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EDITORIAL

It is a year ago since we first launched ourselves on the sea of words and effected some changes in the Journal. Externally it had a change of cover; internally, we preferred feature articles to the brief reports of branch meetings. This policy seems to have met with general approval and Council have for this year entrusted us with a fifth issue and a budget allowance. The Journal will now be published bi-monthly except in December and will become, we hope, more of a news organ of the Council than in the past: witness the fact that this issue contains the Annual Statement of Accounts.

The past year has been of some note for our Institute, because of the more ambitious publication, but much more so for the Association of Scientific Workers, who last July produced their "New Zealand Science Review" with a new look as a monthly publication. We offer our contemporary our congratulations and best wishes for continued success.

LABORATORY DISTILLATION

S. R. SIEMON, Canterbury University College

During recent years the great technical advances made in the art of distillation on the works scale have begun to influence the laboratory still. Thus we have seen the construction of columns with elaborate reflux-controls, of great height and with intricate packings of large surface area per unit volume. These columns have very small output and are expensive in construction, hence it is worth while inquiring whether the same results could be obtained more economically.

Factors Affecting Separation in a Fractionating column.—

The most frequently used conventional measure of separation is the theoretical plate which is a right-angled step on the equilibrium diagram between the reflux line and the equilibrium line. The equilibrium line expresses the relationship between the molal concentration of a component in the liquid phase and that

in the vapour phase in equilibrium with it. The reflux line is a straight line drawn through the point on the diagonal of the diagram of co-ordinates of the product and with a slope $\frac{R}{R + 1}$, where R is the reflux ratio (see Badger and McCabe: Elements of Chemical Engineering or similar source). It can be seen that as R approaches infinity, the slope approaches 1, i.e., the reflux line becomes the diagonal. Also that there is no significant difference between $R = 100$ (say) and $R = \text{infinity}$, so that very large reflux ratios do not materially assist separation. If a step equivalent to a theoretical plate is drawn on an equilibrium diagram, it will be seen that the separation of a binary mixture as measured by the difference of the values of the vapour concentration equivalent to the step is a variable quantity, the value of which is dependent on five factors, viz.:

(a) The system used—the greater the departure of the equilibrium line from the diagonal, the greater the separation in one step at a given reflux ratio.

(b) The position on the diagram—the height of a step varies from zero, at both ends of the diagram to a maximum at some intermediate point.

(c) Vapour velocity—the process is one of diffusion, hence the rate is dependent on the velocity.

(d) Total pressure in the column—the departure of the equilibrium line from the diagonal increases with decrease in pressure.

(e) The reflux ratio used—the larger the value of R, the nearer the slope of the reflux line to 1, hence the greater the value of step height.

It is therefore desirable to think of fractionating columns in terms of the separation that may be accomplished in them, rather than in terms of the number of theoretical plates or height equivalent to a theoretical plate.

Design of Laboratory Columns.—Assuming that columns of very great height are undesirable and that very efficient packings have serious disadvantages, let us see what can be done to obtain separations in a short simple column of the order of those in elaborate columns, together with a very much larger output. The last point is significant not only for saving in time, but also for prevention of decomposition, polymerisation, etc.

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of condensation difficulties. Increase in vapour velocity has been used successfully in the spinning band type column, which is, however, a rather elaborate piece of apparatus. In ordinary packed columns increase in vapour velocity beyond a certain point leads to entrainment of liquid phase, hence to reduction in separation obtained. This leaves one only remaining method of approach, addition to an extracomponent to the system being separated.

Azeotropic and Extractive Distillation.—Improvement in separation is possible if the extra component added to the system increases the deviation from Raoult's Law, i.e., the deviation of the equilibrium curve from the diagonal. Extreme deviations show themselves as constant boiling mixtures (azeotropes) or in the appearance of a second liquid phase. Where the extra component is of relatively low volatility and causes large deviations from Raoult's Law, the process is known as Extractive Distillation or Vapour-Liquid Extraction. Azeotropic Distillation is the term used when azeotropes are formed deliberately to increase separation, the extra component being one of volatility comparable to those of the original mixture.

Selection of the Extra Component.—Formation of azeotropes may be used as an attack on two problems. Firstly, to separate azeotropes there may be added an extra component which forms a minimum azeotrope with one of the components boiling at a lower temperature than the original azeotrope. For example, methanol (b.pt. 64.7°C) and acetone (b.pt. 56.4°C) form an azeotrope (b.pt. 54.6°C). To effect a separation one may add methylene chloride (b.pt. 41.5°C) which forms an azeotrope (b.pt. 39.2°C) with methanol. Thus methanol may be progressively removed from the mixture leaving pure acetone at the base of the fractionating column.

Separation of close-boiling mixtures such as acetic acid (b.pt. 110°C) and water (b.pt. 100°C) which form no azeotrope may be effected by forming the lower boiling azeotrope (b.pt. 90.6°C) of water and butyl acetate (b.pt. 125°C), leaving pure acetic acid.

For selection of suitable azeotropes in a given problem, see Lecat (5). General principles as far as they are known are discussed by Ewell et al. (3).

In the case of extractive distillation the object is to use a relatively involatile substance to distort the vapour pressure curve. Large numbers of extractions have been tried with

success, but the general principles are still rather obscure. Clearly both azeotropism and Raoult's Law deviations are related to internal pressure, hydrogen bonding and dipole moment. For instance, addition of nitrobenzene to a mixture of benzene and cyclohexane will increase the separation achieved in a given fractionating column.

	Mol Fraction	Boiling Point	Internal Pressure	Dipole Moment.
Benzene	0.46	80.1	9.0	0.
Cyclohexane	0.54	81.4	7.8	0.4
Nitrobenzene	0.67	210.8	9.7	4.2
Increased separation, 2.3 times.				

For a discussion of factors influencing deviations from Raoult's Law, see Hildebrand (4). Selection of separating agents in terms of activity coefficients of known systems is discussed by Benedict and Rubin (1) and Colburn and Schoenborn (2). Some theoretical work is also in progress in the Department of Chemistry, Canterbury University College.

- (1) Benedict, M. and Rubin, L: *Trans. Amer. Inst. Chem. Eng.*, (1945), XLI, 353.
- (2) Colburn, A., and Schoenborn, E.: *ibid*, 421.
- (3) Ewell, R., Harrison, M., and Berg., L.: *Ind. Eng. Chem.*, (1944), XXXVI, 871.
- (4) Hildebrand, J. H.: "Solubility," A.C.S. Monograph. Series, 2nd. Ed., Reinhold Pub. Corp., 1936.
- (5) Lecat, M.: "L'Azeotropie," Lamerton, 2 vols., 1942.

N.Z.I.C., R.I.C. CONFERENCE, 1949
22nd-25th AUGUST, AUCKLAND

Up to December 24th, the following themes have been suggested by members in response to the request of the Conference Committee:—

Polarography, Tracer Techniques using Isotopes; Uses and Limits of Spectrography for the Estimation of Trace Elements; Silicates; Fermentation Plant for Antibiotics; Laboratory Organisation; High Vacua; Use of Physical Methods to Elucidate Organic Structures; Fuel; Utilisation of Industrial Waste; The Chemist and the Utilisation of New Zealand's Natural Resources.

Comments and further suggestions will be welcome.

G. L. CALNAN, Secretary,
Dominion Laboratory, Durham St., East, Auckland, C.I.

**RESEARCHES ON FATS AND RELATED CONSTITUENTS
BY NEW ZEALAND WORKERS**

A REVIEW—PART IV.

F. B. SHORLAND, Fats Research Laboratory, Dept. of Scientific and Industrial Research, Wellington.

Fish Liver Oil Industry In New Zealand.

The discovery in 1934 that certain New Zealand fish liver oils were rich in vitamin A aroused little or no attention for some time, apart from the fact that J. O. Shorland rendered annually some 100-144 gallons of ling liver oil at Island Bay, Wellington, for export to the British Drug Houses, London, from 1934 to 1938, when it was discontinued owing to a recession in world prices for vitamin fish liver oils. The experience thus gained indicated that in the event of wartime emergency, New Zealand would be able to replace at least part of the normally imported cod liver oil by local production. Although certain firms in New Zealand showed a keen interest in fish liver oils shortly after the beginning of the war, very little active preparation was made to commence production. Thus the position in New Zealand has been that although our vitamin oil resources were explored some three to five years earlier than in Australia or South Africa, these countries were quicker to realise the possibilities of industrial application, with the result that soon after the war commenced, they were able to replace by local production some of their requirements of cod liver oil.

After a period of preliminary experimentation over a period of years, R. Greenwell established in 1942 at Howick, Auckland, a fish liver oil factory, using modern methods of oil extraction. To Mr. Greenwell goes the credit of being the first in this country to operate successfully centrifugal separation of oil from the soup or pureé produced by mincing and steam digestion of fish livers. The small factory at Howick was replaced toward the end of 1943 by the large factory situated at Beaumont Street, Auckland. The livers for this factory are collected at depots in various parts of the North Island and transported frozen in ten-gallon cans. Where there are no freezing facilities insulated cans are used. In the far north at Awanui, where transport is difficult, there is a subsidiary factory.

Karitane Products Ltd. (as from March 12th, 1948, Adex, N.Z., Ltd.), opened a fish liver oil factory on March 3rd, 1943, at Island Bay, Wellington. This factory is well equipped (c.f. ¹²³) and employs a can collection system, similar to that of R. Greenwell Ltd., Auckland. Recently they have set up another factory at Timaru. Karitane Products Ltd., collect their raw materials from Wellington and South Island ports. Both these firms together handle practically all the available raw materials.

From the annual catch of edible species of fish it may be estimated that there is available not more than 4000 gallons of liver oil, of which ling would contribute 2500 gallons and groper 1000 gallons, yet the total annual production of oil has risen steadily from 20,000 gallons in 1944 to 30,000 gallons in 1947¹³³. This means that some 30,000 gallons of oil last year must have come mainly from sharks, the main contributing species being the school shark. Much further work, however, is necessary before an accurate statement can be made regarding the vitamin A and D resources of the liver oils from fish landed in the various ports throughout New Zealand.

By the application of molecular distillation it was found practicable to increase still further the vitamin A potency of the local fish liver oils. Early in 1946 a large glass falling-film still of novel design¹³⁴ was used to produce from oil containing 30,000 I.U. per gram, 70lb. of distillate of potency ranging from 150,000 to 300,000 I.U. per gram. These successful experiments carried out in the Fats Research Laboratory, D.S.I.R., led to the construction by the Dominion Physical Laboratory, toward the end of 1946, of a commercial spinning disc still, for installation at R. Greenwell's Ltd., where this process has since been successfully carried on.

It may be noted in this connection that according to the statement made by Hickman and Mees¹³⁵, commercial molecular distillation up till this time had been carried out only in the U.S.A., apart from a small plant operating in British Drug Houses Ltd.

Plant Lipids

The relative absence in New Zealand of indigenous botanical species with oil-bearing seeds restricts the field of investigation of plant lipids. The native karaka tree yields a nut, which, because of its toxicity, has been studied by several workers; Easterfield and Aston¹³⁶ noted that the air-dried kernels contained 14-15 per cent. of non-drying oil, while Aston¹³⁷ later recorded 10.9 per cent. oil. Shorland¹³², in the course of

studies of the germination of this nut, observed that as the length of the radicle increased up to three inches, the fat content decreased from 10.3 to 7.3 per cent. of the dry weight. The iodine value varied from 101.4 to 109.8, but could not be correlated with the effect of germination.

Incidental to the isolation of the toxic principle karakin, Carrie¹³⁸ observed that the petroleum-ether soluble fraction of the alcoholic extract of the kernel consisted of an oil containing 12.8 per cent. unsaponifiable matter, 39.8 per cent. stearic acid and 2.5 per cent. oleic acid.

References may be found in the *New Zealand Journal of Agriculture* to the growing of soya beans, sunflower seeds and olives, which in other countries have been used for oil production. Olive trees near Auckland were at one time actually used for oil production, but this was discontinued because the imported oil was cheaper¹³⁹.

Since 1930 ten companies have attempted to grow tung oil trees on a plantation scale in various parts of the North Auckland peninsula. An analysis of the situation in 1938¹⁴⁰ revealed a dismal picture. Out of a total of 4548 acres planted, 55 acres only contained apparently satisfactory trees, the majority of the remainder comprising worthless dead and dying trees.

Linseed Oil

In February, 1943, Dominion Industries Ltd., in response to a war-time shortage, commenced the processing of flax seed supplied from Marlborough, Canterbury, Otago and Southland. A modern mill incorporating mechanised procedures was established at Dunedin, and in 1947 the production had risen to some 450,000 gallons. It may be anticipated that the production will in due course be doubled to meet the whole of New Zealand requirements.

Details regarding the chemical characteristics and composition of New Zealand-grown linseed oil are not yet published. The oil is produced from the seeds of varieties of flax (*linum usitatissimum*), but the chemical constants of the oil vary only slightly from one variety to another. Generally speaking, the iodine value of the oil is higher than the oil available from Europe, indicating a superior drying power in the New Zealand product. The fatty acid composition for oils ranging in iodine value from 194 to 197 have been found to be approximately as follows¹⁴¹:—

					per cent.
Linoleic acid	23-25
Linolenic	27-32
Oleic	28-35
Saturated	remainder

It is generally considered that oils with best drying qualities (high iodine value) are produced in colder climates. For example, oil from the Baltic was for many years, in Great Britain, the standard of high quality (i.e., drying power or degree of unsaturation).

There is in the New Zealand seed a complication which does not apparently exist elsewhere, in that it has an unusually high degree of moisture. This is considered to be the primary cause of hydrolysis and a reason for excessive mucilage. It is understood, however, that the product is of good quality, but requires standing for the purpose of clarification, to compare with the best imported oil. With the further development of the linseed oil industry, it may, in due course, be possible to utilise for oil production other seeds such as those of rape.

Coconut Oil

Practically the whole of the Dominion's requirements of coconut oil are expelled at Abels Ltd., Auckland, from copra produced in Samoa and the Cook Islands. The fatty acid composition of coconut oil from copra supplied by Abels has been determined by Shorland and de la Mare²¹, who found it to be similar to that from other sources (c.f., for example, Longenecker¹⁴²), except that no evidence was found for more than 0.2 mols per cent. of hexadecenoic acid. An interesting feature of this coconut oil is its low iodine value¹⁴³ which may fall below 7.0. Coconut oil obtained from other localities would appear to have a higher iodine value, since the British Standard Specification provides for an iodine value not lower than 7.0 nor higher than 9.5.

Wheat Germ Oil

From 1938 until 1946 Messrs. D. H. Brown and Son Ltd., Christchurch, have produced by use of converted presses about 30 gallons per year, which in 1947, because of the lower demand, was reduced to 15 to 17 gallons¹⁴⁴. Using the Emmerie-Engel method samples of this oil have been found to be rich in vitamin E (300 mg/100 g. oil)¹³².

Montan Wax

This substance is derived from the brown coal of Saxony and Thuringia by distillation with superheated steam, and was investigated by Rigg⁸⁹ in 1911, using a commercial sample having the following characteristics: m.p. 78°, acid value 86.2, saponification value 88.4. It was shown that the acidic constituent of the wax hitherto described as one substance "montanic" acid, was, in fact, a mixture of three acids—cerotic (C₂₆H₅₂O₂), montanic (C₂₈H₅₆O₂) and melissic (C₃₀H₆₀O₂). The nonsaponifiable fraction was found to be an olefinic hydrocarbon C₂₈H₅₆ or C₂₆H₅₂, which was thought to be formed from the ester during distillation of the wax.

Cerotic and melissic acids were separated by systematic fractional precipitation with magnesium acetate of an alcoholic ammoniacal solution of the crude montanic acid. To obtain pure montanic acid it was found necessary to resort to fractional distillation of the ethyl ester of the crude acid under reduced pressure (14-16 mm.), using a special type of distilling flask with an electrically-heated neck. Cerotic acid was also prepared from beeswax, and found to be identical with the product prepared from montan wax. From these purified acids Rigg prepared anilides, amides, ketones, oximes, ethyl and methyl esters, the purity of these compounds being checked by analysis for carbon, hydrogen and nitrogen content. By reduction of cerotone with sodium amyl alcohol he produced for the first time the corresponding alcohol hentricontane—26 ol m.p. 87° and the corresponding acetate m.p. 60.5-61.5°.

To establish the straight chain nature of the higher saturated acids he prepared by Mai's¹⁴⁵ method the hydrocarbon from montanic acid, and found from the mixed melting point with the hydrocarbon obtained by reduction of myristone with hydrodic acid to correspond with a slightly impure n-heptacosane. Although it is now known that the higher naturally occurring mixtures of saturated acids cannot be separated in a pure form by the available techniques, and that by comparison with the pure acids prepared by synthetic methods (c.f. Chibnall et al⁹¹) the melting points are several degrees too low, nevertheless, Rigg's work, viewed in the light of the then existing knowledge, must be regarded as an outstanding contribution.

Wax From Chatham Island Peat

Macpherson and Hughson¹⁴⁶ made an extensive survey of Chatham Island peats which, from previous work, had been

shown to contain a high percentage of wax. The most extensive and important deposits were the moorland or upland varieties, comprising 30,000 to 40,000 acres, with an average thickness of 14 feet. Acres of peat at Kaingaroa, Onenga, Rapunui, Port Hutt and Waitangi West were mapped and sampled, and the wax content, as determined by chloroform extraction, showed an overall average of 9.4 per cent of the dry matter. Extreme variations from 1.9 to 25.4 per cent. wax supported the view that by additional prospecting, peat areas could be outlined containing 12 to 14 per cent. of wax. The properties of the wax resembled those of montan wax obtained from German lignites, the latter yielding 6 to 10 per cent. of wax. The peat wax could, however, be distinguished from montan wax by the fact that it melted at about 10° C. lower, and it contained a higher content of "asphaltic" constituents. The sample of peat wax examined at the Imperial Institute¹⁴⁷ gave the following constants as compared with those of montan wax:—

	Acid value	Saponification value	Melting point $^{\circ}$ C.	Specific gravity 180° C.
Peat wax ..	33.3	129.8	69	1.033
Montan wax ..	20-40	50-90	ca. 80	ca. 1.0

The differences in constants between the two waxes are such as to suggest that it would repay a fundamental investigation of the peat wax to determine the component fatty acids and unsaponifiable constituents.

Lipids of Forage Grasses, Clover and Rape

The complexity of leaf lipids has proved an obstacle in determining in detail their precise chemical nature. The literature in connection with rye and cocksfoot lipids was reviewed by Shorland¹⁴⁸, who also observed that mixed pasture comprising rye grass (55 per cent.), Yorkshire fog (12 per cent.), white clover (11 per cent.), sweet vernal (10 per cent.) and cocksfoot (5 per cent.), contained on a dry matter basis 5.59 per cent. total lipids of the following composition:—

	per cent.
Phosphatides	2.4
Waxes	10.8
Unsaponifiable matter	29.0
Free fatty acids	24.6

together with glycerides and chlorophyll. The high proportion of free fatty acid was attributed to enzyme action during cold storage.

Shorland¹⁴⁸ made similar observations in respect of ten samples of cocksfoot (*Dactylis glomerata*), collected at different periods at Marton. These results are summarised as follows:

	Total lipid	Lipids soluble in acetone at 0°C.			Phospholipids	
		Total	Fatty acids	Unsap.	Waxes	tides
Mean percentage of dry matter	6.12	5.06	3.13	0.96	0.86	0.20
Standard deviation	1.05	0.83	0.70	0.17	0.09	0.07

The fatty acids comprising 2.15 to 4.03 per cent. of the dry weight were found by ester fractionation to have the following mean composition:—

Fatty Acids (weight per cent.)

Saturated				Unsaturated		
C14	C16	C18	as C26	C14	C16	C18
1.4	11.2	2.6	1.5	0.4 (2.OH)	6.4 (2.OH)	76.5 (5.1H)

The presence of traces of oleic acid (ca. 0.6 per cent. of the total C18 unsaturated acids), together with palmitoleic acid, was established by the preparation of the corresponding dihydroxy acids.

Studies on methods of extraction of lipids using cocksfoot (*Dactylis glomerata*), ryegrass (*Lolium perenne*), and white clover (*Trifolium repens*) showed, that to obtain a high yield of phospholipid, together with low free fatty acid content, it was necessary to drop the freshly-cut leaves into boiling alcohol to arrest enzyme action prior to extraction with ether. In this way 1.5 to 1.7 per cent. of phospholipid was obtained, as compared with 0.25 per cent. obtained for cocksfoot by Smith and Chibnall¹⁴⁹.

In a further study¹⁵⁰ on methods of preservation of grass it was found that the free fatty acid and phosphatide contents of grass samples dried in a current of air at temperatures between 35° and 105° were respectively greater than, and less than those found for grass preserved by dropping into boiling alcohol. Grass dried in a commercial drier at 120° C., however, contained less free fatty acid, but the same proportions of phosphatides as grass preserved in boiling alcohol.

Although in the case of rape¹⁵¹ the phospholipids readily yielded both phosphatidic acid and a lecithin-cephalin fraction, only the latter fraction, together with a considerable proportion of unidentified material, could be isolated from the cocksfoot, ryegrass and clover phospholipids. In general the phospholipids tended to resemble the corresponding glycerides as regards fatty acid composition, except that the mean unsaturation of the C18 unsaturated acids tended to be lower in the phospholipids (3.7-4.8H) than in the glycerides (5.0-5.3H).

Shorland¹⁵¹ isolated from the leaf glycerides of rape (*Brassica napus L.*) a hexadecatrienoic acid which had not hitherto been recorded in plant lipids. The composition of the rape glycerides was otherwise generally similar to that of the forage grasses as shown by the following results for two samples:—

Fatty Acids (weight per cent.)

Saturated Mainly C16	Unsaturated		
	C14	C16	C18
16.0	0.7 (2.OH)	11.3 (6.OH)*	72.0 (5.4H)
15.1	0.5 (2.OH)	17.1 (6.OH)	67.3 (5.2H)

*Calculated as hexadecatrienoic acid, but may comprise in addition, small amounts of other C16 unsaturated acids with less than three double bonds.

Examination of cocksfoot, ryegrass and clover lipids failed to reveal the presence of C16 acids more unsaturated than palmitoleic acid.

It is convenient at this stage to consider the composition of the fats of farm animals in relation to the pasture which they eat. Beef and mutton tallow fatty acids comprise 25-30 per cent. palmitic acid and 10-20 per cent. stearic acid, the remainder being mainly mono-ethenoid C18 (oleic) acid with only traces of diethenoid and polyethenoid acids. The virtual absence of oleic acid in pasture and its abundance in sheep and cattle depot fats establishes that the fats of these animals are not derived to any great extent by direct assimilation of the food fats. It has been stated by Hilditch³ that horses fed continuously on grass or green fodder may lay down fat very similar to mutton or beef tallow, whereas the fat of a horse when corn fed is more oily and of lower melting point. A similar statement was made earlier by Armstrong and Allan⁴, but in neither case was reference given to the original work.

The investigations by the author¹³² (to be published later) show, however, that there is a great difference in composition between horse fat and tallow derived from pasture-fed animals. Horse fat is an oil rich in C18 di- and tri-ethenoid acids yielding ethyl ether-insoluble polybromides, m.p. 181° corresponding with the presence of linolenic acid, together with petroleum-ether insoluble bromo adducts which are oily as in the case of the C18 unsaturated acids of grass. This suggests that horses, in contrast to cattle and sheep, may form part of their fats directly by assimilation.

TABLE I.—Comparison between fatty acid composition of beef tallow, horse oil and cocksfoot glycerides.

	SATURATED				UNSATURATED			
	C14	C16	C18	C20 & above	C14	C16	C18	C20
Beef tallow	2.7	27.8	21.6	—	0.3 (2.0H)	2.5 (2.0H)	43.3 (2.05H)	1.8 (6.0H)
Horse fat	1.4	21.9	1.3	—	2.1 (2.0H)	20.1 (2.0H)	53.2 (3.8H)	—
Cocksfoot glycerides	1.4	11.2	2.6	1.5	0.4 (2.0H)	6.4 (2.0H)	76.5 (5.1H)	—

Information on the carotene and chlorophyll content of pastures has been collected from time to time, and certain general observations have been made¹³². It has been found, for example, that the carotene content of mixed pasture fell more or less continuously during the course of the day, being 51 mg./100 g.* at 9 a.m. and falling to 40 mg./100g., at 8 p.m. Chlorophyll showed similar but less marked changes. Cut grass spread in thin layers and kept indoors showed little change in carotene or chlorophyll content over a 24-hour period.

During the period September to February, it has been noted that the carotene content of mixed pasture is approximately 45 to 55 mg./100g, while later in the season when the pasture dries up the content may fall to 20 mg./100 g. or less. The chlorophyll tends to show a similar type of change, and the level of carotene and chlorophyll is well maintained except under drought conditions.

MISCELLANEOUS

Distillation of Fatty Acids for Candle Manufacture

In 1904 Robertson¹⁵² studied the changes in the nature

(*Expressed on moisture free material.)

of the distillate during the course of commercial distillation of tallow fatty acids from an iron retort using superheated steam.

The commonly accepted viewpoint prior to this work was that the solidification point of the distillate rose as the distillation proceeded, but towards the end of the distillation the distillate became brown and began to soften. Robertson, however, showed that the complete picture of the changes was actually much more complex. The proportions of oleic, palmitic and stearic acids were calculated from the iodine values and equivalents of the fractions. In addition, in the later fractions allowance was made for the presence of unsaponifiable matter. During the first hour of distillation, the solidification point fell a little and then proceeded to rise. The proportions of palmitic and stearic acids at the lowest solidification point corresponded to a eutectic mixture. Experimentally it was established that the presence of oleic acid did not alter the relative proportions of palmitic and stearic acids required for the eutectic mixture. The rise in solidification point as the distillation proceeded was accompanied by an increasing content of stearic acid. The sudden fall in the solidification point towards the end of the distillation after a period of about five hours was attributed to the formation of new components in considerable proportions as indicated by the greatly increased saponification equivalent.

By crystallisation from alcohol, stearone $C_{28}H_{56}O$ m.p. 88° identified by the preparation of the oxime which melted constantly at 62° was isolated as well as a more soluble product m.p. 72.3° considered to be the hydrocarbon $C_{28}H_{56}$ formed from stearone by reduction.

Finally the amount of stearone in the distillate became so great that the eutectic point was reached, and the solidification point began to rise. This interpretation was tested by the addition of stearone to the mixture, which showed that the addition of a little stearone after the eutectic point had been reached, caused a rise in the solidification point, whereas the addition of stearone prior to reaching this point caused a reduction in the solidification point. At the present time, stearine (technical stearic acid) is produced by McLeod Bros., at Dunedin.

Some Physical Properties of the Fatty Acids

Easterfield and Robertson¹⁵³ showed that the lower fatty acids—acetic, propionic and butyric, had vapour densities at their boiling points which were higher than those calculated

from their molecular weight. Using the relationship $\frac{ML}{T} =$

K (Trouton's Law), where M is molecular weight, L latent heat and T boiling point (absolute scale), they noted that for these compounds K was considerably lower than the normal constant value of 21.

These phenomena, they considered, could be explained only on the assumption that the molecules are associated in the gaseous state, the extent of the association varying inversely as the square of the molecular weight.

Robertson made many studies on cryoscopy in which fatty acids and their esters were used. Using phenol as solvent, he found that to judge from the freezing point depression, fatty acids¹⁵⁴ associate more or less rapidly with rising concentration. The rates of association of the normal fatty acids alternately increase and decrease for each member. If the even series are considered the association decreases and reaches a minimum probably at C6 and then rises again. This peculiar property was also noted in connection with the differences in melting points and boiling points. From these and other results, Robertson¹⁵⁵ concluded that in a given series of organic compounds we shall find a maximum or minimum in the physical properties, either by taking each member in turn or by taking alternate members.

In contrast to the acids, the esters¹⁵⁶ were found to have a high initial molecular depression and a negative value of association, which, in the case of the ethyl ester series was greatest for ethyl hexoate. It was generally concluded that this abnormally high molecular depression for esters in phenol as compared with the value calculated from the van't Hoff equation, the irregular molecular depression and negative "rate" of association were probably due to the fact that phenol had a great tendency to form molecular complexes, such abnormalities disappearing when substituted phenols such as thymol, guaiacol and o-nitrophenol were used.

McGavin¹⁵⁷, using palmitic acid for cryoscopic studies found that the van't Hoff equation ($D = \frac{0.02T^2}{L}$ where T is the melting point absolute scale, L the latent heat, and D cryoscopic constant), does not hold even at low concentrations.

In the four classes of components studied—acids, alcohols, esters and hydrocarbons, the cryoscopic behaviour was shown to depend on internal pressure and polarity in accordance with the theory of Hildebrand. A general relationship was shown between molecular solution volume, and molecular depression.

Melting Points of the Substituted Amides of the Fatty Acids

Robertson¹⁵⁸ noted the utmost irregularity in the melting points of the amides of the fatty acids, even when a separate comparison was made among the odd or even numbers. To a lesser extent, a similar irregularity was observed in the case of the known anilides. To study further the nature of these irregularities, he synthesised the compounds missing in the anilide series, and in addition, prepared a complete range of p-toluidides and α -naphthylamides.

Among the even numbers of the anilides and p-toluidides, there was a considerable fall in melting point from the second to the fourth member, followed by a slight rise, and then another fall, but after the eighth member, the melting point continued to rise. In the case of the melting points of the amides there was a considerable rise from the second to the fourth member followed by a fall, and then again another rise, and again a fall to the tenth member, each change being in exactly the reverse direction to that observed by either the anilides or p-toluidides. Again among the odd series the same general tendencies were observable, there being a rise followed by a fall in the case of the first three uneven amides, whilst the reverse was true for the other two series.

Evidence was adduced by considering the arithmetical mean of the melting points of the amides and anilides and of the amides and p-toluidides, that the disturbing factor responsible for the melting point irregularities would be eliminated as was actually found to be the case. On taking the means of the two curves, further influences of the disturbing factor, whether lack of symmetry, or some other cause, appeared to be eliminated and the resultant dotted curve was quite regular. Such a curve was considered therefore, to represent a typical melting point curve for compounds of the general formula $\text{CH}_2(\text{CH}_2)_n \text{CO NHX}$ after the disturbing influences of alterations in symmetry had been removed.

Finally, the fatty α -naphthylamides in which the group X was heavier, were investigated. The same alternation between odd and even members persisted, but the other irregularities disappeared. The compounds with an even number of carbon atoms formed a regular series with a minimum at the eighth member, and there was a similar odd series falling to a minimum at the ninth member.

In a subsequent paper, Robertson¹⁵⁹, tabulated the melting points of the amides, anilides, p-toluidides, p-bromanilides, o-toluidides, o-bromo-p-toluidides, 2:4:6 tribromocanilides,

β -naphthylamides, and α -bromo- β -naphthylamides. Particular attention was paid to the purity of the compounds used and where possible the melting points were compared with those obtained by previous workers.

The melting point curves showed that those with higher melting points have a greater initial fall, are flatter in the neighbourhood of the minima and have minima which occur higher up in the series. No connection was found between the initial fall in melting point and the degree of association of the earlier members since this phenomenon is quite marked in the case of the tribromoanilides having a diorthogrouping which would prevent molecular association. The phenomenon is also apparently not connected with the weight of the substituent radicle.

At a certain distance up the series, at about the fourteenth member, the curves tended to become parallel, indicating that the cause of the initial fall in melting point, and the variations in the early part of the curve had been eliminated.

In cases where the substituted amide was of high molecular weight, it appeared that the melting points of the odd and even series fell on approximately the same curve. An unexplained exception was found in the *o*-bromo-*p*-toluidides where the melting points of the odd series was on the average no less than 6°C higher than that of adjacent members of the even series.

Robertson regarded the molecules of a solid as being held together by some force, possibly magnetic, on the magnitude of which depend double refraction in particular and the physical properties of the solid.

An equation was given expressing the melting temperature T_s as a fraction of the specific heat S , the molecular volume, V and the vibration frequency ν .

$$MS.T_s = K.M.V.2/3 \nu^2 \quad (K = \text{const.}).$$

A suitable variation of these values is considered to be capable of causing the observed irregularities in the melting points of a series of compounds. High up the series the density and specific heat of successive members become approximately constant, and it was found that the empirical relationship $T_s = K'.M^{1/6}$ ($K' = \text{const.}$) gave fair agreement in most cases not only for the higher members of the substituted amides but for other compounds also.

Synthesis of Ketones from Fatty Acids

Easterfield and Taylor¹⁶⁰ found that by heating stearic acid with cast iron turnings at 360-365°C over 80 per cent of the acid was converted to stearone as compared with a 50 per cent theoretical yield obtained by the ordinary process of distilling under reduced pressure calcium or barium stearate with slaked lime.

The method was also found to give good yields of ketone, with lauric, palmitic, montanic and melissic acids, and was therefore regarded as a general method for the preparation of ketones of saturated acids with from 12 to 30 atoms of carbon in the molecule.

Ketones of the higher unsaturated acids, including oleic, elaidic and brassidic, which had not hitherto been prepared, were readily obtained by the "iron" method. In the iron stills used for the distillation of the fatty acids of tallow they showed that in addition to stearone, previously reported by Robertson¹⁵², there was also formed oleone which could be isolated from olein pressed from commercial stearine. It is interesting to note that metallic iron powder has been recommended by Grun and has since been used by I. G. Farbinindustrie for the production of ketones¹⁶¹.

Spectrophotometric Estimation of Vitamin A In Fish Liver Oils

Metcalf¹⁶² drew attention to the fact that when the results of spectroscopic estimation of vitamin A were expressed by use of a conversion factor as international units per gram, considerable confusion arose in commercial transactions and in investigational surveys.

In respect of pure vitamin A, it is apparently not feasible to determine accurately the efficiency in I.U./g.m., but on the other hand, the recent values of vitamin A for E(1cm. 1%) at 328 mu. in alcohol have been determined as 1780 ± 50 .

Metcalf therefore, urged that the practice of using a conversion factor to convert to I.U./gm. be discontinued, and that the vitamin A in fish oils be expressed as mg. vitamin A per gram of oil. The factor required to convert E(1cm. 1%) at 328 mu. to mg. vitamin A per gram oil is

1000

$\frac{1000}{E(1\text{cm. } 1\%) \text{ at } 328 \text{ mu. pure vitamin A}}$

For the convenience of analysts, and as an indication of the basis of the estimation E(1cm. 1%) at 328 mu. should also be stated.

Müller and Reinert¹⁶³ have recently emphasised the great difficulty in expressing the biological activity of vitamin A in terms of the international vitamin A standard (β -carotene). They consider that although the suggestion of Metcalf will eliminate many complications, it will not completely dispose of the biological evaluations. For special problems it will now and again be necessary to ascertain whether the quantity of vitamin A determined by the physical method actually corresponds biologically to analogous quantities of pure vitamin A.

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THE COUNCIL

Items from the Minutes of the Annual Meeting of Council-in-Person, held at Wellington, 20/11/48.

Pacific Science Congress: An attempt to be made to include a Division of Physical Sciences or of Chemistry alone in future congresses.

Employment Committee: This committee to include district representatives. Local Committees to include representatives of industry, university and Government. Committee to investigate position regarding non-members, particularly those just leaving school.

Journal: Journal to be placed on a budget basis, budget for 1949 to be £120 above receipts from advertising and non-member subscriptions. Journal to be published 5 times a year in future, one issue to be devoted mainly to Conference business. Subscriptions to local members who are bona-fide students to be reduced to 5/- per annum.

Membership Committee: Mr. W. A. Joiner re-appointed.

Salaries: Dr. Dixon and Mr. J. L. Mandeno appointed to keep Council appointed salary matters for the coming year.

Committees on Standard Methods of Analysis re-appointed.

Finance: Conference Surplus: R.I.C. (New Zealand Section), proportion to be one-fifth; of the remainder £5 to be paid to the Chemistry Dept. of the University of Otago for the purchase of a book for the library, and £14 to be transferred to the Food Parcels Fund; the remainder to be paid into the general funds.

Election of Associates: The following were received into membership: Mr. Maxwell Len McGlashan, Lecturer, Chemistry Dept., Canterbury University College.

Dr. Marion Margaret Cunningham, Karitane Products Society, Wellington.

Dr. Harry Bloom, Lecturer, Chemistry Dept., Auckland University College.

Mrs. Valerie Rose Te Punga, Dominion Laboratory, Wellington.

Mr. John Matheson Climo, N.Z. Farmers' Fertiliser Co., Ltd., Auckland.

Amendment to Rules: The words "in the opinion of the Membership Committee" to be deleted from 9.1.4.

Union Registration and Professional Status: Auckland Branch to be asked to set up a committee to be named "The Committee on Professional Status" to study Union membership and registration, Graduate members of the Institute,

the position of laboratory assistants and technicians, and any further developments regarding the charter.

Contracts of Service: Wellington Branch asked to set up a committee to consider this and also superannuation schemes.

N.B.—Members of the Institute are advised to consider the advantages of entering into a formal agreement with their employers or prospective employers and that, until a suitable draft is officially approved, members who are about to take up a position should communicate with the Hon. General Secretary for advice. (The Royal Institute of Chemistry has a form of Contract of Service, which may be seen by those who so desire).

Resignations were received from the following:—

H. S. Gibbs, Soil Bureau, Wellington.

F. N. Fastier, Medical School, Dunedin.

B. W. Collins, Geological Survey, Timaru.

T. A. Pressley, Sydney.

Registrar: Mr. H. K. Palmer, re-appointed for three years at a salary of £125 per annum.

The Hon. General Secretary was empowered to co-opt an Asst. Secretary.

Book Plate: Design suggested by Mr. Joiner, based on the Institute Seal accepted; details to be worked out.

Balance Sheet: The statement of Receipts and Payments is printed in this issue: the Balance Sheet and Income and Expenditure Account may be seen on request to the Registrar.

It was decided to transfer £15 to the Industrial Chemical Essay Prize Fund and £50 to the Trust Fund. Honoraria of 25 guineas to the Hon. General Secretary, and 10 guineas to the Editor, approved.

Letters of thanks to be sent to the Editor, Business Manager and Distribution Manager of the Journal for the good work done during its first year in Auckland in getting the business affairs organised.

STATEMENT OF RECEIPTS AND PAYMENTS

For the year ended 31st October, 1948

	£	s	d	£	s	d
By Institute Journal—						
Printing (less amounts charged to Conferences)	167	3	0			
Editor's Honorarium, 1947	10	10	0			
Postages, Wrappers, etc.	20	14	0			
				198	7	0
.. Secretary—Honorarium, 1947				21	0	0
.. Registrar—Salary, 1948				100	0	0
.. Travelling Expenses—						
President, Vice-President and Delegates				54	6	11
.. Audit Fee—1947				3	3	0
.. Typewriting & Duplicating				47	11	4
.. Printing & Stationery				52	18	4
.. Postages & Sundry Expenses				27	12	8
.. Branch Expense Allowances—						
Auckland	1	0	0			
Wellington	1	0	0			
Canterbury	1	0	0			
Otago	1	0	0			
				4	0	0
.. Laboratory Assistants' Certificate—						
Typing, Duplicating and Petties ..				18	14	3
.. Chemists' Employment Committee—						
Duplicating, Postages & Petties ...				13	11	2
.. Conference, 1948, Expenses—						
Catering, Postages, Stationery and Sundries				92	4	3
.. Trust Fund—Transfer thereto				50	0	0
.. Balances—31st October, 1948:						
Bank of New Zealand	371	5	5			
Post Office Savings Bank	397	11	8			
In Hand—Petty Cash	3	9	9			
				772	6	10
				£1,455	15	9

SUB-COMMITTEES FOR THE YEAR COMMENCING 1st NOVEMBER, 1948.

1. **CONFERENCE COMMITTEE, 1949:**
 Professor F. J. Llewellyn (Chairman), Auckland University College, Princes Street, Auckland, C.I.
 G. Cainan (Secretary), C/o Dominion Laboratory, Durham Street West, Auckland, C.I.
2. **CHEMISTS' EMPLOYMENT COMMITTEE:**
 L. H. James, P.O. Box 250, Wellington (Chairman).
 E. S. Borthwick, P.O. Box 250, Wellington (Secretary).
 G. M. Smith, P.O. Box 250, Wellington (Acting Secretary).
 K. M. Griffin, Auckland Representative.
 F. Morgan, Wellington Representative.
 F. H. G. Johnstone, Canterbury Representative.
 O. H. Keys, Otago Representative.
3. **EXAMINATIONS COMMITTEE:**
 S. J. Lambourne, 63 Mantell Street, Seatoun, Wellington, E.5. (Chairman).
 T. A. Rafter, P.O. Box 250, Wellington (Secretary).
 H. J. Wood, P.O. Box 250, Wellington (Acting Secretary).
4. **JOURNAL EDITORIAL COMMITTEE:**
 S. G. Brooker, P.O. Box 12, Newmarket, Auckland (Editor).
 Miss M. E. Malcolm, Dominion Laboratory, Wellington (Branch Editor).
 M. L. McGlashan, Canterbury University College, Christchurch (Branch Editor).
 J. Murray, Chemistry Department, University of Otago, Dunedin (Branch Editor).
5. **MEDICAL ADVERTISEMENTS COMMITTEE:**
 L. H. James, P.O. Box 250, Wellington (Convenor).
6. **MEMBERSHIP COMMITTEE:**
 Dr. L. H. Briggs, Auckland University College, Princes Street, Auckland, C.I.
 Professor J. Packer (Acting while Dr. Briggs is on leave).
 Dr. R. Gardner, 41 Dowling Street, Dunedin.
 W. A. Joiner, Dept. Scientific & Industrial Research, Wellington.
8. **SALARIES COMMITTEE:**
 Dr. J. K. Dixon, P.O. Box 250, Wellington.
 J. L. Mandeno, P.O. Box 250, Wellington.
9. **REPRESENTATIVE ON N.Z. STANDARDS INSTITUTE COUNCIL:**
 G. A. Lawrence, Johnsonville.
- 9.1. **CHIEF REPRESENTATIVE FOR ALL STANDARDS INSTITUTE AFFAIRS:**
 M. L. H. Stewart, P.O. Box 1663, Wellington.
10. **STANDARD METHODS OF ANALYSIS.**
- 10.1. **PLANT MATERIALS:**
 Dr. H. O. Askew, Cawthron Institute, Nelson (Chairman).
 Dr. J. Melville, Plant Chemistry Laboratory, P.O. Box 523, Palmerston North (Secretary).
- 10.2. **ANIMAL TISSUE:**
 Dr. C. R. Barnicoat, Massey Agricultural College, Palmerston North (Chairman).
 I. G. McIntosh, Animal Research Station, Wallaceville, P.B., Wellington (Secretary).
- 10.3. **SOILS & FERTILIZERS:**
 Dr. J. K. Dixon, Soil Bureau, 54 Molesworth Street, Wellington.
 Dr. E. B. Davies, Soil Fertility Research Station, Box 490, Hamilton (Secretary).

LIST OF OFFICERS**FOR THE YEAR, 1st NOVEMBER, 1948-31st NOVEMBER, 1949**

President:	Professor J. Packer, Canterbury University College, Christchurch.
Vice-President:	Dr. J. Melville, Plant Chemistry Laboratory, P.O. Box 623, Palmerston North.
Hon. Gen. Sec.-Treas.:	W. G. Hughson, P.O. Box 250, Wellington.
Registrar:	H. K. Palmer, P.O. Box 250, Wellington.
Auckland Delegate:	S. G. Brooker P.O. Box 12, Newmarket, Auckland.
Wellington Delegate:	J. L. Mandeno, Dominion Laboratory, Wellington.
Canterbury Delegate:	F. H. G. Johnstone, P.O. Box 325, Christchurch.
Otago Delegate:	O. H. Keys, P.O. Box 562, Dunedin.
Past President:	Dr. J. K. Dixon, Soil Bureau, 54 Molesworth Street, Wellington.
Editor of Journal:	S. G. Brooker, P.O. Box 12, Newmarket, Auckland.

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Chairman:	S. G. Brooker, P.O. Box 12, Newmarket, Auckland.
Secretary:	G. W. Stace, Dominion Laboratory, Durham Street West, Auckland.
Treasurer:	W. E. Russell, Huia Road, Papatoetoe, Auckland.
Committee:	Professor F. J. Llewellyn, Auckland University College, Princess Street, Auckland, C.I. J. B. Brown, C/o Laboratory, Public Hospital, Park Rd., Auckland. G. S. Lambert, P.O. Box 29, Newmarket, Auckland. M. B. Rands, 252 Mt. Smart Road, Auckland.
Auditor:	A. J. Parker, 10 Ardmore Road, Ponsonby, Auckland.

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Chairman:	Dr. F. B. Shorland, Fats Research Laboratory, D.S.I.R., Wellington, N.I.
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Committee:	C. G. W. Mason, P.O. Box 632, Wellington. R. C. Bell, Vacuum Oil Co., Pty., Box 288, Wellington. B. E. Swedlund, Victoria University College, Box 1580, Wellington. S. E. Wright, Pharmacy College, 59 Cambridge Terrace, Wellington.
Auditor:	G. A. Lawrence, Johnsonville, Wellington.

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Auditor:	G. D. Law, 124 Lichfield Street, Christchurch, C.I.

OTAGO BRANCH

Chairman:	Professor F. G. Soper, University of Otago, Dunedin, N.I.
Sec.-Treasurer:	J. Rogers, School of Mines, University of Otago, Dunedin.
Committee:	O. H. Keys, Dominion Laboratory, P.O. Box 562, Dunedin. C. C. Roberts, King's High School, Dunedin, S.2. Miss R. P. Mauger, Chemistry Department, University of Otago, Dunedin. T. H. Kennedy, Medical School, King Street, Dunedin, N.I.
Auditor:	T. A. Thomson, 4 Cromwell Street, Dunedin, N.W.2.

BOOKS RECEIVED

ORGANIC ANALYTICAL REAGENTS, Vol. III, by Frank J. Welcher, Indiana University. Pp. xi, 493. New York: D. Van Nostrand Co., London: Macmillan and Co., 1947, 8 dollars or £2/4/-.

This is one of a series of four volumes on this subject and covers certain heterocyclic N. compounds (not including "oxine"), oximes and acidic imino compounds. This series should not be confused with a book of the same title written by Yoe and Sarver in 1941, and would be more correctly named "Organic Reagents for Inorganic Analysis," as it does not deal with their applications in organic analysis, such as the α nitroso β naphthol test for tyrosine.

This is a most exhaustive treatise and gives the preparation of each reagent and details of all uses in inorganic analysis cited in the literature. There are 88 pages devoted to dithizone, 62 to dimethyl glyoxime and 46 to cupferron. The treatment is not critical, but there is a value in collecting all possible information, for a method condemned by some workers may yield useful results under other circumstances. It would probably require more than one lifetime to offer a critical estimate of the large number of procedures covered in these volumes.

The reviewer noted only a few points of criticism. The use of diphenyl carbazide as an indicator in the titration of halides, particularly iodides and bromides, with mercuric nitrate is hardly done justice to, (See McCleary, *Anal. Ed., Ind. Eng. Chem.*, 1942, 31), and the Beilstein references are in many cases incomplete, and sometimes omitted altogether. "Zinc purpurate" as a synonym for "Purpuric Acid, Zinc Salt," seems a little obvious. However, these are minor points in a very useful compilation.

HUMOUR AND HUMANISM IN CHEMISTRY, by John Read, F.R.S., University of St. Andrew's. Pp. 388, 1947. London: Geo. Bell & Sons Ltd. 21/-.

This interesting book starts out as a history of alchemy, goes on to a history of chemistry, leading up to the author's experiences at Zurich (under Werner), Cambridge (under Pope), and in Australia, where he made many contributions to the chemistry of the essential oils of Australian plants. The concluding part is a humorous play set in a university chemistry laboratory. The humour here is largely dependent on puns on chemical terms, and there may be two opinions as to whether the play is worthy of inclusion. However, the rest of the book is most interesting, and can be recommended both because of the value of knowing something of the history of our science, and because of the entertaining sidelights. Here is given a full account of what must be the most

famous chemical hoax: an issue of the "Berichte der Durstigen (i.e., thirsty) chemischen Gesellschaft" published in the likeness of the true "Berichte" and bound by a number of people with it in error. It is also said that one editor was so far taken in that he tore it apart and sent the sections to the abstractors in the usual way. For a somewhat similar hoax in our own time, readers may consult the abstract on optically active ice in "The Analyst," Vol. 69 (1944), 97. The famous Glauber, who gave his name to Sodium Sulphate, wrote a book which contained, inter alia, advice on how to perform "certain waggish tricks, such as throwing doped seed to birds so that they may be easily captured." There is also the story of the young lady who applied a bismuth cosmetic to her skin before bathing in the sulphurous waters at Harrowgate; this was very mysterious to the public; but chemists could explain that she came down in group II.

HANDBOOK OF CHEMISTRY, compiled by N. A. Lange, Western Reserve University, Pp. 1767 + 271 + 24. 6th Edition, 1946. Sandusky, Ohio: Handbook Publishers Inc. 6 dollars. The compilers of this useful publication feel that it has reached its maximum size, and new data is therefore included without increasing the size by cutting out some information chiefly on chemical engineering, more usually sought in handbooks on that subject. The chief change is a revised and much enlarged table of inorganic compounds. Briefly the volume seems to contain nearly all that can be expected and few errors have been found. Future editions could have tables on silicon organic compounds and on surface-active materials with advantage, and it is time the archaic practice of including acid values among the "constants" for oils and fats ceased. Thumb-indexing would be valuable. The mathematical tables, compiled by R. S. Burlington, may be obtained as a separate volume at 1.60 dollars. The bindings of both are excellent.

RADIO-ACTIVE INDICATORS: THEIR APPLICATION IN BIOCHEMISTRY, ANIMAL PHYSIOLOGY AND PATHOLOGY. By George Hevesy, Institute for Research in Organic Chemistry, University of Stockholm, and Institute for Theoretical Physics, University of Copenhagen. Pp. 556. 1948. New York and London: Interscience Publishers, 10 dollars. This book, by a recognised authority, summarises the methods and results of the use of radio-active tracers in biochemistry and should be useful to a number of workers in New Zealand as a handbook on the subject, no important aspect of which seems to have been overlooked. There is a complete list of isotopes supplied by the Atomic Energy Commission, references to 1947, and a number of valuable illustrations.

THERMODYNAMICS. by Edward F. Obert, Associate Prof. of Mechanical Engineering, North-Western University. Pp. 571, 1948: New York and London: McGraw-Hill Book Co. 5.50 dollars. This book is described as a "fundamental text in thermodynamics for the engineering student," but it would be useful to many industrial chemists in New Zealand, where they must often be chemical engineers as well. It gives the theory of pumps, blowers, refrigeration, calorime try, power cycles, ejectors, etc., with practical applications and worked examples.

REAGENTS FOR QUALITATIVE INORGANIC ANALYSIS: Second Report of the International Committee on New Analytical Reactions and Reagents of the International Union of Chemistry. Editors: P. E. Wenger and R. Duckert, Geneva. Joint Authors: C. J. Van Nieuwenburg, Delft. and J. Gillis, Ghent, 1948. Published by Elsevier Publishing Co., distributed by Cleaver-Hume Press Ltd., London. 39/6.

This is a collaborative report carried out despite considerable difficulties during the war years. It gives details of tested spot test methods and separations, and with the present very wide literature on this subject it should therefore be most valuable to the general analyst, who does not have the time to test out these procedures for himself. The original French edition came out in 1945, but this English edition is not just a translation as it contains much new data, an enlarged bibliography of 1172 references both to the original papers and to the corresponding abstracts, and finally, a series of splendid microphotographs illustrating those reactions depending on the recognition of crystals under the microscope. The editors claim that the majority of the reagents are in the dealers' catalogues, and details of preparation are given for others. A number of reactions require only common inorganic chemicals. This feature and its authoritative nature will assure a welcome for this volume, and it is gratifying to know that the Committee is continuing its labours under more favourable circumstances.

"QUANTITATIVE ANALYSIS," by W. C. Pierce and E. L. Heenisch, third edition, 1948. New York: John Wiley and Sons; London: Chapman and Hall. 3.75 dollars.

This book should be of great value to any student of chemistry, and contains, besides the usual analytical methods, useful hints on technique and procedure. The book is very well set out with the initial chapters dealing with the preparation of samples and the important subjects of weighing and titration. The following chapters deal with physicochemical methods for determination of end-point in volumetric analysis and the analysis of specific substances. Each chapter is complete in itself and contains, besides the analytical method, notes which point out sources of error and steps to be taken for their elimination. At the conclusion of each chapter, there is a good selection of questions on the work preceding; by working through these the student should have a good grip of each portion of the subject. A chapter is devoted to the use of the literature, with a list of reference works. Five-figure logs, and a good index are provided.

PERSONAL NOTES

Sir Norman Haworth, F.R.S., will be visiting New Zealand this month in connection with the Pacific Science Congress, and it is hoped that many of our members will have an opportunity of meeting him. Sir Norman has recently retired from the Mason Professorship of the University of Birmingham, where he became famous for his researches on the structure of the sugars.

Amongst those who will be attending the meeting of the Australian and New Zealand Association for the Advancement of Science at Hobart, are Prof. Llewellyn, Auckland, Mr. K. J. McNaught, Hamilton, Mr. S. H. Wilson, Wellington, and Mr. S. R. Siemon, Christchurch.

Extracts from a letter received from T. A. Rafter, Dominion Laboratory, Wellington:—

Massachusetts Institute of Technology is as large as any place with a name like that ought to be. With three days to go before leaving here, I have

not seen through one quarter of it and don't intend to. One of my first experiences was to wander through the enormous corridors, twice the length of the Parliament Buildings, and to read the names on the doors of famous American professors in every branch of science. Many I met, but most of them are still just names on the door to me.

I was duly initiated into the Radioactivity Centre and placed under Prof. Irvine, a Chemistry Professor, attached to the Physics Department. The first five weeks were a battle of wits between the Professor and myself. I was given an assignment as if I were to do a Ph.D. Thesis with two to three years to do it in and not just three months. For the first time I found myself dodging work in order to try to make the right contacts to get experience in radiochemistry and its applications. Fortunately, I became tangled up with some analytical difficulties that the Medical Reserve Workers using radio isotopes at Harvard Medical School were having, and I have never been so thankful for the opportunity given me at the Dominion Laboratory to analyse coal ashes. This work kept me away from my useless thesis, the professor gave me up as a bad job; we became the best of friends and the door was open to a wealth of experience and valuable contacts.

For three weeks I worked in the Cyclotron Laboratory and studied the technique of handling cyclotron targets; from there I studied the difficulties associated with plating technique for the deposition of metals prior to radioactive measurements, and then on to the temperamental behaviour of $C(14)O_2$ filled counters and an introduction to vacuum techniques, the application of radio zinc, radio iodine and radio iron into medical research. At the Massachusetts General Hospital, I saw the interesting work of Dr. Franz using starch columns for the separation of the amino acids and ion exchange techniques for the separation of the metals.

The amount of research going on in America is tremendous. While a few years back the research worker timidly asked for an extra 1000 dollars a year for a particular project, he now asks for 50,000 dollars and is assured of getting this amount for a number of years. Incidentally, most of the research money comes from the Government contracts in this part of America. What particularly interested me is how they organise this research and from discussions with research students, technicians, graduates and professors there appear to be all methods from the scatter-brain ideas of busy professors to the preliminary careful scrutiny of the literature prior to an idea that succeeds where others have failed.

Mr. Philip White, late of the Leather Research Laboratory, Wellington, writes that he is still a temporary civil servant, holding an administrative position in Board of Trade Leather Control, and learning about leather manufacture from a new angle. His address is 8, Westhay Gardens, W. Temple Sheen, London, S.W.14.

Prof. L. H. Briggs on refresher leave from Auckland, recently visited Switzerland where he met Prof. Reichstein and Dr. Schlitter in Basle and also visited the laboratories of Profs. Karrer and Rusicka in Zurich. Prof. Rusicka has the largest research group on the continent—over 90 persons studying for advanced degrees or on post-graduate work. Among the latter is Dr. W. I. Taylor, A.N.Z.I.C., graduate of Auckland University College, and a past-pupil of Dr. Briggs. Dr. Taylor is holding a National Research Scholarship awarded by the Council for Scientific and Industrial Research. He is working with Prof. Prelog on the constitution of strychnine. While in Zurich, Prof. Briggs gave a lecture on some recent research work in his laboratory. After a few very pleasant days, there he flew to Stockholm, where he delivered another lecture in the chemical department of the Royal Institute of Technology.

**PAPERS READ BEFORE BRANCHES DURING THE YEAR.
NOVEMBER, 1947, OCTOBER, 1948**

AUCKLAND BRANCH

- October: Annual Meeting. Film, "Masters of Molecules."
 November: "Crystal Chemistry."—Professor F. J. Llewellyn.
 February: Chairman's Address, "The Fatty Acids."—S. G. Brooker.
 March: "Electrochemical Investigation on the Constitution of Molten Salts and their Mixtures."—Dr. H. Bloom.
 April: "Technology and Processing of Rubber."—E. H. Schache.
 May: "Utilisation of Organic Wastes."—Dr. J. K. Dixon.
 June: "Nitroglycerine."—J. Ricketts.
 July: "Pathology and its Relation to Chemistry."—Dr. J. L. Pinniger.
 August: Symposium—"The Teaching of Chemistry and the New Secondary School Syllabus."—P. R. Parr and C. P. Worley.
 September: Students' Papers. (Professor F. J. Llewellyn).
 "Electrokinetic Potentials in Organic Liquids."—G. W. Butler.
 "Application of X-Ray Crystallographic Methods in the Study of Hyponitrites and Nitrosyl Compounds."—I. D. Calvert.
 "Thermal Decomposition of Nitrates."—I. W. Knaggs.

WELLINGTON BRANCH

- October: Annual Meeting.
 "Experiences of a Chemist in the U.S.A., with particular reference to fuel, food processing and waste product utilisation."—G. M. Smith.
 November: "Petroleum as a Chemical Raw Material."—M. L. Stewart.
 March: "Vitamin A."—Dr. F. B. Skörlund.
 April: "The Organisation of Scientific Research In New Zealand."—Hon. T. H. McCombs.
 May: Chairman's Address:
 "The Use of Additives in Petroleum Lubricants."—E. S. Borthwick.
 June: "Phytohormones."—Dr. B. W. Doak.
 July: Mellor Memorial Lecture:
 "British Contributions to Soil Science and Plant Nutrition."—Sir Theodore Rigg.
 August: Students' Researches at Victoria College:
 "Nitrogen Sulphide."—A. G. McDiarmid.
 "A Reaction of Uracil."—P. F. Giles.
 "Adsorption of Proteins."—T. A. Turney.
 "Products of the Bromination of Substituted Ethylenes in Acetic Acid as Solvent."—I. R. C. McDonald.
 September: "The Dyson System of Organic Nomenclature."—B. E. Swedlund.

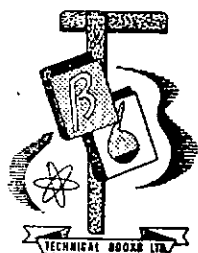
CANTERBURY BRANCH

- March: "Recent Work on Natural Products Done at Auckland University College."—Dr. L. H. Briggs.
 April: "The Application of Electronic Measurements to Industry."—T. R. Pollard.
 May: CHAIRMAN'S ADDRESS:
 "Some Factors Affecting Flour Quality."—L. H. Bird.

June: "Some Aspects of the Chemical Industry in South Africa."—W. F. Rolt.
July: "The Organisation of Scientific Research in N.Z."—Hon. T. H. McCombs.
August: "The Work of a Scientific Liaison Officer in Washington, U.S.A.—
J. A. D. Nash.
September: "The Dyeing of Wool."—R. L. Hutchinson.
October: "Antibiotics."—Dr. M. M. Burns.

OTAGO BRANCH

March: "Substitution Mechanisms."—Prof. F. G. Soper.
April: "Catalytic Hydrogenation."—W. G. H. Edwards.
May: "Unshrinkable Wool."—Dr. L. F. Storey.
June: "The Structure and Properties of Some N.Z. Pottery Materials."—J. T. Linzey.
July: "Uronic Acids in Carbohydrates."—Dr. R. J. McElroy.
September: "Current Research in the Chemistry Department,"
"The Chemistry of Some Acenaphthene Compounds."—W. G. Edwards.
"Mechanism of Formation of Chlorhydrins."—J. K. Martin.



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- Riegel, Chemical Machinery, 1944, 47/6.
- Burns & Schuff, Protective Coatings for Metals, 1939, 66/6.
- Dickey & Bryden, Theory & Practice of Filtration, 1946, 57/-.
- McLaughlin & Theis, Chemistry of Leather Manufacture, 1945, 91/-.
- Burton & Kohl, The Electron, Microscope, 1948, 47/6.
- Robt. H. Boguo, Chemistry of Portland Cement, 1947, 82/6.

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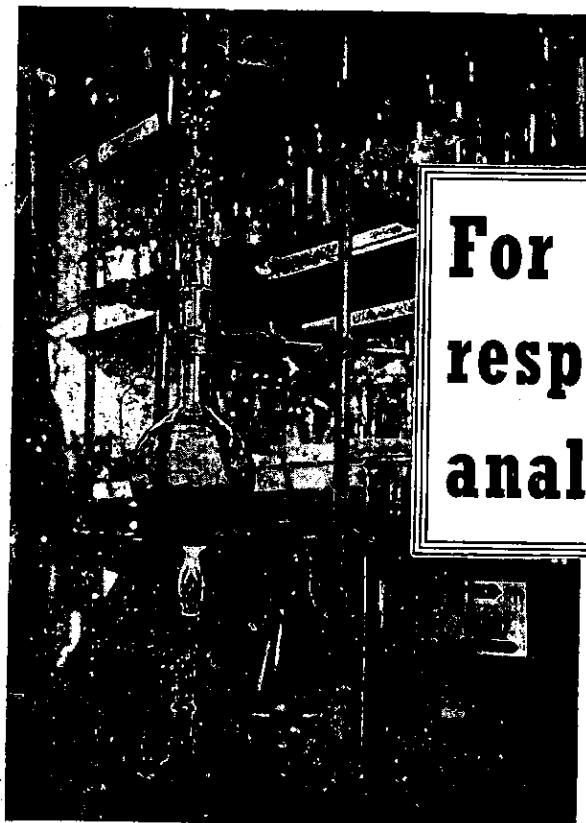
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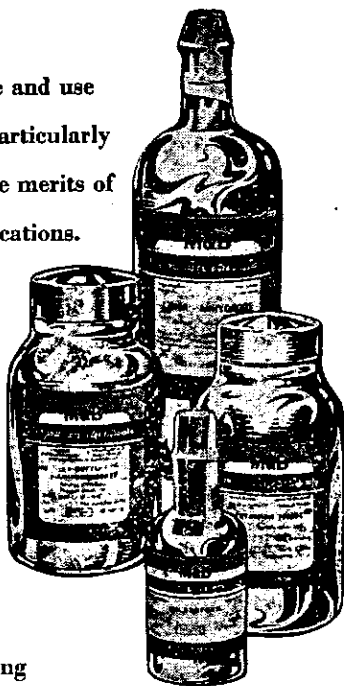
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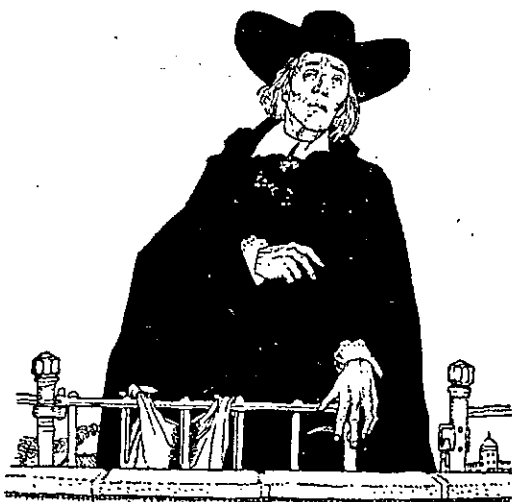
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George Starkey

Chemotherapy—the treatment of infections by means of chemical remedies—is considered one of the most modern developments in medicine. Yet it was being practised in London nearly 300 years ago by George Starkey, the son of an English clergyman in the Bermudas. Starkey was educated at Harvard, Massachusetts—then a British colony—and graduated in 1640. Coming to London, he became an apothecary and showed great skill and versatility in the preparation of chemical medicines such as quinine. He won a high reputation for his “extraordinary knowledge of chemistry”, and was on familiar terms with the leading chemists of the time.

On the outbreak of the Great Plague in 1665, he at once set about seeking a cure, and was reported to have compounded a specific which was always effective. Demands for his services were so great that he became overworked. His health suffered, and he too fell a victim to the Plague. He gave detailed instructions as to how his own remedy was to be administered to him, but his physician made an error and Starkey died, and with him the secret prescription. A contemporary wrote of him “Our friend Dr. Starkey is dead of this visitation, with about six more of them chymicall practitioners the most of them distractedly madd”. The sneer was unworthy for the “chymicall practitioners” had treated Plague patients with complete disregard of personal danger, even going so far as to hold post mortems on victims. From these crude beginnings sprang the science of chemotherapy which 300 years later, was to crown its many great achievements with the development of penicillin, the sulphadiazine drugs and “Paludrine”.

