JOURNAL OF THE
NEW ZEALAND INSTITUTE OF CHEMISTRY

VOL. XX. JUNE, 1956. No. 3.

EDITORIAL

ROYAL AUSTRALIAN CHEMICAL INSTITUTE SALARY SURVEY.

Attention has frequently been drawn to the disparity between scientific salaries in Australia and New Zealand. For this reason the results of the Salary Survey conducted in August of last year by the Royal Australian Chemical Institute are of considerable interest in this country as well as in Australia. Since the report and the recommendations based on it (Proc. R.A.C.I. 23, 25 (1956).) will have only a limited circulation in New Zealand, it seems appropriate to summarise it here.

1547 Associates and Fellows, representing 62.5% of the Institute membership, replied to the questionnaire. These returns showed a mean salary for the 21-25 age group of £1,158. This figure rose steadily with age groups to £2,237 for the 41-45 group and then more slowly to £2,447 for the 61-65 group. The mean income for all groups, excluding those over 65, was £1,775.

As was the case with the New Zealand survey, salaries have also been considered relative to employing body. Considering the three main employers of chemists—Industry, Government and University—it seems that, apart from small differences at certain levels, salaries in the first two sections are roughly comparable but that they are somewhat higher in the Universities. However the point is made that the Universities probably require a higher proportion of more responsible officers than other employers and that a high proportion of moderately good salaries has counterbalanced the lack of highly paid positions. Attention is also drawn to the fact that only Industry pays salaries of £5,000 and over; "some

Published by the New Zealand Institute of Chemistry, G.P.O. Box 250, Wellington.
Edited by W. A. McGillivray, 178 Fitzherbert Avenue, Palmerston North.
Printed by Stylex Print Ltd., 98 Taonui Street, Palmerston North.

University and Government positions surely warrant similar rewards." Returns from chemists outside these three main employment groups were too small for accurate analysis. Nevertheless the position in the teaching profession did seem unsatisfactory and the Institute expresses concern at the low remuneration of the few Associates in the profession and the possible effects on future chemists. A specific recommendation is made that, "The Institute should look carefully into the question of the teaching of chemistry in schools and the remuneration of science teachers . . . salaries may be too low to attract and retain science teachers of the calibre required to inspire young students with the desire to become chemists."

It is apparent that considerable salary increases have occurred since the previous survey in 1953, the mean increase for all age groups being in the order of £400 per annum. But the increases have not been evenly distributed and those on salaries in the middle range have not improved their position as much as those nearer the extremes, the lag being of the order of £200. This lag may explain the greater interest shown in the salary survey by those in the 36-40 age bracket of whom 92.5% replied to the questionnaire against the general average return of 62.5%.

A number of conclusions and recommendations are of particular interest. Despite the salary increases which have taken place over the past two years, the Institute still regards the position as unsatisfactory and considers, in the light of world demands for highly trained scientific workers, that the present rewards are not sufficient to attract enough high-grade students or, presumably, to retain these men in Australia. If this is correct, what can we say of our chances in New Zealand? Attention is also drawn to the fact that, of the various States, Queensland lags behind the others in average salaries to the extent of some £200 to £300 per annum. This, it is pointed out, will make it difficult to retain staff in Queensland. If this small difference is enough to cause an appreciable drift, again what chance has New Zealand?

RECENT WORK ON MILK PROTEINS.

BY C. R. BARNICOAT,

Biochemistry Department, Massey Agricultural College, Palmerston North.

During the last 10-15 years research work on milk proteins has made great progress, partly because of the increased demands for milk proteins in the form of milk powders, but chiefly because of the elegant and precise methods of analysis which have been introduced during this period, viz.:—

(1) *Electrophoresis* which measures the rate of movement of a protein in a buffer solution under an imposed e.m.f. The rate of migration of the protein depends on its net electric charge, which is determined by the difference between the positive charges (amino groups of diamino acids and guanido groups) and negative charges (carboxyl of dibasic amino acids, hydroxyl and sulphydryl groups) on the amino acid residues attached to the peptide chains. When the charges are equal, the protein will not move in the electric field, this pH being the isoelectric point, a characteristic of each protein.

(2) *Ultracentrifugation* which depends on the rate of settling of a protein in an enormously high gravitational field.

(3) *Chromatography* which enables the amino acid composition to be found accurately and quickly, using very little material.

(4) *Electron microscopy* by means of which it is possible to observe objects of one hundredth the size, or even less, than seen in optical microscopes.

The most spectacular advances of all are probably due to the use of isotopes in the field of biochemistry. The degradation and synthesis of proteins and metabolites such as amino acids tagged with N^{15} (heavy) or C^{14} (radioactive), or with deuterium, or radioactive S, P, etc., sometimes in more than one position in the molecules, have been followed by means of appropriate apparatus and the results obtained are quite beyond the capabilities of the older "classical" methods of analysis.

By the application of the newer techniques to the problems of dairy chemistry, the classification and composition of proteins in milk have been completely revised. (Table I).

It is of interest to note that the contents of essential amino acids (i.e., those which the animal cannot synthesize and which must be derived from the food) in the casein of milks of several breeds of cows (ruminants), of mares (herbivora), and of sows (monagastric animals) show no species differences, according to Ray Sarkar (1952).

Blood Precursors (Protein Synthesis in the Mammary Gland): The question whether the proteins of milk come from the blood plasma proteins (a) after degrading to amino acids and resynthesis in the gland, or (b) after degrading to the peptide stage and resynthesis in the gland, or (c) from the circulating free amino acids now appears to have been settled.

TABLE I.

Composition of Typical Milk Proteins

"Classical"		*Per cent.*	
Total Protein (N x 6.38)		3.10	
Casein		2.30	
Whey ("serum") proteins		0.70	
Albumin			0.60
Globulin			0.05
Prolamine (alcohol-soluble)			Present
Milk fat globule-membrane protein			0.03
N.P.N. (x 6.38)		0.10	

"Modern"		*Per cent.*	
Total Protein (N x 6.38)		3.10	
Casein (at least 8 components)		2.30	
Whey ("serum") proteins		0.55	
Immune globulins			0.08
("Lactalbumin"			0.37
(αLactoglobulin	0.11		
(βLactoglobulin	0.23		
(Serum albumin	0.03		
Proteose-peptone (8 components)			0.10
N.P.N. (x 6.38)		0.25	

It has been shown that the immune globulin antibodies of the blood pass into milk. (For this experiment the proteins were labelled with methionine tagged with S^{35}). The principal proteins of milk were studied by Campbell and Work (1952), who injected lactating rabbits with glycine, valine and lysine labelled with C^{14}. The milk proteins were found to be very highly radioactive and of higher specificity than the blood proteins. The specific activities of the casein amino acids were somewhat higher than those of the whey proteins, which suggested that part of the whey proteins originated from the plasma—not more than about 25 per cent., however.

Casein is one of the very few phosphoproteins, and the puzzle of the source of its phosphate groups now appears to have been solved by Barry (1952) who, working with goats supplied with metabolites tagged with P^{32}, found that all the phosphate in casein came from the circulating inorganic phosphate, the process requiring about two hours for completion.

Casein: Linderstrom-Lang and Kodama (1925) demonstrated that casein is a mixture by fractionating it with aqueous alcohol: HCl mixtures. Cherbuliez (1932—) separated α and β caseins and results of the work of American chemists, Warner (1944) Warner and Polis (1945) and Hipp, Groves and McMeekin (1955), employing modern techniques, are summarised in table II.

TABLE II.

Composition and Properties of Components of Casein.

	α *Casein*	β *Casein*	γ *Casein*
N %	15.56	15.89	15.40
P %	0.98	0.55	0.11
S %	0.72	0.86	1.03
Isoelectric point	4.7	4.9	5.9
Proportion in casein (%)	75	22	3
Amino Acid Composition (part)			
Leucine	7.9	11.6	
Proline	8.2	16.0	
Cystine	0.4	0.0+	
Tryptophane	1.6	0.6	
Aspartic acid	8.4	4.9	
Tyrosine	8.1	3.2	

The composition of γ casein is similar to that of the β component.

Mellon, Korn and Hoover (1953) have shown that the terminal basic groups in α and β caseins differ, the relative proportions of arginine and lysine being responsible. Gordon, Semmett and Bender (1953) point out that γ casein has a low content of polar (mainly phosphate) groups, and because of its non-polar nature is soluble in 50% alcohol. It appears to be identical with the alcohol-soluble protein (prolamine) of milk reported in 1918 by Osborne and Wakeman.

Hipp, Groves, Custer and McMeekin (1952) prepared the three proteins α, β and γ casein by fractional precipitation from 50% alcohol, and identical ones from urea solutions of three concentrations. A U.S. patent has recently been taken out by these workers for this process of separating the components of the casein complex.

Clotting of Milk: Results of studies such as have been outlined in the foregoing sections have provided an incentive to workers in one of the oldest and most fascinating (and, incidentally, most characteristic) problems of dairy chemistry—the problem of the clotting of milk by rennet. Moreover, since Berridge prepared crystalline rennin in 1945, it has been possible for workers in this field to follow the reactions brought about by a pure enzyme acting on a pure substrate. Nevertheless, our knowledge of the mechanism of rennet action remains incomplete for the reaction is an amazingly complex one.

Rennin is a protease with optimum pH 3.8 and its primary function in the true stomach of the calf is to digest milk. The fact that cow's milk clots before the (very dilute) rennin has completed its work of digestion is therefore to be regarded as a peculiarity of the milk rather than the rennin.

Nitschmann and Varin (1951) using relatively enormous concentrations of rennin estimated that in extreme hydrolysis only one bond in every 33 amino acid residues was split. They also calculated that only one bond in 1,200,000 was split at the moment

of clotting. Holter and Li (1950) investigated the phosphoamidase activity of rennin and other proteolytic enzymes on casein. Rennin proved to be the most active, the ratio of its milk-clotting activity to its phosphoamidase activity for different rennets being almost equal. They consider that the degradation of casein by rennin may be through the phosphate linkage—i.e., the cross-linkages between peptides.

It is now recognised that the enzymic activity of rennin is not that of clotting milk directly, but rather that of altering it in some way so that it will clot under the appropriate conditions—e.g., at temperatures above 15deg. C and in the presence of calcium ions.

It was formerly believed that the clot is a derivative of casein, named paracasein. Cherbuliez and Baudet (1950) prepared solutions of the "paracaseinate" and on fractionating them found β and γ casein had not been changed, but that α casein had been modified into two proteins (para α 1 and para α 2) which gave double peaks electrophoretically.

The nature of the second clotting mechanism is still obscure. It has, however, an extremely high temperature coefficient which is strong evidence of its being a protein denaturation—i.e., an unfolding of the polypeptide chains followed by their recombination in a more fibrous fashion. Calcium, being a divalent ion, affects the stability of this more hydrophobic complex according to critical experiments made on the stability of other protein systems in the presence of this element.

The physical condition of casein has been studied with the electron microscope by several European workers. Nitschmann (1949) and others found that the casein particles were spherical and varied considerably in size, the median diameter being about 120 mμ. When milk sours the curd consists of threads and irregular masses. There is no preliminary dissolution of casein micelles before clotting with rennin, though there appears to be an alignment of threads of it. The clotting time of milk is inversely proportional to the average size of the casein micelles, and therefore is directly related to the surface area.

With a complex substance such as milk, it is unlikely that any single reaction will explain all the phenomena of clotting. It is therefore not surprising to find that various branches of biochemistry and biophysics are still bringing aspects of the subject to our notice which are not always reconcilable.

Whey ("serum") Proteins: Unlike casein these are denatured by heat. The extents to which they occur in milk are recorded in table I.

Albumin is no longer regarded as the principal protein of whey, the "Classical lactalbumin" having been resolved into several components.

The "Classical globulin" fraction attains enormous proportions in colostrum. The "immune globulins" sometimes in excess of 10 per cent. have been isolated electrophoretically and appear to be identical with or closely related to some of the immune globulins of blood serum (Emil Smith (1946). This immunity factor is still present in later milk.

The "Classical lactalbumin" fraction is composed of

(i) α lactalbumin (Gordon and Semmett (1953)), M.W. 16,500; isoelectric point pH 4.6; easily soluble in water.

(ii) β lactoglobulin (Palmer (1934)), accounting for about 60 per cent. of the whey protein; isoelectric point pH 5.5; insoluble in water but freely soluble in very dilute salt solutions.

(iii) Serum albumin (Polis, Schmukler, Custer and McMeekin (1950)), amounting to less than 5 per cent. of the whey proteins. This protein has the same electrophoretic mobility as blood serum albumin and, indeed, it is identical with it, as confirmed by serological tests.

It is now established that two of the minor proteins of whey are identical with those of the blood though the major constituent, β lactoglobulin, is quite different from blood serum globulin.

Fat Globule-membrane Protein: Renewed interest has recently been taken in this lipoprotein which has been little investigated since L. S. Palmer's studies over 20 years ago. Brunner, Duncan and Trout (1953) "washed" 70 gallons of cream through a milk separator six times and, from the "buttermilk" obtained by churning, isolated a crude protein which they fractionated from aqueous alcohol, equivalent to a 2 per cent. yield on the basis of the milk fat. It had a M.W. of about 47,000, and the electrophoretic patterns indicated that some of their preparations contained more than one component, probably adsorbed milk plasma proteins. By ultracentrifugation, it was found that the principal component was globulin-like. Hare, Schwartz and Weese (1952) obtained about a 1 per cent.. yield of the protein, and as previously noted by Palmer, its N content was low, 13 to 14 per cent. instead of the usual 15 to 16 per cent. The amino acid composition was quite different from that of casein, albumin and β lactoglobulin, which supports the theory that the milk-fat globule-membrane is a distinct entity.

Results of investigations using modern techniques have already opened up new lines of research in applied fields relating to proteins, and they will no doubt prove invaluable to future workers. We must not, however, overlook the amazing contributions of the earlier investigators who established the foundations on which protein chemists of the present day are building so magnificently.

VOLUMETRIC CALCULATIONS ON THE MOLAR BASIS

BY G. A. BOTTOMLEY,
Chemistry Department, University of Otago, Dunedin.

Students always show considerable interest in the technique of volumetric analysis, often reaching a remarkably high standard of dexterity in the actual manipulations. Their enthusiasm, however, is too frequently given a serious jolt when it is found that many experiments, carefully performed with real application and industry, have to be marked incorrect because of errors in the calculations. These errors involve factors such as x2, x½, etc., connected with the "equivalent weight", at an alarming frequency. A few students stumble on the correct answer by having made two such errors which fortuitously produce the correct result.

Anyone with experience in the teaching of volumetric analysis, especially where the analysis is a means to an end as in a physicochemical exercise, is fully aware how dangerous a device is that of "equivalent weight" in all but the most experienced hands. We are inclined to dismiss these errors as due to student inertia, and they, to faulty teaching. My judgment is that "equivalent weight", and its dependent relative "normality", are terms which should not be permitted in a scientific subject. It is unfortunate that in the past a considerable literature using these terms has arisen, and that the tradition still persists, but that is no argument for the continuation of a pernicious practice.

The principal dangers associated with the "equivalent" treatment are set out below.

1. The difficulty of defining "equivalent weight" in a manner which does not demand too great a chemical background from the student, and which leaves him no room for incorrect deductions.

The extent of the difficulty is measured by the space which standard texts devote to definition and illustration of this point.

2. The possibility of the same substance having different equivalent weights in different reactions, sodium carbonate as an elementary example, so that a solution labelled 2.0 Normal is without stoichiometrical significance unless the standardising reaction is quoted fully.

3. The dictum "equivalents react with equivalents" leads students to suppose that volumetric calculations can be done on this basis *without referring to the specific reactions and equations under consideration*—a completely erroneous conclusion in general but one which happens to "work" for a sufficient number of simple cases to ensnare the student into believing in its universal nature. Related to this danger is the situation where a student learns the "equivalent weight" for various reactions by heart, rather than

carry out the deductions from the equations appropriate to the reaction in question, or worse still memorises the statements such as 1 ml. N/50 $KMnO_4$ = 0.0074g I_2.

4. The difficulty of using any literature in which the authors have not clearly and explicitly defined the strength of at least one of the working solutions in terms of grams per litre of a stated substance, or defined their "equivalent weight" in some non-ambiguous manner. One, of course, can usually "guess" what a statement such as 0.01 N HClO means, but there is always the possibility of being wrong. Uncertainty should not be the basis of any science.

Now all these objections would be pointless if no workable alternative could be offered. Fortunately it is quite easy to demonstrate that the molarity basis eliminates all these difficulties without introducing any unmanagable complications either from the theoretical or the purely practical viewpoint. Let us examine the molar method critically.

Definitions.

A *Molar* solution is one containing one gram mole of a stated substance per litre. Designated, M., 1 ml. of this solution contains 1 millemole.

Examples.

Potassium permanganate—15.8g per litre, 0.10 Molar ($KMnO_4$),
Sulphuric acid—98.0g per litre, 1.0 Molar (H_2SO_4),
Sodium aluminate—72.0g per litre, 0.50 Molar (Na_2AlO_2).

In place of the elaborate concept of equivalent weight all that the student need learn is the method of summing atomic weights to produce a formula weight.*

Contrast the distinctness of the molar strength statement with, for example, $KMnO_4$, 0.1 Normal. This may refer to any of the reactions below, with the corresponding molarity indicated.

7e	+	MnO_4^-	+	$8H^+$	=	Mn	+	$4H_2O$	0.100/7 Molar
5e	+	MnO_4^-	+	$8H^+$	=	Mn^{++}	+	$4H_2O$	0.100/5
4e	+	MnO_4^-	+	$8H^+$	=	Mn^{+++}	+	$4H_2O$	0.100/4
3e	+	MnO_4^-	+	$4H^+$	=	MnO_2	+	$2H_2O$	0.100/3
e	+	MnO_4^-			=	MnO_4^{--}			0.100/1
		MnO_4^-	+	Ag^+	=	$AgMnO_4$			0.100/1

*Since the term molecular weight when applied to ionic substances dissolved in ionising solvents (or even to water in the liquid phase) has a less precise significance than when applied to systems in the gas phase, many writers are now using the term formula weight in analytical work, and correspondingly are describing solutions as M formal. Although such a reform is desirable, the usage has not yet taken hold, and in this paper we shall still use molecular weight in the familiar manner as the sum of the atomic weights in the empirical formula.

Which does it refer to?

It is no answer to this type of objection that "it is usually obvious what is meant", the confusion of students is clear evidence that nothing is obvious.

As a second practical example of the dangers of "equivalents" consider $I' \rightarrow \frac{1}{2}I_2 + e$, which can be brought about by a large number of oxidising agents, common to the experience of a student, MnO_4', Fe^{+++}, H_2O_2, S_2O_8'', Cr_2O_7'', etc. The student is liable to believe that the equivalent weight of I' is always the same as its atomic weight. There are a great many scarcely less common reactions where this is not so. A standard physicochemical experiment is the investigation of the equilibrium $I' + I_2 \longleftrightarrow I_3'$ followed by thiosulphate titration. Here the equivalent of I' is half the atomic weight, since that is the amount 'reacting' with $\frac{1}{2}I_2$, the usually accepted equivalent of molecular iodine. Further illustrations of variability of the equivalent of iodide are shown in the following equations.

(1)	$2Cu^{++}$	+	$4I'$		$\rightarrow$	Cu_2I_2	+	I_2	$(4I'$	=	$I_2)$
(2)	IO_3'	+	$6H^+$	+ $5I'$	$\rightarrow$	$3H_2O$	+	$3I_2$	$(5I'$	=	$3I_2)$
(3)	IO_3'	+	$6H^+$	+ $2I'$	$\rightarrow$	$3H_2O$	+	$3I^+$	$(2I'$	=	$3I^+)$
(4)	HgO	+	$4I'$	+ H_2O	$\rightarrow$	HgI_4''	+	$2OH'$	$(4I'$	=	?)

In these more complex illustrations (especially Nos. 3 and 4) there is real difficulty in deciding to what standard the equivalent weight of any reactant shall be referred.

It is not without significance that several textbooks, initially dealing at length with the equivalent weight method, pass without comment or explanation to the molar basis when discussing iodate titration, positive iodine, and hypochlorous acid.

Indicative of the difficulties in the concept of equivalent are the following two student posers asked recently.

"Why is the equivalent of oxygen taken as eight and not sixteen as indicated by the following equation:—

$$H_2 + O_2 \rightarrow H_2O_2$$"

"Copper has a divalent ion Cu^{++}, hence the equivalent of copper is half its atomic weight. Why is it then possible for copper to react in accordance with the equations:—

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

and how is it that the copper here is "equivalent" to 4/3 and 2 "equivalents" of nitric acid respectively. I thought equivalents always reacted with equivalents."

On the grounds of clarity of definition alone the molar basis far excells the equivalent method.

Method of Calculation on a Molar Basis.

The essential steps in the molar calculation method may be summarised:—

1. A knowledge of the chemical processes occurring in the analytical scheme.
2. The formulation and balancing of all relevant equations.
3. A statement of the analytical process in the form F Moles unknown strength reactant = I Mole of known strength reactant.
4. Calculation of the amount (in moles or millemoles) of the known strength reagent which has been used, and multiplication of this amount by the factor F to obtain the amount of unknown strength reagent (in moles or millemoles).
5. Conversion of the amount of the original reagent to grams by multiplying by the molecular weight—including the water of crystallisation where necessary.

Various examples of the molar type of calculation follow.

1. 15.2 ml. of M/10 NaOH was used to neutralise to methyl orange 10 ml. of unknown strength hydrochloric acid. Calculate the strength in grams per litre of the acid.

Reaction 'actually' brought about is $NaOH + HCl \rightarrow NaCl + H_2O$, from which it is clear that

1 gram mole NaOH reacts with 1 gram mole HCl

$$\text{hence acid strength} = \frac{15.2}{10 \times 10} \times 1 \text{ gram moles per litre.}$$

There being no controversy as to what the molecular weight of HCl should be, the required result follows,

$$\text{Strength of HCl} = \frac{15.2}{10 \times 10} \times 1 \times 36.5 \text{ grams per litre.}$$

Experts will omit certain stages of this, but at least the method is simple and free from all trace of ambiguity.

2. Potassium iodide was added to 10 ml. of 0.01 Molar $KMnO_4$. The liberated iodine titrated against sodium thiosulphate required 17.7 ml. of thiosulphate. Calculate the concentration of the thiosulphate in terms of $Na_2S_2O_3$, $5H_2O$ per litre.

Essential equations:—

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$5O + 10HI \rightarrow 5H_2O + 5I_2$$

from which it follows that $2KMnO_4$ liberates $5I_2$ but also:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Hence $2KMnO_4$ equivalent to $5I_2$, equivalent to $10Na_2S_2O_3$ or $5Na_2S_2O_3$ equivalent to 1 $KMnO_4$.

[An ionic method is equally suitable, in fact preferable:—

$$5e + MnO_4' + 8H^+ \rightarrow Mn^{++} + 4H_2O$$
$$I' \rightarrow \tfrac{1}{2}I_2 + e$$
$$I_2 + 2S_2O_3'' \rightarrow 2I' + S_4O_6''$$

It is *not* satisfactory to proceed directly on the basis of the equations,

$$8H^+ + MnO_4' + 5e \rightarrow Mn^{++} + 4H_2O$$
$$2S_2O_3'' \rightarrow 2e + S_4O_6''$$

In this case the correct answer is obtained, but the method overlooks the possibility of electrons (or at any rate some of them) coming from or being used by other reactions than those set down—the same mistake as never permitting the equivalent weight of a substance to vary, but in another guise.]

As for example (1):—

$$\text{Strength of thiosulphate} = \frac{10 \times 0.01}{17.7} \times 5 \times 248 \text{ gram}$$

pentahydrate per litre.

These examples are intended to show that the volumetric calculations can be done at least as well on the molar basis as by using equivalent weights. If the reader will lay out in full the corresponding stages of the equivalent method, he will find that the actual amount of calculation is never less than on the molar basis and is often greater. In general the only real difference between the two methods is the point at which the corrective factors are introduced. It is not true that equivalents simplify volumetric calculations—they merely drive some of the stages of the calculations out of the wholesome glare of publicity!

In cases of any complexity the possibility of error is greater in the equivalent methods than in the molar method, for there is always the difficulty of selecting the correct equivalent weight for the substances under consideration, as well as the possibility of a correct answer being reached through twice applied ignorance. The reader is invited to consider what is meant by an equivalent in the standard azide estimation,

$$HClO + 2HN_3 \rightarrow H^+ + Cl' + H_2O + 3N_2.$$

No case can be made out for the continuation of the "equivalent methods" as far as computation is concerned. Are there any points of practical significance which are sufficient to offset the enormous superiority of the molar basis?

It is claimed by the equivalent weight adherents that equal volumes of two reagents of the same normality will react with the same volume of a given substance, whereas equimolar solutions may differ by a factor of between 1 and 8 in the volume of substance

they will react. Even if this were true, what value is it? It is not a usual practice to change the nature of the fluid in the burette part way through a titration. The claim presupposes that the normality of the solutions is with respect to the same reaction; it would not do, for instance, to prepare a normal solution of perchloric acid as an oxidising agent and then use it in acidimetry. Similarly it is claimed that it is an advantage to know in advance that for this solution about 0.1 normal, volume 25 ml., we shall need about an equal volume of some other reagent of about the same normality to react with it, and thus avoid excessively large or small titrations. Personally, I find that it is little trouble to adjust the volumes of samples so as to obtain roughly equal titrations—or to dilute the solutions on a molar basis by such a factor as will bring about the required equality.

With the molar system it is no longer possible to evaluate an "equivalent weight" for a substance, thus elementary teaching is robbed of one of its most confusing exercises. The significance of the "equivalent weight" as calculated on the normality basis is that it is a simple sub-multiple of, or equal to, the molecular weight of the substance. Precisely the same viewpoint can be achieved on the molar basis as follows. Assume that the substance reacts with the reagent one mole for one mole, and hence calculate the "pseudo-molecular weight", which will be either a simple multiple or sub-multiple of the correct molecular weight.

Conclusion.

The molarity method of volumetric procedure has advantages so greatly superior to the equivalent method that it seems inconceivable that the latter should continue to exist in a scientific subject except by virtue of tradition and historic interest.

The advantages may be summarised.

(a) The concept of molarity is simple to define, readily mastered by elementary students and is *unambiguous*.

(b) Calculations carried out on a molar basis never involve more work than the equivalent basis, frequently less.

(c) As no person can complete a molar calculation unless he has before him the appropriate equations for the reactions involved, the teaching value of the method is greater than that of the equivalent method.

For these reasons it is earnestly hoped that the equivalent method will vanish into obscurity in the near future.

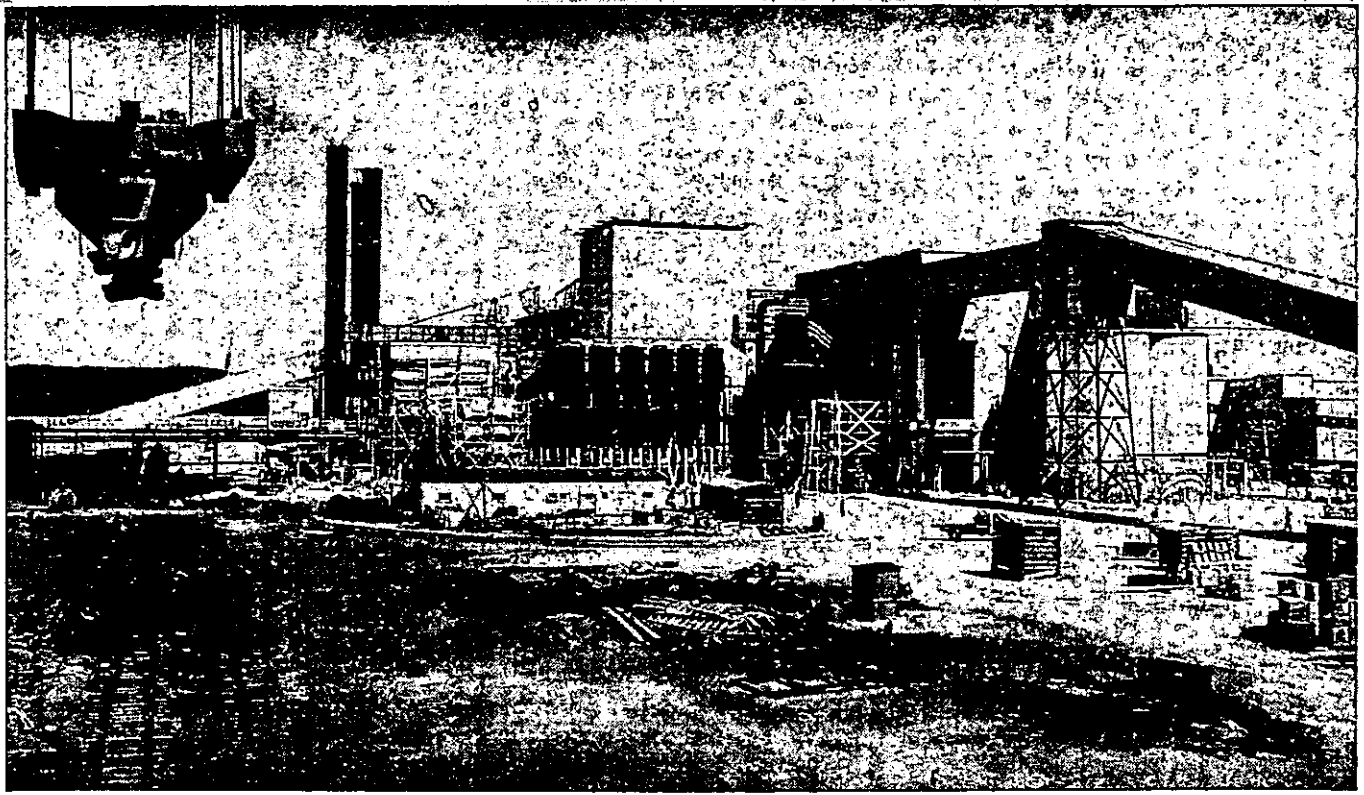
CONFERENCE PERSONALITIES.

Left—

Guest speaker at Conference this year is Dr. Walter Dunkley, Associate Professor of Dairy Industry, University of California.

Right—

The success of a Conference depends in no small measure on the efforts of the Secretary. Mr. H. S. Maslen is seen here at work on the second Conference circular.



A view of a section of the Tasman Pulp and Paper Company's Works at KAWERAU, the focal point of this year's post-Conference excursion.

BRANCH NOTES.

WELLINGTON BRANCH.

Mr. W. G. Hughson has sailed for England where he will be the New Zealand representative on the Commonwealth Committee on Fuel Research. Mr. Hughson, who will be away for four months, will also study the latest methods of coal analysis both physical and chemical and the upgrading of coal. He is hoping to pay a visit to the Continent, especially to Germany, to see the latest coal research there.

Mr. A. H. Swaney has left I.C.I. Wellington, and taken up a position with Ivory Spray Chemicals Ltd., Nelson.

Dr. Walter Dunkley, Associate Professor of Dairy Industry on the Davis campus of the University of California, has arrived in New Zealand under a United States Fulbright Award. He will be working at the Fats Research Laboratory, Wellington, until the end of the year.

Mr. W. A. Joiner, Deputy Secretary of the D.S.I.R., has left New Zealand and plans to spend four months overseas. Mr. Joiner, who will visit Canada, Britain and Europe, will study research administration, with particular reference to the organisation of research associations and assistance to industry.

CANTERBURY BRANCH.

At the March meeting of the Canterbury Branch the Branch Prize for the best Stage II Chemistry student was presented to Miss Sally Page. Miss Page is the daughter of Dr. R. O. Page, a foundation member and past-Chairman of the Canterbury Branch.

OTAGO BRANCH.

A lively discussion followed the Chairman's address to the Otago Branch. Dr. Fastier chose the very topical subject of chemists' salaries in New Zealand. After outlining the need for the fullest utilisation of our scientific manpower, the difficulties in assessing the value of the scientists' contributions to the national economy and the need for increased remuneration, not only because of its purchasing power but for the prestige it can confer, Dr. Fastier pointed out that it was one thing to appreciate the predicament of our profession in New Zealand and another to decide the best means to rectify it. He made the following points:—

1. We have a collective interest in salaries, and if we can boost the earnings of one group, other groups will tend to fall into line. The University scale sets a standard, directly in the case of Medical Research Council salaries for instance, and indirectly for Government positions and industry.

2. Is it fair to blame politicians for the present low salary position? The politician must follow public opinion; therefore we must influence public opinion.

3. Engineers, salaried medical officers, university teachers, etc., are all in a similar position. Can we get together?

After the discussion a motion was passed asking Council to consult with other professional bodies with a view to forming a Combined Professional Association, its primary objective being to look into the question of professional salaries.

MANAWATU BRANCH.

All members will join with us in congratulating Dr. A. T. Johns on his appointment as Director of the Plant Chemistry Laboratory, D.S.I.R., in succession to Dr. J. Melville. Dr. Johns has taken an active part in Institute affairs and is already well known to most members. Born in 1917, he was educated at Christ's College and Canterbury University College, where he graduated M.Sc. with First Class Honours in Physical Chemistry in 1939. As holder of a National Research Scholarship, Dr. Johns worked with Dr. C. R. Barnicoat at the Dairy Research Institute until he joined the Second N.Z.E.F. in 1940. In 1945, a Rehabilitation Bursary took him to Cambridge where he worked in the School of Biochemistry and the A.R.C. Unit of Animal Physiology, obtaining his Ph.D. in Biochemistry in 1949. Dr. Johns then joined the staff of the Plant Chemistry Laboratory and was appointed Chief Chemist in 1958.

In 1951, he was chosen as one of the three New Zealand delegates to the 75th Anniversary Conference of the American Chemical Society in New York and in 1954 was awarded a Commonwealth Fund Civil Service Fellowship. He spent nine months working in the Biochemistry and Virus Laboratories of the University of Berkeley, California, followed by a three-month tour of agricultural research institutions in the United States, two and a-half months in England and attended a C.S.I.R.O. Conference on Ruminant Digestion at Canberra. Dr. Johns is a New Zealand University Rowing Blue and represented Clare College, Cambridge, at Henley Regatta in 1946.

LETTERS TO THE EDITOR.

Sir,—I would like to draw your attention to an article by J. C. Andrews and S. G. Brooker entitled "Twenty-five Years of the Chemist and Industry", in the November issue of the Journal. This article in itself is extremely interesting, and the authors have put together a very readable article. I would, however, like to point out that on page 85 there is a small error.

The last paragraph on page 85 deals with the Plastic Industry in New Zealand, and states that we are still confined to the moulding of imported powders. May I point out that the Company with which I am associated has been engaged in the manufacture of both Phenolic Moulding Powders and Phenolic Resins for the past twenty months. The materials are marketed under the trade name "PHENITE" and current production is in the neighbourhood of 5-8 tons per month. To the best of our knowledge we are the only organisation in New Zealand which is engaged in this process.

J. URLWIN.

Sir,—In the interests of scientific accuracy I feel constrained to draw attention to a misconception that is in danger of being perpetuated in the contribution appearing in the Jubilee issue of the Journal on "The Future of Chemistry in New Zealand."

The authors make two distinct references to the bauxite deposits in Fiordland. Unfortunately no workable deposits of bauxite are known to exist either in Fiordland or in any other part of New Zealand, and in view of the climatic conditions under which bauxite deposits are believed to be formed, there appears little likelihood of any being discovered in this country.

It is true that from time to time the possibility of establishing an aluminium industry in Southland has been seriously considered but the basis of such proposals has been the availability of abundant cheap electrical power from the suggested Manapouri scheme, and it has always been realised that bauxite would have to be imported.

It is, of course, normal practice for bauxite to be transported for reduction to sources of cheap power and it may be of interest to readers to learn that the Guianas, Indonesia and Equatorial Africa which produce 75% to 80% of the world's bauxite produce no aluminium, whereas U.S.A. and Canada are responsible for approximately 80% of the metal production but less than 15% of the bauxite production.

G. S. LAMBERT.

EQUIPMENT PAGE.

The rapid but uniform pouring of chromatographic columns for routine separations may constitute something of a problem. Polythene wash-bottles have been found most convenient for this purpose in Dr. McGillivray's laboratory. The bottle is about one-fifth filled with adsorbent and an equal volume of eluent is added. The mixture is shaken and squirted into the chromatography tube. The method is rapid and highly uniform columns result.

A heater of the type now fitted in the "Radiometer" pH meter, and referred to in the last issue, will probably solve many of the problems previously encountered in mains-operated pH meters. Instability seems inherent in Macbeth meters in this country, but the problem was completely overcome by the installation of an 8-watt heating coil which was left permanently "on".

Where numbers of routine microkjeldahl determinations are carried out, a simple innovation for facilitating the acid digestion of samples has proved time-saving in the experience of Dr. Mangan. This is to replace the gas burners by a ten-inch 600-watt electric bar element. The racks themselves are made of galvanised iron sheet (plentifully drilled with holes to avoid buckling) and lined inside with "polite" or similar insulating

sheet. Digestion proceeds at a uniform pace and the operation may be safely carried out overnight, thus effecting a considerable saving in working time.

The use of an electrolytic desalter in the preparing of solutions for paper chromatography often seems impracticable because the volumes of solution required are too large. This difficulty has been met in a desalter currently used at Plant Chemistry Laboratory employing a continuously renewed mercury cathode and a copper anode. A cellophane membrane surrounds the anode. The dimensions of the cell have been scaled down so that volumes of solution of 2-5 ml. can be conveniently and rapidly desalted. Amino-acids are quantitatively recovered in general; organic acids and even sugars may be recovered in high yield. This is because the desalting is accomplished so rapidly that little diffusion occurs across the cellophane membrane into the dilute acid solution surrounding the anode. Further details may be obtained from Dr. A. T. Johns, Plant Chemistry Laboratory.

Wastage of buffer solutions often occurs because of bacterial or fungal contamination during storage. This can be avoided by the addition to the solution of agar cubes containing mercuric iodide. Mercuric iodide is prepared by precipitation, carefully washed and then added to a 2% agar solution. The agar is allowed to set in Petri dishes and cut into cubes which may be stored indefinitely in a stoppered bottle under water.

Drying of glassware in laboratories is always a problem. One solution is the provision of racks under the washing-up bench, to hold wire-netting baskets containing the washed glassware. A heater/fan combination provides for fairly rapid drying and the glassware may be readily distributed to appropriate cupboards from the wire baskets. This system has considerable advantages in terms of time, space and convenience over the usual "drying rack" system.

The measuring out of many equal portions of fluid may be considerably speeded up by the use of an automatic pipette such as the "Aupette". This pipette is essentially a glass piston within a graduated barrel. When the piston is pushed into the barrel (with moderate thumb pressure) the preset volume of fluid is dispensed through a jet. The piston is rapidly restored to its original position by a return spring and the pipette refills at the same time through a supply tube and valve unit. In this way any predetermined volume of fluid may be delivered over and over again with considerable precision and rapidity. The volume dispensed is easily adjusted with a simple screw collar. This automatic pipette has been found convenient for filling test-tubes as it may be taken to the tubes and is easily operated with one hand. The range of fluids which may be handled is probably limited by the corrodibility of the stainless steel valve unit and jet. The valves proper are of buna rubber and the supply tube of tygon—both resistant to many chemicals. The whole apparatus may be sterilised by autoclaving and is suitable for the aseptic dispensation of biological media, etc.

At present the pipettes are available in 5 ml. and 10 ml. capacities, graduated to 0.2 ml., but it is probably possible to adapt them to take other capacity barrels.

BOOK REVIEWS.

ESSAYS IN BIOCHEMISTRY. Edited by Samuel Graff. Published by John Wiley & Sons, Inc. (New York). 1955. 345 pages. Price 6.50 dollars.

Twenty-seven leading authorities, all former students or academic associates of Professor Hans Thacker Clarke, have contributed these essays on the occasion of Professor Clarke's retirement as Professor and Chairman of the Department of Biochemistry, College of Physicians and Surgeons, Columbia University. So often, because of the wide range of subjects covered, a collection of essays of this type is of interest only to those who know the person in whose honour they are written. It would be unfortunate if this book were overlooked on account of this general criticism for there will be few biochemists, whatever their field, who will not find interest and stimulation in all of these essays.

The style varies considerably. Some essays are reviews, some are discussions of the present status of the subject, and others, perhaps the most interesting, can best be described as "frankly speculative or deliberately provocative". Most are well illustrated and adequately referenced. Some indication of their scope and nature can be gained from the following titles, chosen at random: "On the bigness of Enzymes", "The very big and the very small: Remarks on conjugated proteins", "On the nature of cancer", "Some thoughts on the biochemistry of steroid hormones", "Glycogen turnover", "On determining the chemical structure of proteins", and "The chemical basis of heredity determinants".

—W.A.McG.

COLLEGE CHEMISTRY (2nd Edition) by Linus Pauling. Published by W. H. Freeman and Company, San Francisco, June, 1955. 685 pages. Price 6.00 dollars.

In this second edition an endeavour has been made to increase the clarity of presentation of the subject and a considerable revision of the first part of the text has been made with the object of introducing the student more gradually to chemical concepts and terminology. Nevertheless the book still remains a very comprehensive introduction to modern chemistry.

The book has now been divided into six parts; an introduction, some aspects of chemical theory, non-metallic elements and their compounds, solutions and chemical equilibria, metals and their compounds, and organic chemistry, biochemistry and nuclear chemistry. An excellent feature is an introduction to each part which indicates the general nature of the topics to be embarked on and the reason for their being studied at that particular stage.

More organic chemistry is included and is first introduced in the chapter dealing with carbon and its compounds. A later chapter is entirely devoted to it.

A completely new chapter gives an account of the experiments carried out over the period of 20 years dating from about 1895, which led to the discovery of the election and atomic nuclei.

It is of interest to recall that "College Chemistry" was originally written to provide a text giving a simpler and less mathematical introduction to modern chemistry than does Professor Pauling's well-known "General Chemistry", which is designed more especially for students aiming to proceed eventually to more advanced chemistry courses. The latter book gives a more detailed treatment of various aspects of theoretical chemistry as, for example, in the sections dealing with quantum theory and with chemical equilibria and reaction rates. Otherwise the two books

contain so much material in common (including some identical or virtually identical complete chapters) that one wonders whether the purchase of both books could be justified by libraries having only limited resources. Nevertheless, "College Chemistry" should be a valuable acquisition not only in university libraries, but also in those secondary schools in which candidates are being prepared for university scholarship examinations.

The book contains no fewer than 202 excellent illustrations, including two colour plates and these in no small measure contribute to the undoubted attraction of the book as a whole.

—C.V.F.

RESONANCE IN ORGANIC CHEMISTRY, by G. W. Wheland. Published by John Wiley & Sons, Inc., New York, 1955. Price 15 dollars.

Wheland's, "The Theory of Resonance and Its Application to Organic Chemistry" is well known to organic chemists interested in the more theoretical aspects of the subject. The book under review is much more than merely a new edition of its predecessor although the original style of presentation is retained. The greatly increased size is the result of the inclusion of much new material, including a table of bond lengths and bond angles in organic compounds, and a long chapter on the mathematical basis of resonance. The latter section contrasts sharply with the non-mathematical and predominantly qualitative treatment used in the remainder of the book, and the chemist whose mathematical background is limited will not find it easy to master. It is perhaps debatable whether the inclusion of this material is justifiable in a book written primarily for organic, rather than theoretical, chemists. However, the non-mathematical sections of the book are easy to read and follow, and provide a very complete and up-to-date coverage of the subject matter. The book is well produced, printed and indexed, but the price of 15 dollars is too high for it to find its way into the libraries of individual chemists.

—W.E.H.

AUTOMATIC PROCESS CONTROL FOR CHEMICAL ENGINEERS, by Norman H. Ceaglske. Published by John Wiley & Sons, Inc., New York, 1956.

Automatic control or "automation" has taken such an important place in industry that a familiarity with the fundamentals of automatic control is essential to the chemical engineer. The aim of this book is to present the basic theory of control systems as applied to chemical process control—a more fundamental approach than the usual descriptive account of the construction and operation of industrial instruments and controllers.

The first two chapters give an introduction to the essential parts of a control system and of the four basic modes of control: on-off, integral or reset, proportional and rate. The properties of these modes and of combinations of them are clearly set out. A brief description of a few industrial instruments connects theory and practice.

The remaining five chapters of the book are devoted to a mathematical analysis of control systems. The differential equations for each section of a control system are derived. (An explanation of the Laplace transformation which is extensively used preceeds this section). The equations are then applied to find the response to three standard input changes—step change, ramp input and sinusoidal input—first for the individual parts of a system and then for complete control systems. In the final chapter, analyses of simple control systems indicate the effect of the system parameters on steady-state error, stability and response to random disturbances of the system.

The book should be of definite value to those for whom it is primarily intended, viz., students of chemical engineering and practical engineers who desire an elementary review of the mathematical principles of process control. Chemists who would not consider the mathematical treatment elementary but who may have occasion to work with automatic control systems will find the first two chapters give a very useful insight into the properties of the various modes of control. In the remaining chapters they may also find information which will be of use in their particular problem.

—R.M.D.

THE ROGER ADAMS SYMPOSIUM. Published by John Wiley & Sons, Inc. (New York), 1955. 140 pages. Price 3.75 dollars.

On the occasion of the retirement of Professor Roger Adams from the chemical faculty of the University of Illinois, a symposium was held in his honour, the papers being delivered by former students who have reached eminence. Roger Adams achieved distinction during his forty years at Illinois, not only in the brilliance and the range of his researches in organic chemistry, or in the large number of distinctions (including the Hon. C.B.E.) won by him in America and abroad, or in his service to the profession of chemistry in his many years' leadership of the A.C.S., but mainly in the many successful chemists he trained. Those who contribute to the symposium now published in book form are Ernest Volwiler (Adams' career), W. R. Brode (Steric effects in dyes), John R. Johnson (Structure of Gliotoxin), Samuel McElvain (Structure of Nepetalic Acid), Ralph Shriner (Chemistry of Flavylium salts) and Wendell M. Stanley (Some chemical studies on viruses). The symposium is a very fitting tribute and all those who knew Professor Adams will be glad to have this book. To others, although the essays are excellent in their way, such a mixture may make less appeal.

—S.G.B.

BIOCHEMICAL PREPARATIONS, Volume 4, Edited by W. W. Westerfield. Published by John Wiley & Sons, Inc., New York, 1955. 108 pages. Price 3.75 dollars.

A further volume in this series is to be welcomed. This volume is of the same good quality as regards to information given and setting up as we have come to expect of the series. There are a further 21 preparations listed with a cumulative index to the four volumes and a useful reference to "compounds of biochemical interest which have appeared in 'Organic Syntheses' ".

—G.M.W.

Messrs. Watson Victor Ltd., advise that their list of scientific instruments and industrial control equipment for immediate delivery ex stock, is now available. This list—No. 256—is in booklet form and readers who have not yet received a copy may have their names placed on the mailing list.