JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

VOL. XV. AUGUST, 1951 No. 4.

CONTENTS


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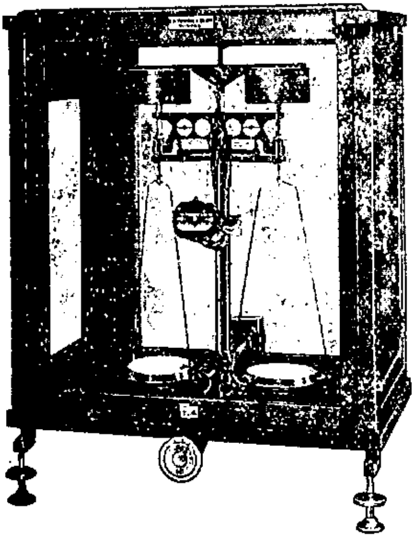

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WIDNES — ENGLAND

JOURNAL OF THE

NEW ZEALAND INSTITUTE OF CHEMISTRY

VOLUME XV. AUGUST, 1951 No. 4

PUBLICATIONS RECEIVED ON EXCHANGE—JUNE, 1951

The following is a list of the publications now being received on exchange for the Journal of the New Zealand Institute of Chemistry. Through the generosity of the Auckland Institute and Museum, they are now housed in that Institute's Library, and members who wish to borrow them may do so by writing to the Librarian, Auckland Institute and Museum, Newmarket, Auckland, including stamps to cover the cost of postage.

Acta Chemica Scandinavia. Vol. 4, 1950 . . .

Anales de la Asociacion Química Argentina. Vol. 36, 1948 . . . .

Boletin da Associação Química do Brasil. Vol. 8, 1950 . . . .

Chemistry in Canada. Vol. 1, 1949 . . . .

Chimie Analytique (Paris). Vol 31, 1949 . . . .

Industria y Química (Buenos Aires). Vol. 12, 1950 . . . .

Irish Chemical Association Journal. 1946-47 . . . .

Journal of the Royal Institute of Chemistry, Vol. 69, 1945 . . . . (Formerly: The Royal Institute of Chemistry Journal and Proceedings.)

Journal of the South African Chemical Institute. New Series. Vol. 1, 1948 . . . .

Lantbrukshogskolans Annaler (Annals of the Royal Agricultural College of Sweden), Vol. 1, 1933-34. . . .

Lectures Monographs and Reports of the Royal Institute of Chemistry. Irregular. 1945 . . .

Organization for Scientific Research in Indonesia. Various publications, 1948 . . . .

Proceedings of the Royal Australian Chemical Institute. Vol. 15, 1948. (Formerly: Journal and Proceedings of the Australian Chemical Institute.)

Reviews of Pure and Applied Chemistry (Melbourne). Vol. 1, 1951.

The South African Industrial Chemist. Vol. 1, 1947 . . . .

THE QUENCHING OF FLUORESCENCE

W. S. Metcalf

The Mechanism of Fluorescence Emission

Fluorescence, the subsequent emission at longer wave-lengths of absorbed radiation, is found in solids, liquids, and gases. For example, anthracene in all three states at suitable concentrations is blue when illuminated by ultraviolet light. The simplest mechanism of fluorescence in gases and liquids which is consistent with experiment is as follows (3).

Light is absorbed by a molecule (benzene will serve as an example) and the electrons in it change their mode of motion. This changes the binding force between the atoms and sets the excited molecule vibrating. This vibrational energy is lost by collisions and appears as heat. After a short time—about 10^{-8} seconds—the electrons return to their original mode of motion with emission of fluorescence and change again the inter-atomic binding forces. Vibration follows as before, and this also is lost in collisions. The energy change on emission is less than that on absorption by the vibrational energy lost in the excited and ground states. The frequency of the fluorescence is less than that of the absorbed light as is required by the proportionality between frequency and energy.

The Lifetime of Excited Molecules

Three methods are available for measuring the average life of excited molecules, and in the case of fluorescein (17, 24) all three methods agree within the approximations of the theory used in the interpretation of the data, though the discrepancies considerably exceed the experimental error.

Firstly, the area under the absorption band is proportional to the probability of both the absorption and the emission processes (11, 13). There is a little arbitrariness in the assessment of the contribution to the area of the various bands when they overlap, but a more serious difficulty lies in the fact that the precise calculation of the lifetime from this area makes use of the assumption that the molecules are isolated, and this, while nearly so in the gas phase, is far from true in solution. Corrections amounting to about 50% have been proposed, using the refractive index of the solvent, but their validity is doubtful (15). There is another difficulty. Molecules of anthracene absorb longer wavelength ultraviolet light in one direction only—believed to be along the length of the molecule. If all the anthracene molecules were held the same way and light polarised in the most favourable direction were used, the absorption spectrum would be three times as great as usual. This would make it appear that molecules excited in this way would have a much longer life than those excited in the normal manner. This is hardly credible, and it is necessary to decide which absorption spectrum to use in the calculation of lifetimes. Expressions derived so far do not cover this situation, and they probably give average lives several times too long in the case of anisotropic molecules (5).

A second method of lifetime measurement presents an interesting picture of the rotation of molecules in solution (17). In viscous solutions fluorescence excited by polarised light is itself polarised. The forward and reverse transitions are associated with a definite direction in the molecule, which in viscous solutions can scarcely rotate during its lifetime. In solutions of low viscosity the fluorescence is depolarised, because at the moment of emission the excited molecules have rotated to a random position. If the lifetime is known, this provides a direct method for observing rotation in solution, and in the future it may be much used for this purpose. If the lifetime is not known, further assumptions are required. If the excited molecule is regarded as a sphere moving in a homogeneous medium whose viscosity is that of the solvent, hydrodynamics and the theory of Brownian motion allows an exact computation of the rotation in a given time, and hence a deduction of lifetimes from depolarisation measurements. In the case of fluorescein dissolved in water, this theory describes well the variation of depolarisation with the viscosity of water-glycerol mixtures in which it is dissolved. With anthracene dissolved in paraffin mixtures, a case where the solvent and the solute sizes are more nearly equal, and less in conformity with the postulated model, the agreement is not good (8). The anthracene rotates faster than theory requires in very viscous solutions (25).

A third method of lifetime measurement is more direct (24). No mechanical shutter can be made to operate fast enough to show that the emission process follows the absorption process after 10^{-8} second. Nitrobenzene in an electric field passes suitably polarised light more readily perpendicular to the field than parallel to it. It is possible to change this field 10^8 times a second, and a sufficiently agile shutter can thus be made, with which the lag in fluorescence emission can be measured. This method can only be used for substances which can be excited by wavelengths that nitrobenzene will transmit, a condition which excludes anthracene.

Quenching in Gases

The fluorescence of anthracene gas is reduced if oxygen or sulphur dioxide is added. This quenching process is considered to be due to reaction between the excited and quencher molecules, which destroys the excited molecules. The number of quanta emitted is then less than the number absorbed and the fluorescence is reduced accordingly. The competing reactions and their rates are set out below.

		Rates
Absorption	$A + h\nu \rightarrow A^*$	$k_a I_{abs}$
Fluorescence	$A^* \rightarrow A + h\nu^1$	$k_f [A^*]$
Quenching	$A^* + Q \rightarrow$ products	$k_Q [A^*] [Q]$

A — anthracene.
A^* — excited anthracene.
Q — quencher.
I_{abs} — amount of light absorbed per second.

The fluorescence is steady, so that $[A^*]$ is constant. Its formation by absorption must equal in rate its disappearance by fluorescence and quenching. Therefore:

$$k_a I_{abs} = k_f [A^*] + k_Q [A^*] [Q]$$

$$\therefore \quad [A^*] = k_a I_{abs} / (k_f + k_Q [Q])$$

In the absence of quencher (that is $[Q] = O$)

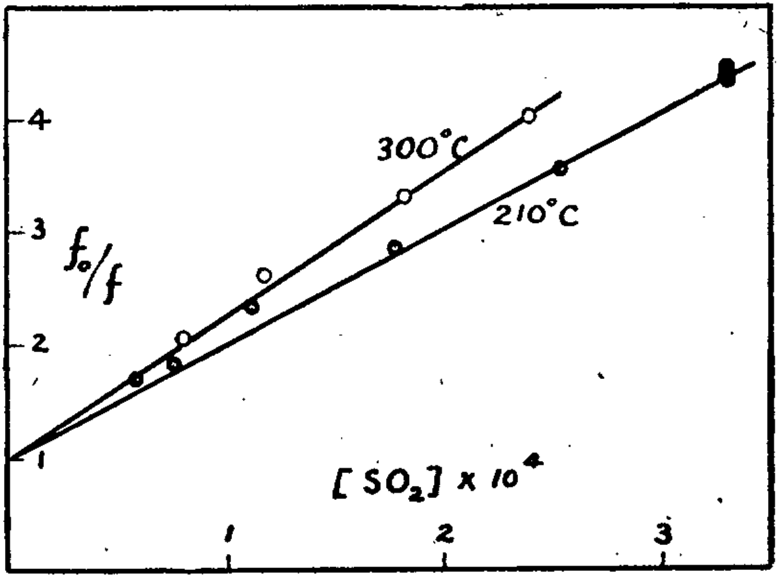
$$[A^*] = k_a I_{abs} / k_f$$

If f is the fluorescence intensity in the presence of quencher and f_o in its absence

$$f_o/f = 1 + (k_Q/k_f) [Q]$$

because f is proportional to $[A^*]$.

This expression (23) predicts a straight line if f_o/f is plotted against the quencher concentration. Fig. 1 shows such a plot for the quenching of anthracene fluorescence by sulphur dioxide at two temperatures (5).



The slope of this line is k_Q/k_f. k_f is the inverse of the average life, and is known from the absorption spectra to be 0.75×10^8. k_Q can thus be calculated, and has the value 0.75×10^{11} at 210°C, and 0.9×10^{11} at 300°C. In the case of oxygen the figure 0.6×10^{11} was found at 210°C.

The low temperature coefficient and the similarity between these values suggests that there is no large activation energy required for quenching, and that nearly every collision is effective. It is possible to calculate k_Q on the assumption that every collision is effective. The expression is:

$$k_Q = (N/10^3)\ \pi\ (r_A + r_Q)^2 \left\{ \frac{8RT}{\pi} \cdot \frac{M_A + M_Q}{M_A M_Q} \right\}^{\frac{1}{2}}$$

where N is the Avogadro number,
r_A and r_Q are the molecular radii of anthracene and quencher,
M_A and M_Q are the molecular weights of anthracene and quencher.

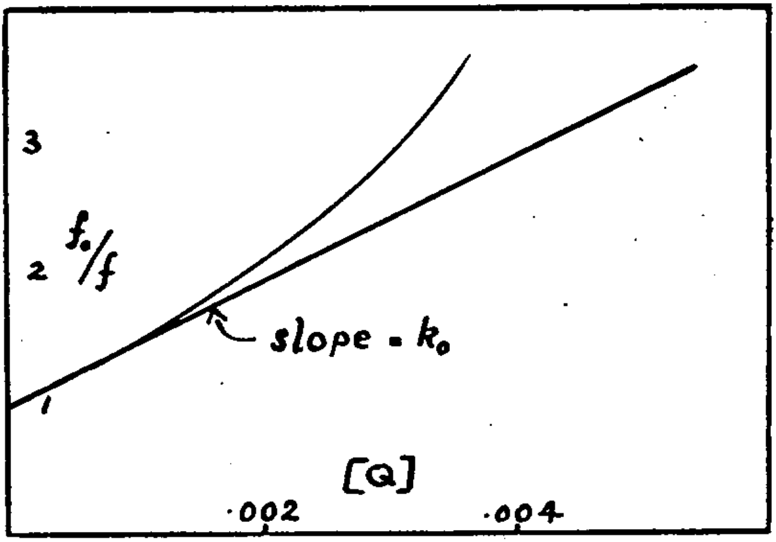
The result is 3×10^{11} for sulphur dioxide, and
3.5×10^{11} for oxygen.

Taking into account all the errors and uncertainties, one may say that for the quenching of the fluorescence of anthracene molecules by oxygen or sulphur dioxide, from two to seven collisions are needed.

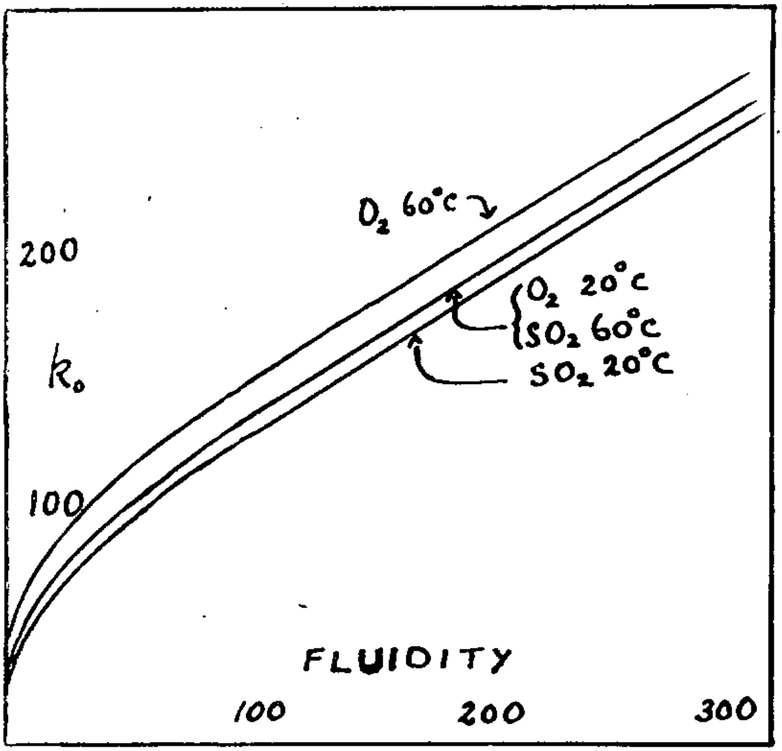
Quenching in Solution

A reaction which occurred on every collision would be most valuable for the study of the collision frequency in solution. Many ways of calculating this quantity have been proposed (6, 7, 14, 16), some of them contradictory. The high efficiency of the quenching reactions already discussed has suggested their use for this problem. Anthracene, oxygen and sulphur dioxide are soluble in all the common organic solvents (with the possible exception of pure glycerol) and anthracene fluoresces in most of them.

Paraffin fractions and mixtures have been chosen for solvents as these provide a large range of viscosities, and would not be expected to react with any of the solutes. The graph (Fig. 2) of f_0/f against [Q] is not quite straight—a fact whose significance will appear later. The value to which the slope tends as the concentration of quencher is reduced, is termed the quenching constant in dilute solution, k_0. k_0 is conveniently regarded as the reciprocal of the concentration of quencher which reduces the fluorescence approximately 50%.



In Fig. 3 k_o is plotted against the fluidity (that is the reciprocal of the viscosity).

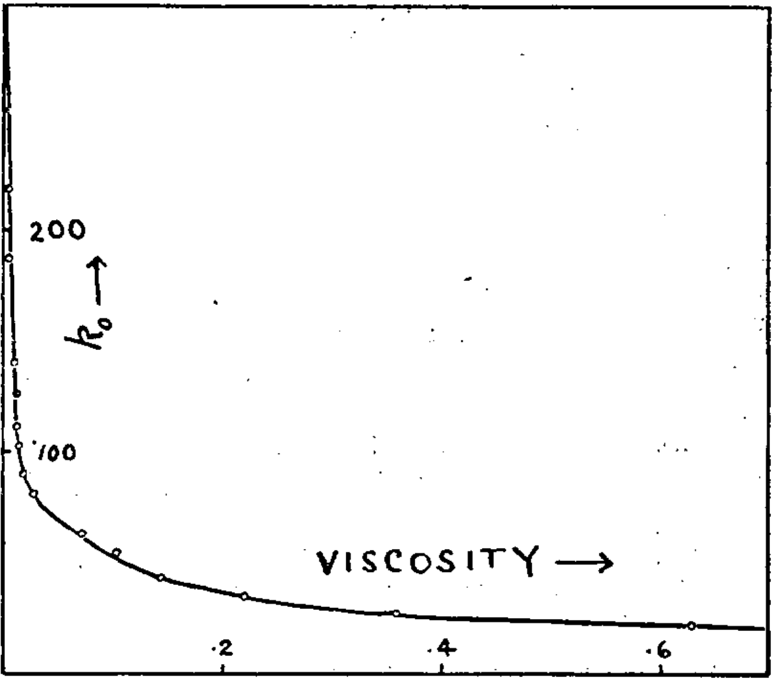


Quenching is seen to be much less than in the gas phase, and to vary with the fluidity. Although it falls off steeply at high viscosities it is not zero even in the solid state, being easily seen by eye when the fluorescence of anthracene dissolved in solid paraffin wax is quenched by sulphur dioxide in solid solution. Apart from the concomitant change of viscosity, the effect of temperature is small but definite.

Collisions in Solution. The Gas Analogy. (2)

The collision frequency between two gases A and B is little affected by the addition of a third gas C, since a change in direction due to a collision with a C molecule does not change the probability that an A molecule will strike a B molecule. The distribution of B molecules is on the average the same in every direction. The presence of C molecules in large concentration reduces the volume in which A and B move, and the consequent reduction in path between AB collisions increases their frequency by only a few times even when C is so concentrated that it can be regarded as a liquid in which A and B are dissolved.

If this theory is applied to fluorescence quenching, it predicts a value of k_o equal to that in the gas phase. It may be that the collision efficiency is somewhat different from the value 1/2 to 1/7 found in the gas phase, and allowance must also be made for the shorter average life of excited molecules in solution. When this is done, a value of k_o, not less than 300 and independent of viscosity is predicted. Fig. 4 shows the quenching constant to be approaching some such value at low viscosities, but at the viscosity of any common solvent, the theory is clearly inadequate.



The Solid Analogy

There is very little space in a liquid which is not occupied by the known volume of the molecules. To get them in they must be efficiently packed. It is of interest to examine the consequences of regarding a liquid as a collection of closely-packed spheres. The assumption of spherical shape is not so unreal as it first appears, because molecules in a liquid rotate rapidly and in consequence they occupy an effectively spherical volume. Molecules in such a structure are supposed to move about either by occupying holes which by chance appear beside them, or, as seems more likely, by changing places with their neighbours. This process involves less congestion than does the movement of a single molecule independently of its neighbours. Collisions between A and Q molecules in a solvent S will occur in sets, "encounters" (1, 9,10, 12, 19, 21) being frequently repeated while any two A and Q molecules are neighbours in the structure and being separated by longer periods when A and Q molecules wander about surrounded by only S molecules.

This process has been illustrated in two dimensions by a mechanical model due to Rabinowitch and Wood (20). Balls are added to a shaking tray. At first the collisions between any two balls are single. As the area of the tray becomes more and more covered with balls it is found that the collisions occur in sets. The number in each set is small at first but rises very rapidly when about two-thirds of the tray is covered with balls.

The distance d between sites in a hexagonal lattice is $2^{1/6} V^{1/3} N^{-1/3}$ where V is the volume of one gram mol of solvent, and N is the Avogadro number.

When neighbours change places they move this distance. If they change places every t seconds on the average, it follows from the work of Einstein on diffusion that

$$D = d^2/6t$$

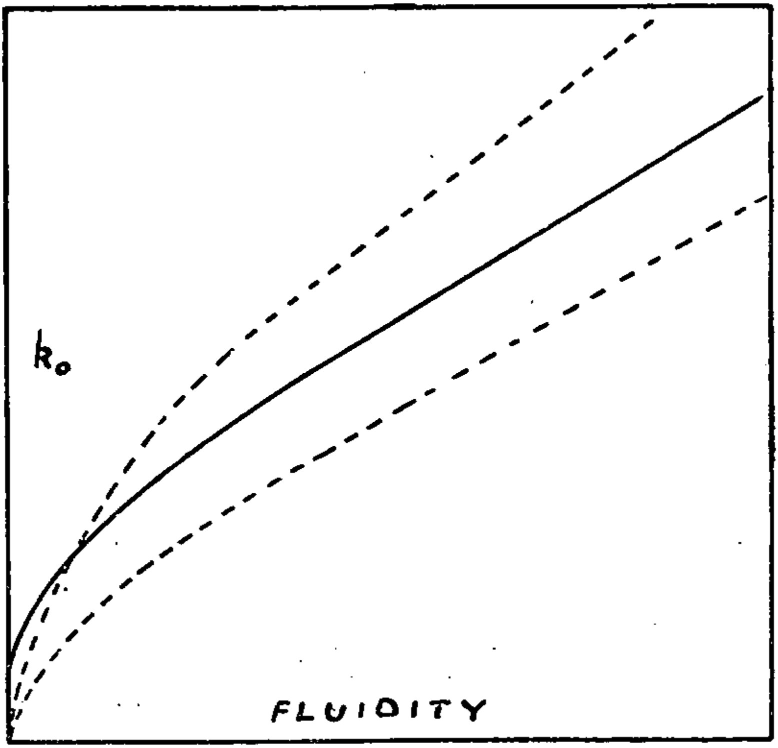
D, the diffusion coefficient of a dissolved solute, is measurable by observing the blurring of a boundary between solution and solvent. In this way we can calculate t.

From d and t the frequency of sets can be deduced. Each A molecule enters $1/t_A$ new neighbourhoods a second. The probability that a neighbourhood contains a Q molecule is approximately $12\ n_Q/n_S$, assuming there to be 12 neighbours for each molecule as a hexagonal close packed lattice requires. n_Q and n_S are the numbers of Q and S molecules per cc. Each A molecule thus undergoes $12 n_Q/n_S t_A$ new encounters per second. This is an over-estimate. When A and Q are neighbours, 5 out of the 12 possible jumps an A molecule can make do not separate it from Q and so are not available for the formation of new encounters. Correcting for this, and counting in the encounters undergone by molecules, the number of encounters per cc. per second is:—

$$\frac{7n_A n_Q}{n_S}\left(1/t_A + 1/t_Q\right) = 42\,\frac{n_A n_Q}{d^2 n_S}\left(D_A + D_Q\right)$$

In this approximate theory, account has not been taken of any nett forces between A and Q molecules, nor has proper consideration been given to size and differences between A, Q and S molecules. It represents an ideal case to which experiment conforms more closely than might have been expected.

In applying this theory to fluorescence quenching, it is clear that if quenching occurs on nearly every collision, it will also occur early in every encounter, or set of collisions between excited molecules and quencher molecules. The rest of the set of collisions will be wasted. Thus the encounter frequency replaces the collision frequency in the expression for the quenching constant k_Q, and the result is:



$$K_Q = \frac{42}{\sqrt{2}} d \, (D_A + D_Q) \times N/10^3$$

If $k_o = k_Q/k_f$, it may be calculated, and in Fig. 5 it is compared with the experimental value. The wide limits given for the calculated values are due to uncertainties in the diffusion coefficients, and in k_f, the latter being the more serious.

The main discrepancy with experiment lies at low fluidities. The encounter frequency in solids is too small to account for the observed quenching in paraffin wax. No new ideas are needed to explain this. By an oversight those molecules of anthracene which are in an encounter at the moment of excitation and which are therefore immediately quenched without diffusing, were not considered. The fraction of anthracene molecules in encounters is not a kinetic quantity, but depends on the equilibrium—

$$A + Q \rightleftharpoons AQ$$

which is not expected to change with viscosity. Quenching on this account is present at all viscosities, but is the only quenching of importance at very low viscosities. When it is included in the scheme, there results the equation—

$$f_o/f = \left(1 + \frac{k_Q}{k_f}[Q] \right) \left(1 + K[Q] \right)$$

where K is the equilibrium constant [AQ]/[A] [Q].

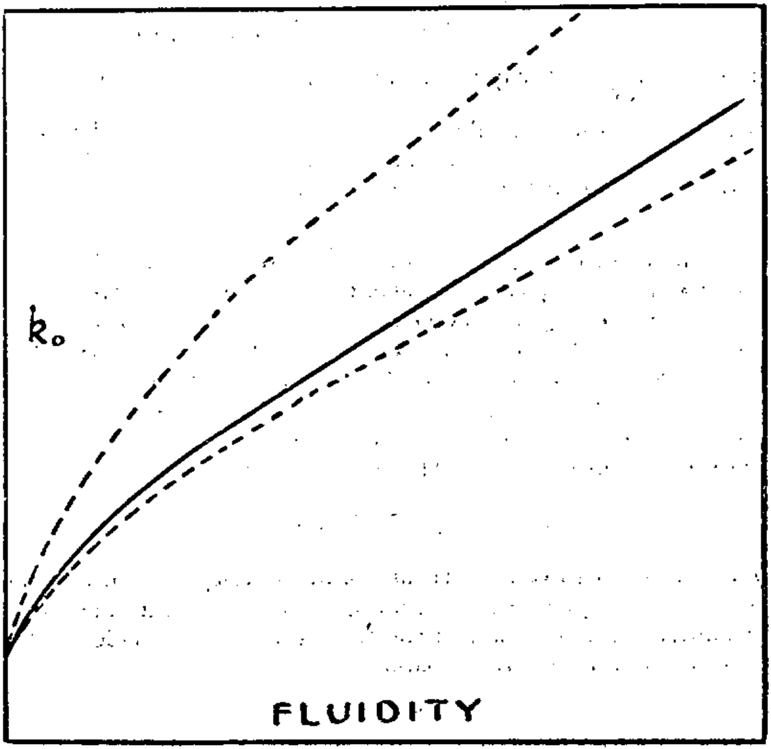
When k_Q/k_f is small in viscous solutions, this becomes—

$$f_o/f = 1 + K[Q]$$

and $k_o = K$.

When both k_Q/k_f and K are not negligible the plot of f_o/f against [Q] is curved, and from the curvature, both K and k_Q/k_f can be obtained. The value of K so obtained is found to be independent of viscosity and equal to the value in very viscous solutions as the theory requires.

Fig. 6 shows that when this correction is made, the agreement of theory with experiment is all that could be expected, in view of the uncertain lifetime of the excited molecules.



Weak Quenchers

The elucidation of any quenching process in solution is greatly simplified if it is known to occur on nearly every collision, as the foregoing examples show. At the other extreme are those quenching reactions that are so inefficient that diffusion is not a limiting factor. These may be called weak quenchers, and they are distinguished by the fact that quenching is independent of viscosity. In hexane as solvent, carbon tetrachloride and bromobenzene quench anthracene fluorescence by 50% if they are present at concentrations of about molar (4). Oxygen or sulphur dioxide at M/200 would have the same effect. The distribution of collisions is not important for weak quenchers because many more collisions are required for quenching than occur in any one set. The ratio of the quenching constants for the weak and strong quenchers above suggest that the number of colisions in an encounter is less than 100. This figure can also be found from the ratio of the collision frequency assumed to be the same as in the gas phase, and the encounter frequency. The result for ordinary fluid solvents is about ten. A careful study of quenching by bromoform which is intermediate in type may be expected to fix this figure more exactly.

Quenching by carbon tetrachloride (4) has a temperature coefficient from which an activation energy sufficient to account for the low efficiency can be calculated. This activation energy is very sensitive to the solvent, quenching being more efficient in polar solvents. Bromobenzene quenching on the other hand has no marked temperature co-efficient, and is not affected by the polarity of the solvents. By extending the data already available (4) on quenching by halogen compounds it may be possible to find out why bromocompounds are inefficient quenchers, although there is no direct evidence of an activation energy.

The effect of pressure on quenching will provide an interesting test of the mechanism of quenching that has been proposed. Pressure increases the difficulty of changing sites in the liquid structure and should reduce the quenching of strong quenchers. On the other hand pressure reduces the free volume in a liquid and so should increase the collision frequency. Since the latter quantity is the controlling factor for weak quenchers, their quenching ability should increase with pressure. Experiments are planned to test the point when facilities become available.

The quenching of dyes by ions in water as solvent has been the subject of a great deal of investigation (18). The efficiency of the quenching process is usually unknown, but the viscosity dependence often found shows it to be high in many cases. The complexities due to ionic interaction and solvation have hindered interpretation, but now that quenching due to the existence of encounters (which may in some cases be synonymous with "ion pairs" and "intermediate complexes") and to their formation by diffusion have been differentiated, the picture is becoming clearer. Quenching of dyes is often a reaction between ions, and the effect of ionic strength commonly observed in such cases is observed here (22). Only experiments at known or constant ionic strengths can be interpreted. Such dyes often form acid-base systems like indicators. Unless the solutions are buffered the amount of dye in each form is unknown, and may be affected by the addition of quencher, which is confusing to interpret.

Notwithstanding these difficulties, it is interesting to find the same phenomena occurring in so different a system. The same curvature of the graph of f_o/f against Q, and the same effect of viscosity when water-glycerol mixtures are used, appear in the quenching of dyes by iodide ions as are found in the anthracene-oxygen-paraffin system.

A great deal of experimental work is needed to tidy up our present knowledge of the quenching process. New aspects continually invite us to explore new fields. The importance of the subject in clarifying our views on the distribution and motion of molecules and ions in solution, on the mechanism of the fast steps of chemical reactions, and on the relations between concentration, activity and reaction rate, makes one chafe at the laborious nature of the fact-collecting process.

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NEW ZEALAND INSTITUTE OF CHEMISTRY–ROYAL INSTITUTE OF CHEMISTRY CONFERENCE

PROGRAMME

Monday—August 20th:

MORNING—

9.00—Registration.

9.30—Opening ceremony.

10.30—Official photograph.

10.45—Morning tea.

11.15-12.30—Lecture Session. Chairman, Dr. J. C. Andrews.
"Problems Connected with Food and Agriculture in New Zealand."
Speakers: Dr. M. M. Burns,
Dr. J. Melville,
Dr. C. P. McMeekan.

AFTERNOON—

2.00—Excursions to

(a) N.Z. Co-operative Dairy Co's factory at Waitoa (a large modern milk-powder factory handling up up to 100,000 gallons of milk daily. Interesting features are the bulk receiving, bulk packing, boiler equipment and Mojonnier apparatus).

(b) Rukuhia Soil Research Station, Ruakura Animal Research Station, and associated chemical laboratories in Hamilton East.

EVENING—

7.30—Annual General Meeting of the N.Z. Institute of Chemistry.

Tuesday—August 21st:

MORNING—Lecture Session.

A—INDUSTRIAL. Chairman, Dr. R. Gardner.

9.15-10.20—1. "The Heat Pump for the Evaporation of Milk." N. W. Vere Jones.

2. "A Simplified Process of Preparing Vitamin A Concentrates from Fish Liver Oils." L. Hartman.

10.45-12.30—3. "Recovery and Utilization of Lanoline from Wool-scouring Effluents." H. A. L. Morris.

4. "Sewage Purification": Review. R. Hicks.

5. "Chemistry of Pulp and Paper Manufacture." L. Neubauer.

B.—AGRICULTURAL. Chairman, Mr. R. E. R. Grimmett.

9.15-10.20—6. "Determination of Available Molybdenum of Soils." J. L. Grigg.

7. "Some Recent Work on Cobalt Deficiency in N.Z." E. D. Andrews and C. J. Alton.

10.45-12.30—8. "Nutrient Studies in the Early Development of Seedlings." R. M. Greenwood.

9. "The Nature, Occurrence and Transformation of Pectic Substances." R. P. Newbold.

10. "The Newer Plant Therapeutants." P. J. C. Clarke.

AFTERNOON—Lecture Session. Chairman, Mr. G. Lambert.

2.00-2.30—"Phosphatic Fertilizer Processes." Dr. A. Bridger.

2.30-3 p.m.—Instrumentation: Exhibit of Apparatus. W. G. Whittleston. Discussion.

4 p.m.—Annual General Meeting of Royal Institute of Chemistry, N.Z. Branch.

6.30—Buffet Dinner at Peachgrove Road Hall.

8 p.m.—Presidential Address: "The Chemist and Food."

Wednesday—August 22nd:

MORNING—Lecture Session.

A.—ACADEMIC. Chairman, Prof. F. P. Worley.

9.15-10.20—11. "Gas Adsorbtion by Solids" (with special reference to water vapour). H. D. Orchiston.

12. "Amino Acid Constituents of Urine." N. O. Bathurst.

10.45-12.30—13. "The Structure of Hiptagenic Acid." L. D. Calvert.

14. "Occurrence of Branched Chain Acids in Butter-fat." F. B. Shorland and R. P. Hansen.

15. "Asperuloside." L. H. Briggs.

B.—AGRICULTURAL. Chairman, Dr. J. K. Dixon.

9.15-10.20—16. "The Application of the Glucose Tolerance Test to Sheep."—N. D. Jamieson.

17. "Further Observations on the Carotene Metabolism of Ruminants." W. A. McGillivray.

10.45-12.30—18. "A Review of Recent Work on Milk Proteins." C. R. Barnicoat.

19. "Purity of Dairy Products." G. M. Moir.

20. "How Safe are Phenolic Anti-Oxidants in Foodstuffs?" G. M. Richardson.

AFTERNOON—Lecture Session. Chairman, Mr. C. G. W. Mason.

2.00-3.30—pH Symposium.

21. Historical and Theoretical Introduction. H. Bloom.

22. Determination of pH of Soils. E. B. Davies.

23. Automatic Control of pH in Industry. R. L. Ledger.

4 p.m.—Break-up ceremony.

BRANCHED-CHAIN FATTY ACID IN BEEF-FAT

R. P. Hansen and F. B. Shorland.

Following the isolation from butter-fat of branched-chain fatty acids, further investigations in the Fats Research Laboratory by Hansen and Shorland have revealed the presence of methyl side-chain acids in beef suet. Amongst the acids isolated is a C17 branched-chain saturated fatty acid also recently identified in butter-fat.

TRIBUTES

It is with sincere regret that we publish the following tributes to three late members of the Institute.

IVOR TING

The loss of Mr. Ivor Ting, who has been presumed to have been drowned on February 2nd, while returning to New Zealand on the "Rangitiki," has already been referred to in this journal, 1951, *15*, 58, and although he had been in the chemical profession for only five years, nevertheless, his extreme conscientiousness and charming personality merit appropriate record.

He received his secondary education at Wellington College, where he showed himself a very capable student. Proceeding to Victoria University College, he interested himself in French, but later switched over to chemistry and eventually took his M.A. in that subject. He served on the Executive Committee of the Students' Association and took a keen interest in hockey, in which he played a prominent part, being for several years the club captain, as well as a North Island representative.

He joined the staff of the Fats Research Laboratory in March, 1946, where he quickly established himself as a research worker and published papers on "Preliminary Investigations of the Determination of Fully Saturated Glycerides in New Zealand Butterfat," in the N.Z. Jour. Sci. and Tech., 1948, *29A*, 240-246, and (with J. S. George) "The Prevention of the Formation of Copper Oxide in a Copper Vacuum System," in the Journ. Sci. Inst., 1951, *28*, 123.

He took special leave as from September, 1949, to take up a French Government Bursary, and proceeded to Paris to work at the Institut de Recherches pour les Huiles et Oleagineux in Paris under the direction of M. Loury, on "L'interesterification des glycerides par catalyse a basse temperature." M. Loury has commented that Mr. Ting brought "all his perseverance and all his intellectual and experimental skill into his research." M. Loury, in addition, had not failed to note his pleasant disposition and good fellowship, in which connection M. Desclos, Director of the College Franco-Britannique also commented most favourably.

Mr. Ting also visited various laboratories in Great Britain, where he was invariably well received. Professor T. P. Hilditch, F.R.S., of Liverpool University, mentions that Mr. Ting had a long talk with him during his visit in October last, and impressed him with his knowledge and interest in the field of fats.

Something of the impression which Mr. Ting created during his visit overseas may be gleaned by quoting Dr. E. H. Callow, Head of the Meat Section of the Low Temperature Research Station. He states: "I remember so vividly the talks we had about work and the enthusiasm he showed for it. It is a bitter blow to think that so promising a young life has ended so suddenly."

Those of us in the Fats Research Laboratory who have worked with Mr. Ting will always remember his versatility, tact, and his wide understanding which enabled him to be equally at ease with chemical or administrative work. All the tasks that were allotted to him he performed cheerfully and with ability. —F.B.S.

B. C. ASTON, C.B.E., F.R.S.N.Z., F.R.I.C.

When, two years ago, the writer was invited to deliver a memorial address on "Bernard Cracroft Aston—First N.Z. Official Agricultural Chemist," to the Society of Animal Production, he did not anticipate so soon being asked to add to his tribute.

B. C. Aston, born in Kent, England, in 1871, died in Wellington on May 31st, 1951.

A full obituary will be published in the Transactions of the Royal Society of New Zealand, for to that body Aston gave a lifetime of service. Although he was not actively associated with the New Zealand Institute of Chemistry, he regarded it with friendly interest and encouraged the chemists working under him to join and play their full part in its meetings and organisation. As a fellow of the Royal Institute of Chemistry he was, of course, concerned indirectly with its birth and early development.

"B.C." was a man of marked personality. No one working with him could fail to be influenced by his zeal, tenacity and enthusiasm. As a friend he was engaging and lovable, albeit at times somewhat temperamental and unexpected in his reactions. No finer companion could be sought for week-end tramps in search of native plants, or for expeditions to remote areas of undeveloped country where problems of soil or nutrition were suspected.

As a pioneer agricultural chemist at the period when that subject was just emerging as a science, Aston held a unique position in this country. No single person now could or would attempt to cover the field as he did. Arising in large part out of his early efforts have grown many of the activities now engaging large staffs in organisations for chemical research or servicing of the agricultural industries of this country. His influence on the training of chemists now in leading positions has been marked.

Aston dearly loved the pumice country, and his long-cherished vision of it as a district of green and prosperous farms became, in large measure through his efforts, a reality during his later years. If any memorial is to be dedicated to him, I am certain nothing would please him better than that one of the natural "ignimbrite" monoliths that dot the Mamaku Plateau as residuals rising above the pumice showers should be selected for this purpose. If in addition a small area of native bush surrounding it were set aside as a plant and bird sanctuary, it would serve a worthy object dear to Aston, and become a place of rest and beauty in an area now scarred by the milling of timber. That was "Aston's Country," and long will his influence there continue. —R. E. R. GRIMMETT.

MISS EDA SWANBERG

It is with regret that we have to announce the death of one of our Associates, Miss Eda Swanberg, after a long illness. Miss Swanberg graduated B.Sc. from Auckland University College in 1935, and after a period of teaching joined the staff of the laboratory at the Waitemata Brewery, Otahuhu, in 1941, as Assistant Chemist, which position she retained until August of last year, when ill-health overtook her. Some weeks before her death, the Auckland Branch decided to send flowers to Miss Swanberg in hospital. They were personally conveyed by the President, Mr. Parr, and Mr. J. Ricketts, and much appreciated. Until the last fortnight, she was always interested in the affairs of the Institute and looked forward to receiving copies of the Journal, from which she derived a good deal of pleasure.

ITEMS FROM THE MINUTES OF COUNCIL MEETING, 11th MAY, 1951

Present: Mr. P. R. Parr, President (Chairman), F. H. G. Johnstone, Canterbury Delegate; A. P. Oliver, Wellington Delegate and Assistant Secretary; B. E. Jackson, Proxy for Auckland; E. P. White, Proxy for Waikato; I. C. McDowall, Proxy for Manawatu; L. H. James, Proxy for Otago; W. G. Hughson, Hon. General Secretary; H. K. Palmer, Registrar.

Laboratory Assistant's Certificates: Resolved that Council approve the issue of certificates to the following:—

Lionel Stanton Bush, Auckland.
Joan Philippa Cook, Palmerston North.
Judith Eleri Fisher, Palmerston North.

James William Dickinson, Wellington.
Vigette Victoria Russell, Auckland.

Journal: Council decide to accept with thanks the generous offer of the Auckland Institute and Museum to house Journals received on exchange by this Institute. The Journals will remain the property of the N.Z.I.C. and may be borrowed by members on application to the Librarian. The publications will be catalogued in the serial list of publications in New Zealand Libraries. (A list of these Journals is published elsewhere in this issue.)

Resolved that Volumes XII to XIV constitute the third binding of the Journal and that two sets be bound, one for the Editor and one for the Hon. General Secretary.

Resolved also that a complete set 1936-1950 be bound in three bindings and lodged with the Librarian of the Auckland Institute and Museum.

Professional Status Committee: Resolved that the Professional Status Committee be asked to compare the standards for admission to various grades in all the Empire Chemical Institutes.

Institute Prizes: Resolved that the Imperial Chemical Industries of Australia and New Zealand be thanked for their offer of a medal to accompany the prize and that the design submitted be approved in principle. The President and Vice-President, with power to co-opt, were appointed examiners for the I.C.I. prize for 1951.

Resolved that, in accordance with the regulations, the President and Vice-President, with power to appoint one or more assessors, be appointed examiners for the Morcom Green and Edwards Prize, 1951.

Addressograph: Resolved that Branch Secretaries be instructed to advise the Registrar of all changes of address not later than the first day of the month preceding the month of issue of each number of the Journal.

Life Membership: Resolved that the Registrar be asked to draw up a draft regulation for submission to the August meeting of Council on the same annuity basis as already submitted but terminating at the age of 65 instead of 70; i.e., members over 50 years of age may pay a life subscription on the basis of an annuity for the number of years' difference between 65 and the member's age.

Accounts totalling £100/19/4 were passed for payment.

Associates: The following were elected:—
L. W. Bruce, Fats Research Laboratory, Wellington.
G. S. Walter, Korma Mills, Auckland.
R. B. Nevin, Dental School, University of Otago.
A. J. D. Robb, Dominion Industries, Ltd., Christchurch.
D. Hall, Auckland University College.
Marianne Beilschowsky, Ph.D. (Freiberg), Medical School, Dunedin.
I. W. Knaggs, Auckland University College.
D. B. Adams, Proven Paint Products Ltd., Dunedin.
R. S. Malthus, Nutrition Research Dept., Medical School, Dunedin.

Resignation of P. A. Ongley was accepted with regret.

Waikato Branch: Resolved that the boundary between the Auckland and Waikato Branches run East through Ohinewai so as to include Thames in the Auckland Branch, and Te Aroha, Paeroa and Waihi in the Waikato Branch.

"SPECTOGRAPHIC ANALYSIS"

By Mr. J. E. Allen, Rukuhia Soil Research Station, Hamilton.
Summary of Address delivered to the Waikato Branch on June 5th.

"Mr. Allen dealt first with the theoretical aspect, outlining the origin of spectral lines as a movement of electrons from an active to the normal state. This was explained in terms of energy levels and quantum numbers.

The production of spectral lines by the flame, the D.C. arc, the high-voltage spark, and the pulsating arc, was outlined. Methods of introducing powders and solutions into the arc were discussed.

Mr. Allen then turned to the analytical use of spectography, particularly as applied to agricultural problems, and mentioned particularly his own experiences in analysis of soil and plant materials for major and trace elements. The use of spectrographic analysis for qualitative, semi-qualitative, and quantitative analysis was assessed. Particular consideration was given to the comparison of healthy and unhealthy plants using the D.C. arc, and the quantitative estimation of exchangeable bases in soil and of the major cations in plant ash, using flame excitation. It was considered that the pulsating arc technique, when available, would allow a considerable advance in the use of this type of analysis."

BOOK REVIEWS

SAFETY IN THE CHEMICAL LABORATORY. By H. A. J. Pieters, Head of the Chemical Works Safety Department of the Netherlands State Mines, with the collaboration of J. W. Creyghton, Head of the Medical Department of the Joint Netherlands Coal Mines. 258 pages. 1951: Butterworths Scientific Publications, London. Our copy from Butterworth & Co. (Australasia) Ltd., Wellington. 21/-. This book started as a booklet issued by Dr. Pieters to the staff of his laboratory at the Netherlands State Coal Mines in 1930. In 1942, and again in 1947, it was rewritten and enlarged in collaboration with Dr. Creyghton, and it is now claimed that the text has been brought up to date for the first English edition. Chapter headings are:—General safety considerations; Precautions with glassware, platinum, gas and electricity; Fire hazards; Explosion hazards; Cylinders containing compressed gases; Physiological effects of chemical substances; Handling toxic and injurious substances in the laboratory; Toxic gases and dusts; Protective devices and first aid; Analytical procedures relating to toxic and hazardous substances (this covers about half the volume), and finally there are a number of tables of information on toxic substances, their effects and detection, inflammable substances, gas masks, codes for compressed gas cylinders, first aid, etc. It is the first full-sized book on the subject and it can be said without enquivocation that it should be in every laboratory and the first part at least should be read by every member of the staff. There will be less need for the analytical methods to be generally known, and they could have been issued separately to make a cheaper safety manual more readily available. The book covers all the recognised and some unrecognised laboratory hazards. In writing such a book the authors have obviously had to choose between a discursive readable style and imperative mood where directions are easily followed in an emergency: they have wisely chosen the latter, but the book is still readable. It may be pointed out that the notes on analytical methods and certain preventive techniques are by no means exhaustive, and in the section on ether peroxides, the simple test of shaking with potassium iodide solution, widely used in the United States, is not mentioned, and there are more usual methods of preserving ether than those outlined. The reagents mentioned by Williams should be used in .05% concentration, and not 5%, as stated. In closing, it may be mentioned that the book sells in England for 15/-, and it is pertinent to ask why there should be a 40% mark-up in this country.

"CHYMIA," ANNUAL STUDIES IN THE HISTORY OF CHEMISTRY. Vol. 3. Henry M. Leicester, Editor-in-Chief. 251 pages. 1950. Philadelphia: University of Pennsylvania Press. $4.50. The current volume of this work contains a number of articles of interest to all chemists. There is an introductory study of Tenney L. Davis, first Editor of "Chymia"; an illustrated description of Lavoisier's equipment, still preserved in Paris; and biographical articles on Henri Sainte-Claire Deville, Bunsen, Mohr, Boyle, and his French contemporary Bayle. Bayle was not a scientist, but merits comparison with Boyle because he was probably the most famous seeker after truth and toleration in an intolerant age. Karl Friedrich Mohr commemorated in Mohr's salt (ferrous ammonium sulphate) ,the pinch clamp for the burette, and in Mohr's burette is the "father of Volumetric analysis" and author of the first book on the subject. This volume was quickly accepted in Germany, where it went through seven editions, but Mohr could not interest any English publisher in a translation. Mohr also introduced the cork-borer and the present method of cutting and folding filter-papers. Sainte-Claire Deville has an amazing list of achievements, including the industrial production of aluminium when it was only known as a few minute crystals in the laboratory. This volume will appeal to all those who have more than a purely lucrative interest in their profession.

QUANTITATIVE INORGANIC ANALYSIS. By I. M. Kolthoff and E. E. Sandell, University of Minnesota. Revised Edition. 794 pages. 1950: Macmillan & Co., Ltd., London; 30/-. This is an English reprint of a well-known and excellent text-book covering both the theoretical and practical aspects of the subject in a way that is useful both for the student and the practising analyst. It is, however, disappointing to find that it is not a new edition, but the second (1943) American edition which has been faithfully copied, even to the American spellings, such as "Sulfide," "color," and "buret," which is rather rubbing it in.

Volume 6 of the *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY* (Interscience, New York, $20.00), which has just been issued, contains a very comprehensive article running to 127 pages on Fatty Acids, and 76 pages on Fertilizers, which is very topical because it deals with the methods of treating rock phosphate without using sulphuric acid. Other long articles are on Explosives (91 pages), Extraction (49 pages), Fats and fatty oils (32 pages), Fuels, including synthetic liquid fuels (90 pages), Fluorine and its compounds (115 pages), Filtration (24 pages), and Food and food processing (33 pages). The section on Fermentation (58 pages) includes details of the manufacture of alcohol, acetic and citric acids, butanol, etc., and a discussion on pumps is included under Fluid mechanics (41 pages). Each new volume of this work enables us to see more clearly the pattern of the whole. There is no doubt that it contains some very fine articles even if they are almost exclusively concerned with American practice. Judgment must still be reserved as to the completeness of the coverage, but they certainly make a very handsome set of volumes for any chemist's library.

LES METHODES D'ANALYSE DES REACTIONS EN SOLUTION. By G. Charlot, Professor at the Ecole Superieure de Physique et Chimie industrielles, and R. Gauguin, also of the Ecole Superieure de Physique et Chimie industrielles. Masson et Cie., Paris (1951). 328 pages. Price 2200 francs. This book is rather different in its method of attack—theory is cut down to the very minimum, being mostly an abridged mathematical derivation of the formulae required. The bulk of the book is used to discuss examples taken from published papers (mostly very recent). The examples are very well chosen and complete references are given to the originals, as well as references to other papers on the same subject. Topics dealt with include chapters on fundamental types of reactions, oxidants and reductants, complexes, acids and bases, change of concentration during a reaction, different types of titration curves, the use of instrumental methods, precipitation reactions, different solvents, effect of gas phase, indicators, reaction rate, irreversible reactions and activity in solution. The book includes an excellent appendix on ionization and hydrolysis constants of the various chemical compounds, listed systematically. The quality of paper and binding are disappointing and the lack of an index is a disadvantage, but in general the book is a very worthwhile addition to a chemical library. H.B.

PHYSICS IN CHEMICAL INDUSTRY. By R. C. L. Bosworth. Macmillan & Co. Ltd. (London), 1950; 928 pages. Price £3/10/-. If the aim of this book were merely to assist the chemist in industry in the understanding of physical problems, the reviewer would be forced to the conclusion that the book had failed in its purpose. The author, however, points out that this is only one of the objects and that others are (1) to provide basic background knowledge to students who will later take up positions in chemical industry, (2) "to indicate to those in academic positions some of the more pressing of the fundamental problems of industry," and (3) to encourage two-way exchange of information between academic chemistry and industry. In these three objects the book ought to succeed. It does indeed give an excellent theoretical background of certin physical topics, written in an interesting manner. The practical side, including the discussion of scientific instruments, is, however, weak and is better covered in books of Industrial Chemistry. The book is in four parts: I, Mathematical introduction, including mechanical mathematics and statistical methods; II, the properties of matter, including the atomic theory, thermodynamics, the properties of gases, solids and liquids, rheology and adsorption; III, movement of matter, including flow of heat, electricity, liquids, etc.; and IV, scientific instruments, including the measurements of length, area, volume, mass, pressure, viscosity, elasticity; also a discussion of optical, electrical and temperature measuring instruments. The book is very well indexed and documented, the type is clear, the symbols used systematic. H.B.

A TEXTBOOK OF PHYSICAL CHEMISTRY, 2nd Edition. By J. Newton Friend. Charles Griffin & Co. Ltd., London (1948), 566 pages. An abridgement of the first edition, which appeared as two volumes—Volume I in 1932 and Volume II in 1935. The more elementary portions of the first edition have been omitted and new matter included, but the book can best be described as an elementary one which will be mainly of interest to second and final year Chemistry degree students. The printing is excellent and the book fully indexed. H.B.

NEWS AND NOTES

Dr. J. Melville, Fellow, has been appointed Director, Grasslands Division, Department of Scientific and Industrial Research, succeeding Mr. Bruce Levy. He will retain his position as Director, Plant Chemistry Laboratory, Palmerston North, although this laboratory will in future cease to be known as such, having been combined as an integral part of the Grasslands Division.

Miss A. C. Gladding, Associate, who resigned from the laboratory of Abel's Ltd., Newmarket, in February, is now on the staff of the laboratory of Messrs. J. Lyons and Co., Hammersmith, London, where a staff of 200 is employed under the direction of Dr. L. H. Lampitt.

Chemists from New Zealand attending the Brisbane Congress of the Australasian Association for the Advancement of Science in June were Professor L. H. Briggs, Professor P. A. S. Smith, and Dr. C. R. Barnicoat. Professor Briggs was President of Section B (Chemistry), and the subject of his presidential address was "Plant Products of Australasia." Professor Briggs while in Sydney gave an Exposition Lecture to the New South Wales Branch of the Royal Australian Chemical Institute on "Potentialities of Australian Plant Products." Professor Smith, of the University of Michigan, who holds a Fulbright Fellowship at Auckland University College, gave a paper on "Julolidine," and Dr. Barnicoat read a paper for Dr. Shorland.

Addresses at recent Auckland Branch meetings have included the following:—

Mr. F. J. Lowe, of Candy Filters (N.Z.) Ltd., on "New Aspects of Water Treatment." Of particular interest to members was Mr. Lowe's demonstration of the new method of Biedermann and Schwarzenbach for determining total and calcium hardness in water, using disodium dihydrogen ethylene diamine tetraacetate as a sequestering agent and Eriochrome Black T and ammonium purpurate as indicators.

Mr. W. Agnew, on "Phosphate Fertilizer Production and the Sulphur Shortage." Mr. Agnew described several processes of producing phosphatic fertilizer not using sulphur. In a lively discussion which followed it was pointed out that these processes required cheap coal or electric power, both of which were short in New Zealand.

Professor P. A. S. Smith, on "Some Aspects of Wartime Research on Penicillin." This entertaining address gave members an insight into the difficulties of co-ordinatiug research by widely separated teams of workers under the secrecy and haste of wartime conditions.

On the eve of his departure from New Zealand, Dr. S. Ma addressed the Auckland Branch on "Microchemical Techniques."

The Royal Australian Chemical Institute has changed its editorial policy and now issues two journals, the monthly "Proceedings" and the quarterly "Reviews of Pure and Applied Chemistry." The first issue of the latter has now been received and contains four articles as follows: "The Mechanism of Chemical Change," by F. G. Soper, Dunedin; "The Impact of Chemistry in Biology and Medicine," by A. R. Todd, Cambridge; "Chemical Engineering Problems in the Generation of Nuclear Power," by J. P. Baxter, Sydney; and "The Change of Surface and Interfacial Tensions with Time," by K. L. Sutherland, Melbourne. We congratulate our sister Institute on a useful addition to the chemical literature.

At the June 5th meeting of the Waikato Branch, very feeling reference was made to the late Mr. B. C. Aston, under whom many of the members had worked in the chemical laboratory of the Department of Agriculture when it was in Sydney Street, Wellington. The following motion was passed: "That the Waikato Branch of the New Zealand Institute of Chemistry records its deep sense of loss in the death of Mr. B. C. Aston, C.B.E., F.R.S.N.Z., F.R.I.C., and records its sincere sympathy with his relatives."

No meeting of the Canterbury Branch was held in May as the Royal Society Seventh Science Congress was being held in Christchurch. The Section "B" Chemical Sciences programme contained the following papers:

1. Biochemistry:

   "Chemistry and the Farmer," Dr. J. Melville (Chairman's address).

   "Fatty Acid Oxidation," Dr. R. L. Blakley.

   "The Biosynthesis and Metabolism of Pyrimidine Compounds," Dr. J. McT. Ploeser.

2. Chemical Physics:

   "The Nature of Non-electrolyte Solution," Dr. H. N. Parton.

   "Impurity Activated Phosphors," Mr. F. A. Johnson.

3. Bioassay:

   "Statistical Methods of Biological Assay," Mr. H. R. Thompson.

   "Assay Methods for Antibiotics," Dr. T. R. Vernon.

   "The Microbiological Assay of Amino Acids and Vitamins," Mr. N. O. Bathurst.

   "The Bioassay of Hormones," Mrs. E. G. Bassett.

At the June meeting of the Canterbury Branch the President, Mr. P. R. Parr, spoke on the subject, "The By-products of the Meat Freezing Industry." Mr. Parr prefaced his address with some observations on his recent trip to Australia.

The congratulations of all who know him will go to Mr. S. R. Siemon, Senior Lecturer in Applied Chemistry at Canterbury College, who has been awarded a Fellowship of the Nuffield Foundation which will enable him to carry out advanced studies and research in Britain during the 1951-52 academic year. Mr. Siemon will be accompanied by his wife and is planning to leave New Zealand at the beginning of September and return for the first session in 1953. In England Mr. Siemon intends to investigate the technology of powdered solids under Professor T. R. C. Fox at the Department of Chemical Engineering, Cambridge.

Mr. A. F. R. Adams, Soil Chemist at Lincoln College, expects to leave this year to spend six weeks in Australia studying spectrographic methods particularly as applied to soils and plants. He expects to spend the greater part of his time at Waite Agricultural Research Institute, Adelaide.

Dr. R. H. Locker has been awarded a National Research Fellowship. These Fellowships are offered annually on the recommendation of the Council for Scientific and Industrial Research to enable applicants with postgraduate experience to study in New Zealand or overseas.

Mr. L. C. Baker, of W. Gregg and Co., Ltd., Dunedin, has left for United States to attend the foreign student summer project at the Massachusetts Institute of Technology from June to September of this year.

He will go on to Britain and expects to return shortly before Christmas.

The vacancy in the Otago Branch Committee created by the departure of Mr. R. A. Green has been filled by Mr. D. H. McLean, of Ross and Glendining Ltd.

Mr. A. D. Campbell has been appointed lecturer in charge of the Micro-chemical Laboratory at Otago University, vice Dr. T. S. Ma, who has gone to Purdue University, Indiana. Mr. Campbell has been forced by pressure of work to relinquish the position of Secretary of the Examinations Committee, where he put in a lot of work necessitated by the change-over to Dunedin, but he remains on the Committee. The new Secretary is Mr. C. R. Edmond of Dr. Gardner's laboratory.

We congratulate Dr. F. B. Shorland (once again!) on his election to the Fellowship of the Royal Society of New Zealand, this being the only distinction necessary to make him co-equal with Prof. Briggs. Both of these scientists, rather than going overseas to the larger and better equipped establishments, have elected to remain in New Zealand and have founded schools of research which are attracting world-wide attention. The discovery of branched-chain fatty acids in butterfat (Hansen and Shorland, this Journal, 1950, *14*, 142) is of a significance which has been considerably appreciated overseas.

Mr. J. K. Heyes, of the Fats Research Laboratory, Wellington, is going to study plant chemistry under Prof. Todd, Cambridge, on a Shirtcliffe Scholarship.

Mr. E. L. Richards, of the Dominion Laboratory, leaves shortly for England as a member of the Defence Science Corps.

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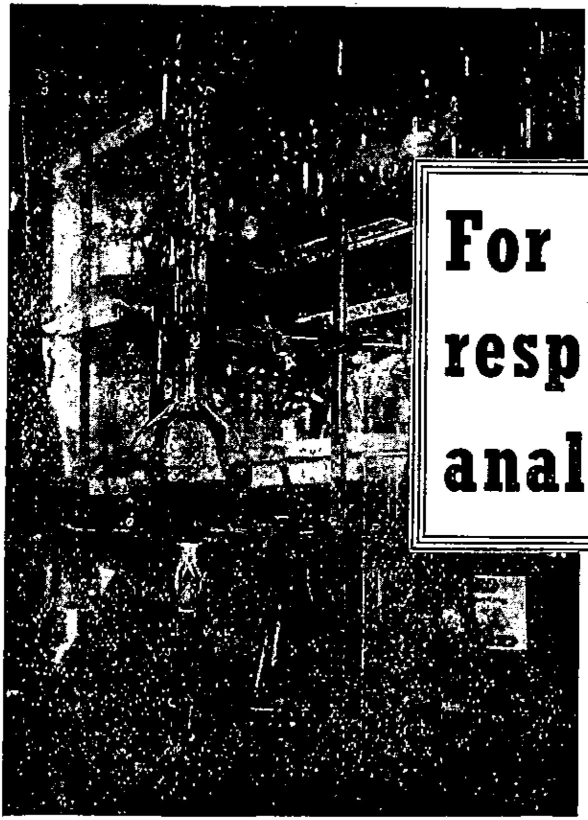

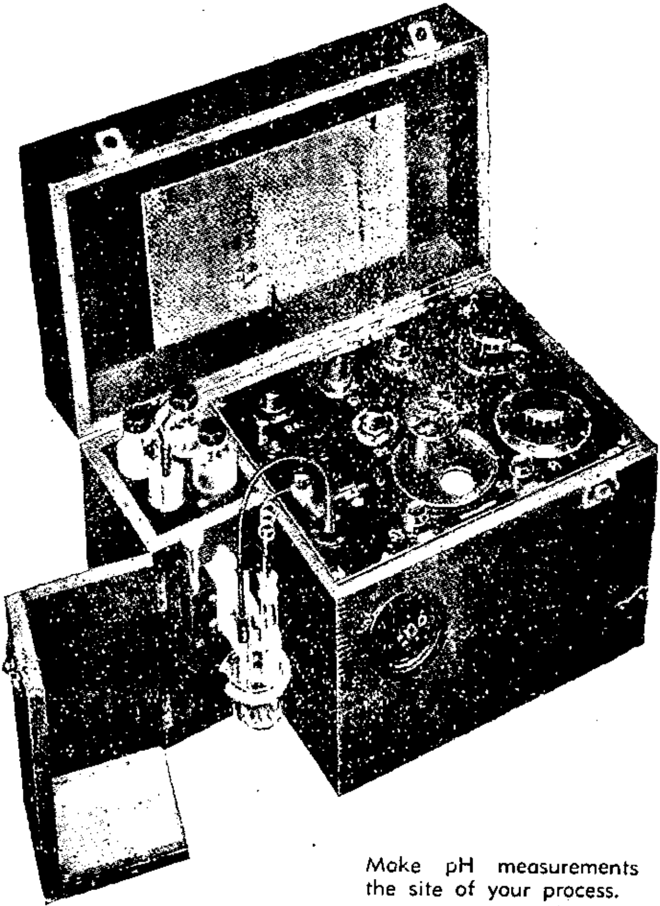

Inert gases

Over 99% of the air we breathe is a mixture of oxygen and nitrogen. The remaining 1% contains, in addition to the carbon dioxide which we breathe out, no less than five other gases. Though these were not discovered until recently, as long ago as 1785 the English chemist Henry Cavendish noticed that a fraction of the air differed from both oxygen and nitrogen. This observation was confirmed more than a century later when an English physicist, Lord Rayleigh, discovered that nitrogen extracted from the air was heavier than nitrogen obtained from ammonia. Working together in 1894 Lord Rayleigh and Sir William Ramsay found that the difference was due to a gas which later they named argon—a Greek word meaning lazy—because of its reluctance to combine with any other chemical substance. In the following year Ramsay discovered another gas by heating the mineral cleveite. He proved that this was helium, an element which in 1868 Lockyer had observed in the sun. Shortly after Ramsay's discovery it was confirmed that helium existed in the earth's atmosphere also. Finally in 1898 Ramsay and his colleague Travers fractionating liquid air discovered three other gases which they named krypton, xenon and neon. Called the "inert" gases because of their characteristic chemical laziness, these elements have many practical uses today.

Helium is used in airships and in deep diving apparatus. Argon, a filling for incandescent electric bulbs, is now used in certain welding processes. Krypton and xenon are used in photographic flash lamps, and neon, together with certain of the other inert gases, in the brilliant electric signs that bear its name.

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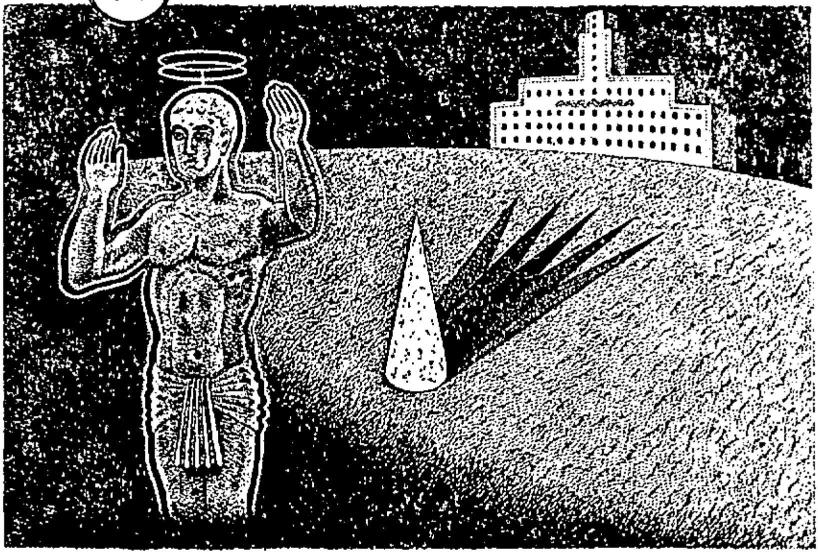

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