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THE PRINCIPLE OF CORRESPONDING STATES

By M. L. McGLASHAN

The substance of this article was recently given as Chairman's Address to the Canterbury Branch of the Institute.

There seemed to me several good reasons for choosing the Principle of Corresponding States as the subject for my Chairman's address. I know of no text-book of physical chemistry in which there is any useful discussion of the Principle. What is more I believe that those text-books which do mention it, since they all tie it closely to van der Waals' or some other equally unrealistic equation of state, are downright misleading. The Principle has consequently been neglected by Chemists, though many recent publications[1] reveal the fact that Chemical Engineers are, more and more, recognising its predictive value.

A statement of the Principle of Corresponding States asserts that if we compare the behaviour of different substances, not at the same values of P, V and T, but at **corresponding** values of these quantities, then the behaviour of all substances obeying a Principle of Corresponding States will be the same.

Corresponding values of a quantity X for a series of substances are obtained by expressing X as a fraction of some **characteristic** or invariant value of X for each substance. Such characteristic points are the triple point (P_t, V_t, T_t) and the **critical point** (P_c, V_c, T_c); not of course the boiling point or melting point. Instead then of comparing $P—V—T$ results for different gases we should compare, for example, values of the **reduced** quantities P/P_c, V/V_c, and T/T_c. Incidentally such procedure has the further advantage that the quantities being compared are now dimensionless numbers and the heartbreaking business of fumbling at once with grams and pounds, centimetres and feet, B.T.U.'s and several indifferently defined calories, all disappears.

The Principle of Corresponding States can be rigorously deduced from a simple model[2, 3]. In this model we assume that the energy of interaction ϵ of each pair of molecules in

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the system depends only on the distance r between the two molecules. If we express ϵ as a function of r according to the equation

$$\epsilon = \epsilon_0 \, \Phi \, (r/r_0), \qquad (1)$$

where ϵ_0 and r_0 are the energy and distance corresponding to the minimum of the potential energy "well", then we assume further that the function Φ is the **same** function for all substances. It should be noticed that we have not said anything, and shall not need to say anything, about the precise mathematical form of the function Φ. We have said only that, whatever its form, it is the same for all the substances which we shall expect to obey the Principle. As a matter of fact very little is known about the exact form of Φ except at very great distances where ϵ is inversely proportional to the sixth power of the distance[4].

Various other assumptions must also be made [2, 3]. Here it is sufficient to say that the Principle deduced from the model will not be expected to apply at all well to polar molecules, to long chain molecules even if non-polar, or to molecules like helium and hydrogen which have sufficiently small masses so that they display quantal effects at accessible temperatures. The Principle will be expected to apply best of all to the heavier inert gases, only a little less well to gases like methane and nitrogen, and so on. Finally the Principle will be expected to apply better to gases than to liquids, and better to liquids than to solids. All these expectations are borne out by experiment.

By the ordinary methods of statistical mechanics it can be deduced from this model[2, 3] that the Helmholtz free energy $F(T, V)$ of any substance is given by

$$(2) \quad F(T, V)/RT = f(kT/\epsilon_0, V/{}^4/_3\pi r_0^3) + \ln (VT^{\frac{3}{2}}) + \text{const.},$$

where f is the **same** (albeit unknown and probably complicated) function for all substances, and ϵ_0 and r_0 are a characteristic energy and distance for each substance.

A little thought will make it obvious, by the way, that whenever we carry out any theoretical treatment intended to apply to each of a group of substances we are in fact assuming a principle of corresponding states to apply to these substances. For example if Debye's well-known model of a crystal is correct, then all crystalline solids will have the same values of C_p/R say, if they are compared not at equal values of T, but at equal values of T/Θ_D where Θ_D is a temperature characteristic of each solid[5].

From equation (2) all the other thermodynamic functions can be deduced by the appropriate differentiations. In particular using the conditions,

$$(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0, (T = T_c, P = P_c, V = V_c), \quad (3)$$

to define the critical point we deduce that ϵ_0/kT_c and $\frac{4}{3}\pi r_0^3/V_c$ are universal constants, that is to say they have constant values which are independent of the particular substance under consideration. We can therefore express all our results as universal functions of P/P_c, V/V_c, and T/T_c.

I shall now quote without proof a few of the more useful formulae deduced from equation (2) and shall try to show, by means of tables and diagrams, how well the Principle of Corresponding States is obeyed by some simple substances. I shall use the symbol u to denote any universal function, and the symbol uc to denote any universal constant.

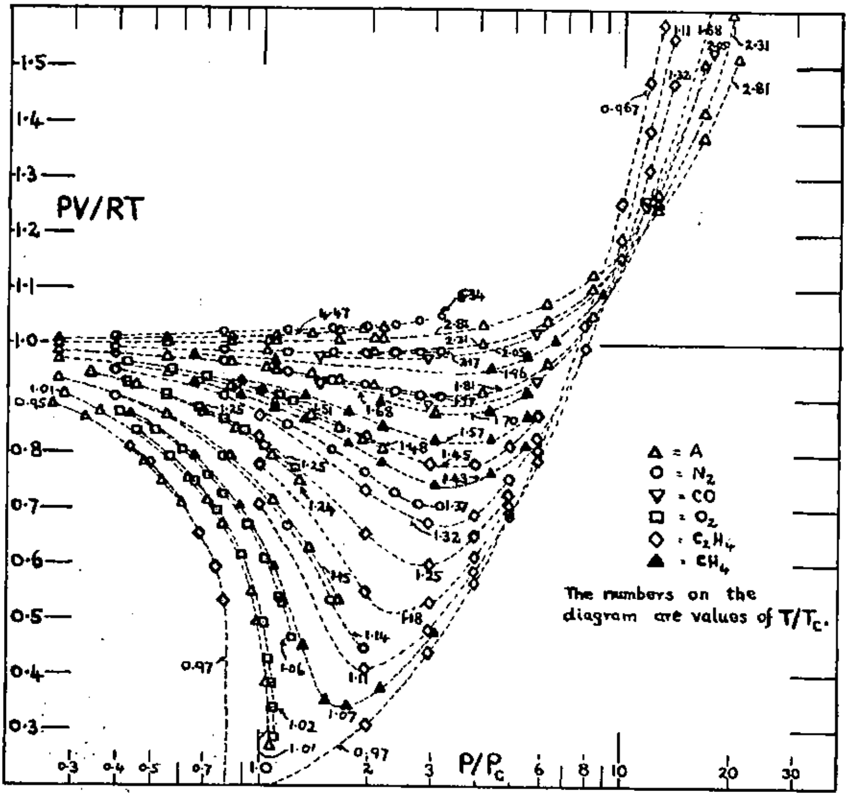

Fig. 1

Some Applications of the Principle of Corresponding States

1. $PV/RT = u_1(T/T_c, V/V_c)$

In Fig. 1 values of the "compressibility factor" PV/RT are plotted against P/P_c for six gases. It will be seen that over a wide range of pressures and temperatures the resulting curves form a family such that where measurements on different gas happen to have been made at exactly the same value of T/T_c the curves for the different gases coincide. The predictive value of such a diagram for gases on which no, or insufficient, measurements have been made should be obvious. The reader wishing to study further the use of "compressibility charts" is referred to Hougen and Watson[6].

2. $P_cV_c/RT_c = uc_1$

Values of P_cV_c/RT_c are shown for several substances in the second colunm of Table 1. The value of P_cV_c/RT_c is always close to O.29.

TABLE 1

	P_cV_c/RT_c	T_B/T_c
Ne	0.305	2.70
A	0.292	2.73
Kr	0.290	2.74
Xe	0.293	—
N_2	0.292	2.59
O_2	0.292	—
CO	0.294	2.60
CH_4	0.289	2.58
C_2H_6	0.287	—

3. $B/V_c = u_2(T/T_c)$.

4. $C/V_c^2 = u_3(T/T_c)$.

Here B and C are the second and third virial coefficients in the theoretical equation of state for an imperfect gas[7 8 9].

$$PV = RT\left\{1 + B(T)/V + C(T)/V^2 + \text{------}\right\}$$

In Fig. 2 values of $|B|/V_c$ and of $|C|^{1/2}/V_c$ are plotted for several gases against T/T_c on double logarithmic paper. It is seen that the values of the reduced second virial coefficient all lie close to a common well-defined curve and that the values of the reduced third virial coefficient, in spite of considerable experimental uncertainties in their values, also scatter about a common, though less well-defined curve. These curves have been used extensively[10] in theoretical studies of the mathematical form of the function Φ of equation (1). It is also interesting that in a similar diagram which I drew in 1950 the points for the second virial coefficient of ethane

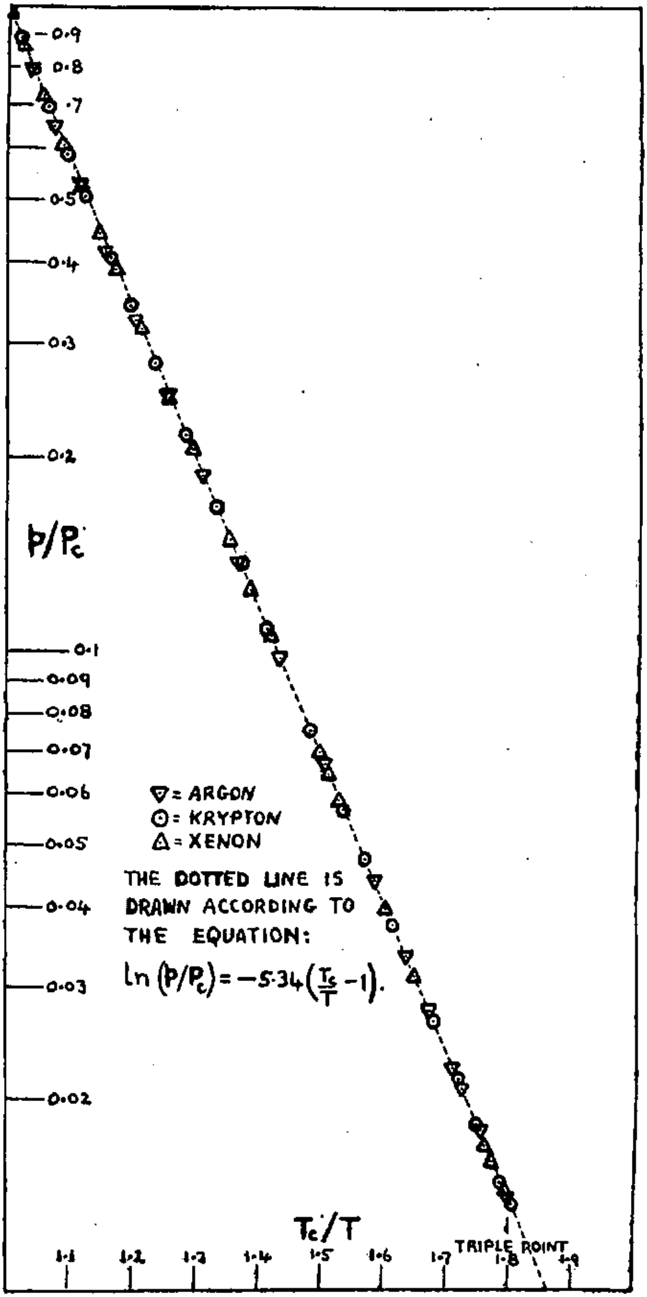
0·9
0·8
·7
0·5
0·4
0·3
0·2
p/P_c
0·1
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
▽ = ARGON
⊙ = KRYPTON
△ = XENON
THE DOTTED LINE IS
DRAWN ACCORDING TO
THE EQUATION:
$\ln(p/P_c) = -5{\cdot}34\left(\frac{T_c}{T} - 1\right)$.
T_c/T
1·1
1·2
1·3
1·4
1·5
1·6
1·7
TRIPLE POINT
1·8
1·9

Fig. 2.

showed considerable deviations from the common curve. This raised the question whether the deviations were due to inaccurate data or to real deviations from the Principle of Corresponding States. This question has recently been settled by Hamann and McManamey[11] who first showed that there were other data, ignored by me in 1950, which lie right on the curve, and then did a series of measurements themselves the results of which also closely follow the Principle of Corresponding States.

5. $$T_B/T_c = uc_2$$

Here T_B is the "Boyle Temperature" at which the second virial coefficient changes sign. Inspection of the third column of Table 1 and Fig. 2 shows that T_B/T_c is close to 8/3 for all substances considered.

6. $$\Delta_e H/RT_c = uc_3$$

Trouton's rule in its classical form compared values of the latent heat of evaporation $\Delta_e H$ of liquids divided by the boiling points T_b. According to the Principle of Corresponding States we should, however, compare values of $\Delta_e H/T_c$ since normal boiling points are not corresponding temperatures. Nevertheless T_b/T_c and therefore $\Delta_e H/T_b$ are approximately constant for a number of liquids (T_b/T_c is usually about 0.6) but this is not a **direct** consequence of the Principle of Corresponding States. Values of $\Delta_e H/RT_c$, $\Delta_e H/RT_b$ and T_b/T_c are shown for several substances in Table 2.

TABLE 2

	$\Delta_e H/RT_c$	$\Delta_e H/RT_b$	T_b/T_c
Ne	5.00	7.75	0.65
A	5.21	8.99	0.58
Kr	5.19	9.06	0.57
Xe	5.24	9.21	0.57
N_2	5.32	8.68	0.61
O_2	5.31	9.10	0.58
CO	5.47	8.91	0.61
CH_4	5.38	8.82	0.61

7. $$p/P_c = u_4\ (T/T_c)$$

Here p is the equilibrium vapour pressure of the liquid at temperature T. In Fig. 3 $\ln(p/P_c)$ is plotted against T_c/T for argon, krypton and xenon. It is seen that the results can be accurately expressed from the triple point right up to the

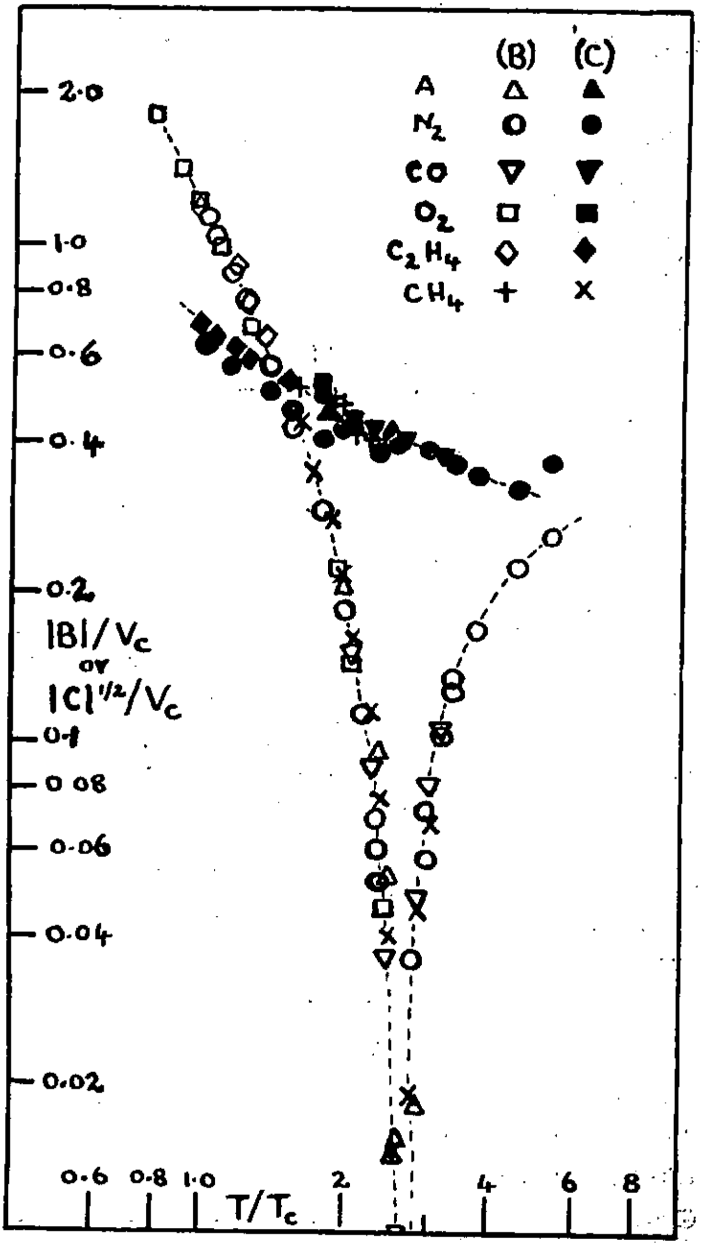
(B) (C)
A
N2
CO
O2
C2H4
CH4
2.0
1.0
0.8
0.6
0.4
0.2
|B|/Vc or |C|^1/2/Vc
0.1
0.08
0.06
0.04
0.02
0.6 0.8 1.0 2 4 6 8
T/Tc

Fig. 3.

critical point by a linear equation. From this equation, since $d \ln p/dT = \Delta_e H/RT^2$ we derive

$$\Delta_e H/RT_c = 5.34.$$

This result should be compared with the values calculated directly from calorimetric latent heat data in the second column of Table 2.

8. Finally there are shown in Table 3 values of the ratios T_t/T_c, $\Delta_f H/RT_t$ and P_t/P_c for four inert gases, where $\Delta_f H$ is the latent heat of fusion.

TABLE 3

	T_t/T_c	$\Delta_f H/RT_t$	P_t/P_c
Ne	0.549	1.64	0.0158
A	0.557	1.69	0.0142
Kr	0.553	1.69	0.0133
Xe	0.557	1.71	0.0139

These examples of the use of the Principle are only a few chosen from many. The interested reader will be able to find others in the works referred to at the end of this article.

The Principle of Corresponding States has been extended to surfaces by Guggenheim[3], to mixtures of gases by Guggenheim and McGlashan[8], to polyatomic molecules by Trappaniers[12], to polar gases and to the transport properties of gases by Rowlinson and others[13], and to gases like helium and hydrogen which do not obey the simple Principle for quantal reasons by de Boer and others[14]. In the last case the extended principle has been used to predict the properties of the interesting gases He^3, T_2, HT, and DT before these gases were prepared in sufficient quantities to allow measurements to be made.

References

[1] See for example Hougen and Watson, "Chemical Process Principles", Wiley, (1947).

[2] Pitzer, J. Chem. Phys. **7**, 583, 1939.

[3] Guggenheim, J. Chem. Phys. **13**, 253, 1945; "Thermodynamics", North-Holland Publishing Co. (1949).

[4] London, Trans. Faraday Soc. **33**, 8, 1937.

[5] See for example Fowler and Guggenheim, "Statistical Thermodynamics", C.U.P., (1939), p. 145.

[6] Ref. 1, Chapter XII.

[7] Mayer and Mayer, "Statistical Mechanics", Wiley, (1940).

[8] Guggenheim and McGlashan, Proc. Roy. Soc. A **206**, 448, 1951.

[9] Guggenheim, Rev. Pure Applied Chem. (R. Aust. C.I.), **3**, 1, 1953.

[10] See for example refs. 8 and 9.

[11] Hamann and McManamey, J. Chem. Phys. **21**, 1953.

[12] Trappaniers, Physica, **17**, 501, 1951.

[13] Rowlinson, J. Chem. Phys. **19**, 827, 1951. Rowlinson and Townley, Trans. Faraday Soc. **49**, 20, 1953.

[14] de Boer, Physica, **14**, 139, 1948. de Boer and Lunbeck, Physica, **14**, 510. 1948.

STOP PRESS

We have just received advice that the Corday-Morgan Fellowship, for which applications were called in 1952, has been awarded by the Council of the Chemical Society to Dr. A. D. Campbell, of the University of Otago. This is an honour both to Dr. Campbell and to New Zealand, and we extend to him our heartiest congratulations. He is at present in charge of the Michrochemical Laboratory at Otago, and has been granted a year's leave to take up his fellowship at the University of Glasgow to work under Prof. J. W. Cook, F.R.S. Dr. Campbell is an active member of this year's conference committee.

WOOD

By L. G. NEUBAUER

Chairman's address given by Dr. L. G. Neubauer to the Wellington Branch at their May meeting (summarised).

Since wood is a raw material of considerable importance to New Zealand a few words on its composition was considered not inappropriate. After describing the methods whereby the wood is formed during growth, the development of heartwood and the deposition of heartwood extractives was outlined.

Cellulose is chemically identical from all sources, but cottonseed hairs are most frequently used for cellulose studies because of their freedom from polysaccharides other than the "alpha-cellulose" of Cross and Bevan. Hydrolysis of cellulose yields glucose as the only end product, Methylation, acetylation and nitration of cellulose showed that each glucose unit in the molecule had three hydroxyl groups, and hydrolysis of fully methylated (trimethyl) cellulose yielded 2, 3, 6, trimethylglucose. The uniformity of the glucosidic bonds in cellulose was proved mathematically from the kinetics of the hydrolysis reaction, and from polarimetric studies of the series cellobiose, cellotriose, cellotetrose, cellulose. Thus cellulose was shown to be a polyglucopyranose, linked 1, 4 by betaglucosdic linkages. That the chains of glucose units were long was deduced from the fact that there were few end units, as shown by the very low copper reducing power and the small yield of tetramethyl glucose on methylation and subsequent hydrolysis.

The chain length of the cellulose molecule (or its degree of polymerisation) is not a constant value, a considerable degree of polymolecularity being exhibited. Solutions of cellulose and its derivatives can be fractionated, by precipitation, into chemically identical fractions that differ markedly in their solubility and other physical properties. This is due to the extent of the polymerisation. The average degree of polymerisation of a sample of cellulose can be determined chemically (end group methods), or physically using properties such as viscosity, osmotic pressure and ultracentrifuge sedimentation, and it has been shown that the degree of polymerisation is dependant not only on the source of the cellulose but also on the method used for its isolation.

X-ray examination of cellulose fibres showed a measure of crystallinity, and now the fringe micellar theory of cellulose structure is widely held. By this theory it is postulated that the cellulose chains in a fibre, which had previously been shown to be oriented roughly parallel to the fibre axis, became so placed at random intervals that interaction between neighbouring chains created regions of crystallinity. The dimensions of the unit cell responsible for this crystallinity have been measured, and the measurements agreed with primary valence forces operating along the b axis of the cell (this is the direction of the cellulose chains), with hydrogen bonding along the a axis, and van der Waals forces along the c axis. These randomly placed areas, where the parallel cellulose chains are so placed for crystallisation, are contained in larger areas in the fibre where ideal conditions do not exist, the amorphous region.

It is possible to estimate from X-ray diagrams the relative proportions of amorphous and crystalline cellulose in a fibre, and it was found that this ratio was the same as that between the readily reactive and less reactive portions as determined by chemical means. Cellulose exhibits both inter- and intramicellar swelling, the first occurring with water which penetrates only the amorphous region leaving the X-ray pattern of the crystallite unaltered. Intra-micellar swelling occurs to a limited extent with agents such as 18% sodium hydroxide solution, in this case the crystallite is penetrated sufficiently to distort it, causing a definitely new X-ray pattern, and to an unlimited extent with cupramonium hydroxide when the crystal lattice is destroyed and eventually solution takes place. The swelling of cellulose is a matter of considerable importance in the preparation of derivatives, since the ideal is to obtain a very reactive cellulose before processing, without degradation of the cellulose chains.

Closely related chemically and intimately related physically with the true or alpha-cellulose in wood are the hemicelluloses. The hemicelluloses contain sugar or uronic acid units and were first differentiated from alpha-cellulose by their solubility in alkali and their ready hydrolysis to constituent monosaccharide units by dilute mineral acids. There are two subdivisions, the polyuronide hemicelluloses which contain uronic acid groups and are amorphous substances forming part of a system interpenetrating and encrusting the cellulose fabric of the cell wall, and the cellulosans which are orientated in the micellar structure of the cellulose fabric. The cellulosans are composed of chains of monosaccharide units united in the same fashion as in cellulose but the chain length is smaller. Indeed the glucosans may be considered as fragments of cellulose chains. In hardwoods the cellulosans are glucosans and xylans, whilst in softwoods mannans also occur.

Also found in intimate physical association with the cellulose of the cell-wall is the non-carbohydrate, lignin, and there is much indirect evidence that there is a chemical linkage between the lignin and the polyuronide hemicelluloses. Lignin can be isolated from extractive-free wood by destruction of the polysaccharide material by hydrolysis and subsequent solution of the simple sugars so formed, or by solution of the lignin leaving the carbohydrates as a residue. The first type of isolation is exemplified by the standard 72% sulphuric acid method for determining lignin, and the second by the convential sulphite process for the pulping of wood. Unfortunately all isolation methods for lignin involve the use of either strong acid or alkali or high pressure and temperature, therefore it is not surprising that the nature of the lignin depends on the method of isolation used, and in all cases there is more or less alteration during isolation. Lignin is aromatic in character, and contains methoxyl and hydroxyl groups, a fraction of the latter being phenolic. From the results of degradation reactions such as alkali fusion, oxidation, high pressure hydrogenation, etc., it has been shown that lignin is a polymer based on units of a phenyl-propane carbon skeleton, but as with research on other wood constituents the absence of reliable criteria of purity has been a serious hindrance to the elucidation of structure. In common with other high polymers lignin exhibits a high degree of polymolecularity.

In conclusion there were a few brief remarks on the application of our knowledge of the reactions and structure of wood components to the wood using industries, notably pulping.

1953 Combined Conference of the New Zealand Institute of Chemistry and the New Zealand Section of the Royal Institute of Chemistry, Dunedin, 25-28th August.

CONFERENCE PROGRAMME:

(All functions will take place at the University.)

Tuesday, 25th August. 7.30-8 p.m.: Registrations, Allen Hall.
8 p.m.: Official Welcome, Allen Hall, followed by supper.

Wednesday, 26th August. 9.30-12.20:

(1) Economic aspects of chemical science and industry in New Zealand. Chairman Mr. O. H. Keys. Papers by Dr. R. Gardner, Mr. F. Callaghan and Dr. T. Hagyard.

12.20: Conference photograph.

2.30-4; tea. 4-4.30; 4.30-5.30; Two concurrent Sessions (2) and (3).

(2) Chemical Technology (Chairman, Mr. S. R. Siemon).

C. W. Weston—Recent Advances in Industrial Instrumentation.
N. W. Vere-Jones—Biochemical Engineering.
A. D. Monro—Future Uses of Iron Sand.
G. M. Moir—Casein for Industrial Use.
W. M. Billinghurst—Alternative processes of phosphate fertilizer manufacture.

(3) Biochemistry (Chairman, Prof. N. L. Edson).

F. B. Cousins—The lactic acid oxidase of the mycobacteria.
C. E. Arcus—The tolyol hydrogenase of acetobacter suboxydans.
R. D. Batt—The catabolism of pyrimidines.
J. M. Ploeser—The metabolism of hydropyrimidines.

8 p.m.: Presidential Addresses. Dr. J. K. Dixon (R.I.C.): "Some applications of Clay Mineralogy." Dr. H. E. Annett (N.Z.I.C.): "Soil Moisture in Relation to Pasture Production."

Thursday, 27th. 9.30-11; tea. 11-11.30; 11.30-12.30, two concurrent sessions. Sessions (4) and (5).

(4) Organic Chemistry (Chairman, Prof. J. Packer).

R. S. Robertson and J. Vaughan—Hydrogen Cyanide Tetramer.

A. G. McInnes—Ozonolysis and Gas-liquid Chromatography in determining the constitution of unsaturated fatty acids.

A. J. Ellis—Mechanism of Amine Chlorination.

R. E. Corbett and W. G. Hanger—The Structure of Metrosiderene.

L. H. Briggs—The Constitution of Asperuloside.

(5a) 9.20 a.m.: Particle Size and Particle Shape Factors in Industry. Chairman, Mr. W. Vose.

R. S. Jones—Methods of determining particle size.

J. T. Linzey—Size distribution relationships in particulate materials.

I. C. McDowall—Shape factor and its technical significance.

(5b) 11.30: Analytical Chemistry (Chairman Mr. F. Hurst).

T. A. Mitchell—Spectrophotometric determination of magnesium with thiazole yellow dyes.

L. Hartman—Rapid estimation of glycerol with periodates.

Thursday. 2 p.m.: Professor Emeleus.

3.15 p.m.: Tea break.

3.45: N.Z.I.C. Annual General Meeting.

5.00: R.I.C. (N.Z. section) General Meeting.

Thursday Evening—Discussion Groups.

Friday. 9.30-11; tea 11-11.30, 11.30-12.30. Two concurrent sessions (6) and (7).

(6) Physical and Inorganic Chemistry (Chairman, Prof. F. G. Soper).

M. L. McGlashan—Mixtures of molecules of single and double size.

L. E. Sutton and C. J. Wilkins—The molecular structure of some silicon compounds.

W. S. Metcalf—Some fast gas reactions.

R. S. Malthus and G. M. Richardson—Aqueous vapour pressures of salt hydrate pairs by an isopiestic method.

G. A. Bottomley—Reaction of aromatic compounds with hydrogen peroxide.

(7) Agricultural Chemistry (Chairman, Dr. M. M. Burns).

E. D. Andrews—The role of Vitamin B12 in the cobalt metabolism of sheep.

A. D. Care—The use of I^{131} in the investigation of the presence of goitrogens in sheep feeding stuffs.

N. D. Jamieson—The **in vivo** control of the blood ionizable calcium in the sheep.

G. A. Holmes—Molybdenum for crops and pastures.

F. H. McDowall—The steam distillation of cream for the removal of taint.

Friday afternoon—Visits.

Friday evening—Conference Dinner.

OFFICIAL NOTICE

A GENERAL MEETING OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.) WILL BE HELD IN THE CHEMISTRY LECTURE THEATRE, UNIVERSITY OF OTAGO ON THURSDAY, 27th AUGUST, 1953 at 3.44 p.m.

AGENDA

1. Confirmation of Minutes of previous General Meeting held at Victoria University College, Wellington, on 26th August, 1952.
2. Business arising from Minutes will be dealt with below under respective headings.
3. Presidential Remarks.
4. Activities of Institute Sub-Committee Representatives:—
    1. Membership Committee.
    2. Journal Committee.
    3. Professional Status Committee.
    4. Salaries.
    5. Examinations Commitee.
    6. Medical Advertisements.
    7. Standards Institute Committees.
    8. Employment Representative (N.Z.I.C. and R.I.C.)
    9. Conference Committee. (N.Z.I.C. and R.I.C.)
    10. Patents Representative.
    11. U.N.E.S.C.O.
5. Finance—Statement of Receipts and Payments.
6. Institute Prizes.
7. Amendments to Rules—Report on Progress.
8. General.

W. G. HUGHSON,
Hon. General Secretary.

RADIO-PHOSPHORUS IN AGRICULTURAL RESEARCH

Summary of an address given to the May meeting of the Waikato Branch by Mr. F. D. Dorofaeff of the Rukuhia Soil Research Station.

Radiophosphorus is one of the most widely used of the radio-active isotopes. This can be attributed to two causes, firstly that phosphorus is one of the major elements in biological processes and consequently it is of importance to know something of phosphorus mechanism. Secondly the isotope P^{32} is very convenient for research purposes. It has strong β-emission, 1.69 Mev. and a half-life of 14.3 days.

The production of this isotope is mainly by way of adsorption of slow neutrons by sulphur in a uranium pile reactor. This adsorption of neutrons produces an unstable energy state within the nucleus, which undergoes rearrangement according to the Laws of Probability.

Detection and measurement of radiation is carried out by a Geiger-Müller Counter. A Geiger-Müller tube is essentially a high gain, gas-filled amplifying diode operating at potentials below continuous discharge voltage. For β-counting the end-window type is used. This has a thin mica, duralumin or glass window permeable to the radiations emitted.

The radioactive material is wet-digested with nitric, perchloric and sulphuric acids and total phosphorous determined by the Lorenz gravimetric method. This precipitate is dissolved in ammonia, and the phosphate precipitated as magnesium ammonium phosphate, which is mounted on a brass ring and placed under a Geiger tube by means of a rigid slide which ensures standard reproducible geometry.

The first experiment carried out at the Rukuhia Soil Research Station was a preliminary trial to compare utilization by pasture of animal manure and superphosphate. The animal manure was obtained by grazing sheep on radiophosphorus topdressed pasture, and the comparison was carried out on two contrasting soil types, Te Kowhai loam and Horotiu sandy loam. The main conclusions that could be drawn from the experiment were that in the Horotiu sandy loam plot more phosphate was taken up from the soil than in the control plot, while in the Te Kowhai loam plot the amounts taken up from the soil in the super-treated and in the control plot were similar.

The second experiment was a large-scale mowing trial in sextuplicate to compare reverted superphosphate and superphosphate, both top-dressed on a high fixing soil. Preparation of the reverted and straight super was undertaken by T. A. Rafter and co-workers of the Dominion Laboratory with 60 millicuries of P^{32} added to the sulphuric acid used for acidulation. The period of time from when the radio isotope left Oak Ridge to that of topdressing was a little over a week. The final result of the trial was that over a five monthly growing period the super plots returned 14.3 per cent., and the reverted plots 10.1 per cent. of the applied fertiliser. Yield figures were significantly greater for superphosphate plots for the first 2 months only. Results for the last 3 months were parallel. The conclusion of the experiment was that no advantage was gained through the use of reverted superphosphate on Horotiu sandy loam over the five month period.

Work at present being carried out is a study of what is termed "available soil and fertilizer phosphorus," and much time is being devoted to the question as to whether radiophosphorus in the plant gives a true indication of fertilizer uptake.

TRENDS IN THE USE OF PESTICIDES

Summary of a lecture to the Wellington Branch at their March meeting by Mr. P. J. C. Clark of the Dominion Laboratory.

The chemistry of pesticides has mushroomed to such an extent in the past decade that the speaker narrowed the field of his address to the organic phosphorus compounds which of all spray materials are exciting the most interest. They are the most poisonous, most effective, the least selective and being synthetic are very suitable for mass production. Their very poisonous nature, however, has the effect of inspiring workers in fields other than organic phosphorus compounds to renew their search for very much safer insecticides. Structurally the organic phosphorus compounds fall into two groups.

1st — based on organic groupings round the phosphate molecule.

2nd — based on organic groupings round the pyrophosphate molecule.

The first group is represented by parathion, perhaps the best known, methyl parathion, paraxon and EPN, and the second group by tetraethylpyrophosphate (the active constituent of HETP or hexone) tetraethyldithiopyrophosphate and Schradan or Pestox 3.

Two others, Malathon and Systox, both of which come into the first group, are also growing in popularity in Great Britain. Of these compounds Schradan and Systox are systemic poisons, i.e., absorbed by the plant, both leaf and root and translocated within the plant mainly to the growing points.

A systemic pesticide which has proved its worth is Hanane, or a mixture of bis dimethylaminofluorophosphene oxide and Schradan; this has been used with phenomenal success against mealy-bug. This bug is the vector by which the virus disease called swollen shoot is transmitted to cocoa. Spraying with contact insecticides is of no avail, because the ants which domesticate the mealy-bugs for the honeydew which they exude, build a protective tent over them. Control is obtained by planting gelatine capsules containing Hanane at the base of each tree, the Hanane within the capsule is liberated as the capsule dissolves and is absorbed into the tree as a systemic. After 5 to 8 weeks no toxic residues are found in the cocoa beans.

Mr. Clark then discussed the toxicity of the organic phosphorus compounds in comparison with other well-known insecticides. The work has mainly been done on rats, rabbits, and, in a few cases, on dogs.

Added difficulties arise because all animals do not react in a similar way to the same insecticide. An instance here is the case of Isopestox which causes paralytic symptoms in man, dogs, and fowls but not in other test animals.

Mr. Clark concluded his lecture with a brief reference to the amount of poisonous residues on fruit which can be regarded as a safe tolerance.

WOOD EXTRACTIVES

This is a summary of a lecture given by Dr. W. E. Harvey to the April meeting of the Wellington Branch. Dr. Harvey has recently returned from Sweden where he had been doing research on wood chemistry. Now lecturer in organic chemistry at Victoria College, Dr. Harvey had been with the Dominion Laboratory since he returned and prior to this present appointment.

The substances which may be extracted from wood with solvents such as acetone, although only minor constituents on a weight basis, have assumed increasing importance in recent years. An extremely wide range of chemical types of compounds are represented, but the extractives may be classified roughly into groups.

The terpenes appear commercially as turpentine which may be manufactured directly from stump wood, or alternatively obtained as a by-product from pulping operations. Resin acids and fatty acids are the chief components of tall oil, and with the advent of improved methods of purification the demand for this material has increased greatly and tall oil has become a valuable by-product of the suphate pulping industry.

The tannins, which occur mainly in the bark, have long been in considerable demand for the leather industry. The chemistry of the tannins is complex and much still remains to be done in this field. The wood colouring matters vary widely in type, and although of no commercial value, are of interest especially to the producer of mechanical pulp since, if a bright pulp is desired the colouring matters must be removed as completely as possible—a process which may present considerable difficulties.

Phenolic compounds may be of considerable importance in determining the durability of the wood. Thus, in the case of the pines, the durability closely follows the content of pinosylvin (3:5-dihydroxystilbene) and its monomethyl ether in the heartwood. The pinosylvin phenol content of a particular tree appears to depend mainly on hereditary (as distinct from climatic for example) factors. The distribution of the pinosylvin phenols in the wood is not uniform but follows a fairly well defined pattern. Pinosylvin shares with certain other reactive phenols the property of inhibiting sulphite cooking, and it was in fact studies on this phenomenon which led to the original isolation of pinosylvin.

Of course not all phenols are toxic to fungi, and compounds other than phenols may be responsible for the durability of certain woods. Of the latter compounds the tropolones, α, β, and γ-thujaplicins (isopropyltropolones) and nootkatin (an isopropylisopentenyltropolone) thujic acid (4:4-dimethylcycloheptatriene carboxylic acid) and the chamic acids (derivatives of carene) are worthy of mention.

NEW HONORARY FELLOWS

MR. R. L. ANDREW

Mr. R. L. Andrew was born at Thames in 1883. His forbears were Cornish miners, and it was not surprising that he went to the Thames School of Mines, and acquired in his youth an interest in gold mining that he has never lost. He joined the staff of the old Colonial Laboratory in 1906 and spent four years doing analytical work for the Mines Department and the Geological Survey. In 1910, he commenced a task that was to occupy him for many years: the analysis of samples collected under the newly promulgated regulations of the Food and Drugs Act. He did pioneer work on the freezing point and reductase tests for milk and this not only led to his making useful contributions to the literature as the result of his long experience, but also to a great improvement in Wellington's milk supply. Mr. Andrew looks back to this work as the most satisfying of his career.

Mr. Andrew also did much work on the determination of iodine in soils and waters. This work also has two important consequences. On the one hand it showed the connection between the incidence of goitre and the amount of iodine in the soils and waters; on the other it led to a critical examination of the methods of extracting iodine from natural products. He was doubtful if this element could ever be completely extracted, and this conclusion was borne out by a thorough investigation in the laboratory of the Government Chemist in Great Britain. He also investigated (with G. W. Stace) the loss of iodine from iodised salt, and showed that it had migrated to the container in many cases.

Mr. Andrew's last six years in the Department of Scientific and Industrial Research were spent in administrative duties as Director of the Dominion Laboratory. He retired in 1946, and spends his leisure in gardening, photography, reading the classics, and entertaining his grandchildren. He has written to the Editor to say "No honour in my old age could have been more acceptable than the one Council has been pleased to confer on me."

MR. F. T. SEELYE

In addition to the notes published in our last issue, which bear testimony to Mr. Seelye's reputation as an outstanding analyst of rocks and minerals, we are pleased to be able to add the following biographical details. He was born in Dunedin in 1879, and after leaving Otago Boys' High School, went to the Otago University School of Mines in 1898 and gained the diploma of A.O.S.M. in both the Mining and the Geological divisions, and also the certificate of Metallurgical Chemist and Assayer. In 1902 he was appointed assistant to the late P. G. Morgan, Director of the Waihi School of Mines. Besides being instructor in chemistry, assaying and mathematics, he carried out many analyses for the general public.

In 1920, Mr. Seelye joined the staff of the Dominion Laboratory, Wellington, where his whole time has been spent on the analysis of rocks, clays, minerals and sands, largely for the Geological Survey and the Soil Bureau. These samples came not only from various parts of New Zealand, but also from some of the Pacific Islands. One of his most interesting discoveries was the large amount of boron (up to 4.8 per cent. of boric oxide) in the ash of Waikato coals; he also found (with T. A. Rafter) that monazite and almost all highly refractory minerals can be decomposed at quite a low temperature in platinum vessels by fusion with sodium peroxide.

In 1944, Mr. Seelye was elected a Fellow of the Royal Society of New Zealand. He now lives in retirement at Lyall Bay.

(We hope to publish an account of the career of Mr. H. Rands, the third new Honorary Fellow in our recent issue.—Ed.)

OBITUARY

MR. R. M. BRUCE

The death occurred recently in Wellington of Mr. Robert Marshall Bruce, formerly a mathematics and science master in a number of secondary schools in New Zealand, and latterly an examiner of patents in the Government Patent Office.

Mr. Bruce was the second son of the late James Bruce, one of the earliest instructors in agriculture in New Zealand—he was appointed about 1906—and who was particularly well known in the Nelson district.

Mr. Bruce was born in Dunedin and educated at the Otago Boys' High School and Nelson College. He later received his science degree from Victoria

University College, where he obtained the Sir George Grey Scholarship on two occasions. He also assisted the late Sir Thomas Easterfield at the college as demonstrator and lecturer in chemistry until the First World War, in which he served for some time in the Divisional Signallers in France, where he was severely gassed.

He was granted an Expeditionary Force scholarship and attended the Royal College of Mines, London, where he recieved his associateship a few years later. He was also an early associate of the Royal Institute of Chemistry of Great Britain and a foundation member of our Institute.

Mr. Bruce taught as a mathematics and science master at a number of secondary schools, including the Wanganui Technical College and the Christchurch Boys' High School. While at the latter school he also acted as a consultant in metallurgy, and later accepted an industrial appointment as chief chemist to a Dunedin firm. A few years later he was appointed as chief chemist and metallurgist to the New Zealand Railways at Lower Hutt, and during the Second World War he served in the Munitions Department, Wellington, from which he later retired owing to ill health.

For the last few years Mr. Bruce was employed in the Government Patent Office as an examiner of patents.

NEWS AND NOTES

At the June meeting of the Wellington Branch Dr. R. M. Williams of the Applied Mathematics Laboratory, D.S.I.R. discussed "Some Applications of Statistics to Chemistry."

The Wellington Branch prize to the best Chemistry I student at Victoria College in 1952 has been awarded to Miss A. M. Long.

At the invitation of the Auckland Institute and Museum several members attended an evening at the Museum to listen to an informative address by Professor Briggs who is President of the Auckland Institute and Museum this year. Professor Briggs lectured on the impact of chemistry on our everyday existence.

At the regular June meeting of the Auckland Branch Mr. Odell of the Chemistry department, Auckland University College, discussed the magnetic properties of complex salts and illustrated his lecture with examples from the work he and his associates have been doing at the University. Before supper, Mr. Odell showed members the magnet and measuring apparatus he has developed for carrying out his research and the radioactive laboratory in which they are endeavouring to use tracer techniques to relate chemical reactivity with the physical structures derived from the study of the magnetic susceptibility.

Mr. K. E. Seal of Amalgamated Brick and Tile Co. Auckland, discussed the value of chemistry and, in particular, physical chemistry to the Ceramics industry at the May meeting of the Auckland Branch. Mr. Seal gave examples of the value of the application of scientifically derived information to an industry which until recently has depended more on native skill than on science.

For his Chairman's address to the Otago Branch, Mr. Keys chose the subject "Water." The chemistry of water is in large measure the chemistry of the small amounts of impurities present. The problems of supplying large urban populations with an adequate safe supply were considered, and sewage pollution of rivers. In recent years there has been an alarming increase in the pollution of rivers in the U.S.A. and purification difficulties have increased with the use of synthetic detergents in large quantities. Water treatment varies considerably but one of the standard methods is coagulation and filtration followed by sterilisation, usually by chlorine. Chlorine supplies in N.Z. must be imported. Ozonisation is considered quite a good method and has the advantage that it leaves no residual taint.

Vigilance is always necessary with water supplies and regular analyses are essential. An analysis should include the hardness, pH, free and combined chlorine, oxygen demand, nitrates, nitrites, and a microscopic examination of the sediment. Nitrites are rarely determined quantitatively; traces should be regarded with suspicion as they indicate that organic matter is still being oxidised.

Mr. Keys also discussed boiler waters, Dunedin's water supply, breakpoint chlorination and concluded his address by a brief reference to methods for obtaining drinking water from seawater.

"Recent Advances in Tanning Techniques" was the title of an address by Mr. N. P. Lino, in which he outlined the practices he observed in overseas tanneries and discussed the methods used by his own company.

Professor F. J. Llewellyn has recently been delivering a course of lectures at Otago University, and on June 24th he addressed the Otago Branch, his subject being "The Solid State." The Professor was guest of honour at an informal dinner attended by about twenty branch members who appreciated the opportunity to meet him socially before his address. The success of the dinner will encourage the Branch Committee to repeat the experiment from time to time.

Mr. A. H. Lewin, who until recently was with the Oamaru Woollen and Worsted Mills Ltd., has now joined the staff of Cadbury Fry Hudson Ltd., Dunedin.

Mr. H. R. Boswell, of the Mosgiel Woollen Mills, has been awarded an International Wool Secretariat Scholarship, and will spend a year at Leeds.

Mr. L. P. Chapman, until recently with the D.Y.C. organisation in Auckland, is now with the Oamaru Woollen and Worsted Mills Ltd.

At the June meeting of the Waikato Branch, members heard an interesting address by Mr. K. M. Griffin, Government Analyst at Auckland, on "Forensic Chemistry." Mr. Griffin illustrated his talk with anecdotes from his experiences over the last 30 years and revealed both amusing and grim episodes.

The May meeting of the Canterbury Branch was addressed by Dr. B. R. Penfold who took as his subject "X-ray Diffraction and Chemical Structure." Dr. Penfold outlined the basis of the chief methods for the determination of crystal structure and illustrated his discussion by reference to some recent interesting results. Dr. Penfold returned to his position on the staff of the chemistry department at Canterbury University College towards the end of last year after receiving his Ph.D. degree for work done at the Cavendish Laboratory, Cambridge, on the structures of glutamine, δ-pyridone and δ-thiopyridone.

At the last Council Meeting Dr. Penfold was elected an associate and is to be congratulated in contributing to his Branch activities so promptly.

R. V. Peryman was last year admitted to the degree of Ph.D. by the University of Leeds for a thesis on "Some Relationships between Swelling and the Behaviour of Animal Fibres in Felting and Milling." He resigned his position with New Zealand Woollen Mills Research Association in 1950, and from November of that year has been a Senior Scientific Officer in the Woollen Mills Research Association, Leeds.

The first issues of a new publication of the American Chemistry Society, "Journal of Agricultural and Food Chemistry," have arrived, and, as expected, it proves to be a magazine which will be of considerable interest to all those connected with either of these fields of chemistry. It contains original papers, reviews, and "hot" news; it is well produced and illustrated. There are two curious features in this journal. Firstly, the publishers have adopted a larger page size, which is out of harmony with the rest of the A.C.S. publications, and will cause difficulties in filing. Secondly the Journal is numbered straight through from cover to cover, advertisements and all. This will cause problems in binding and is certainly unusual in a scientific journal. It is also unusual for such a journal to publish tributes to itself from individual readers. Never-the less, many others besides ourselves will look forward to seeing each issue—when it arrives. (Number 1 took exactly three months to reach the Editor's desk.) It is published fortnightly at $6.00 per annum, plus $1.50 postage.

BOOKS RECEIVED

Lange's Handbook of Chemistry. Compiled and edited by Norbert A. Lange. 8th Edn. 1952. 2014 pages 5⅜ x 7⅞ in. Fabricoid binding. Sandusky, Ohio. Handbook Publishers, Inc. $7.00. It may be said at the outset that the coverage of this volume is excellent and there is little information that one would expect to find that is not included. It does not pretend to deal with actual methods of quantitative analysis but this is not a defect as such information is better obtained from books on analysis and its omission leaves more space for data which is properly included in a handbook. Some topics such as ceramics may have too much space allotted to them and tables on surface-active agents and antibiotics would have been useful additions. On the other hand the compiler has chosen wisely and there is not much that any reasonable user would suggest could be left out. The reviewer has checked the information given at several points and finds a high standard of accuracy.

This edition contains 78 more pages than the last and the following new tables: Ionization potentials of the elements; Classification of clay minerals; Glossary of inorganic chemical nomenclature; Titrimetric indicators (mixed, oxidation-reduction and fluorescent); Molar equivalent of a litre of gas; Density of moist air. Several other tables have been revised and the compiler is apparently active in keeping the work up to date. The general get-up of the book makes it pleasant to handle. There is a good clear type and an excellent binding, but the print shows through the paper so badly that it can be clearly read from the other side. The price is reasonable.

Kurzes Handbuch der Chemie. By Waldemar Koglin. Vol. 2, Bixin-K, 1953. Gottingen: Vandenhoeck and Ruprecht. 49 DM (74s). This book confirms our good impression of the first volume reviewed in our February issue, and we would make only two criticisms. In some places the print shows through the paper, and the data on glycerol could have been enlarged to include e.g. boiling points of mixtures with water at various pressures.

Traité de Chimie Organique. Published under the direction of Victor Grignard, G. Dupont, R. Loquin and P. Baud. Vol. XXI. Various Heterocyclic Compounds. 1147 pages. 9,300fr. Vol. XXII. Organic Chemical Industries. 1290 pages 11,000fr. 1953. Paris: Masson & Cie. With the publication of these two volumes and two more scheduled for later in this year—Vol. XX on Heterocyclics and a general index—Grignard will be complete. This monumental and unique work has thus been spread over eighteen years, a long delay due largely to the war and other difficulties which merit our sympathetic consideration. Nevertheless it is certainly unfortunate that in some sections in Vol. XXI only the literature up to 1933 has been considered, and in many others the work has ceased in 1942. The publishers have apparently preferred to print manuscripts received so long ago, rather than to endure further delays by waiting for these manuscripts to be brought up to date. There is something to be said for this point of view as they have produced even with these limitations the most recent full review of the field, but it is to be hoped that they contemplate an early revision of these parts of the work.

Vol. XXII is much more recent in its scope, covering the field into the present decade. Noteworthy features are lengthy articles on soaps with a full discussion on the physical chemistry of soapmaking; on synthetic polymers; on dyestuffs; and on chemotherapeutics. The production of antibiotics and the fermentation industries are also discussed and there is a section on general methods in the organic chemical industry. This is a very useful volume and we envy French chemists who have this work in their own language.

Messrs. Macmillan and Co. have forwarded a copy of Schmidt and Rule's Textbook of Organic Chemistry, edited by Neil Campbell (32/-). This book was reviewed by Prof. Slater in our issue for April, 1951, and seems to us to be very good value for the money.

We have also received a copy of another very well known book, Gattermann's **Practical Organic Chemistry**, edited by H. Wieland. First published in 1894, and now in its 34th edition, its still maintains a modern outlook on the subject, and has a judicious mixture of the newer and classical methods. An unusual feature for a practical book is the inclusion of a chapter on electron theory and reaction mechanisms. This would be an excellent book for those who wish to learn German and organic chemistry at the same time. It is published by Walter de Gruyter and Co. of Berlin at DM.26 (45/6).

Applied Inorganic Analysis 2nd Edition by G. E. F. Lundell, H. A. Bright and J. I. Hoffman. 1034 pages. 1953. John Wiley and Sons, New York $15.00. The first edition of this book by Hillebrand and Lundell twenty-four years ago, gained a fine reputation among analysts, and this new edition is a worthy successor. This is esesntially a practical man's book, and the theoretical material required for students is conspicuous by its absence. The book is complete as far as can be ascertained, and should be found useful in any laboratory. Compared with the first edition, which was slightly smaller, there have been many changes, although much of the wording remains unaltered. The sections on rock analysis have been reduced and the space used to introduce some more modern methods, such as polarography, X-ray methods, chromatography and mass spectroscopy. The chapter on "Special Operations and Techniques" has been much expanded. There is an abundance of references. The book is not expensive for the wealth of material contained.

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(Subject to Final Confirmation)

August	16	Sunday	Arrive Auckland.
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	18	Tuesday	Auckland — Hamilton.
	19	Wednesday	Hamilton — Rotorua.
	20	Thursday	Rotorua — Hamilton.
	21	Friday	Hamilton — Palmerston North.
	22	Saturday	Palmerston North — Christchurch.
	23	Sunday	Christchurch.
	24	Monday	Christchurch.
	25	Tuesday	Christchurch — Dunedin.
	26-28	Wednesday-Friday	Dunedin.
	29	Saturday	Dunedin — Wellington.
	30	Sunday	Wellington.
	31	Monday	Wellington.
Sept.	1	Tuesday	Depart Wellington for Sydney.

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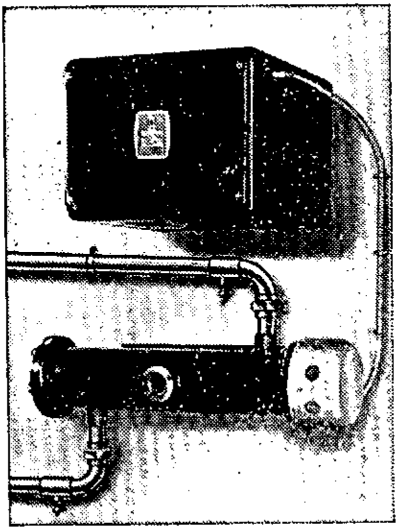

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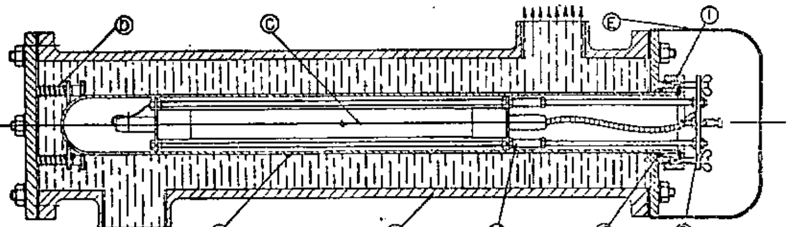

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