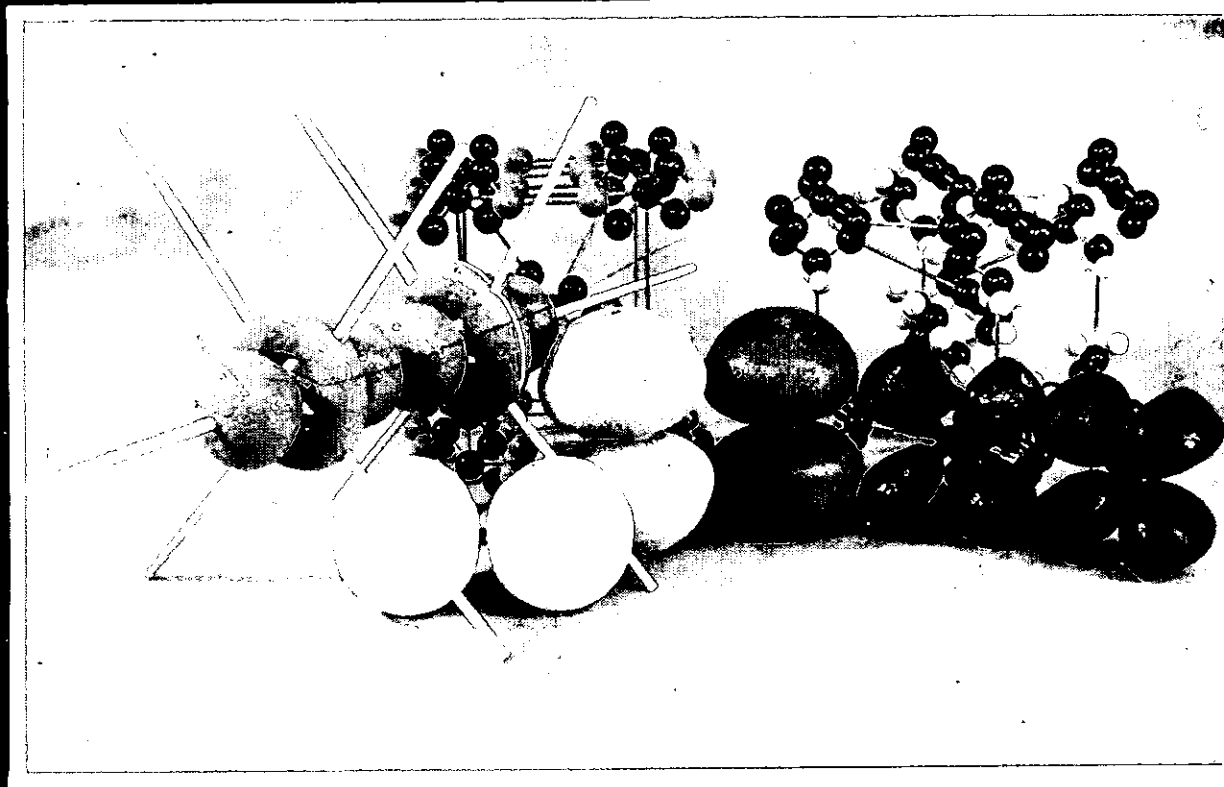


# CHEMISTRY IN NEW ZEALAND

JOURNAL OF  
THE NEW ZEALAND  
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Vol. 32, No. 2, April 1968

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## Journal of The New Zealand Institute of Chemistry

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## Review . . .

## THE HISTORICAL DEVELOPMENT OF THE CONCEPT OF MULTIPLE BONDING

*J. E. Fergusson, M.Sc., Ph.D.*

Chemistry Department, University of Canterbury

CHEMISTS have for over one hundred years found it necessary to postulate multiple bonds between atoms in a number of compounds. It is interesting to find that the early concepts are still the basis of our ideas today, though this is not always apparent due to the sophistication of modern chemistry.

### Earliest Concepts up to 1916

One of the earliest descriptions of a bond was that of Leucippus (430 B.C.), who suggested that atoms became entangled with one another by means of hooks.<sup>1</sup> This concept was forgotten, due to the influence of Aristotle, until the 17th century when Mayow and Boyle revived it. It was not until late in the 18th century that the first diagrammatic representation of bonds as lines was suggested by Higgins.<sup>1</sup>

The first firm ideas on bonding arose in the mid-19th century. These stemmed from Frankland and Kekulé. The former suggested

that there is an attraction between atoms which could be variable; for example, nitrogen has a valency of five or three.<sup>2</sup> Kekulé,<sup>3</sup> on the other hand, held firmly to the belief in a constant valency for any particular atom. His arguments were based on his study of the chemistry of carbon. He represented an atom's valency in diagrams as follows (1861).<sup>3</sup> (Fig. 1.)

Though it has never been pointed out, some of these diagrams are in fact the first reported descriptions of multiple bonds.

Kekulé's immediate problem was to resolve the difficulty encountered in such compounds as  $C_2H_4$ ,  $C_6H_6$ , and  $PCl_5$ , where variable or unexpected valencies were suggested by the compositions. For the first two compounds he maintained the constant quadrivalency of carbon and proposed double bonds to satisfy this requirement. In 1865 he represented the structure of benzene as in Fig. 2.<sup>3</sup> To arrive at this diagram he used

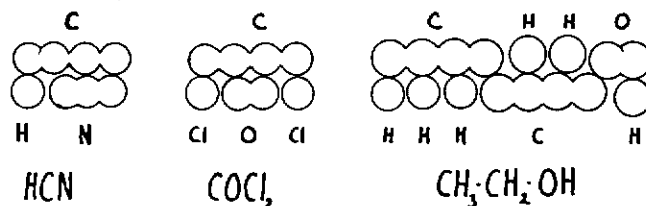
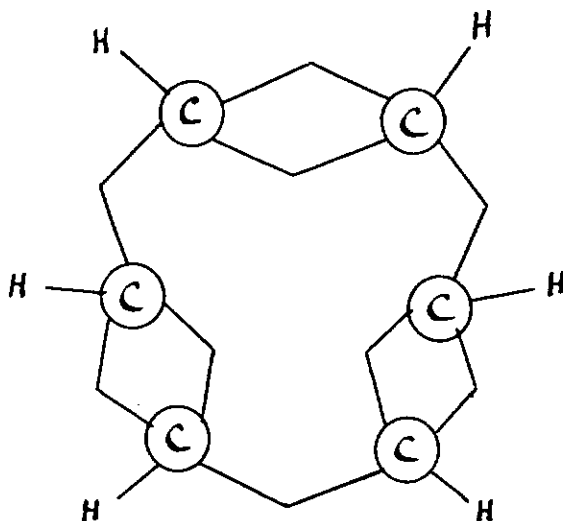


Fig. 1.



Frankland's concept of a bond and Brown<sup>4</sup> and Couper's<sup>5</sup> pictorial representation of it. This diagram is quoted as the first example of the use of multiple bonds in chemistry. For  $\text{PCl}_5$  Kekulé was wrong in advocating a constant valency; he was forced to write the compound as  $\text{PCl}_3 \cdot \text{Cl}_2$ .

The concept of multiple bonding between carbon atoms was fundamental to the development of the structural chemistry of unsaturated compounds. Even so, it did not achieve easy acceptance. As late as 1904 some chemists were still using single bonds for  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$ .<sup>1</sup> Kekulé himself seemed to be undecided about  $\text{C}_2\text{H}_4$ . In his book of 1865<sup>3</sup> he first proposed  $\text{CH}_2\text{—CH}_2$  but

later suggested  $\text{H}_2\text{C} \langle \rangle \text{CH}_2$  though he did not attach much importance to the latter idea.

Kekulé made two further statements concerning multiple bonds which are remarkable in anticipating later ideas and experimental results. Firstly the two bonds  $\text{C} \langle \rangle \text{C}$  were said to be equivalent, and secondly they were said to be more compact than a single bond. Implicit in the second statement was the prediction that multiple bonds would be

found to be shorter than single bonds; there is now, of course, experimental confirmation of this.

The next major problem was to describe how multiple bonds, though overall stronger than a single bond, were more reactive. It was not until twenty years later, in 1885, that Baeyer<sup>6</sup> proposed his strain theory. He

claimed that the angle  $\theta$  in  $\text{C} \rangle \theta \text{C}$  must be less than the tetrahedral carbon bond angle proposed by van't Hoff (1867)<sup>7</sup> by as much as  $55^\circ$ . Therefore, the double bond was under strain and easily ruptured. Thiele (1899)<sup>8</sup>, on the other hand, suggested what is perhaps a less satisfactory theory: that only a part of the combining power of the carbon is involved in the double bond. This leaves what is termed a partial valency on each carbon atom involved in the double bond  $\text{>C}=\text{C}<$ .

The heat of formation of ethylene indicates that the strength of the  $\text{C}=\text{C}$  double bond is less than twice the strength of a single bond (Thomson 1887)<sup>9</sup>. This fact could be used to support either the strain or partial valency theories.

Werner<sup>10</sup> tried to represent the double bond as made up of two bonds of different strengths as in Fig. 3.

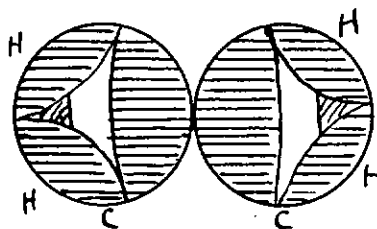


Fig. 3.

The blank areas are said to correspond to the second  $\text{C—C}$  bond. Forces radiating from these areas are only in part directed between the carbon atoms.

It must be kept in mind that all the ideas so far mentioned, some of which anticipate modern theories, were suggested before the discovery of the electron by Thomson (1895-1897). Soon after the discovery it was realised that the electron was the fundamental particle involved in bonds. From that time onwards chemists considered bonds in terms of electrons.

A number of ingenious ideas were put forward to explain chemical bonding between the time of the discovery of the electron and the postulation of the concept of the electron pair in 1916.

Falk and Nelson (1910)<sup>11</sup> represented bonds as arrows to symbolise electron migration. The compounds  $R_2C=CR_2$  should therefore exist in two forms,  $R_2C\rightleftharpoons CR_2$  and  $R_2C\leftarrow CR_2$ , while the compounds  $R^{1/2}C=CR_2$  had three possible forms  $R^{1/2}C\rightarrow CR_2$ ,  $R^{1/2}C\leftarrow CR_2$ , and  $R^{1/2}C\rightleftharpoons CR_2$ . Instability of certain forms was the reason given for the non-existence of some. Lewis in 1913<sup>13</sup> criticised the general argument because it rested on the assumption that the electrons in the bonds were distinguishable.

Stark (1915)<sup>12</sup> represented bonds as tubes of force between the atoms and electrons (2 tubes per bond). For double bonds the two sets of tubes of force were postulated as being at right angles to each other (Fig. 4).

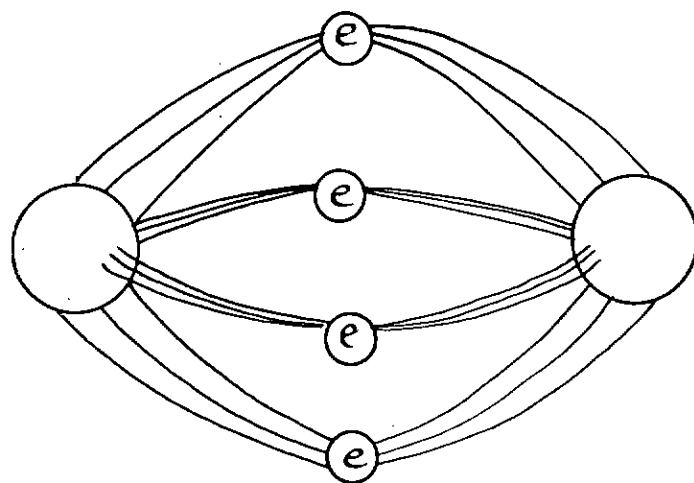


Fig. 4.

### Lewis-Kossel-Langmuir Period

In 1916 Kossel<sup>14</sup> and Lewis<sup>15</sup> independently published theories on bonding which depended on the stability of an outer electron shell of 8 electrons. Lewis claimed in his paper that his ideas were actually formed in 1902. Clearly he did not suffer from the present-day fear of delay in publication. Kossel was mainly concerned with ionic compounds, but Lewis also considered electron sharing in a covalent bond, and for this reason his work is more applicable to the present study.

On the basis of his cubic arrangement of electrons in the outer shell, double bonds were represented as the sharing of faces of a cube (Fig. 5).

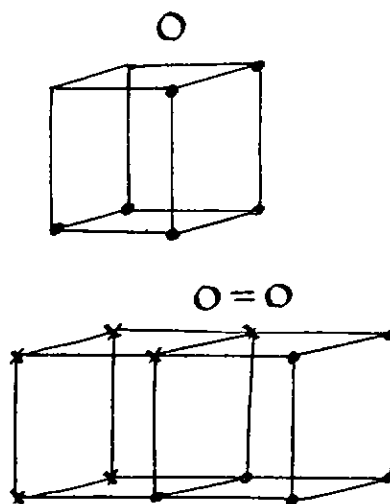


Fig. 5.

One wonders if this is, in fact, very different from the ideas of Stark.

It was soon obvious to Lewis that this representation could not be used for triple bonds. He therefore suggested that the octet of electrons could be grouped in pairs to give a tetrahedron of electron pairs. A bond would then be formed by (a) sharing a corner, to give a single bond as in  $H_3C:CH_3$

(b) sharing an edge, to form a double bond as in  $\text{H}_2\text{C}::\text{CH}_2$  and (c) sharing a face to give a triple bond as in  $\text{HC}:::\text{CH}$ . The reduced stability of the second and third components of multiple bonds (and also the shorter bond length) is due to the closer proximity of the atomic nuclei (see Fig. 6).

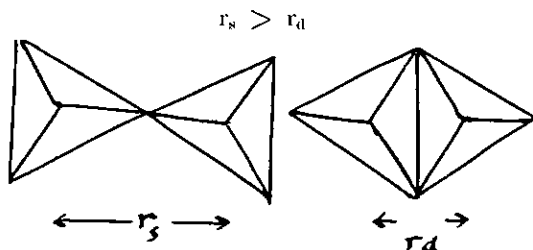


Fig. 6.

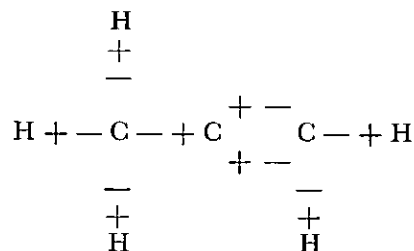
The repulsion between the nuclei weakens the second and third bonds.

Langmuir (1919-20)<sup>16</sup> considered these ideas further and developed a formula for the number of bonds in a compound, viz.,  $p = \frac{1}{2}(8n - e)$  where  $n$  = number of octets,  $e$  = number of valence electrons. For carbon dioxide  $n = 3$ ,  $e = 16$ ; hence  $p = 4$ , (i.e., four bonds or two double bonds, as in  $\text{O}=\text{C}=\text{O}$ ). For acetylene  $n = 2$ ,  $e = 10$ ; hence  $p = 3$  (or a triple bond,  $-\text{C}\equiv\text{C}-$ ). The C—H bonds have been ignored, presumably because the hydrogen has no octet of electrons.

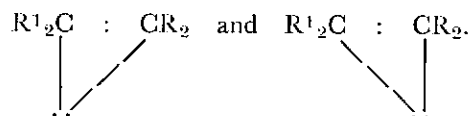
In 1923 Lewis<sup>17</sup> pointed out that in double bonds the two pairs of bonding electrons cannot both lie on the line joining the bonded atoms, hence there must be an angle between the two bonds. He also emphasised that multiple bonds do not necessarily imply unsaturation (cf.,  $\text{C}\equiv\text{O}$  and  $\text{N}\equiv\text{N}$ ); it was the first time that this point had been clearly made. The value of the theories of Lewis, Langmuir and Kossel to chemistry has been considerable, and some of the ideas, particularly the concept of the electron pair in bonds, are still used, although with modifications imposed by quantum chemistry.

## Organic Chemistry 1920-1930

During the nineteen-twenties the implication of multiple bonds in organic chemistry were considered in terms of bond polarity. Cuy (1920)<sup>18</sup>, for example, suggested formulae such as the following:



Attack by  $\text{H}^+\text{Br}^-$  at the double bond is such that the  $\text{H}^+$  goes to the negative end and  $\text{Br}^-$  to the positive end of the bond. Lowry in 1923<sup>19</sup> supported this concept; others thought it went too far. Similar ideas were suggested by Kharasch and Darkis<sup>20</sup> who proposed electro-isomers



Carothers<sup>21</sup> discussed active and inactive double bonds;  $\text{R}^1_2\text{C} : \text{CR}_2$  and  $\text{R}^1_2\text{C} : \text{CR}_2$  were active,  $\text{R}^1_2\text{C} : : \text{CR}$  was inactive. Which active isomer exists depends on the relative electronegativity of the  $\text{R}_2\text{C}$  groups. Other workers such as Lucas and Jameson,<sup>22</sup> Robinson and Kernack<sup>23</sup> and Sidgwick<sup>24</sup> suggested only partial polarity in the multiple bonds; the electrons in the second C—C bond lie a little closer to one or other of the carbon atoms.

Some clarification of the situation began in 1926-28 with the work of Robinson and coworkers and Ingold and his coworkers. The latter group considered that polarity in the bonds was small in the free compound but could be affected by the attacking reagent. This led to the mechanistic treatment of reactivity of multiple bonds which has

been such a powerful concept in organic chemistry.

Looking at the nineteen-twenties from this distance, we see clearly that if further progress were to be made, bonding theories would need to be put on a more quantitative basis. This fortunately came in the form of the Quantum Theory, although the general impact of this theory on chemistry has been felt only in the last decade or two.

### Quantum Theory (1927-1937)

The application of Quantum Mechanics to bonding, and in the present context to multiple bonding, was foreshadowed somewhat by Sidgwick in 1923.<sup>24</sup> He suggested that a double bond was made up of two dinuclear orbitals forming a circle, as in Fig. 7.

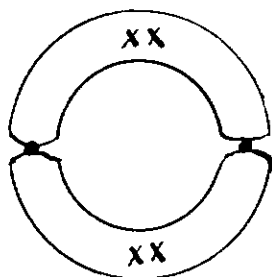


Fig. 7.

This arrangement is under strain because of the smallness of the circle. As the circles become larger (more atoms included) the strain is reduced. This concept is very similar to the Baeyer Strain Theory.

In 1930 the first quantum mechanical description of the double bond was given independently by Dunkel<sup>25</sup> and Huckel.<sup>26</sup> The two separate bonds were labelled  $\sigma$  and  $\pi$ , the names being derived from those given to the molecular orbitals for diatomic molecules.  $\sigma$ -Bonds have cylindrical symmetry about the internuclear axis,  $\pi$ -bonds do not. Therefore a double bond was written as  $\sigma^2\pi^2$  and a triple bond as  $\sigma^2\pi^4$ . Penny and

Mulliken (1933-36)<sup>27</sup> described the  $\sigma$ -bond in ethylene as the overlap of  $sp^2$  hybrids, one from each carbon; the  $\pi$ -bond arises from the overlap of the remaining  $2p$ -orbitals on each carbon (Fig. 8).

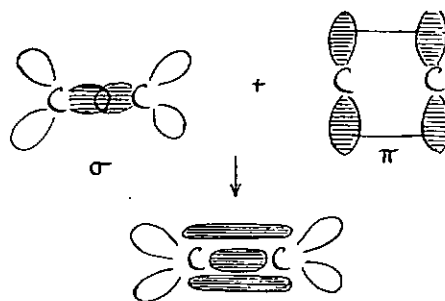


Fig. 8.

Concurrent with this description, which is based on the Molecular Orbital Theory, was the development of the Valence Bond Theory. Pauling<sup>28</sup> and Slater (1931)<sup>29</sup> independently said that the double bond in  $C_2H_4$  was obtained by overlap of two  $sp^3$  hybrids from each carbon giving two bent bonds (Fig. 9). Pauling claims that this arrangement gives better overlap than a  $\sigma + \pi$  description.

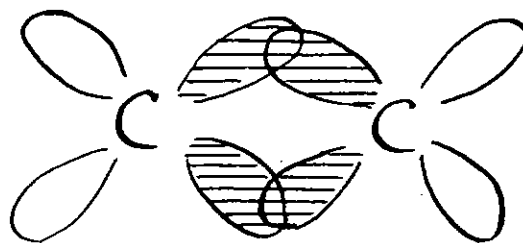
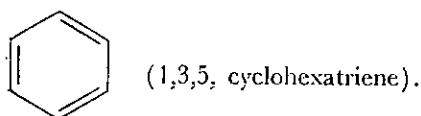


Fig. 9.

It is clear that these two approaches give rise to different stereochemical implications, i.e., in the use of  $sp^2$  or  $sp^3$  hybrids on the carbon atoms. This point will be held over until we consider the ideas that have arisen in the last twelve years.

It is obvious from the chemistry of benzene that its properties are not adequately represented by the structure



In 1937 Lennard-Jones<sup>30</sup> demonstrated that the bonding may be composed of a  $\sigma$ -bond framework and a delocalised  $\pi$ -ring above and below the plane (Fig. 10). The electrons (6) involved in the  $\pi$ -orbitals were termed "mobile".

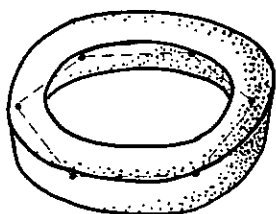


Fig. 10.

The diagram in Fig. 10 gives only one of the six possible  $\pi$ -orbitals.

The alternative valence bond approach considers contributions from canonical forms, such as the two shown in Fig. 11.



Fig. 11.

### Inorganic Chemistry (1935-1945)

In the period 1935-45 the main inorganic interest in multiple bonding appears to be particularly in covalent halides and oxides of elements. This is perhaps a consequence of the development and use of electron diffraction techniques for studying volatile compounds and obtaining information on bond lengths.

The multiple bonding found here is different from that which we have been considering. The second or third bond may not always involve the overlap of semi-filled atomic orbitals but may involve the overlap of an empty and a filled orbital to form a dative  $\pi$ -bond. For example, in  $\text{SiCl}_4$  it is possible that the lone pairs of electrons in the valence shell of the chlorine atoms could be donated to empty, low-lying  $d$ -orbitals of the silicon as represented in Fig. 12.

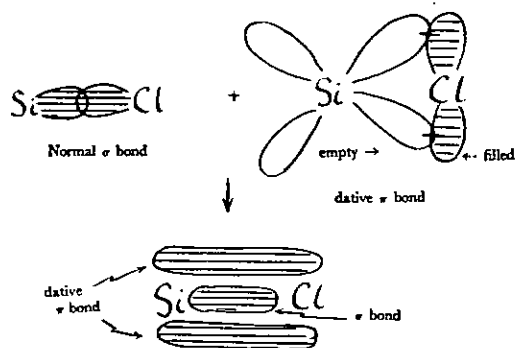


Fig. 12.

The total number of  $\pi$ -bonds in  $\text{SiCl}_4$  can be four, giving one effective double bond per Si-Cl. Such multiple bonds will not occur for the first short period elements due to the absence of accessible  $d$ -orbitals. The  $\sigma + (d\pi - p\pi)$  bonds invoked to explain the chemistry of covalent halides and oxides have been justified by Moffitt (1950)<sup>31</sup> and by Craig et al. (1954)<sup>32</sup> on the basis of Molecular Orbital Theory and overlap integrals respectively.

One of the major consequences of multiple bonding is bond-shortening relative to single bonds. The reason for the short bonds in systems such as Si-X, P-X, As-O, P-O and S-O has been attributed to  $\pi$ -bonding, as described above, by Sutton (1937-45)<sup>33-35</sup>, Pauling (1940-1950)<sup>36</sup>, Brockway (1934-1938)<sup>36-38</sup> and Stone and Seyferth (1955)<sup>40</sup>. Pauling and his coworkers suggest only par-

tial  $\pi$ -bonding, and they propose various canonical forms, e.g.,  $\text{SiCl}_4$  in Fig. 13.

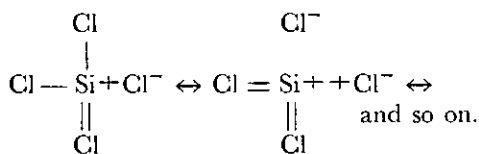


Fig. 13.

Pauling therefore relates bond-shortening to an increased proportion of double bond character. On the other hand Sutton and coworkers suggest complete double bonding and they point out that in some cases the shortening is even less than expected for a double bond.

The concept of multiple bonding involving a dative  $\pi$ -bond has not been accepted easily by chemists. Wells (1949)<sup>41</sup>, for example, completely discounts the possibility of such double bonding. There has also been considerable disagreement among the different schools about the amount of double bonding in any one compound and the relative abilities of elements to form double bonds.<sup>42</sup>

### Inorganic Coordination Compounds 1935-

Another sphere of chemistry in which multiple bonding plays a significant role is that of transition metal coordination chemistry.

A study of transition metal compounds leads to a consideration of yet a third type of  $\pi$ -bond which is the reverse of the dative  $\pi$ -bond discussed above and where the central atom (transition metal) acts as the  $\pi$ -donor. This bond type  $d\pi$  (metal)  $\longrightarrow$   $\pi_{\text{orbital}}$  (ligand) was first proposed by Pauling in 1940,<sup>39</sup> largely as a mechanism to get rid of the accumulation of negative charge placed on the central metal atom by the dative  $\sigma$ -bond ligand  $\rightarrow$  metal originally proposed by

Sidgwick (1927).<sup>43</sup> Chatt in 1950<sup>44</sup> called the  $\pi$ -component a "dative"  $\pi$ -bond and

therefore the complete bond  $\text{M} \overset{\pi}{\rightleftharpoons} \text{L} \overset{\sigma}{\rightleftharpoons} \text{L}$  a "dative double bond". In what follows, the  $\sigma$ -component will be assumed to be already present and most discussion will be on the  $\pi$ -component. Theoretical justification for the  $\pi$ -bond comes from the work of Jaffé (1954)<sup>45</sup> and Craig et al. (1954)<sup>32</sup>.

It may also be noted that special types of  $\pi$ -bonds have been proposed by Chatt (1949)<sup>46</sup> for the olefin complexes of platinum(II). The Pt-olefin double bond involves the double bond of the olefin itself (Fig. 14).

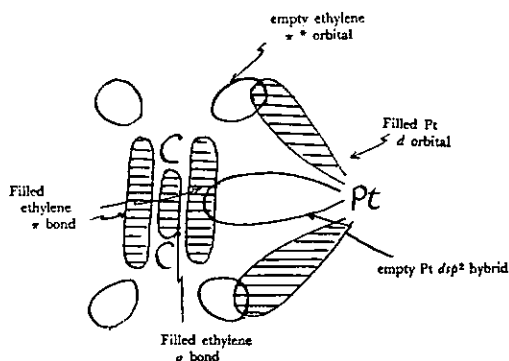


Fig. 14.

We shall not pursue this aspect any further except to say that these compounds were the first examples of what is today an ever-increasing number of transition metal  $\pi$ -complexes.

The structure of  $\text{Ni}(\text{CO})_4$  was determined in 1935<sup>47</sup> and the Ni—C bond length suggested that some double bonding was present. Nyholm in 1952<sup>48</sup> demonstrated that the  $\nu(\text{C}\equiv\text{O})$  stretching frequency in the infrared could be accounted for by some Ni—C double bonding which in consequence reduced the C—O bond order from three to almost two.

A considerable amount of our present knowledge of double bonds in transition metal complexes comes from the investigations of Chatt and coworkers. For example, Chatt<sup>49</sup> related the change in the  $\nu(\text{N—H})$  stretching frequency for the nitrogen ligand in the complexes  $[\text{LPtX}_2(\text{N-ligand})]$  to the  $\pi$ -bonding ability of various ligands L (1955). In 1951 Chatt and Williams<sup>50</sup> pointed out that the phosphorus trifluoride complex of platinum(II) could only exist by virtue of  $\pi$ -bonding since the  $\sigma$ -component is negligible. The failure of  $\text{PF}_3$  to react with the Group III metal halides (e.g.,  $\text{AlCl}_3$ ), which can only bond via  $\sigma$ -bonds, supports this contention.

In 1952 Chatt and Wilkins<sup>51</sup> showed that *cis*- $\text{PtCl}_2\text{L}_2$  (where L can form  $\pi$ -bonds with platinum) is more stable than *trans*- $\text{PtCl}_2\text{L}_2$ . This is explained by the fact that in the *cis* configuration the ligands L have a greater share of the  $\pi$ -bonds. The ability of  $\pi$ -bonding ligands to labilise ligands *trans* to themselves and direct less powerful  $\pi$ -bonders to that position is also explicable in terms of  $\pi$ -bonding (Chatt et al. (1955)<sup>52</sup>, Orgel (1956)<sup>53</sup>).

Without doubt, a great number of properties of transition metal complexes (e.g., stabilisation of low oxidation states) are readily explained in terms of double bonding. Quite recently<sup>41</sup> the concept of  $\pi$ -bonding in platinum metal compounds has been attacked from a consideration of Pt-ligand coupling constants derived from NMR studies.

### Latest Developments 1950-

In the last 10 years some thought has been given to the difference between the two concepts of double bonds,  $\sigma + \pi$  and bent bonds. We will restrict the discussion to a  $\text{C}=\text{C}$  double bond. Lennard-Jones and Hall (1950)

and Pople (1957)<sup>54-56</sup> showed that the two concepts were really equivalent. One can combine the  $\sigma$ -bonding orbital with the  $\pi$ -bonding orbital of ethylene to give two new Equivalent Orbitals  $\chi_1$  and  $\chi_2$

$$\chi_1 = 1/\sqrt{2} (\psi(\text{C—C})\sigma + \psi(\text{C—C})\pi)$$

$$\chi_2 = 1/\sqrt{2} (\psi(\text{C—C})\sigma - \psi(\text{C—C})\pi)$$

These are in fact bent bonds with angles approximating to the tetrahedral angle. This appears to be a happy union of the two concepts.

However, in 1958 and 1960 Pauling<sup>57</sup> claimed the two models were different and if, in the case of the bent bonds of the Valence Bond Theory, one uses not pure  $sp^3$  hybrids but  $sp^3 + 4\%3d + 2\%4f$ , the result is a far better bonding orbital (Fig. 15).

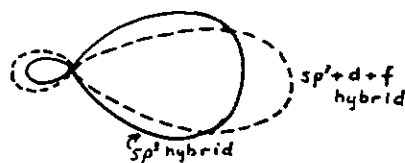


Fig. 15.

The new orbital has a much better concentration of charge in the bonding direction and will give better overlap. Pauling also points out that on this basis the angle  $\text{X—}\hat{\text{C}}=\text{C}$  would be close to  $125^\circ$ . In fact a number of compounds have this angle, e.g., propylene  $124.75^\circ$ , 1,1 dichloroethylene  $123.2^\circ$ , (ethylene has an angle of  $120^\circ$ ). Further, if one constructs two arcs 1.54 Angstrom units long ( $\text{C—C}$  single bond length) and inclined to each other at the tetrahedral angle, the  $\text{C}=\text{C}$  distance is 1.32 Angstrom units which is the same as the observed value (Fig. 16).

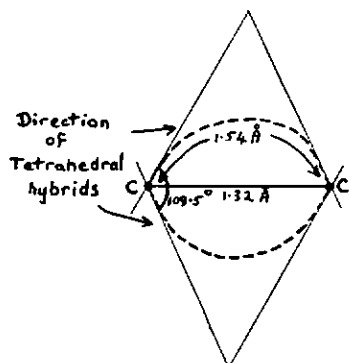


Fig. 16.

Pauling claims that in time the  $\sigma + \pi$  concept will disappear entirely from chemistry in favour of bent bonds!

To date, the main criticism of his theory has come from Coulson (1961)<sup>58</sup> who agrees that if  $d$  and  $f$  orbitals were included, one would get stronger and better bonds. But he considers that the energy required to incorporate the  $3d$  and  $4f$  levels would *not* be compensated for by the improved bonding.

Chemists are going to use both ideas freely for a long time to come because both have useful features which are dominant in different situations. It is important to realise that the theories are only working models and suffer from certain limitations which do not, however, remove their overall usefulness.

In conclusion, it is of interest that certain dimeric compounds of trivalent rhenium, e.g.,  $K_2[Re_2Cl_8]^{60}$  and divalent molybdenum  $Mo_2(\text{acetate})_4^{60}$  have been obtained in which there is a direct metal-metal bond suitably described as *quadruple* ( $\sigma^2\pi^4\delta^2$ ). In the rhenium compound the Re-Re bond is very short and the  $ReCl_4$  groups (Fig. 17) are in the eclipsed configuration. Both these facts strongly support the formation of the  $\delta$ -bond and a resultant Re-Re bond order of four, which is probably the maximum bond order that can be obtained between any two atoms.

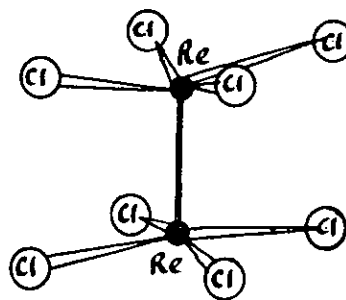


Fig. 17.

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## FOOD, DRUGS AND THE FOOD AND DRUGS SECTION

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### Introduction

We live in an age when our food supply is becoming increasingly sophisticated and when there is an increasing demand for "convenience foods" which can be prepared quickly and easily. Inevitably this has caused the introduction of an ever-increasing range of food additives. Before wide-scale use of these it is necessary to decide when and where there is justification for their introduction.

In 1956, the Food and Agriculture and World Health Organisations convened a Committee on Food Additives.<sup>1</sup> This Committee was asked to establish general principles governing the use of these compounds and they concluded that their use could be justified when they serve at least one of the following purposes:

- (a) the maintenance of the nutritional value of food;
- (b) the enhancement of keeping-quality or stability with a resulting reduction in food wastage;
- (c) the making of foods attractive to the consumer in a manner which does not lead to deception;
- (d) the providing of essential aids in food processing.

The Committee also pointed out that there are certain situations where the use of additives would not be in the best interests of the consumer and should not be permitted. These are:

- (a) to disguise the use of faulty processing and handling techniques;
- (b) to deceive the consumer;
- (c) when the result is a substantial reduction of the nutritive value of the food.

In New Zealand food standards are administered by the Health Department and controlled by the Food and Drug Regulations which aim at ensuring that additives are used properly and that the food itself is of good quality. In addition, there is an attempt to protect the consumer from misrepresentation. The present regulations were promulgated in 1946 and have been amended whenever developments in the field made amendment desirable. Recently the Health Department issued the draft of a complete revision for comment by interested parties. New Zealand has been rather conservative with new techniques or additives, preferring to wait until other countries have gained experience before deciding whether the innovations should be permitted.

The joint F.A.O.-W.H.O. Committee on Food Additives recommended that the legal control of food additives should be based on the principle of a permitted List.<sup>1</sup> This has been the traditional method used in New Zealand. It has the advantage of specificity and allows the following criteria to be used to decide whether an additive is suitable.

- (a) the additive must be harmless at the levels used;
- (b) there must be a need for its use;
- (c) there must be a reliable quantitative method for determining how much of the additive is present;
- (d) the use of the additive must not affect the consumer's interests adversely.

Unfortunately, much emotional nonsense has been written about food additives. Many books and articles have selected evidence so as to produce a spurious case against them and have misled a substantial proportion of the population. Publication of a balanced

case about food additives would remove many irrational fears. Of course there are potential hazards but these can be controlled and minimized by the application of scientific knowledge. In this country approval is given for the use of a specific additive only when the evidence about the additive indicates that the consumer's interests are best served by its use.

### **Food Additives**

Food additives fall into two categories—incidental and intentional. Incidental additives enter the food during growing, cleaning, processing, packaging or storage and serve no useful purpose in the final product. They include pesticide residues and heavy metals. Intentional additives are used to produce a desirable result and there are many examples of these.

Anticaking agents are used to keep salts and powders in a free-flowing condition even during humid weather conditions. These include calcium hydroxyphosphate and silicate, edible bone phosphate, magnesium carbonate and sodium aluminosilicate. The draft regulations also permit the addition to salt of up to 10 parts-per-million of potassium or sodium ferrocyanide as an anticaking agent.

Inorganic chemicals may also be added to canned fruits and vegetables to prevent them from becoming soft and disintegrating during processing. The present regulations permit the use of calcium chloride or sulphate in canned tomatoes, while the draft revision extends this provision to all vegetables.

Bleaching agents such as chlorine and potassium bromate are used in the milling and baking industries. Not only is the colour of flour lightened, but also the elasticity and stability of dough are improved by their use. These agents have enabled millers to avoid the months of natural ageing which were required to "mature" flour.

A large number of additives are used to improve the texture, homogeneity and thickness of foods. Methyl cellulose, methyl ethyl

cellulose and sodium carboxymethyl cellulose are used in foods such as salad dressings, processed cheese and ice cream. Similar use is made of naturally occurring polysaccharides such as acacia gum, agar, alginic acid and its salts, and pectin.

Although gelatin is a protein it has many properties similar to those of the plant gums. Particularly useful are its elastic consistency, property of holding air and water and inhibition of the crystallisation of sugars. Gelatin may be found in processed cheeses, brawn, corned tongues and ice cream but since it lacks the aminoacids tryptophan and tyrosine it cannot be considered as the sole source of dietary protein.

Mono- and di-glycerides may be used as emulsifying agents in bread, shortening, processed cheese and ice cream. In bread mix they may be present up to a level of 20 percent of the amount of fat used imparting to the bread a fine grain, smooth texture and lasting softness.

Only two artificial sweetening agents are permitted for use in foods, saccharin and the cyclamate salts. Saccharin is about 400 times sweeter than sugar and the cyclamates are about 100 times sweeter. None of these has nutritive value making them useful in the preparation of low calorie or diabetic foods. The presence of artificial sweeteners must be indicated on the labels of the products.

Consumer acceptance of a food often depends on its pH. Recognition of this fact has led the food industry to employ many acids, bases and buffering agents. Proper acidulation is essential in beverages to produce the best flavour. Commonly citric, phosphoric, and tartaric acids are employed; however, lactic and malic acids may be used. The regulations are somewhat restrictive by insisting that if the acidity of a fruit juice is adjusted then the product cannot be described as fruit juice but must be labelled as "flavoured drink". In preparing jams, fruit, jellies and marmalade it may be necessary to adjust pH in order to achieve proper gel formation. If the fruit used is deficient in acid, citric,

TABLE 1 — PRESERVATIVE SUBSTANCES

<i>Unrestricted Preservatives</i>	<i>Restricted Preservatives</i>	<i>Antioxidants</i>
Acetic acid, Vinegar	Benzoic acid	Ascorbic acid
Herbs and Spices	Boric acid	Butylated hydroxyanisole
Sodium and Potassium Nitrate*	Sorbic acid	Isoascorbic acid
Sodium and Potassium Nitrite†	Sulphurous acid	Propyl gallate
Salt, Sugar		Tocopherols
Wood Smoke		

\* Level restricted to less than 14 grains per pound (as potassium nitrate) in manufactured meat.

† Level restricted to less than 1½ grains per pound (as sodium nitrite) in manufactured meat.

malic or tartaric acid could well be added to produce a more satisfactory product. The existing and proposed regulations do not provide for these additions.

Preservatives are added to foods to inhibit microbial growth or oxidation and thus prevent spoilage. There are three groups—those whose use is largely unrestricted, those whose use is restricted, and antioxidants. Table 1 lists substances in these categories.

For many years boric acid has been used as a preservative for bacon but the proposed regulations withdraw permission for its use. They also restrict the levels of nitrate and nitrite in corned, cured or salted fish as well as abandoning the imperial system of units. At present, sulphurous acid may be used as a preservative for minced meat, sausage meat or saveloy meat at levels of up to 3½ grains-per-pound as sulphur dioxide. Modern refrigeration facilities make the use of this preservative unnecessary and possibly undesirable since sulphite may be used as an antidote for unhygienic handling procedures. It is proposed to withdraw the provision for use of sulphur dioxide in meats. This would require improvements in the techniques used by some butchers.

Benzoic and sorbic acids are used to preserve sauces, fruit pulp and juice, rennet, and beverages. Sorbic acid is regarded as the more effective of the two against mould formation. In man, sorbic acid is said to be metabolised to carbon dioxide and water in the same manner as are the fatty acids of foods.

In other countries sequestering agents are used in some foods to overcome the effects of adverse ions. The agent complexes the interfering ions and inhibits their effects which may include the production of off-colours, off-flavours or turbidity. The soft drink industry may use sequestering agents to overcome problems of precipitation. The most common agent is calcium disodium edetate (E.D.T.A.-calcium complex) which has been suggested for use in salad dressings and sandwich spreads, but there has been no provision made in New Zealand for its use in foods.

The remaining category of additives consists of the colouring agents. Today's consumer expects his food to have an appetizing and characteristic colour and provides economic pressure for the use of colouring materials. Naturally occurring agents include caramel, cochineal, annatto, carotene, chlorophyll, flavine (from quercitrin), saffron and turmeric. In addition there are 18 synthetic colouring substances which are permitted by the current regulations for use in foods. No levels are specified and the control is purely qualitative.

Some compounds, including vitamins and minerals, are added to food to improve its nutritive properties. The Health Department has encouraged salt manufacturers to add 40 to 80 parts per million of potassium iodide to their products which has greatly reduced the incidence of simple goitre in New Zealand. A proposed regulation requires vitamin and mineral claims on labels to be specified in quantitative terms. This

type of regulation has become necessary to combat dubious advertising practices. There must be more misleading nonsense published about vitamins than about any other group of food constituents. Contrary to the claims of some manufacturers, New Zealand is not suffering from widespread vitamin deficiency and to promote a multivitamin preparation as a type of "pep pill" is ludicrous.

The Food and Drug Regulations do not confine themselves to food additions but protect the consumer by specifying standards for the food itself and by attempting to prevent misleading labelling and presentation of food products. They also define standards for the preparation, storage and packaging of foodstuffs.

### **Enforcement of Regulations**

The Food and Drugs Section and the branch laboratories of Chemistry Division collaborate with Health Department to check compliance with regulations and to investigate problems which may arise. Analyses are performed under the supervision of Analysts appointed under the Food and Drugs Act 1947. Apart from a few empirical tests, the regulations do not specify analytical methods. Responsibility for the choice of method rests with the Official Analysts.

A wide range of techniques is employed by the Food and Drugs Section, including colorimetry for heavy metals,<sup>2</sup> thin layer chromatography for antioxidants,<sup>3</sup> paper chromatography for synthetic colouring matters<sup>4</sup> and infra-red spectroscopy for detecting adulteration such as butter in cocoa butter.<sup>5</sup> Often two different methods are used for a particular analysis—a rapid, less accurate method for screening samples coupled with a slower, more accurate method for use when required. More attention is paid to preservative levels in meat than to any other additives or foods. In 1966, approximately one meat sample in fifteen had excessive levels of preservative. Prosecutions were instituted in about half of these cases.

The Section also analyses foods to determine their quality as foods, e.g. estimating

the fat content of milk (3.25 percent minimum), the meat content of sausage (75 percent minimum), the acetic acid content of vinegar (4 percent minimum), or determining whether a sample of almond paste is made from almonds or from a paste flavoured with benzaldehyde.

A number of recent cases illustrate our work in these fields. Imported raisins from the United States were shown to contain the antioxidant butylated hydroxytoluene, the use of which is not permitted in New Zealand. A check on the Vitamin C content claims of a local manufacturer of beverage concentrates showed that there were insufficient levels in most of his products. He was prosecuted. The same manufacturer also produced a lemon essence which was found to contain only one-tenth of the required content of lemon oil. Another manufacturer produced a "double strength" orange essence. Although the latter product had a high content of orange oil, the regulations do not specify a required level so that the description "double strength" is meaningless. This is a good example of labelling calculated to deceive. A survey of Vitamin A and D capsules failed to detect any clear-cut cases of sub-standard preparations.

### **Contamination**

Contamination in foodstuffs provides us with some of our most varied problems. Apart from the usual run of rodent droppings, we have had a case of a mouse embedded in a pound of butter and another mouse embedded in a loaf of bread. A razor blade in a sample of dates proved to have been introduced in the Middle East. A hat pin in a loaf of bread was traced to a small boy in a grocer's shop. Invisible contamination provides its usual collection of headaches. Copper in lemon squash was detected rapidly but a fish pie defeated all attempts to explain why a class of school girls became ill. Even guinea pigs seemed immune to it and it is possible that the pie was not connected with the illness.

The number of food complaints submitted to us is only a small proportion of those sub-

mitted to the District Health Offices. In spite of this the number has almost doubled in the last four years. This is due mainly to increased public awareness of the action to be taken when encountering examples of contamination.

### Research Projects

The section has conducted a number of research projects. Various analytical techniques have been devised.<sup>4,5</sup> One project demonstrated the feasibility of producing almond-like products from apricot kernels<sup>6,7</sup> which are a waste product from the fruit industry. A local manufacturer has become actively interested as a result of this study. Currently, an investigation of the chemistry of lemon juices is being done in collaboration with Fruit Research Division of D.S.I.R. This project will compare local juices with those of other countries and will assist in determining whether products labelled as "pure lemon juice" are genuine.

We are collaborating with the Customs Department in a project on the production of brandy in New Zealand. Seven vineyards have been licensed and six of these have distilled brandy spirit. Samples are taken every six months and we have been following the maturing process by chemical analyses. An evaluation of these analyses in the light of organoleptic testing conducted by the Department of Agriculture in 1966 revealed that the analyses were lacking in the discrimination required for a chemical evaluation of the quality of brandy. We hope to apply gas chromatography to this problem.

### Water Supplies

The Section also analyses potable water supplies and checks the fluoride levels in fluoridated systems. In 1966 approximately 320 samples were analysed for chemical indices of pollution, pH and carbon dioxide as a check for possible corrosion problems, hardness, and toxic or troublesome trace metals such as iron, copper and manganese. An interest has developed in the use of PVC

pipng for high-pressure water systems. It is necessary to inhibit the depolymerisation processes of PVC by adding stabilisers such as dibasic lead stearate but these materials migrate into water passing through the pipe. This situation represents a potential health hazard whenever PVC piping or spouting is used to transport drinking water. A study of the kinetics of lead release is in progress in an attempt to improve the present unsatisfactory Standard Specification.<sup>8</sup>

Standards for water supplies are based on the specifications of the World Health Organisation.<sup>9</sup> While there can be little argument about the tolerances given, the scope and frequency of chemical testing are unrealistic for New Zealand waters. W.H.O. specifications are designed for highly industrialised areas such as in Europe where most water sources are subject to industrial pollution and where water may be used and re-used five or six times. Our own environment is completely different from that of Europe and our pollution problems are insignificant compared with theirs. Unless this is appreciated, there is a tendency to introduce over-zealous testing schedules. At a time when the country's analytical facilities are very limited it is important that they be used to the best advantage.

### Drugs

The aim of official control is to ensure that the right drug is present at the specified concentration and in a form which is absorbed with reasonable reproducibility and efficiency into the bloodstream. There should be no significant levels of impurities other than compounding agents. The variation in individual dosage forms such as tablets and capsules should not be significant. Finally, the stability of the drug must be compatible with the labelled expiry date.

The Food and Drug Regulations traditionally link their standards to those of the British Pharmacopœia and the British Pharmaceutical Codex. These define standards of purity for drugs and of concentration for a limited number of formulations.

There is also a standard for the disintegration of tablets into particles. The British Pharmacopœia makes no attempt to check whether the drug particles will dissolve sufficiently rapidly to be absorbed efficiently except in the case of griseofulvin where a limitation is placed on particle size. Obviously the smaller the particles, the more rapidly they will dissolve. We shall be attempting to develop suitable procedures for evaluating the availability of drugs from tablets.

Variations in the content of individual tablets are unlikely to be detected by those pharmacopœia methods which use a sample of twenty tablets. Methods of assaying individual tablets are desirable. In addition, the pharmacopœias do not establish stability standards for formulations, except indirectly by specifying formulæ for a limited number of cases. Even within their limited range of standards, the British Pharmacopœia and Pharmaceutical Codex do not always specify methods which are as satisfactory as those of the United States Pharmacopœia and the National Formulary. It could be advantageous for these sources to be incorporated into the regulations.

No specific provision is made for controlling the quality of non-pharmacopœia drugs or non-pharmacopœia formulations. However, a 1962 amendment to the Food and Drugs Act 1947 requires certain information to be supplied whenever a new drug is to be introduced to the local market. This includes reports of tests to establish the safety of the drug and tests to control the strength, quality, purity and safety of the drug. This information should provide a starting point for official control. The validity of results of an assay depends on the method used. One has only to consider a hypothetical assay for morphine hydrochloride by titration with silver nitrate to realise how misleading such an assay procedure could be for a sample contaminated with sodium chloride. The method of synthesis is important because a major change in the synthesis of a drug will change most of the likely impurities and hence alter possible side effects and toxicity.

Some authorities have even suggested that if the synthesis of a drug is changed, the biological testing of the drug should be repeated. Again, this emphasises the importance of evaluating control procedures rather than merely accepting their results.

Little official attention has been devoted to checks on drug quality for some years. This has created a situation where an inadequate number of analysts is available for this important work. Recently, the authorities became more actively interested. The National Research Advisory Council made an eloquent comment on a potentially dangerous situation when it recommended that an additional eight analysts be appointed to Chemistry Division for quality control of drugs.

In spite of staff shortages we have analysed a number of formulations during 1966 and detected a batch of paracetamol tablets which did not disintegrate sufficiently rapidly for efficient absorption. Paracetamol is an analgesic which appears to lack some of the toxic side-effects of phenacetin, to which it is closely related.

Another investigation involved suspensions of the antibiotic chloramphenicol palmitate which has crystalline and amorphous solid forms. A suspension of the amorphous form (the less stable and more soluble) on standing reverts to the crystalline form unless it is stabilised by the presence of methylcellulose. The crystalline form has such a low solubility in aqueous solutions that it is not absorbed efficiently. Suspensions therefore should contain only a small proportion of crystals. Infra-red spectroscopy has shown that the two available brands of suspension are satisfactory.

At present we are also investigating a range of the cough mixtures which are available in New Zealand. A great variety of formulations is involved and almost every cough mixture presents a unique analytical problem. It seems clear that some of the formulations do not contain therapeutic levels of any of their constituents and must produce their effects (if any) by psychological mechanisms.

## Conclusion

The Food and Drugs Section of Chemistry Division is active in fields which are particularly prone to the introduction of new compounds and techniques. There is a constant stream of analytical problems which provide stimuli for research projects. From time to time the Section's interest in quality control reveals new areas where controls should be developed and these provide another source of projects. The Health Department is concerned with similar problems in formulating legislative controls for food and drugs.

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## Question and Answer . . .

### THE EMPLOYMENT OFFICER

*We have been asked why the Institute has an Employment Officer, and what he does. So we asked Mr E. S. Borthwick to give an account of himself, and this is how he answered the two questions:*

#### Why?

Some years ago, in the post-war period, when there were numbers of chemists competing for a considerably smaller number of jobs, the Institute maintained an Employment Bureau. For a small fee the Bureau registered the names, qualifications and employment aspirations of Institute members who wished to use the service, and issued to them regular circulars listing positions vacant. This information was collated by a central Employment Officer from material sent in by prospective employers and by specifically appointed Branch representatives.

Later, when the employment tide turned and there were more jobs than chemists, the Bureau lost most of its customers and was closed down. But like many things in this life which, although officially dead, refuse to lie down, there still persisted a small demand for advice and help upon employment matters generally. So Council decided to retain an Employment Officer to deal with these enquiries on their behalf. Hence myself as present incumbent.

#### What?

In brief, I am rather like the 'Pub with no Beer', running a Labour Exchange without any labour to offer—or almost so. If I were to write a dissertation on "How to be a Successful Chemists' Employment Officer", I would paraphrase Mrs Beeton and start with "First catch your chemist . . .". My function nowadays is largely confined to dealing with overseas correspondence (18 letters last year) and giving brutally frank advice to egotistically youthful applicants who, on the basis of "sitting Finals for Higher National Certificate" and with an obviously inflated record of experience, expect as of right to obtain an immediate assisted passage and a job with management status to boot.

Nevertheless, every now and then the sincere and genuine enquiry comes in the mail and makes the job well worthwhile. If and when I can satisfactorily bring such an applicant and an appropriate employer together to their mutual advantage, I find it a truly rewarding human experience.

## Current Chemistry . . .

## VISCOSITY-CHARGE RELATIONSHIPS IN CLAY-WATER SYSTEMS

R. M. Carr, M.Sc.(Hons.), Ph.D., D.I.C.

Chemistry Department, University of Otago

THE viscosity relationships in clay-water mixtures are of importance in the ceramic industry, especially in the widely used slip casting process. When a natural clay is mixed with water it remains sticky and plastic until a substantial amount of water has been added. Under a microscope it can be seen that individual clay particles are grouped together in aggregates, i.e. the clay is flocculated. If a small quantity of sodium silicate is added to the system a spectacular change occurs. The fluidity is greatly increased (the viscosity is lowered) and the individual particles are separated or deflocculated. In such a state a fluid suspension can be formed with a relatively small amount of water (sometimes as low as 15-20%). A small decrease in the liquid content changes the system from a fluid one to a plastic one with a rather high yield point, i.e. a thixotropic system which is characterised by the fact that a given force must be applied to the material before any movement is produced. In the slip casting process a clay slurry is poured into a porous mould which extracts the water. The clay-water mixture changes from a fluid to a plastic state with high yield point and this allows moulds to be manipulated without causing damage to the cast. The origin of flocculation-deflocculation effects is related to the charges carried by the clay particles. A thorough understanding of such relationships and their origins is necessary for the scientific control of the slip casting process in the ceramic industry.

The structure of typical clay minerals has been described (*J.N.Z. Inst. Chem.* 31, 170, 1967) in terms of layers of silica and alumina polyhedra with some substitution of hydroxyl

for oxygen in the alumina layers. Clay particles usually possess a small residual charge which may originate from broken bonds at the edges of sheets, replacement of the exposed hydrogen atoms on hydroxyl groups by cations, or from substitutions ( $Al^{3+}$  for  $Si^{4+}$  or  $Mg^{2+}$  for  $Al^{3+}$ ) within the framework structure, the latter being the most likely origin of the charge. The interaction of charged particles with electrolytes is the cause of flocculation-deflocculation effects in clay-water systems. The model of a negatively charged clay particle immobilising either a shell of water molecules or attracting hydrated cations can be used to explain viscosity-charge relationships. The relative attraction of ions to the clay surface can be calculated from simple electrostatic theory and it is found that the binding energies are high for  $H_3O^+$  and  $Al^{3+}$  but decrease through the alkaline-earth and alkali metal cations. The effect of competition between exchanging ions can be used to determine the nature of a clay-water system. For example, if all clay particles are neutral they will gather together due to the action of weak dispersion forces, so flocculation results. If all particles carry like charges they will deflocculate as a result of electrostatic repulsions. The relative size of the exchanging ionic species is another important parameter in the interpretation of viscosity relationships. Some aspects of this general theory have been investigated in kaolinite-water systems.

Two types of measurement were made: viz. an electro-osmotic test for the determination of the sign of the charge on the clay particles, and viscosities of clay-water-electrolyte mixtures using a Brookfield viscometer. Increasing amounts of each of the

bromides of lithium, potassium, ammonium, tetramethyl ammonium, and cetyl trimethyl ammonium were added to a 20/80 clay-water suspension. The initial clay carried a negative charge and the system became more viscous as electrolyte was added. Only cetyl trimethyl ammonium bromide showed substantial flocculation which was closely followed by development of positive charge and deflocculation. All of the other electrolytes showed a small flocculation effect and little tendency to deflocculate despite the development of positive charge on the particles. This

type of behaviour is not in strict accord with the predictions of the theory outlined above. Much more experimental work is required to elucidate the mechanisms involved in clay-electrolyte interactions.

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#### N.Z. GEOCHEMICAL GROUP

At the 40th ANZAAS Congress at Christchurch in January the Geochemical Group in association with the ANZAAS committee was able to arrange an extensive series of papers on geochemical topics both from New Zealand and overseas. A notable visitor to the Congress was Prof. K. Rankama of the University of Helsinki. At a geochemistry symposium chaired by Dr J. Rogers papers were presented from Otago University on aluminosilicate stability relationships, from the Institute of Nuclear Sciences on isotope geochemistry, and from Massey University on geochemical prospecting. Dr J. F. Levering of the Australian National University presented a review paper on the geochemistry of the lower crust and upper mantle. A separate session on Mineral Development in New Zealand contained papers from both the Geological Survey and Chemistry Division on metal genesis and hydrothermal alteration in the Coromandel region, and on halloysite clays of Northland.

In all some 15 papers of a geochemical nature were presented.

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*R.I.C. Monograph for Teachers No. 14.* "Principles of the Colloidal State" by Dr G. D. Parfitt. 64 cents.

While the colloidal state is not included in school general science or chemistry examination prescriptions, this topic is usually treated in biology when the properties of protoplasm are considered.

In this Monograph, after a brief but useful introduction in which he outlines the scope of the subject and its everyday applications, the author divides his attention between lyophobic sols and lyophilic sols in the ratio of about three to one.

Sections are devoted to the stability, electrical charge, sedimentation, colligative properties and preparation of sols.

Minor topics of interest are the determination of Avogadro's Number from Brownian movement, a discussion of the behaviour of the surfaces of oxides in contact with water, salting out and the grouping of detergent molecules into aggregates (micelles).

The Monograph is rounded off with a list of a dozen suggestions for further reading.

A. F. BAKER.

*Copies will be available from the Registrar shortly.*

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## Branch Notes

### AUCKLAND

Preparations for the 1968 Conference are underway and will be reported in following month's Notes.

In **university circles** the Chemistry Department's move to the new staff and research accommodation in the "Stage B" building was completed in time for the present teaching session. Student numbers have increased at almost all levels this year. Enrolments in Chemistry I are approaching 800, excluding the first intake for the Medical School but including 280 taking B.E. (Intermediate).

Dr C. L. Nobbs has left the staff of the University Chemistry Department.

At the **Auckland Technical Institute** the enrolment in Chemistry III has exceeded 100 this year.

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### WELLINGTON

#### Recent appointments

##### *Chemistry Division:*

Dr G. D. MacAdam has joined the Metallurgy Section and will be concerned with the current research programme on the processing of N.Z. ironsands. Dr MacAdam was formerly head of the Metallurgy Section in B.S.A.'s Research Centre at Birmingham.

Mr W. J. Edge will be doing research work with the Food and Drugs Section. Mr Edge was previously in charge of Quality Control at Geigy Pharmaceuticals at Macclesfield, Cheshire.

Mr G. G. Page, a corrosion chemist and former graduate of C.U., has been a corrosion consultant in England. He has recently joined Chemistry Division.

Miss J. Hemmingson, a recent graduate from V.U.W., has joined the Organic Section.

Dr P. P. Williams and Dr K. R. Markham have recently returned from overseas trips. Dr Williams spent a year at the University of Aberdeen on a Nuffield Fellowship working on crystal structures of calcium alumi-

nates. Dr Markham held a Post-doctoral Fellowship at the Cell Research Institute at the University of Texas, Austin, for 2½ years. He was studying the use of phenolic natural products, particularly flavenoids, as species indicators and intends to continue work in natural product chemistry with emphasis on biologically active compounds.

Dr B. Findlayson from the University of Hawaii is working with Dr Ellis for a year.

Two Australian chemists have been working with Dr Golding during the vacation period. Dr A. H. White, a lecturer at the University of Western Australia, has been working, theoretically and experimentally, on manganese dithiocarbamates. Mr E. Sinn, a Ph.D. student at the University of N.S.W., has been studying the c.s.r. and Mossbauer spectra of trinuclear transition metal complexes.

##### *Soil Bureau:*

Mr P. L. Searle has been seconded to the C.S.I.R.O. for 3-6 months. He will be working at the Division of Chemical Physics in Melbourne and the Division of Soils in Adelaide.

#### New Instrument

Geological Survey have recently acquired A.E.I.'s SEM2 scanning electron probe micro-analyzer which is capable of analyzing quantitatively all elements down to Atomic No. 5. The principle of the instrument is the analysis of the X-rays emitted from the sample when it is bombarded by a stream of electrons. The emitted X-rays have wavelengths characteristic of each element present in the sample. The X-ray spectrometer has four fully focussing curved crystal analyzers to cover the whole range of elements. The take-off angle of 30° is higher than in other spectrometers and makes the specimen preparation for quantitative work less critical. The electron probe can be focussed down to 0.25μ and variable scanning conditions can be selected to give an accurate picture of the elemental distribution in the sample. Optical,

electron and X-ray micrographs can also be recorded.

The electron probe can be used to investigate all types of materials: metals and alloys, ceramics, soils, biological materials, fibres, etc. It is the only one of its kind in N.Z. and is available for use in research projects from other laboratories.

All enquiries should be directed to the Director of Geological Survey.

### CANTERBURY

Mr S. R. Gay, a foundation member of the Canterbury Branch, has retired from the position of General Manager of Southland Co-op. Phosphate Co., Invercargill, and has returned to live in Christchurch.

Mr D. J. Higgins has been promoted to Works Manager of Kempthorne & Prosser's fertiliser works at Hornby while retaining his existing position as Chief Production Officer for all works of the company.

Dr J. M. Austin has returned to the Chemistry Department, University of Canterbury, following a year's sabbatical leave spent partly in the United States and partly in U.K.

Dr W. S. Earl has returned to be Lecturer in Chemical Engineering, University of Canterbury, after two and a half years in Canada on leave without pay as project engineer for the Shawinigan Chemical Company, Montreal. Dr Earl worked at the East Montreal plant, first on the design, construction and initial production for a \$600,000 plant producing bisphenol used to manufacture polycarbonate plastics and epoxy resins, and later in the expansion of the main phenol plant to raise production from 50 million pounds to 100 million pounds a year and to provide capacity for 150 million pounds. On his return Dr Earl said this practical experience was easily as valuable as any post-graduate study he might have undertaken.

Two post-doctoral fellows have been appointed to the Dept. of Chemical Engineering. They are Dr S. O'Neill from University of Toronto and Dr N. F. Judd from University of Exeter.

Dr M. H. G. Munro, an Otago graduate, has been appointed Lecturer in Chemistry at Canterbury University. He has been doing post doctoral work at the Robert Robinson Laboratories, University of Liverpool. Dr Munro is an organic chemist with training in bio-genetics and is interested in problems in biological chemistry.

Dr K. Emerson, Associate Professor of Chemistry at Montana State University, Bozeman, Montana, will arrive at University of Canterbury in September on a Fulbright travel award. He will undertake crystallographic research.

Professor C. J. Wilkins has received a supplementary grant from the Selenium-Tellurium Development Association of New York for the continuation of his researches on these two elements.

The University of Canterbury has received a research fund award from the University Grants Committee for the purchase of an A.S.C.D. (Automatic Single Crystal Diffractometer) for the automatic determination of crystal structures. The diffractometer is controlled by its own digital computer and is almost wholly automatic in operation. The diffractometer will be used in the chemistry department for studies in organic, inorganic, and biochemistry. Among current projects are investigations of the unknown structures of two copper complexes which chemists in the laboratories of the Wool Research Organisation have found will promote an increase in the length of wool fibres.

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In January, immediately preceding the ANZAAS Congress in Christchurch, the Teachers' Refresher Course Committee held a national course in Chemistry. Course members stayed at Christchurch College and the lectures and workshops were held in the Science Block, University of Canterbury, Ilam. The course work was based on the new U.E. syllabus.

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The February meeting of the branch took the form of a buffet tea at Lincoln College, followed by an inspection of the newly completed teaching block, to be known as the Hilgendorf Wing after a former Director of the College. In an introductory talk before the inspection, the present Director, Dr M. M. Burns, referred to the low cost of the building (\$12 per square foot) which he attributed to large scale off-site prefabrication and to careful limitation of services. He said it had been decided to "wheel-in" special services rather than have them piped throughout the building. The low cost has apparently drawn

favourable comment from the Minister of Finance.

### Junior Chemical Society

The Canterbury Junior Chemical Society held its first meeting for the year early in March when Dr R. C. Claridge of the Canterbury University Chemistry Department gave a lecture-demonstration on "Radiation Chemistry"; using, among other equipment, the department's CAT (time averaging computer) he showed a large audience something of the study of very fast reactions.

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## THE CHEMICAL ESSAY PRIZE.

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(Conditions as decided by Council, November 1966)

1. The New Zealand Institute of Chemistry shall offer annually a prize for an essay or review on a chemical topic.
1. The prize shall be open to anyone who has not attained the age of 25 years before April 30th 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 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.)

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## BOOK REVIEW

*Mechanisms of Inorganic Reactions*, Second Edition by F. Basolo and R. G. Pearson, John Wiley and Sons Inc., New York, 1967. 701 pages. \$17.95.

Basolo and Pearson have assessed fairly the further results and understanding achieved in this field since the publication of the first edition of *Mechanisms of Inorganic Reactions* in 1958. There has been much research activity in the field, a fact indicated by a four-fold increase in publications since 1958. The authors accept most of the postulates presented in the earlier text and have successfully vindicated them by resource to recent results. There are some new sections in this edition, e.g. Reactions of Transition Metal Organometallics; and significant expansions of the texts relevant to fields in which most research is being done, viz. reactions of geometric and optical isomers, isomerism, racemisation, applications of Molecular Orbital Theory, physical properties and reactions of platinum(II) complexes, and metal-ion catalysis. It is apparent that many advances stem from the availability of new ligands which can be tailored to influence the stereochemical pathway and mechanism of a reaction.

The book benefits from two introductory chapters which outline the basic premises of Coordination Chemistry. The reader is introduced to relevant details concerning nomenclature, stereochemistry, stability and the nature of the coordinate bond. The latter section on The Theory of the Co-ordinate Bond is well presented; the authors make clear the failure of the Valence Bond Theory to describe the physical properties of co-ordination compounds.

The authors' frequent use of the term 'Hard and Soft Acids and Bases' is regrettable as the concepts have only limited empirical significance. The early classification into class (a) and class (b) acceptors (Ahrlund, Chatt and Davies) was based on thermodynamic data which was not strictly comparable in that it was not all appropriate to the one phase (or solvent). One feature of this classification is that the cations (Lewis Acids) most comprehensively studied in aqueous solution are in general classed as 'borderline'.

However, the general quality of this text is by no means borderline and the book is a valuable reference for all interested in the synthesis and reactions of transition metal co-ordination compounds.

H. K. J. POWELL.



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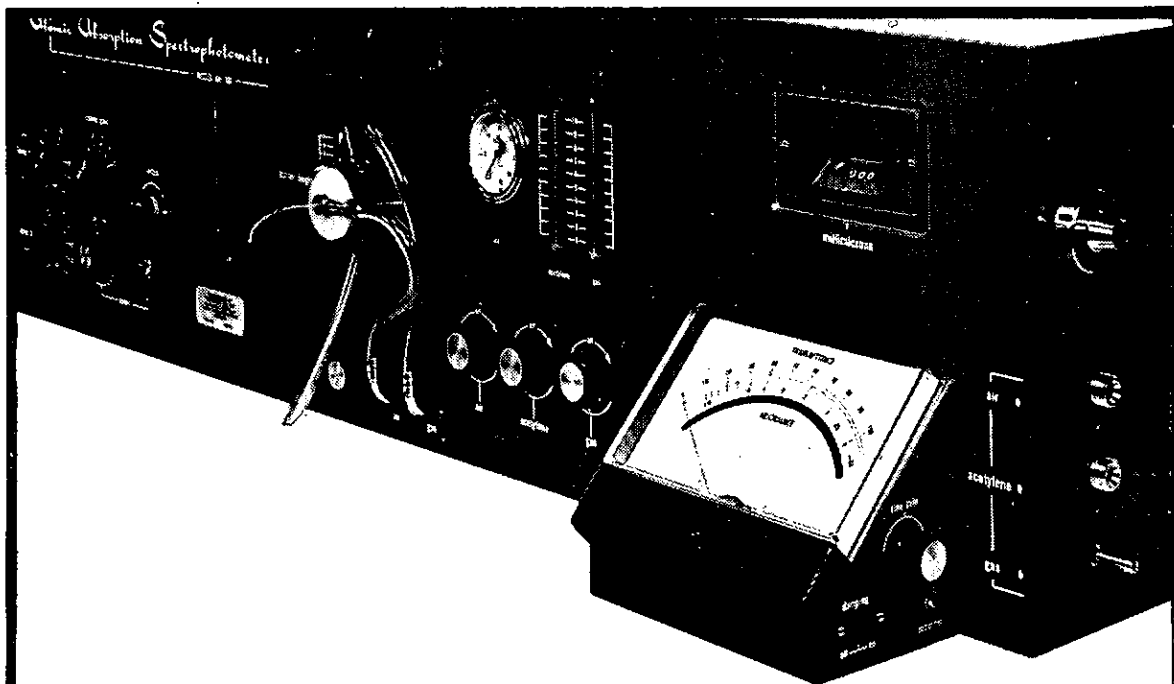
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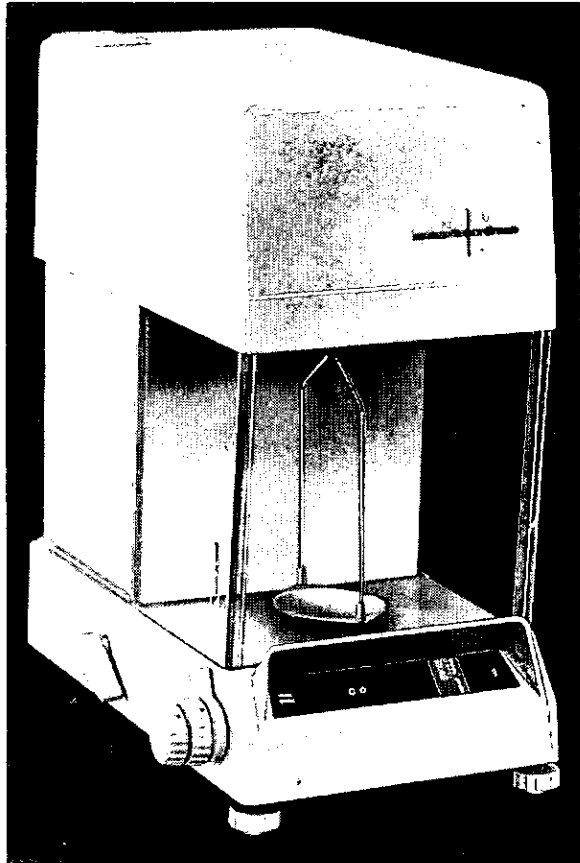
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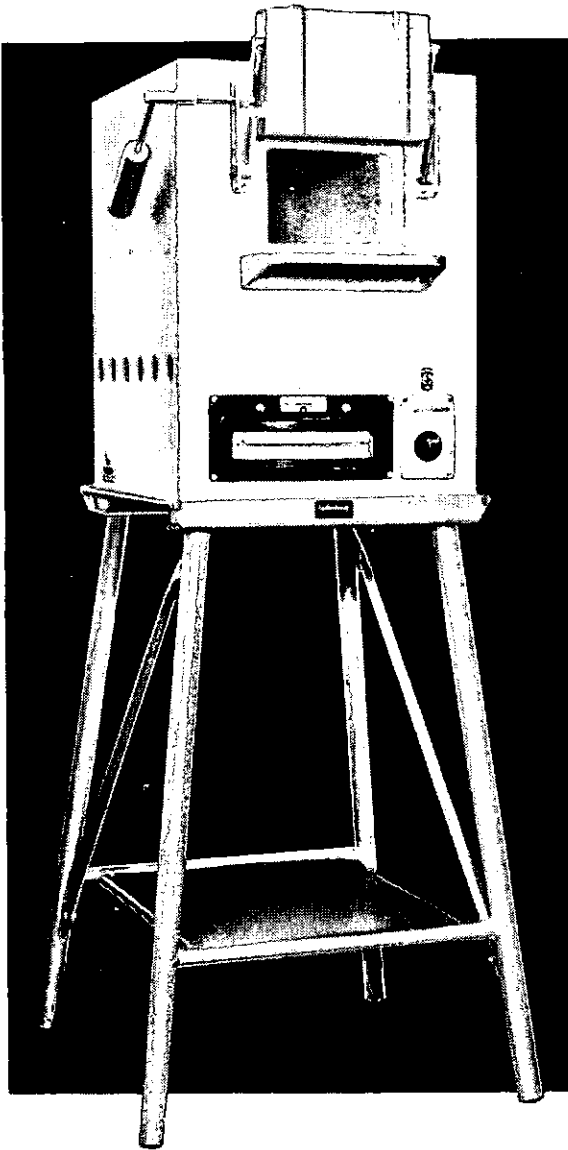


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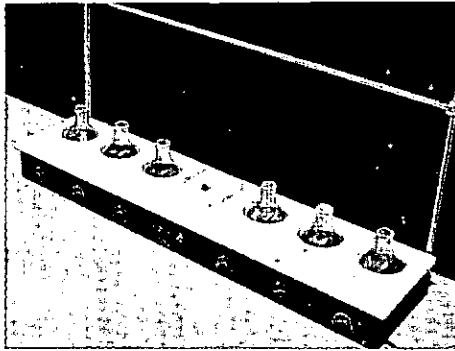
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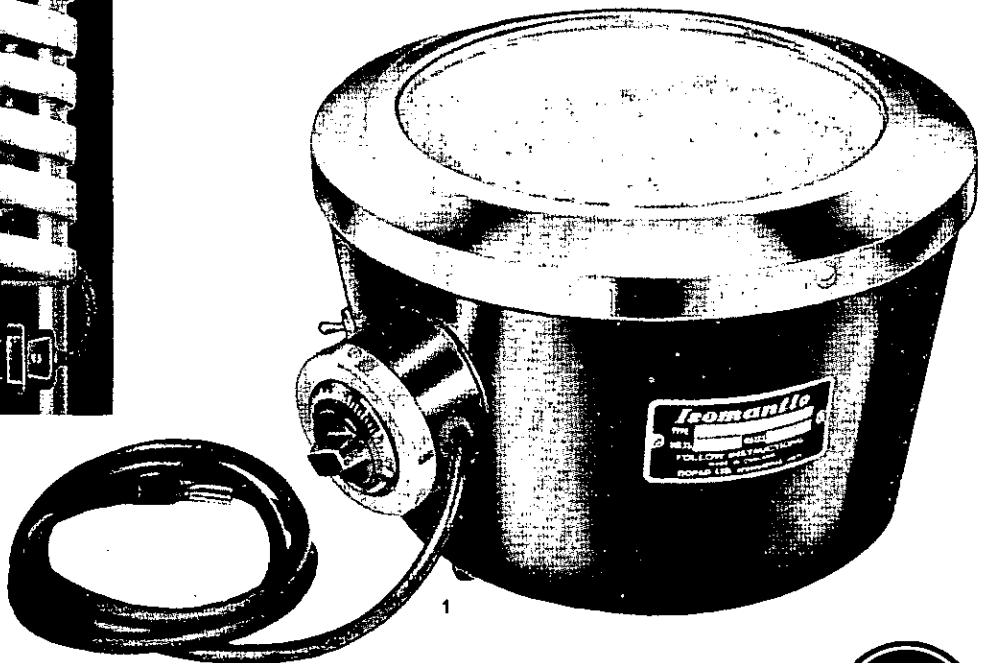
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