly find a place alongside "Steroids" and "Steroid Reactions".

Discussed in chapters of functional group reactions, the chemistry of steroids is extensively reviewed to give an easily read and thorough account of steroid reactions and their mechanisms. The authors have combed the literature very carefully and the review, although not a critical one, serves as a compilation of an enormous volume of work in the steroid field.

Earlier works have shown the importance of steroids in the understanding of the principles of conformational analysis. The authors follow this same approach but extend it by their consideration of detailed reaction mechanisms. The result of this nicely balanced approach is two-fold—firstly it illustrates strikingly the dependence of mechanisms on conformation, and secondly it leads to a much better understanding of conformational analysis.

The presentation is clear and pleasingly free from error. Although the high price (not excessive when one considers its reference value) may prevent this book being widely bought I hope it will be widely read. For the organic chemist with interests in alicyclic chemistry, this title is highly recommended.

P. K. GRANT.

Halides of the First-Row Transition Metals, by R. Colton and J. H. Canterford, published by Wiley—Interscience, London, 1969. 580 pages. Price Aust.$21.25.

This book is an examination of the halogen chemistry of the elements from titanium to copper. It is not confined to the simple halides but also discusses in detail the chemistry of the adducts formed by the halides. References are complete up to 1968 with addenda to January 1969.

The first chapter, a general survey, is concerned with preparations of the halides and halide complexes and general structural features. The remaining eight chapters deal separately with each element, cobalt, nickel and copper receiving rather more space than the earlier members.

Under each element the arrangement is by oxidation state, the different halides, oxide halides and halide complexes then being discussed separately. The result is an extremely orderly treatment, ideal in a reference work. An obvious disadvantage is that it does not provide much scope for discussion of trends or comparisons.

Thermodynamic data is tabulated at appropriate points throughout the text and there are very clear illustrations, being for the most part reproductions from the original cited references.

SALARY SURVEY 1971

Because of the effects of inflation with Government salary scales increasing approximately 40 percent in two years, another salary survey has been circulated to members. It is the same as that of 1969 in order to make direct comparisons.

Please fill yours in and return it promptly.

Structural findings and the results of spectroscopic and other physical measurements receive due weight, making this a valuable book for workers in these fields as well as in transition-metal chemistry.

M. J. TAYLOR.

Introduction to Spectroscopy (2nd edition), ed. R. L. Manning. Pye-Unicam Ltd., Cambridge, England, 1969, pp. 27.
Atomic Absorption Spectrophotometry by Peter Cooke. Pye-Unicam Ltd., Cambridge, England, 1969, pp. 44.

These two paperbacks are intended to provide straight forward introductions to their subjects and in this they succeed admirably.

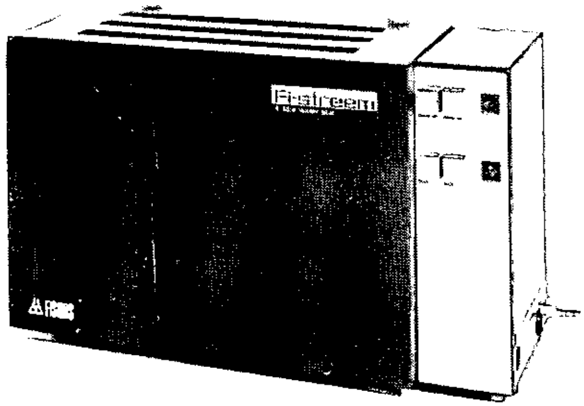
The first book begins by reviewing the basic theory of light and radiation with a painless discussion of radiant energy, simple quantum theory and the function of a spectrophotometer. This latter section is then expanded into a discussion of the design, construction and use of the various types of spectrophotometer beginning with the simple colorimeter and progressing through single and double-beam instruments. The author deals thoroughly with the important problems of instrumental errors and specifications. Subsequent sections cover the related techniques of flame emission spectroscopy, atomic absorption, fluorescence and atomic fluorescence spectroscopy.

"Atomic Absorption Spectroscopy" is more specialised and gives this important analytical technique a more vigorous treatment than does the previous book. Although the discussion is orientated around the Pye-Unicam SP90 instrument it is generally applicable to all AA instrumentation. Topics covered include burners and flames, nebulisation, hollow-cathode lamps, the preparation of standards and calibration curves, together with the problems and snags commonly encountered in AA analysis. The latter third of the book is devoted to a detailed review of the methods of sample preparation for a wide variety of materials; this being supplemented further by an extensive bibliography.

Both of these books may be recommended with confidence to laboratory workers and students who require a concise and inexpensive practical introduction to spectroscopy. It should be of particular value in technician training courses.

J. R. L. WALKER.

N.B.—These books are available in New Zealand from Philips Electrical Industries Ltd. (Professional and Industrial Division).



FI-STREEM

A new water distillation unit from Fisons Scientific Apparatus—Fi-streem 4 litre water Still. Developed, manufactured and marketed by Fisons, the water Still represents considerable rationalisation of facilities and design.

It is totally enclosed giving a compact and very safe unit ideally suited for wall or bench mounting. Silica sheathed elements and hard (borosilicate) glass boiler and condenser give an 'all glass' boiling and condensing unit for additional purity of the pyrogen-free distillate. The distillate is at a rate of 4 litres per hour and meets all European Pharmacopeia.

Cleaning is greatly simplified by the incorporation of a 'push-button' syphoning device that empties the boiler directly into the waste line before and after an 'acid wash'. Also incorporated with the Fi-tsreem Still is the facility for automatic level control in a remote reservoir of the customers choice whereby the Still is switched off when the reservoir is full and automatically switched on to replenish any drain-off of distillate.

The Still has been successfully sold in the U.S.A. and the journal "Laboratory Equipment" of August 1969 selected it as "Product of the Month".

For further information, please write to: Geo. W. Wilton & Co. Ltd., Box 9071, Newmarket, Auckland, or Box 367, Wellington.