chemistry in new zealand

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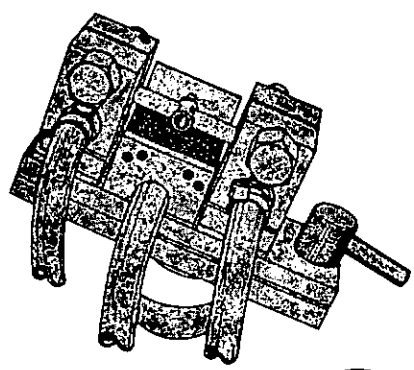

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NZIC AUCKLAND BRANCH SALARY SURVEY MARCH 1976

This salary survey was designed to cover the salaries of industrial chemists in the Auckland region and to compare these with groups having a structured salary scale. Members of the NZIC Auckland Branch employed by industry were asked to complete a questionnaire giving age, salary as at March 1st 1976, academic qualifications, length of time in the practice of chemistry, job description, estimated degree of responsibility and to include an assessment in terms of salary of additional benefits, such as use of a company car, etc (taking taxation into account).

The total response was 61 from an estimated 120 industrial members. For nearly all members experience correlated with age, and the degree of responsibility replies were all high or medium. These two factors have been omitted from the results. One reply was omitted from the survey in that it was uniquely atypical and could have been assigned to an individual, its omission has not altered the given figures.

Table I gives total income (salary plus additional benefits) as a function of age, and also lists the non-salary benefits separately. These are compared with salaries for chemists employed by DSIR. It should be noted that the Government figures are not restricted to NZIC members, nor to the Auckland region and have been taken from official government sources with the permission and willing co-operation of The State Services Commission.

Table Ia gives standard deviations for the three larger sample groups in Table I. A simple interpretation of standard deviation is that approximately 2/3 of the sample lie within one standard deviation of the mean. Applying Students t test shows that differences in mean total incomes between Government and Industry are statistically different at the 95% level for the 26-30 and 46-50 age groups, but not for 31-35.

In Table 2, academic qualifications have been split, each into two groups of approximately equal size. BSc includes all bachelor degrees and NZCS, MSc/PhD all higher degrees including BSc(Hons). For job description, Other includes mainly R+D and Quality Control. Sample sizes were too small for statistics to be applied meaningfully, and the mean figures are presented without any attempt at interpretation. Some small samples have been omitted to preserve anonymity.

The normal criticisms of all surveys can (and doubtless will) be levelled at this one but we hope the results will be of some use and interest.

A.C. Herd, K.R. Laing, J.R. Yolland
for NZIC AUCKLAND BRANCH

TABLE I — INCOME VERSUS AGE, INDUSTRY AND GOVERNMENT.

AGE GROUP	INDUSTRY SAMPLE SIZE	INDUSTRY TOTAL INCOME/$	INDUSTRY NON SALARY/$	GOVERNMENT SAMPLE SIZE	GOVERNMENT TOTAL INCOME/$
21-25	2	7,433	0	15	7,325
26-30	14	9,488 [1]	763	38	8,235 [4]
31-35	15	10,497 [2]	1,342	27	10,453 [5]
36-40	4	13,115	1,090	8	11,831
41-45	6	15,175	1,250	7	11,818
46-50	11	14,975 [3]	1,592	17	13,408 [6]
51-55	5	15,869	1,420	13	13,980
56-60	0	-	-	4	14,982
61-65	3	16,102	1,933	2	11,682

TABLE Ia — STANDARD DEVIATIONS

Number	Standard D.	Number	Standard D.
1	1,876	4	1,080
2	2,840	5	2,720
3.	3,280	6	3,300

TABLE 2 — QUALIFICATIONS & JOB DESCRIPTION - TOTAL INCOME

Age Group	Industry BSC	Industry MSc/PhD	Government BSc	Government MSc/PhD	Industry Management	Industry OTHER
21-25	-	-	7,606	6,722	-	-
26-30	8,561	10,415	7,407	8,348	10,521	9,074
31-35	11,183	10,962	8,075	10,383	12,706	9,316
36-40	8,160	14,766	9,884	12,198	15,150	11,080
41-45	14,030	20,900	10,260	12,755	16,100	13,325
46-50	15,544	13,638	11,767	14,136	17,700	12,250
51-55	10,892	19,188	11,780	14,473	19,188	10,892
56-60	-	-	11,869	15,652	-	-

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Cover: Auckland Branch Diamond Jubilee. Mr. A. Kennett, Professor P. de la Mare and Mr. L. Spackman with commemorative plaque.

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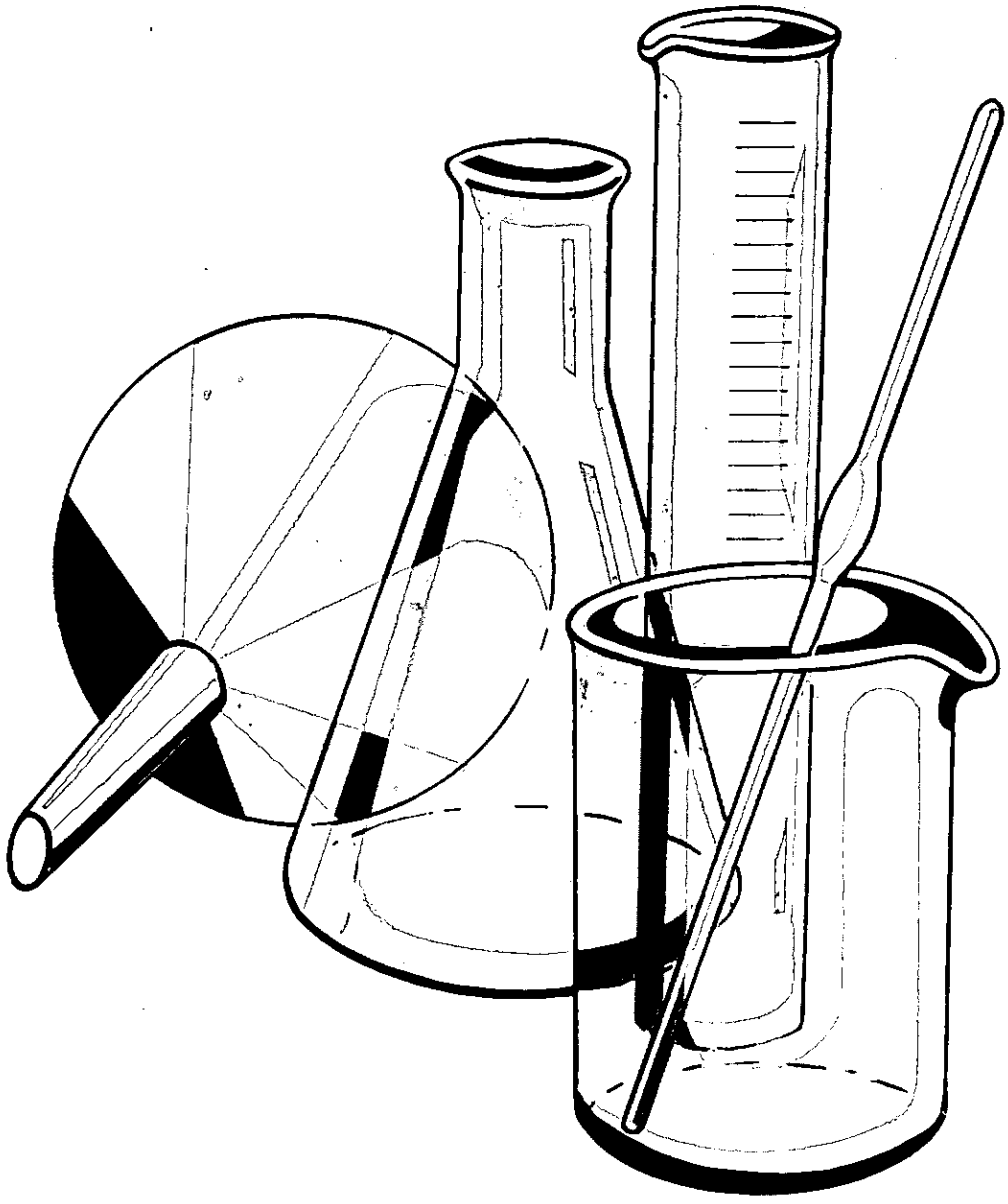

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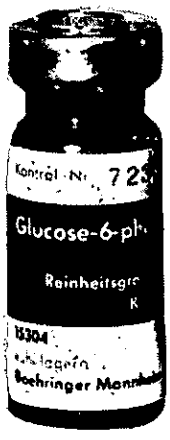
analytical bio chemistry

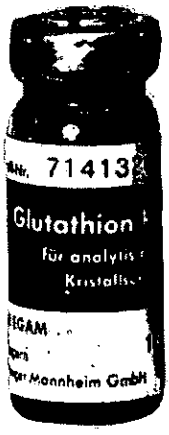


For the solution of a variety of considerably complex questions, many analytical methods are employed by the biochemist. An almost classical method of analytical biochemistry came into existence from biochemistry itself, viz. the enzymatic analysis.

Enzymatic analysis means determination of metabolite concentration with the aid of enzymes, measurement of activities and study of the characteristics of enzymes in vivo and in vitro, and analysis of the control and regulatory functions within the cell and in organ metabolism.

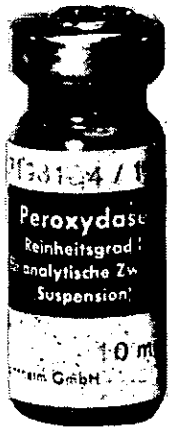
molecular biology

The research fields of protein and nucleic acid biosynthesis are nowadays lumped together – unfortunately – under the term "molecular biology." In our program we offer enzymes, substrates, templates, primer, inhibitors and auxiliary reagents, all of which are indispensable for the study of molecular action mechanisms.



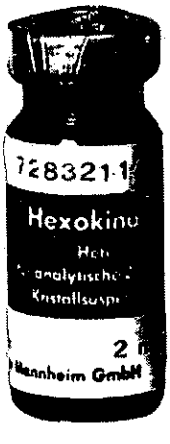
enzymology

Enzymologic research revolutionizes biology not only because of the mushrooming number of newly-discovered enzymes. To the extent to which the biologist advances into cellular regions, he will become an enzymologist; to the extent to which the enzymologist interprets biological functions of cell components enzymatically, he will become a biologist. Thus, enzymology has become one of the main pillars of all biological disciplines.



food analysis

The first knowledge of biochemical processes, of the role enzymes play in them and the first experiences with enzymatic analytical methods were gained with foods. Analyses with the aid of enzymes have many advantages in food analysis: enzymatic methods are fast, safe and reproducible. The measurement of enzyme activities as a criterion of the condition of foods is supplemented more and more by enzymatic analysis of the components of foods.



clinical chemistry

This program is noted for its search for ever more specific and predictable test methods for medical research and routine diagnosis while adhering to the rising requirements for precision and accuracy of laboratory data. On the other hand, such a program must also take into consideration the requirements for simplification and rationalization. The ideal requirement is reached when simplification of actual labour allows, at the same time, for an increase in precision.

Our program for clinical chemistry offers numerous examples of this ideal.

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Editorial

This issue of the Journal marks a change in publication policy. There will be three issues of the Journal per year, carrying the records of prominent lectures and Institute prize-winning papers etc. Reports of Branch News and information required for speedy dissemination will be found in the Newsletter produced from Manawatu.

Institute Officers 1975-76

PRESIDENT

John Pollard is Engineer-In-Charge of Technical Services with British Pavements (Canterbury) Ltd. He says his association with the Institute dates back to 1946 when Mick Hughson went out of his way to welcome a new student attending his first conference. He was admitted as an associate in 1947, and became a Fellow in 1962. For some years he convened the List of Members Committee. In 1968 he was appointed to the Membership Committee, a post he held until his election as President.

A graduate from the old Canterbury, College, Mr Pollard subsequently took the College's Diploma in Industrial Chem-

One of the functions of the chemical engineer is to catalyse the interaction between scientists and engineers, something to which Mr Pollard hopes he has contributed as a former chairman of the Canterbury Branch of both the Institue and the New Zealand Institution of Engineers. He is a former council member of the latter and a Fellow of both it and the Institution of Chemical Engineers.

Non-technical pleasures run to walking short distances over small hills, driving long distances over obscure roads, a workshop and the happy contemplation of his wine rack. istry and joined the Chemical Engineering Section of the Dominion Laboratory in 1947. Whilst working in the Section he sat the examinations for the Institution of Chemical Engineers and was admitted as a graduate in 1949.

In 1950 Mr Pollard joined the Christchurch Gas Company where he succeeded W. O. R. Gilling as Chief Chemist in 1956. After developing a predilection for road tar he transferred to British Pavements in 1960. The name notwithstanding, this is a Canterbury firm with a long tradition for building and producing much of the plant and materials involved in the construction of the roads of Canterbury.

Along the way the requirements of these various occupations have left their residue of interests and enthusiasms—the broader aspects of energy utilisation and their implications, the fundamental behaviour of paving materials, the design of obedient plant, and the wider recognition of the fact that New Zealand offers specific and fascinating challenges for the technologist.

To atone for the sins of his plants he sits on the Canterbury Regional Authority's Air Pollution Technical Committee, and on some days he is seen in decidedly non-chemical company as a member of the N.R.B. Road Research Unit's Pavements Committee. A long affection for the University of Canterbury is fostered as an Associate Member of the Engineering Faculty.

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Ashley Wilson gained his B.Sc., M.Sc., and Ph.D. degrees at the University of Canterbury. In 1958 he held a post-doctoral fellowship at Florida State University working on free radical reactions and he stayed in North America working in industry for a further six years. For most of this period he did development work on cellulose acetate flake and fibre production at Chemcell's plant in Edmonton, Alberta.

Dr Wilson returned to New Zealand in 1964 to take up a research position in the Technical Centre of N.Z. Forest Products Limited in Auckland. In 1969 he was transferred to the company's mill at Kinleith as Technical Superintendent with responsibility for quality control, environmental and technical development work. He returned to the company's Technical Centre in 1974 as deputy to the Chief Chemist. In this position he is responsible for monitoring the technical work being done at the Technical Centre and overseeing the work done at the company's mill laboratories.

Dr A. F. Wilson

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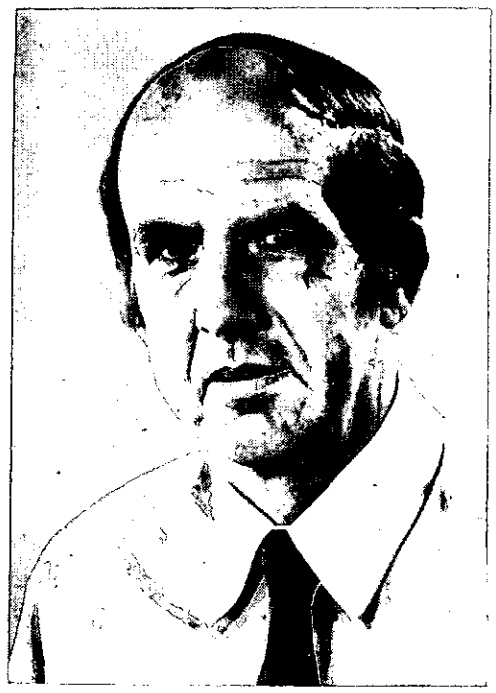
Everit Payne is Leader of the Chemistry Section at the Ruakura Animal Research Station, Hamilton. He graduated B.Sc. (Hons.) in Biochemistry at the University of Queensland in 1959 and joined the Biochemistry Laboratory at the Animal Research Institute, Brisbane. After working for some years on changes in rumen metabolism and clinical chemistry in ruminants fed grain he began studies in lipid metabolism of runminant tissues resulting in the award of a Ph.D. from the University of Queensland in 1971. In parallel with these studies he carried out studies on urea toxicity in sheep and the use of liver enzyme activities as indicators of protein intake in sheep.

In 1972 he came to Ruakura to head the Analytical Chemistry Group. Since coming to Ruakura he has continued his interest in lipid biochemistry of ruminants and has also become heavily involved in the radioimmunoassay of hormones.



Dr E. Payne

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Dr Roger Reeves is a Reader in Chemistry at Massey University. He graduated M.Sc. from Victoria University of Wellington in 1961, and after a short period on the staff of the Chemistry Department at the University of Canterbury he went to the United States on a Fulbright Travel Award. He studied in the field of molten-salt electrochemistry with Professor George J. Janz at Rensselaer Polytechnic Institute, Troy, New York, and graduated Ph.D. in 1964. At the end of that year he returned to New Zealand and joined the staff of Massey University as a Lecturer in the Department of Chemistry and Biochemistry.

During the following years he was closely associated with the development of Chemistry courses for the B.Sc. and M.Sc. degrees at Massey. He has developed research interests in the field of trace analysis, particularly in analytical atomic spectroscopy and electroanalysis.

In 1971-72 Dr Reeves spent a sabbatical leave at the University of Florida working with Professor James D. Winefordner on the use of electrothermal atomizers for atomic absorption and fluorescence. In recent years Dr Reeves has taken a particular interest in the teaching of third and fourth-year courses in Analytical Chemistry at Massey.

He has been a member of the N.Z.I.C. since 1965, and was Secretary of the 1970 N.Z.I.C. Conference.

Dr R. D. Reeves

Wellington

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Branch Hon. Auditor: Dr L. P. J. Chapman

Alan Turner joined Shell Oil as a laboratory assistant in 1952 and at the same time attended Victoria University graduating B.Sc. in 1958. In 1960 he was sent by Shell to their research laboratories in Amsterdam to study lubricants technology and manufacture with particular emphasis on greases. Additionally, he studied other aspects of oil industry operations in Belgium, Germany, United Kingdom, South Africa and Australia. Returning to New Zealand he was appointed the Technical Adviser, firstly in the Auckland Area and later in the South Island. In 1967, he returned to Wellington to senior marketing positions and was appointed Technica Manager for Shell Oil New Zealand Limited in 1973. He is in control of technical services and manufacturing and quality control. Prior to this appointment he had a familiarisation assignment in Australia, Canada, U.S.A., United Kingdom, Holland and Japan. Alan is a graduate of the International Marketing Institute of New Zealand and his other associations include the Institute of Fuel and the Institute of Petroleum.

Mr A. A. Turner

Christchurch

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Editor:	Dr I. L. Weatherall

Dr House gained his B.Sc., M.Sc., and Ph.D., (1964) from Victoria University of Wellington where he was a Junior Lecturer in Chemistry (1960-63). During the summer of 1963-64 he was a member of the 8th Victoria University of Wellington Antarctic Expedition investigating the chemistry and physics of some permanently ice covered lakes. Then followed two years of post-doctoral work at the University of California, Los Angeles, with Professor C. S. Garner where he developed an interest in chromium(III) chemistry. In 1966 he joined the staff at the University of Canterbury and was promoted to Senior Lecturer in 1971. During 1971-72 he worked with Professor F. Woldbye at the Technical University of Denmark investigating the properties of optically active transition metal complexes. His current interest is now in the field of inorganic reaction mechanisms and he is the author of two major reviews and over eighty research publications.

Dr House became a member (associate) of the NZIC in 1961 and was secretary for the University of Canterbury NZIC Conference committee in 1973.

Dr D. A. House

Otago

Chairlady:	Associate Professor M. Robinson
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Editor:	Dr B. M. Peake
Committee:	Professor A. D. Campbell, Mr C. W. Thompson, Dr J. F. Cutfield, Associate Professor R. Laverty.

The Otago Branch has elected its first lady chairperson. Dr Marion Robinson is an Associate Professor of Nutrition at the University of Otago School of Home Science. She graduated M.H.Sc.(N.Z.) with First Class Honours in Nutrition in 1946 and then worked for two years with the late Dr Muriel Bell at the Otago Medical School investigating the nutritional importance of fluoride in New Zealand. It was this work which first drew attention to the importance of fluoride for dental health in this country.

With the award of a Post Graduate Scholarship in Science Dr Robinson went to the University of Cambridge in 1948 to work with Professor R. A. McCance in the Department of Experimental Medicine. Here she studied the storage of iron, copper and zinc in the liver and gained her Ph.D. in 1952.

Dr Robinson joined the staff of the Nutrition Department in Dunedin in 1958 as a part-time lecturer and since 1969 has directed the M.R.C. project on Trace Elements in Human Nutrition.

During 1965 and 1975 she returned to work in Cambridge as well as visiting many laboratories in Britain and U.S.A. In May 1975 she was invited to deliver the first Muriel Bell Memorial Lecture of the Nutrition Society of New Zealand: the lecture was entitled "The Moonstone: More About Selenium". Her husband, Dr James R. Robinson is Wolff Harris Professor of Physiology at the University of Otago and is a former chairman of the Otago Branch of the New Zealand Institute of Chemistry.

Associate Professor M. Robinson

* 1974 Easterfield Address.

Some Quantitative Aspects of Coordination Chemistry*

by Kipton Powell,

To prepare a paper summarising the highlights of one's work over a five-year period is a fair challenge, particularly when one has dabbled in several areas of chemistry rather than staying in one. A book published about the time my research work started was "Modern Co-ordination Chemistry" by Lewis and Wilkins. The chapter by Rossotti on "Thermodynamics of Metal Complex Formation" was a great stimulus, and this fired an interest in energetic and quantitative aspects of co-ordination chemistry which has shown up in many subsequent research activities. This paper will outline several small facets of my research interests, with the theme of energetics linking these separate facets in some diffuse way. Firstly the problem of measurement of equilibrium constants will be considered, followed by a brief look at the chelate effect, oxygenation of cobalt complexes, enthropy titrations and the co-ordination of oximes.

Measurement of Equilibrium Constants

When studying the thermodynamics of a metal complex reaction, e.g. M + L → ML, we want to derive the thermodynamic parameters, K, $\triangle H$ and $\triangle S$. Now, in reality a system is rarely as simple as metal + ligand to give complex, for the ligand may well be the conjugate base of a polyprotic acid, e.g. EDTA, and as such will be in equilibrium with protonated species LH, LH_2 etc., and the complex ML is probably in equilibrium with higher complexes ML_2, ML_3 etc. When we study such a system the factors which we are likely to know at the beginning of an experiment are the total concentrations of metal, of ligand and of protons in our system, and the pK values for the protonated ligand. The determination of the K values for formation of the complexes $ML(K_1)$, $ML_2(K_2)$ etc., and the measurement of $\triangle H$, are best, though not necessarily, done in separate experiments.

Equilibrium constants will probaby be determined from an experiment in which alkali titre is added to a solution containing protonated ligand and metal ions. With increasing titre the ligand will be deprotonated, and will complex with the metal. The pH will be recorded as a function of titre. To obtain equilibrium constants from the titration data, one must solve a series of mass balance equations, e.g.

$$C_M = [M] + [ML] + [ML_2]$$
$$C_L = [ML] + 2[ML_2] + [L] + [HL] + [H_2L]$$
$$C_H = [H] + [HL] + 2[H_2L] - [OH]$$

These equations express the equilibrium concentrations of all the species in solution in terms of the stoichiometric concentrations (C) of metal, ligand and ionisable protons in the system. The equations shown would be valid for the complexing of copper with the ligand ethylenediamine; that is, where a bis-ligand species, CuL_2, is formed, and the ligand can take up two protons, H_2L.

If each equilibrium concentration is now expressed in terms of known or unknown equilibrium constants then, after appropriate substitutions, these three equations will reduce to one of the form

$$C_L = fn(K_1, K_2, pK, C_H, C_M, [H^+])$$

All simple problems will lead to an equation of this general form in which the unknown equilibrium constants K_1 and K_2 are a function of the stoichiometric concentrations of ligand, metal and acid, of the pK's for the ligand, and of the equilibrium hydrogen ion concentration. An equation of this type can be set up for each data point in the titration, and the total set of N equations for N data points must then be solved by some general non-linear least-squares process to determine the best parameters K_1 and K_2.

To perform this calculation satisfactorily the equilibrium hydrogen ion concentration at each data point must be known with considerable accuracy. This presents a major problem—how can hydrogen ion concentrations be determined accurately from the reading given by a pH meter? The answer is that they can't, unless some special method of calibration is used for the electrodes

Why? Briefly, there are two problems.

Chemistry Department, University of Canterbury.

pH Measurements

Firstly, there is a problem of residual liquid junction potentials. Usually for determining pH a glass electrode and a calomel electrode will be used. The cell is standardised by dipping the electrodes into a solution of defined pH, i.e. in one of the standard buffers. The emf of the cell E_s is given by equation (1) where E° is the emf of the reference electrode, E_{as} is the asymmetry potential of the glass membrane and E_{LJ} is the liquid junction potential for the cell.

$$E_s = E^\circ + E_{as} + E_{LJ} + pH_s\,(2.303RT/F) \quad \ldots\ldots (1)$$

$$E' = E^\circ + E_{as} + E'_{LJ} + pH'\,(2.303RT/F) \quad \ldots\ldots (2)$$

$$pH' = pH_s - \frac{(E_s - E') + (E'_{LJ} - E_{LJ})}{2.303RT/F} \quad \ldots\ldots (3)$$

When the electrodes are placed in a solution with unknown acidity pH', the emf is given by equation (2) which features a liquid junction potential E'_{LJ}. Equation (3) relates the pH of the test solution to E_s and E'. The pH given by this equation is not what is recorded on the pH meter (pH_m) unless $E'_{LJ} = E_{LJ}$; i.e.

$$pH_m = pH' + \Delta E_{LJ}(F/2.303RT) = p[H^+] - \log \gamma_{H^+} + \Delta E_{LJ}(F/2.303RT) \quad \ldots\ldots (4)$$

Only if $\Delta E_{LJ} = 0$ will the measured pH correspond with the conventional pH scale on which the standard is defined. This will seldom be the case, for the ionic strength and ionic composition of the unknown solution will probably not match those of the standard buffer.

Secondly, there is a problem with activity coefficients. pH is a measure of a_{H^+} whereas for calculation of equilibrium constants the $[H^+]$ is required. Activity coefficients could be calculated using the Debye-Huckel equation, or an extended form of it (e.g. the empirical Davies equation), but these equations hold only for dilute solutions of single electrolytes, and to use them in a mixed electrolyte system—metal salt + ligand salt + inert electrolyte—is an erroneous simplification.

$[H^+]$ Buffers

In order to avoid these two problems it is necessary to calibrate the pH assembly against buffer solutions which are (i) of known $[H^+]$ and (ii) have the same ionic strength and ionic composition as any test solutions to be studied, i.e. a calibration relating pH_m and $p[H^+]$ is required (equation (4)). Unfortunately there are very few buffer systems which can meet these requirements, and only two have been used so far, although many workers have used the less accurate method of calibrating against dilute solutions of strong acids around pH 1 – 2 and extrapolating the calibration through the entire pH range.

What is required is a buffer for which equilibrium concentration quotients are known at a fixed ionic strength. (That is we require a non-thermodynamic constant which is a product of concentrations rather than a product of activities.) One such example is the acetic acid/sodium acetate buffer which has been used by several workers. Electrode calibration as a $[H^+]$ probe is effected by titrating NaOH into acetic acid solution at fixed ionic strength, and for each data point measuring the pH, and calculating the equilibrium $[H^+]$ from the solution stoichiometry and the equilibrium concentration quotients. These constants for acetic acid were determined by Harned and Hickey using a cell without liquid junction.[1] This calibration with acetate buffers is limited to the pH 4 – 5 range.

This range has been extended significantly by use of the ethylenediamine(en)/ethylenediammonium buffer system.[2] Pinsent and Everett[3] determined concentration quotients for this system using the cell

$$Pt,\ H_2 \mid HCl(1),\ en,\ NaCl \mid KCl(3.5M) \mid HCl(2),\ NaCl \mid H_2,\ Pt$$

The $[H^+]$ in the R.H. half cell was known. The L.H. half cell contained the buffer. Because the two half cells have equal ionic strength the cell emf is related to the ratio of $[H^+]$ in the two half cells. At the limit of zero buffer concentration in the L.H. half cell the two liquid junction potentials can be equated, and the cell emf can be used to calculate the concentration of H^+ in equilibrium with en (eq(5)):

$$E = E_{LJ(1)} - E_{LJ(2)} - 0.059 \log \frac{aH^+_{(1)}}{aH^+_{(2)}}$$

$$= -0.059 \log \frac{[H^+_{(1)}]}{[H^+_{(2)}]} \text{ at zero buffer concentration} \quad (5)$$

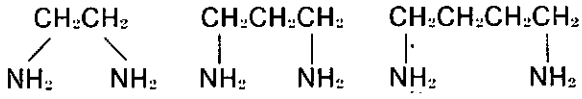
Ignoring the small residual liquid junction potential, concentration quotients were calculated for low buffer concentration. These constants were then extrapolated to zero buffer concentration to eliminate the effect of liquid junction potentials.

Use of this buffer system for pH calibrations has extended the range of $[H^+]$ buffers from pH 6.5 to 10.3. Calibration is extremely simple, involving the titration of NaOH into an ethylenediammonium solution. The $[H^+]$ at each data point is calculated by means of a simple computer program. A linear relationship is observed between $-\log$(calculated $[H^+]$) and pH_m. Further, the calibration is colinear with that for acetic acid and for dilute solutions at HCl at lower pH. If the approach is correct, then measurements at different ionic strengths should give parallel curves. This is observed. In fact in the ionic strength range 0.05 to 0.20 M NaCl the curves are coincident within experimental error.[2]

Conventiently, for a given pair of electrodes the calibration need be made only once; the calibration is relative to the electrode response to the NBS standard buffers and only this latter response need be checked on a day to day basis. The data of Pinsent and Everett are available for the temperature range 10° to 60° and I = 0.07 to 0.30M (NaCl), so data could be obtained to suit most experimental conditions, e.g. 37°, 0.135M.

Reactions of chelating ligands

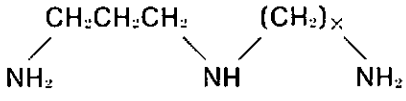
The stability of a complex involving a chelate ring is dependent on the size of that ring. Five-membered chelate rings are the most stable, stability then decreasing with increasing ring size. The ligands ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane, which give respectively 5, 6 and 7-membered chelate rings afford an example.



Chelate ring size		
5	6	7
log K_{CuL}		
10.5	9.6	—

As noted by the stability constants for the 1:1 copper complexes the smallest 5-membered ring gives the most stable complex. In contrast, for the 7-membered ring (and larger rings), complex stability is so low that reaction of the ligand with copper in aqueous solution leads to precipitation of copper hydroxide.

Another approach to the relative stabilities of complexes with 5, 6 and 7-membered chelate rings has considered ligands in which these rings are added onto a common ring which by itself gives a stable complex.[4] One example is a set of tridentate ligands coordinating through three nitrogen atoms:



Ring sizes	log K_{CuL}	△
6,5	16.6	7.0
6,6	14.2	4.6
6,7	11.6	2.0

The size of one ring remains constant while the other increases. The constants decrease with the increasing size of the second ring. △ represents the difference in stability between the complexes shown and that complex having only one 6-membered ring corresponding to the left half of the ligand. From the △ values it is seen that addition of a 5-membered ring adds 10^7 to the stability of the complex whereas addition of a 7-membered ring adds only 10^2 despite the fact that the latter ligand is by far the more basic.

We could make a similar comparison for ligands in which the common ring is a 5-membered one. But now a problem emerges. We do not see a regular trend in the log K values.

Combination of ring sizes	log K_{CuL}
5,5	15.8
5,6	(16.6)
5,7	13.4

For a combination of linked 5 and 6-membered rings the value appears to be high.

An observation of this type led to the very popular, but I believe misleading, conclusion that a combination of alternating five and six-membered rings in a ligand imparts extra stability to a complex. The observation has also been made for combinations of three linked chelate rings, $NH_2(CH_2)_xNH(CH_2)_yNH(CH_2)_xNH_2$, where the ligand with alternating 5 and 6-membered rings gives the most stable complex, and the one with two 6 and one 7-membered ring gives a complex of much lower stability.[4]

A rationale which has been offered to explain the stability associated with different ring sizes is in terms of accumulated ring strain. We know from structure determinations that within a single chelate ring the bond angles will not all be ideal. The ring is said to be strained. When a second ring is joined on, strain is transmitted through the linking atom. When a third ring is added, the transmitted cumulated strain may be such as to force the third ring into an unstable configuration, For example whereas a single 5-membered ring will adopt a gauche configuration, and a pair of linked 5-membered rings will do likewise, in a chain of three of these rings the cumulated strain is such that the final ring must adopt the less stable eclipsed configuration if the terminal nitrogen is to coordinate with a metal ion in planar coordination. Models show this clearly and also show that for a 5,6,5 combination of rings the two outer 5-membered chelate rings can adopt the gauche configuration and the central 6-membered ring its favoured chair configuration. With inclusion of a 6-membered ring there has been a release of strain. However, this argument overlooks one fundamental point. The ligands with different combinations of ring sizes are in fact of different basicity, and when comparing the relative stabilities of the complexes formed we are considering the combined effect of *both* ligand basicity *and* stability associated with ring size. To consider only the stability associated with the ring system our comparison should consider the reaction for the conversion of the metal complex into a solvated metal ion plus protonated ligand:[4]

$$CuL^{2+} + nH^+ \rightarrow Cu^{2+} + H_nL^{n+} \quad (\log K')$$

i.e. the relative affinities of both metal and protons for the ligand should be considered, and ring stabilities expressed in terms of log K'. Now a different sequence of ring stabilities emerges.

Triamines	log K'	Tetra-amines	log K'
5,5	7.2	5,5,5	8.5
5,6	9.6	5,6,5	9.2
5,7	13.3	6,5,6	12.5
6,6	13.7	6,6,6	19.0
6,7	17.4	6,7,6	22.9

In the table the smallest value of K' corresponds to the most stable ring system. For both the triamines and tetra-amines we see greatest ring

stability for linked 5-membered chelate rings. The conclusion must be made, that despite ring strain, linked 5-membered chelate rings give the most stable ring system. This stability of 5-membered rings is, I believe, entirely a geometric effect. The free ligand which can give a 5-membered chelate ring has its donor groups suitably positioned for coordination with a metal ion. For a ligand giving a larger chelate ring, these donor groups must be drawn closer together, against the repelling effect of their mutual dipoles or charges, before coordination can occur. This drawing together of dipoles will be an endothermic effect, destabilising the complex with larger chelate rings.

Addition of Molecular Oxygen to Metal Complexes

Some cobalt(II) complexes with amines, amino-acids, schiff bases and porphyrins can reversibly oxygenate in a manner similar to haemoglobin. They do this in the absence of the enveloping protein, globin; under these circumstances haem would irreversibly oxidise. So these cobaltous complexes are useful model compounds for a reaction of biological importance. The reactions of cobalt complexes with O_2 are of two types—to give either 1:1 adducts or 2:1 adducts.

The reaction to form 2:1 adducts[5]

$$2CoL_n + O_2 \rightarrow CoL_n-O_2-CoL \qquad (K_{O2})$$

is very exothermic, *circa* −125 kJ mol^{-1}. This reaction can be rationalised in terms of three steps which finally give an adduct which is essentially a cobalt(III) peroxy species:

$$CoL_n^{2+} \rightarrow CoL_n^{3+} + e \qquad (6)$$

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \qquad (7)$$

$$2CoL_n^{3+} + H_2O_2 \rightarrow \{CoL_n-O_2-CoL_n\}^{4+} + 2H^+ \qquad (8)$$

oxidation of the cobalt complex(6); reduction of O_2 to H_2O_2(7), and coordination of peroxide(8). The high exothermicity originates in the reduction of O_2 to H_2O_2; the oxidation and coordination steps are slightly endothermic.[5]

In connection with studies of this type our attention was drawn to earlier work on oxygenation of a cobalt ornithine complex. Ornithine (HL) is 1,4-diaminopropanoic acid, $\overset{+}{N}H_3(CH_2)_2CH(NH_2)COO^-$. The earlier study had been rather incomplete and (unfortunately) like so many publications today reported too little experimental data to allow recalculation or reinterpretation of results. (Do journals still look on chemistry as an *experimental* science?) It reported the formation of a mono and a bis ornithine complex, $Co(HL)^{2+}$ and $Co(HL)_2^{2+}$, in which the ornithine is acting as a bidentate (glycinate type) ligand, with the terminal amino group still protonated. It reported that $Co(HL)_2^{2+}$ is oxygen-sensitive and forms a 2:1 adduct with O_2 at pH 9 – 10 with K_{O2} *circa* 10^5. This result was surprising in that no other cobalt amine or amino-acid complex with fewer than three nitrogen atoms coordinated was known to be oxygen-sensitive. Further, the potentially tridentate character of ornithine had been overlooked—at high pH the very basic terminal amino group will have started to deprotonate, allowing an additional 7-membered chelate ring to form (L^- coordinates). A full analysis of this system[6] has now established that in addition to the above species, which have their maximum concentrations at pH 7.3 and 8.8 respectively, a complex $Co(HL)L^+$ forms at high pH (L^- = tridentate ligand). The metal-ligand system is oxygen-sensitive only in the pH range where the species $Co(HL)L^+$ is present (pH > 9), and for the formation of $Co(HL)L-O_2-Co(HL)L$ $K_{O2} = 2 \times 10^7$. Complexes with fewer than three coordinated nitrogen atoms (e.g. $Co(HL)_2^{2+}$ which represents > 50% of total cobalt at pH 7.7 – 9.9) were not oxygen-sensitive.

The uptake of O_2 was determined by polarographic oxygen sensor. The oxygenation reaction was studied in a small thermostatted cell having no airspace and air-tight except for a capillary venting tube. The O_2 sensor and a combination pH electrode passed through the lid of the cell. The cell was filled with air-saturated ornithine solution. The pH was adjusted to *circa* 10 and cobalt solution was then added in increments from a micrometer syringe. Complex species formed, as noted by a drop in pH, and the amount of adduct formed was given by the change in $[O_2]$. The composition of the solution in equilibrium with the adduct was determined from the measured pH and the stoichiometry of the solution.

Entropy Titration

It was stated above that the enthalpy change and the equilibrium constant for a reaction were best determined in separate experiments. However under certain conditions they can be obtained from a single experiment.

One bright spot which appeared in the field of solution thermochemistry in the mid 1960's was the reporting of the 'entropy titration' technique[7] In this a titration is carried out inside a calorimeter, and from the measured heat change both the equilibrium constant and the enthalpy change for an unknown reaction are determined. This is possible, in principle, provided the equilibrium constant for the reaction lies between 100 and 10,000; i.e. provided the reaction proceeds significantly but not to completion. Consider a general reaction, A + B → AB. Ignoring activity coefficients, a concentration quotient K can be written in which [A] is the equilibrium concentration of A and is equal to the total concentration of A (C_A) minus the equilibrium concentration of AB. Likewise for B (equation (9)).

$$K = \frac{[AB]}{[A][B]} = \frac{[AB]}{(C_A - [AB](C_B - [AB])} \qquad (9)$$

$$[AB] = \frac{Q_{abs}\ (J)}{V(ml).\triangle H(kJ\ mol^{-1})} \qquad (10)$$

$$\frac{\triangle H}{K} = D(\triangle H)^2 + E\ \triangle H + F \qquad (11)$$

The heat change measured on reacting A and B, Q_{obs}, is a function of the amount of AB formed; equation (10). Substituting this expression into equation (9) yields equation (11) which relates the two unknowns $\triangle H$ and K; D, E and F are expressions relating Q_{obs}, V, C_A and C_B. An equation of this type can be set up for each data point in the calorimetric titration. Solution of a set of equations from a single titration can, in principle, lead to the values of $\triangle H$ and K.

However, in our experience, data can rarely be obtained with sufficient accuracy to carry out the necessary least-squares calculation. Careful analysis of published data has shown that where the method has been applied less-than-rigorous methods of computation have often been used. Recent articles have critically assessed the use of this method [8, 9]. The principle may however be applied in a non-rigorous fashion and this can be illustrated by an example of an ion-pairing reaction.

Trivalent lanthanide ions form very stable 1:1 contact ion pairs with sulphate ion in aqueous solution. Further there has been some debate as to whether the lanthanide ion would accept a second sulphate ion in the ion pair. When titrant $(Me_4N)_2SO_4$ is added incrementally to lanthanide perchlorate solution in a calorimeter the calculated values of $\triangle H$ for formation of the 1:1 ion pair are constant up to the point where the sulphate-lanthanide ratio is approximately unity. At higher sulphate ratios the calculated $\triangle H$ increases; this was considered indicative of the 1:1 ion pair undergoing a subsequent reaction to give a 2:1 ion pair. For this subsequent reaction neither K nor $\triangle H$ was known, but they can be determined by a simple graphical analysis. The reaction being studied is given by equation (12)

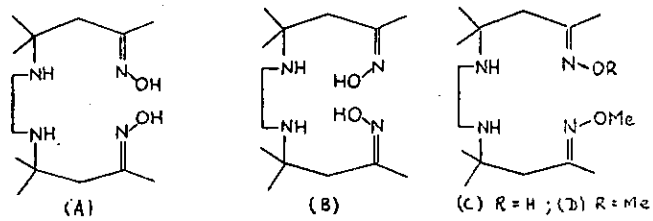
$$MSO_4^+ + SO_4^{2-} \rightarrow M(SO_4)_2^- \ (K_2) \qquad (12)$$

$$\triangle H_2^\circ = \frac{1000\ Q_{obs}\ fn(\gamma)}{K_2^\circ\ V[MSO_4^+][SO_4^{2-}]} \qquad (13)$$

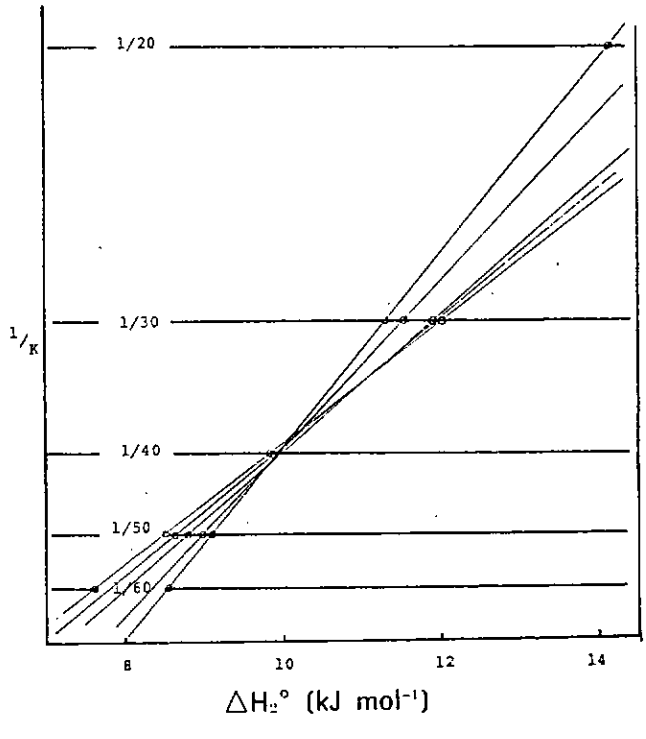
In equation (13), which derives from the equilibrium expression, $[M(SO_4)_2^-]$ has been expressed in terms of the enthalpy change for formation of the 2:1 ion pair ($\triangle H_2^\circ$) and of Q_{obs} (that part of the measured heat change which does not correspond to formation of the 1:1 ion pair or heats of dilution etc.). The graphical analysis involves choosing a range of K_2 values in the region of the expected value, and for a given data point (i.e. a given value of Q_{obs}) calculating values of $\triangle H_2^\circ$. The $\triangle H_2^\circ$ values will be inversely proportional to K as shown on the graph. The calculation is done for each data point and the resultant family of straight lines intercept in a region which defines the values of $\triangle H_2$ and K_2 and their error limits (i.e. for the correct value of K_2 all data (errors excepted) will give the same value of $\triangle H_2$).[9]

Some Aspects of Oxime Chemistry

Sometimes the chemist may want to look at the coordination of a functional group which is not amenable to study by potentiometric measurements. Examples of this would be the carbonyl group and the oxime group. The carbonyl group is an extremely weak base. The oxime group is amphiprotic, protonating at the nitrogen, deprotonating at the hydroxyl. But the nitrogen atom is protonated only at a pH below 1 and the hydroxyl group is deprotonated only at pH > 11. To study the coordination of these donor groups in near-neutral solution it is necessary to include them into a ligand which contains a strongly basic functional group which can be used as a probe in pH studies. Examples of this type of ligand are the oximes A and B and the diketone from which they are derived.



The oxime ligand can, in principle, occur in three isomeric forms. Only two have been isolated as salts, viz (A) having a *syn* methyl configuration and (B) having an *anti*-methyl configuration. The two isomers have been characterised by n.m.r. spectroscopy, using as a probe the resonance for the methyl and methylene groups α to the oxime group. The positions of these resonance absorptions is somewhat dependent on the solvent used, but in trifluoroacetic acid both absorptions move



Entropy titration analysis for

$GdSO_4^+ + SO_4^{2-} \rightarrow Gd(SO_4)_2^-$

upfield by approximately 0.4 p.p.m. when the oxime group has the *syn* methyl configuration. Interconversion of the two isomeric forms is essentially instantaneous in aqueous solution in the presence of acid, base, or metal ions. This has been established by n.m.r. studies, and by potentiometric and spectrophotometric measurements on metal-ligand systems. In the solid state coordination to a metal ion is through the two oxime nitrogens and the amine nitrogens, with the ligand in the *syn* methyl configuration, irrespective of whether the metal is added to a solution of the *syn* or *anti* isomer[10, 11].

Thermodynamic data have been obtained for the co-ordination of the oxime ligand and these are compared with data for (1) ethylenediamine, which is the diamine residue in the ligand, and (2) the tetra-amine ligand derived from the diamine-dioxime by reduction with sodium in pentanol.

	log K	$\triangle S$/J mol^{-1}K^{-1}
Cu^{2+} + dioxime →		
Cu (dioxime)$^{2+}$	13.2	70 ± 2
Cu^{2+} + en →		
$Cu(en)^{2+}$	10.5	25
Cu^{2+} + tetra-amine →		
$Cu(tet.)^{2+}$	22.4	80 ± 4

The first question to be answered is whether the weakly basic oxime does in fact coordinate in solution, and if so, how strongly. A clue to its coordination is found in the entropy change; the observed $\triangle S$ is very similar to that for the co-ordination of the related tetra-amine. We can deduce that the reactions are of similar type, i.e. metal + ligand to give a complex, plus four water molecules liberated from the metal coordination sphere. Visible absorption spectra also afford evidence for coordination of the oxime nitrogen. The log K values give an estimate of the strength of coordination of the oxime group. Relative to ethylenediamine the stability constant increases by a factor of only 1000 on adding the oxime functions, whereas coordination of two additional amine functions is seen to increase the stability by 10^{12}.

One important reaction in oxime chemistry is the deprotonation of a coordinated oxime group. This reaction is of fundamental importance in the analytical application of oximes for it leads to metal complexes of zero charge and this contributes to their low solubility in water. Oxime deprotonation facilitates the development of a hydrogen bridged structure which is well known in the dibridged nickel dimethylglyoxime complex. Such bridging units introduce significant additional stability to a complex. The stability of this bridging unit can be gauged from the fact that in formation of dimethylglyoxime complexes the second stability constant is greater than the first. This rarely happens with other types of ligands. The development of one such hydrogen bridge is possible with the diamine dioxime ligand (A). The following data show how readily this reaction will occur.

LH_2 = dioxime

		log K
$Cu^{2+} + LH_2 \rightarrow$	$Cu(LH_2)^{2+}$	13.2
$Cu(LH_2)^{2+} \rightarrow$	$Cu(LH)^{+} + H^{+}$	−3.2
$LH_2 \rightarrow$	$LH^{-} + H^{+}$	−12.2
$Cu^{2+} + LH^{-} \rightarrow$	$Cu(LH)^{+}$	22.1

The first entry is for the coordination of the non-ionised dioxime. The second is for dissociation of an oxime proton from the coordinated ligand. The dissociation constant of $10^{-3.2}$ is to be contrasted with that of $10^{-12.2}$ for proton dissociation from the uncoordinated oxime. That is, coordination of the oxime to a metal has caused an increase of 10^{9} in the acid dissociation constant for the oxime. Acid dissociation from the coordinated oxime could be considered to occur in two steps: (i) Dissociation to give an oximato group which is resonance stabil-
hydrogen bridge between the oxime and oximato functions. It is not yet clear what the relative contributions of these factors will be. (C) and (D) are two ligands which we are studying in order to clarify this point.

Whereas (A) can both deprotonate and then hydrogen bridge, (C) can deprotonate but not hydrogen bridge, and (D) can do neither.

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Acid Catalysed Reactions

by Charmian J. O'Connor

Many kinetic investigations have dealt with the dilute acid region, where activity coefficient variation of reaction species can be either ignored or reasonably treated using Debye-Huckel type approximations. However, in dilute acids reactions often proceed at inconveniently slow rates, and it is difficult to achieve much variation in the concentration (or activity) of one important reaction species, water, unless more concentrated acids are used.

On the other hand, in more concentrated solutions, these difficulties are replaced by other serious problems which are largely concerned with the theoretical interpretation of results. Some of these arise from the use of acidity functions to represent variations in the acidity of a reaction medium. Because of these difficulties this field of reaction mechanism has been in an uncertain state for many years; nevertheless valuable kinetic information can be obtained. The purpose of this paper is to show the progress made in recent work carried out in the Chemistry Department at the University of Auckland.

Acidity Functions

An acidity function, H_X, is defined as the quantitative measure of the ability of a medium to protonate a particular type of base X.

$$X + H^+ \rightleftharpoons XH^+$$

$$h_X = a_{H^+} f_X / f_{XH^+}$$

$$-\log_{10} h_X = H_X = pK^{\oplus}_{X} + \log_{10}(C_X / C_{XH^+})$$

Thus h_X and H_X are extensions of the C_{H+} and pH scales into concentrated acids. It is now well recognised that no one acidity function, e.g. H_0,[1] based on primary aniline indicators is generally applicable to the protonation behaviour of neutral bases of different structural classes; we must define appropriate H_X scales for typical organic substrates in acid catalysed reactions e.g. we use the H_A scale[2] for amides and ureas. It is true however that all H_X scales are linearly related to H_0, the first acidity function to be defined.

$$H_X = mH_0 + C$$

Chemistry Department, University of Auckland.

Summary of a paper presented to the Auckland Branch, N.Z.I.C., 15 October, 1974.

Criteria of Reaction Mechanisms

Acid catalysed reactions can be broadly classified into two general classes, depending on whether the conjugate acid formed in a rapid pre-equilibrium

$$\underset{(1-\alpha)}{S} + H^+ \rightleftharpoons \underset{\alpha}{SH^+}$$

undergoes rate determining unimolecular decomposition −A1

$$SH^+ \xrightarrow{\text{slow}} \neq \rightarrow \text{products}$$

or is attacked by a water molecule in the rate determining step −A2.

$$SH^+ + H_2O \xrightarrow{\text{slow}} \neq \rightarrow \text{products}$$

Table 1 summarises the development and extension of this theory.

The first quantitative attempt to treat rate-acidity dependence in non dilute acids was made by Zucker and Hammett.[3] Based on the data then available reactions were grouped into two categories. Application of this criterion depended on plots of $\log_{10} k\psi$ *vs.* $-H_0$ or *vs.* $\log_{10} C_{H+}$ having unit slope. The example quoted to illustrate an A1 reaction was mutarotation of sucrose in HCl at 25°C. We have carried out this reaction[4] in HCl, H_2SO_4, $HClO_4$ and H_3PO_4 at 25 and 0°C, and find that in fact it is only in HCl at 25°C that the criterion of unit slope is fulfilled e.g. in HCl at 0°C, and in H_2SO_4 at 25°C the slopes are 0.85 and 0.80 respectively. It is thus a tribute to their genius and their luck that modern theories are based on Zucker and Hammett's original classification. Unfortunately very few reactions fit their theory cleanly; plots are either curved or have slope ≠ 1. A more sophisticated treatment was obviously needed, and in 1961 Bunnett[5] introduced his hydration parameter treatment. Empirically he found that plots of $(\log_{10} k\psi + H_0)$ are linear or very nearly linear in log a_{H2O} of the reaction medium. The water activity dependence w corresponds closely to the number of water molecules required to convert a protonated substrate molecule to transition state, or the approximate 'order' of the reaction in water. A further linear free energy relationship developed by Bunnett and Olsen[6] in 1966 defines a parameter ϕ whose magnitude is useful to characterise the kinetic effect

of changing the reaction medium. Generally Bunnett-Olsen l.f.e.r. plots are more nearly linear than Bunnett w plots e.g. for hydrolysis of acetanilide[7] in H_2SO_4 at 80°C the correlation coefficients of these two plots are 0.998 and 0.987 respectively.

In acid catalysed reactions the observed rate constant, $k\psi$, must be corrected for the fraction, α, of substrate which actually undergoes hydrolysis, $\alpha = h_x/(K_{SH^+} + h_x)$, and it is these corrected values which are substituted into the various kinetic equations.

My interest in this field was first aroused after a series of studies on the ^{18}O exchange of carboxylic acids with solvent water. The rate of exchange of acetic acid[8] increased up to 35% (w/w) HCl and was much faster than that in other mineral acids for which the rate decreased in the order $H_2SO_4 > HClO_4 > H_3PO_4$. This trend is frequently observed in reactions in concentrated acid media. Moreover the profiles for these last three acids were bell shaped, and this again is typical of profiles for hydrolysis of many substrates. One early explanation for the bell shape was that the rate increased as the proportion of conjugate acid increased, but as an increase in solute concentration reduces water activity, when this activity is proportionally greater than the effect in enhancing acidity, the rate of hydrolysis fell.[9] This explanation is now inadequate to explain the detailed effects of structure, solvent etc on the magnitude and position of the rate maximum.

It seems unlikely that the presence of different counterions such as HSO_4^-, ClO_4^-, and Cl^- could alter the basic mechanism to such an extent that the role of water in the rate determining step would be significantly changed. Further, since all strong mineral acid solutions eventually exhibit the same activity coefficient behaviour, all w and ϕ plots for a given hydrolysis in different acids should extrapolate to the same point in dilute acid. Unfortunately this very rarely happens but the hydrolysis of sucrose is one example which illustrates this point well.[4]

Hydrolysis of Esters

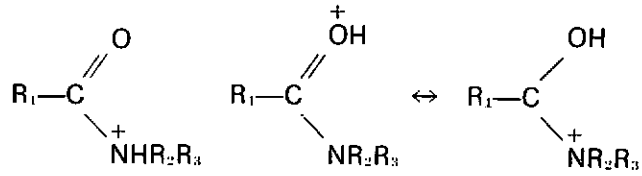
Much of the work covered in the literature deals with the hydrolysis of oxygen bases e.g. Yates[10] has reviewed the extensively differing behaviour of esters. Primary alkyl acetates, and secondary alkyl, benzyl (except p-MeO), and allyl acetates have hydrolysis profiles characterised by an initial steady rate of increase with acid concentration, passing through a maximum at intermediate acidities, falling to a minimum at higher acidities and then increasing again. These compounds, and also vinyl and phenyl acetates whose profiles do not exhibit a rate maximum but continue to increase in moderately concentrated acid, all have Bunnett w plots whose slopes are originally linear and positive ($w \approx 2$) and then after a small region of curature w becomes linear and ≈ -0.2. These plots confirm that the mechanism of hydrolysis changes from A2 to A1 with increasing acidity. t-Bu and p-MeO-benzyl acetates however exhibit only a monotonic rate increase at low acidity and their w plots are linear and indicate only an A1 mechanism ($w \approx -0.6$).

Similar differences in profile shapes and changing mechanisms of hydrolysis with increasing acidity have been found among the hydrolysis studies we have made on nitrogen bases i.e. amides, dipeptides, nitriles, and ureas. Thus weak bases, dipeptides and nitriles do not exhibit a rate maximum;[11] the maximum for ureas[12] which are stronger bases than amides occurs at a relatively lower acidity; and acetanilides[13] and phenylureas[12] frequently exhibit a change in mechanism from A2 to A1.

Hydrolysis of Amides

The rate constants of hydrolysis of aromatic amides are dependent on the nature of the mineral acid. Thus for benzamide[14] at any one acidity the bell shaped profiles decrease in the order $HCl > H_2SO_4 > HClO_4 > H_3PO_4$. Moreover substitution on nitrogen decreases the rate in the order 1° > 3° > 2°. Bunnett w and Bunnett-Olsen l.f.e.r. plots are curved.[14]

The first step in the acid catalysed hydrolysis of amides is a protonation step, the exact position of protonation being the subject of much discussion in recent years. Amides can theoretically protonate on either nitrogen, (I), or on oxygen, (II) and (III), which are mesomerically stabilised.



I II III

In practice, the position of protonation depends on whether or not the mesomeric stabilisation which can be achieved by the O-protonated amide is important enough to outweigh the inherently greater basicity of the nitrogen site. Certainly O-protonation is thermodynamically more stable by orders estimated from 10^3-10^7, but evidence suggests that the minor component of the N-protonated conjugate acid is kinetically more reactive.

Because the theories, (Table 1), involving only a one-term mechanistic pathway involving an O-protonated transition state seemed to be inadequate for hydrolysis of amides, we formulated[14] a new reaction scheme involving two transition states, arising from two distinct mechanistic paths involving protonation on both oxygen and nitrogen. The Bronsted-Bjerrum rate equation and correction for α and $(1-\alpha)$, the amounts of O-protonated and unprotonated amide respectively, gave equation (1).

$$k\psi = k_N C_{H^+} (1-\alpha)\, a_w + k_O\, \alpha\, a_w \qquad (1)$$

Application of eq. (1) correlated the data for benzamide, *N*-Me and *N,N*-diMe benzamides well (> 0.998), but the plots in H_2SO_4 were slightly curved at high acidities, leading to relatively large standard deviations in slope and intercept. As a result, when values of k_N and k_O evaluated from eq.(1) were used to try and reproduce theoretically the rate profiles for a series of *N*-substituted 4-chlorobenzamides,[15] the position but not the absolute magnitude of the rate profiles could be accurately predicted.

Comparison of our results[15(b)] on the acid hydrolysis of a series of (a) ring substituted acetanilides and (b) *N*-substituted 4-chlorobenzamides suggests that correction of the rates for the concentration only of *N*-protonated conjugate acid is more appropriate. Although this quantity has not been directly measured, the ratio of *N*-protonated to unprotonated amide is related to the ionization ration, $I = C_{ROH^+}/C_{RO}$, by an amount = $c' I^n$ where c′ and n are constants. This leads to formulation of a kinetic equation (2) for the bimolecular reaction between water and the *N*-protonated conjugate acid.

$$k\psi = k_N\, c'\, I^n\, a_w^r\, f_{RNH^+}/f \neq \qquad (2)$$

k_N is the psuedo first-order rate constant for the reaction. If we make the long standing assumption that r, the number of water molecules involved in formation of the transition state, is equal to three, then application of eq. (2) to 60 sets of literature data invariably gives excellent fit and back substitution produces theoretical curves which exactly fit experimental profiles.

Hydrolysis of Ureas

The hydrolysis of ureas has not been as extensively studied as that of amides. Shaw and Walker[16] studied the hydrolysis of mono-, di- and trimethylthioureas and of the unsubstituted thiourea in dilute acid solutions, and suggested that these ureas decompose by intramolecular hydrogen transfer and dissociation of the activated complex. Moodie *et al.*[17, 18] studied the hydrolysis of urea and some of its derivatives and concluded that the reaction occurred via two distinct paths. They suggested that at low acid concentrations the reaction was a unimolecular decomposition of the unprotonated urea, and in moderately concentrated and concentrated acid solutions the reaction was a bimolecular one between water and the diprotonated urea.

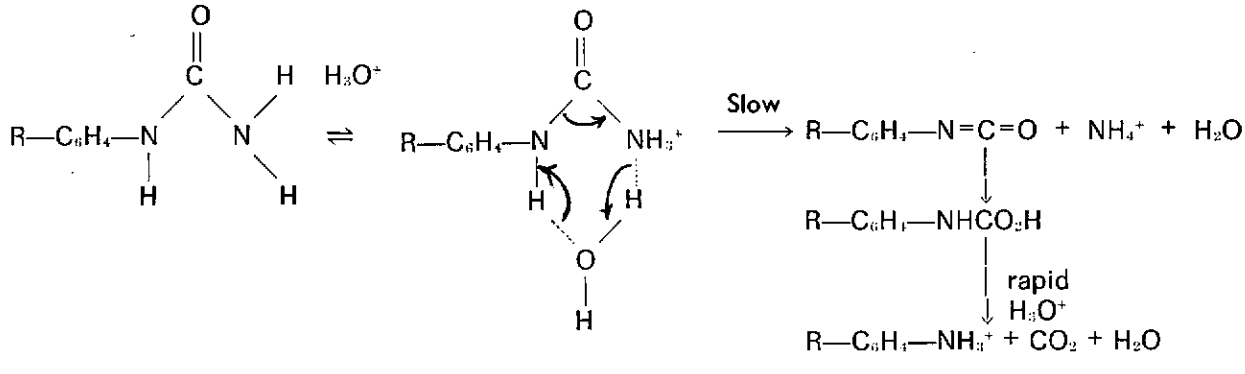
We have hydrolysed twelve substituted phenylureas[12(b)] in aqueous solution (pH 6.5) and in H_2SO_4, HCl and $HClO_4$ over a wide range of acidities at 101.0°C. In acid solutions the hydrolysis products were identified as the corresponding substituted anilines. The rate constants of hydrolysis, $k\psi$, vary with acidity, first increasing to a maximum and the decreasing as the acidity is increased, but the two term rate equation (3)

$$k\psi = k_{up}[K_{SH^+}/(K_{SH^+} + h_A)] + k_p[h_A/(K_{SH^+} + h_A)] \qquad (3)$$

(where k_{up} and k_p are the specific first order rate constants of unprotonated and protonated bases respectively), postulated by Moodie *et al.*[17] predicts a sigmoidal shaped curve. The acidity at which $k\psi_{(max)}$ occurs is related to the basicity constant (K_{SH^+}) of the urea suggesting that the hydrolysis reaction depends on the initial formation of a protonated species. Once again we suggest that it is the *N*-protonated urea which is the reactive entity. Also, independent of the nature of the counter anion, the rates are relatively close at the same water activity in the different acids. Arrhenius parameters[12(a)] suggest that in < 45.0% (w/w) H_2SO_4 solutions, the hydrolysis of phenylurea occurs via a unimolecular mechanism. We therefore propose[12(b)] that hydrolysis of phenylureas occurs by Scheme I.

Such a mechanism involving a proton transfer by water in a cyclic transition state in the r.d.s. should show general acid-catalysis and evidence for this has been obtained.[19] Hammett plots also support this scheme. Phenylisocyanates are readily attacked by water to form the corresponding carbamic acids and these decompose instantly to the corresponding aniline salt on addition of mineral acid.

Variation in the substituent R- produces only a very small variation in $k\psi$ at pH 6.5. This result



SCHEME I

is not unexpected since R- would have opposing effects on the protonation and dissociation steps.

The solvent isotope effects for hydrolysis of 4-Me- and 4-Cl-phenylureas have been measured in H_2O/D_2O (k_H/k_D = 2.42 and 2.04), 10.8% (w/w) H_2SO_4/D_2SO_4 (k_H/k_D = 1.29 and 1.15) and 41.0% (w/w) H_2SO_4/D_2SO_4 (k_H/k_D = 2.12 and 1.68), respectively. These values of k_H/k_D are similar to those observed for the general acid catalysed mutarotation of glucose[20] in neutral and acid solutions. In deuterated solvent the *N*-bound protons undergo rapid exchange and the ratios of k_H/k_D therefore confirm that an N-H, or N-D, bond must be broken in the r.d.s. The solvent isotope effect on this second proton transfer more than counterbalances the inverse solvent isotope effect which would be expected for pre-equilibrium protonation of urea.

In all solutions the values of k_H/k_D are smaller for the hydrolysis of 4-Cl- than for 4-Me-phenylurea. This difference confirms the proposed scheme as, compared to the methyl group, the electron-withdrawing chloro-substituent will favour breaking of the N-H, or N-D, bond and this will lead to a smaller degree of bond-breaking in the transition state.

K_{SH^+} is a measure of the equilibrium involving the *O*-protonated cation which we suggest is unreactive. Correction of the values of $k\psi$ for reaction of the unprotonated species, k_{up} = $k\psi/(1-\alpha)$, followed by application of the standard criteria of mechanism (Table 1), gives good results.

Conclusion

Although some of the fundamental difficulties in interpreting kinetic acidity dependence are not likely to be quickly resolved, approaches based on the hydration treatment still remain the most satisfactory presently available. They are much more widely applicable than other treatments and have clearly demonstrated the singular importance of water activity as a reaction variable. Also, despite some of their difficulties in a purely numerical sense, they can be very useful to chemists in drawing qualitative and sometimes quantitative conclusions about the nature of reaction mechanisms in a more chemically descriptive way than perhaps more mathematical treatments would do.

Continued testing of hydration parameter treatments may in future lead us to more satisfactory solutions to the complex problems of reaction kinetics in concentrated acids.

Acknowledgements

I sincerely thank my students Dr. C. Janet Giffney (nee Hyland), Dr. J. W. Barnett and Mr. A. J. G. Milbank who carried out much of the experimental work described above.

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TABLE 1

Theory	Slope of Plot	Role of water
Zucker Hammett (1939)		
$\log_{10}k\ \psi$ *vs.* $-H_0$	1.0	A1 none
$\log_{10}k\ \psi$ *vs.* $\log_{10}C_{H^+}$	1.0	A2 involved in r.d.s.
Bunnett Hydration Parameter (1961)		
$(\log_{10}k\psi + H_0)$ *vs.* $\log_{10}a_{H_2O}$	$w \leqslant 0$	none
	$1.2 < w < 3.3$	nucleophile
	$w > 3.3$	proton transfer agent
Bunnett-Olsen l.f.e.r. (1966)		
$(\log_{10}k\psi + H_0)$ *vs.* $(H_0 + \log_{10}C_{H^+})$	$-0.34 < \phi < 0$	none
	$0.18 < \phi < 0.47$	nucleophile
	$\phi > 0.47$	proton transfer agent

This invited article from USSR will be of considerable interest to N.Z. clinical chemists

Detection of Hereditary Diseases

By Yuri Veltischev,

Director, Scientific Research Institute of Pediatrics and Children's Surgery,

Ministry of Public Health, Russian Federation.

A mass screening of newborn babies is a new important stage in the development of Soviet medicine. Its main aim is to spot the danger, to get the disease in good time, and to prevent hereditary disorders of metabolism threatening a child's development.

The screening programmes existing in the USSR at present consist of two main stages: firstly economical and simple tests which can be applied to screen large populations are carried out. Any positive results of these checks justify the second stage, a more profound examination of the children with the use of modern methods of analytical biochemistry and load tests.

The main link in this mass screening of children for spotting hereditary anomalies of metabolism is the centralised biochemical laboratory. This new form of medical service makes it possible to carry out both basic stages of mass check-ups. Such a laboratory was opened in Moscow in 1972 as part of the system of public health bodies with direct participation of the Scientific Research Institute of Pediatrics and Children's Surgery. The laboratory was entrusted with the following tasks:

(1) To work out and introduce the programme of mass screening of the children's population, starting with newborn infants;

(2) to introduce the latest methods of analytical biochemistry to the practices of public health services;

(3) to examine children and their nearest relatives applying to the medico-genetics laboratory;

(4) to carry out speedy biochemical investigation in urgent cases;

(5) to develop and introduce standard methods of biochemical diagnostics for Moscow biochemical laboratories, and to exercise control over the quality of biochemical investigations in various laboratories.

Research for the screening programmes occupies the main place in the activities of the laboratory. Microbiological methods, based on the use of auxotrophic mutants of *Bacillus coli*, are used in the first stage of checking for anomalies of amino-acid metabolism. These methods differ from the Guthrie method, widespread in the United States and Europe, which utilises the addition of chemical inhibitors of microorganism growth to the nutrient medium. There is no need for such inhibitors in the application of auxotrophic mutants, which makes the auxotrophic methods more economical but no less informative. The growth of microorganism in the medium to which the blood of the child under investigation is added indicates increased concentration of the corresponding component. Just as with Guthrie method, the blood of a child in the maternity home is taken onto filter paper and is sent to the centralised laboratory by post. Discs are made there by a special device and introduced into media with microorganisms. In each case of a positive result in this first stage the parents are invited with the child to a specially organised medicogenetics centre for clinical and biochemical investigations, all done at State expense.

General (mass) and selective screenings are carried out in the USSR at present as follows:

A. Mass Screening

1. Phenylketonuria and histidinemia

Microbiological tests are used in the first stage; high-voltage electrophoresis of the free amino-acids of blood plasma and urine and the investigation of amino-acids spectrum on an automatic analyser are used in the second stage. Where diagnostic difficulties occur with suspected phenylketonuria, the alpha ketoacids of urine are studied. To diagnose histidinemia thin-layer chromotography on silica gel is used and urocanic acid and the imidazole compounds determined in sweat and urine, as well as the histidase activity in the child's skin. This programme is taken care of by one doctor and three laboratory assistants.

2. **Mucoviscidosis**

For the first stage the meconium is tested for albumin. The colour reaction of soluble proteins with bromophenol blue is used. Practice has shown that this reaction gives a high percentage of false positive results. In view of this it is now being checked by an immunochemical method (immunodiffusion in agar against antialbumin).

The second stage: after three or four months the parents are invited with the child to the medico-genetics centre to determine chloride content in sweat (after pylocarpine stimulation) and blood is taken for determining isoenzymes of the serum amylase. This programme is carried out by one doctor and two laboratory assistants.

Mass screening programmes carried out in Moscow cover about 80,000 newborn infants a year. Mass check-ups of newborn infants for detecting phenylketonuria are carried out in Leningrad. Selective screening programmes are carried out in other large Soviet cities.

B. Selective Screening

1. **Galactosemia**

Checked for this metabolic anomaly are children kept in the Departments of the Pathology of Newborn Babies because of protracted jaundice and hepatomegaly, as well as older children who, the medico-genetics consultation center suspects, may have genetic disorders.

The first stage includes the microbiological test for galactose in blood using a mutant defective for the key enzyme in galactose metabolism—galactoso-1-phosphate-uridyl-transferase. Benedict's test on urine is done at the same time.

In the second stage the galactose content of blood and urine is detected by thin-layer chromotography of mono- and di-saccharides on silica gel; the activity of galactose-1-phosphate-uridyl-transferase in erythrocytes is determined by two methods: (a) using an auxotrophic mutant of galactotransferases. Erythrocytes are incubated with ATP, galactose and UDP-glucose. The presence of the zone of microbial growth after incubation points to the satisfactory activity of enzymes in galactose metabolism; (b) incubation of the child's erythrocytes with galactose in anaerobic conditions (atmosphere N_2 and CO_2) with subsequent determination of lactates in the incubation medium by photometry. With the presence of an enzymatic block the essential increase of lactic acid is not seen. The programme is taken care of by one doctor and one laboratory assistant.

2. **Respiratory distress—newborn infants' syndrome**

In the first stage amniotic fluid is tested for air bubble stability under various concentrations of ethyl alcohol.

In the second stage thin-layer chromotography on silica gel is used to determine the correlation of lecithin and sphyngomyelin in the amniotic fluid and the child's blood. The tests are carried out by two doctors and three laboratory assistants.

3. **Hyperlipoproteinemia**

No biochemical methods are used in the first stage as yet, but school children with high arterial blood pressure, detected through mass check-ups, are to be examined. Lipidograms of blood serum (thin layer chromotography on silica gel), as well as fractionation of lipoproteins, are studied by disc electrophoresis in polyacrylamide. The programme is taken care of by a postgraduate and a laboratory assistant.

4. **Cystinuria**

Must be checked for in children with durable changes of urine sediment. To detect increased cystine excretion an iodine-azide test is used in the first stage (with cyanide/nitroprussic test used more rarely); renal clearance of cystine and diaminocarboxylic acids, arginine, ornithine and citrulline, is determined in the second stage. High-voltage electrophoresis of the free amino-acids of blood and urine is used for this purpose, with subsequent chromotagrophy of amino acids.

5. **Oxaluria**

Stable calcium oxalate crystalluria, combined with changes in urine sediment, is an indication for checking for this disorder. Quantitative determination of oxalates and glyoxylic acid in urine is carried out in the second stage by spectrophotometric methods. The cystinuria-oxaluria programme is taken care of by one doctor and one laboratory assistant.

6. **Pyridoxin dependent conditions** (Knapp-Komrower syndrome, Tad syndrome, cystathioninuria)

Under test is a microbiological method of semi-quantitative determination of pyridoxine. Specially tested are children whose urine after high-voltage electrophoresis shows the bright fluorescence of tryptophan metabolites (kynurenine and its derivatives). The latter are quantitatively determined by thin-layer chromotography on silica gel before and after a peroral load with tryptophan (50-70 mg/kg).

7. The investigation of children for the pathology of the renal transport of imino acids (proline, oxyproline) and glycine is done by microbiological tests, and high-voltage electrophoresis of the imino acids of blood and urine (done by a doctor and a laboratory assistant).

The study of the genealogical tree is a necessity in the investigation of children in screening programmes. At present the laboratory searches for indications of disease such as hereditary nephritis and immunodeficient conditions.

Standard International Units in Soil Science

M. A. Wilson and R. T. Baker

It would seem that Standard International Units (S.I.) are to be adopted throughout the world in many branches of science and technology and as the official standard of weights and measures. In New Zealand a continuous conversion from Imperial and other units to the S.I. system has already begun and in some fields is well advanced. Within industry[1, 2] and our university[2] and technical institutes[3], S.I. units are being adopted for the measurement of chemical quantities. However some objections have been raised to S.I. units both in local[4, 5] and other journals[6]. Some scientists consider the problem of conversion a real one. In particular, although there have been some moves towards change[7, 8], soil scientists both locally and internationally have used and will probably continue to use non S.I. units for some time[4, 5]. Thus milliequivalent percent (i.e. per 100 grams of soil) has been used to express the concentration of certain ions in the soil environment, rather than moles or millimoles per kilogram.

We have followed with interest the arguments of soil scientists locally[4,5,7,9] concerning the introduction of standard international (S.I.) units and thought these problems might be of interest to chemists in general. A conversion from milliequivalents percent to equivalents per kilogram of soil presents little problem because it involves only a conversion factor of 10^{-2}, and of course the number of equivalents present can be readily converted to the number of moles present by use of the ion charge number or similar conversion factor. However, one of the major problems seems to be to find a way to express the cation exchange capacity (C.E.C.) of a soil. The cation exchange capacity of a soil is an arbitrary concept with a number of definitions depending on the procedure by which it is determined. For example, some traditional procedures[8, 10] for determining C.E.C. involve displacement of the cations held by the soil by ammonium ions, and then displacement of these cations by either sodium ions or by distillation with magnesium oxide and then titration. Other methods are also in use, but if the method is standardised the procedure should measure the total capacity of the soil to hold cations in an exchangeable form. Dominant ions include aluminium, hydrogen, potassium, magnesium, calcium and sodium. Normally the C.E.C. of a soil has been expressed in the units 'milliequivalents percent' but as others[9] have pointed out it is strictly more correct chemically to state the species exchanged and the eluant used e.g. equivalents or moles of ammonium ion by sodium ions, because of the arbitrary nature of the concept. This is important because only those sites which ammonium and sodium are capable of displacing ions from are under consideration. The ability of a soil to exchange cations for ammonium ions or other cations may depend on a number of intrinsic properties of its constituent mineral and organic matter. Thus the C.E.C. of a soil might vary with the nature of the eluant, the species exchanged, or with pH. Also in use is the similar term, total exchangeable bases (T.E.B.) which usually represents the total exchangeable alkali and alkaline earths but not aluminium and hydrogen. This has also been expressed in terms of milliequivalents percent. It can be determined from the initial exchanged eluate by summation from the estimation of the amounts of individual ions present, or by back titration of an acidic solution of the residual ash after pyrolysis of organic matter and removal of ammonia. One advantage of expressing T.E.B. and the proportion of individual cations in milliequivalents may be because the former can be equated to the sum of the amounts of the latter (Equation 1):

Eq. 1

$$\text{T.E.B.} = [Ca^{2+}] + [Mg^{2+}] + [K^{+}] + [Na^{+}] \text{ etc.}$$

(Lecturers in Chemistry, Lincoln University College, Canterbury.)

It can be argued that this quantity should be retained in its present form, i.e. that it is the proportion of exchange sites occupied by these cations which is significant, so to express this quantity if the individual cations are recorded in moles per kilogram of soil Equation 2 must be used:

Eq. 2 T.E.B. =
$$2[Ca^{2+}] + 2[Mg^{2+}] + [K^{+}] + [Na^{+}] \text{ etc.}$$

Thus these values in moles per kilogram of soil are multiplied by the charge number because divalent ions are displaced by twice the amount of ammonium ions used in the determination (Equation 3):

Eq. 3 $2NH_4^+ + R^{2-}\,M^{2+} \rightarrow M^{2+} + R^{2-}\,(NH_4^+)_2$
(where R = the exchange site)

The terms, 'total exchangeable bases' and 'cation exchange capacity' are now meaningless when the concentration of individual ions are expressed as moles per kilogram, unless expressed in terms of the chemical procedure used. Thus C.E.C. becomes moles of ammonium ions absorbed per kilogram of soil and T.E.B. becomes moles of protons neutralised by bases displaced by ammonium ions per kilogram of soil. They are somewhat awkward expressions. The term moles of positive charge has been suggested[7] but has not been liked by others[9]. Percentage base saturation (Equation 4):

Eq. 4 $$\% \text{ B.S.} = \frac{\text{T.E.B.}}{\text{C.E.C.}} \times 100$$

causes smaller problems since it is without units and becomes unchanged in value no matter what units are used if T.E.B. and C.E.C. retain their original meanings. The name remains meaningful if considered as the percentage of exchange sites occupied by 'base' ions.

Equivalents have been found to be of use in other allied fields as well. In water analysis it is often desirable to balance cations and anions. In studies of plant uptake of elements it has often been observed that there is a ratio between the sum of the cations (calcium, magnesium, potassium, and sodium in milliequivalents percent) and anions (nitrogen, sulphur, phosphorous, chlorine) taken up by the plant. Other problems encountered by analytical chemists have been described[11] and it is interesting to note that a recent *ad hoc* IUPAC working group has recommended that the terms equivalent and normality be retained[11].

On the other hand, the term equivalent lost favour in many branches of chemistry long before the introduction of S.I. units because it is not applicable on a molecular scale. When equal numbers of molecules are present equal numbers of moles are present, not necessarily equal numbers of equivalents. Plant biochemistry and thus soil fertility is ultimately on the ionic and molecular scale involving unimolecular or bimolecular pathways so there is every reason to measure quantity in terms of the number of molecules present. Thus when describing a system as having equal equivalents of potassium and calcium ions present we are double weighing the real number of calcium ions present, so an S.I. system is more logical. In chemical studies some of the last bastions of equivalents were some aspects of electrochemistry. In this area of study because one equivalent of material was deposited by one Faraday (96,500 coulombs) of electricity the equivalent unit was retained until recently for a whole range of conductivity functions and constants. In some texts all this has now been scrapped[2, 12, 13] and a new set of values based on S.I. units has been introduced. In the writers' opinion this has greatly simplified the teaching of this subject, again largely because the association with the molecular level becomes obvious, but the awkwardness of reintroducing equivalents for applied studies still exists. We would be interested in hearing from others who have encountered similar problems.

We thank Professor T. Walker and Mr. A. F. R. Adams for helpful advice.

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AUCKLAND BRANCH DIAMOND JUBILEE 1975

The Branch celebrated its Diamond Jubilee with a Dinner attended by about eighty people at the Waipuna Lodge Motel on 10 July. Dr A. F. Wilson acted as Master of Ceremonies, the Chairman, Mr A. C. Kennett delivered his Chairman's Address entitled "50 years and on" and proposed a toast to the Auckland Branch and Mr O. H. Keys replied on behalf of the Branch. The Chairman, on behalf of the Auckland Branch, then presented a plaque to the memory of the late Emeritus Professor L. H. Briggs to the Head of the Chemistry Department of Auckland University, Professor P. B. D. de la Mare. The plaque is to be mounted in the Chemistry Department.

To publicise its Diamond Jubilee, the Branch mounted a display in the display cabinet of the Auckland Savings Bank for the month of July. This took the form of a large insignia of the Institute of Chemistry, announcing it was our Diamond Jubilee and displaying the first page of the original Minute Book of the Auckland Chemical Society. The Institute motto was spelled out in English, and books, a balance and a retort of the early 1900s were contrasted with modern textbooks, the most modern digital analytical balance, and quickfit distillation equipment.

The Auckland Chemical Society 1925-1934

To Commemorate the Fiftieth Anniversary of the Founding of the Auckland Chemical Society

By R. W. Oliff, M.Sc., Ph.D., M.N.Z.I.C.

"By the invitation of Professor Worley a meeting was held at his residence on Saturday, 21st March, 1925, to consider the desirability of inaugurating a Chemical Society in Auckland."

So begins the first Minute of the Auckland Chemical Society. Present at the meeting were: Mrs. K. Short, Prof. F. P. Worsley, Messrs A. H. Bowell, W. F. Short, K. M. Griffin, R. H. Inder, A. V. Johnson, F. H. V. Fielder, J. R. Hosking, Turner, Leonard, J. C. Andrews.

After general discussion the following motion was passed (Moved Prof. Worley, seconded Mr. Short) "That a Society, to be known as the Auckland Chemical Society, be formed."

A temporary Committee, with powers to draw up a provisional constitution, was elected. These were: President, Prof. Worley, Hon. Sec./Treasurer, Mr. Short, Committee, Messrs Bowell, Hosking, Grffiin.

The draft rules of the Society were considered at the first full meeting of the Society held on Tuesday, 21st April, 1925, in the Chemistry Lecture Theatre, Auckland University College, and were adopted with a few amendments.

The following Officers were then elected as the first full Committee of the Auckland Chemical Society: President, Prof. F. P. Worley, Vice-President, Mr. K. M. Griffin, Hon. Sec./Treasurer, Mr. W. F. Short, Committee: Messrs A. H. Bowell, J. R. Hosking, T. E. Perks, P. R. Parr.

The President gave the Inaugural Address to the Society on 2nd June, 1925, when he spoke on "Chemical Research at A.U.C., 1883-1925." In it he described the work done by the 29 Honours students who had been in the Department in that period. Indeed the description of current research in the Chemistry Department formed a significant part of meetings until recent years.

Regular scientific meetings were held from then on, with an even balance between academic and applied chemistry. One feature of these early meetings was the announcement of important scientific discoveries and demonstrations of new equipment. For example at one meeting Prof. Worley announced the reported discovery of two new elements, Masurium (43) and Rhenium (75) and pointed out the relationships of these elements to other members of the Periodic Table.

Space does not allow the reporting of all the meetings held by the Society but a few of interest can be mentioned.

Mr. K. M. Griffin read a paper entitled "The Analysis of Milk" (7 July 1925) in which he described the methods used and the results obtained. He pointed out that one of the main problems in milk from some areas was the presence of dirt in the milk, and he emphasised the necessity of educating the producers in the handling of clean milk. The lecture was "profusely illustrated throughout with experiments."

On 28th July, 1926, the Minutes recorded, "The President announced that Mr. J. C. Andrews had met with an accident and was therefore unable to deliver his address as proposed." The meeting then took the form of a discussion on the transmutation of the elements, including the transmutation of mercury to gold. This had been shown fairly conclusively to be due to small amounts of gold in the apparatus.

On 19th July, 1927, Dr. H. E. Annett spoke on "Recent Work on the Opium Poppy" in which he described the collection of opium from the poppy capsules and a new colorimetric determination of the morphine content. This technique enables 60 morphine estimates to be made in one day.

"The Chemistry of Linseed Oil" was the subject of an address by Mr P. R. Parr (10 Oct., 1927) where he dealt with the extraction, composition and uses of linseed oil. He described the drying of linseed oil paints and the effects of additives which could reduce the drying time from 72 hours

(Chemistry Dept., University of Auckland).

a circular letter was sent to Chemists throughout New Zealand. Replies were received from Otago and Wellington. The first of these reported the formation of a Chemical Society associated with the University of Otago, and the second that the Guy Fawkes night the meeting was postponed until the beginning of the following season."

"The Determination of Hydrogen Ion Concentration" formed the subject of a panel discussion on 22 September, 1932, the speakers being Prof. F. P. Worley, Mr. L. S. Spackman and Mr. K. M. Griffin. Various methods were described and demonstrated including the new instrument belonging to the Chemistry Department.

On June 28, 1934, Dr. T. J. Hughes presented a "lantern lecture" on "The Filaria Parasite and Leprosy." His lecture covered the diseases elephantiasis, leprosy and plague, and the efforts being made to prevent their entry into New Zealand.

The last scientific meeting of the Society was on October 30th, 1934, and took the form of two reports on Research in the Chemistry Department, the speakers being Dr. L. H. Briggs and Dr. R. A. Robinson.

Membership, Finances, etc.

The annual subscription to the Society was originally set at 5/- and remained at this figure until the Society was dissolved. However at the 1931 A.G.M. the following motion was carried.

"That all those members of the Auckland Chemical Society who had been financial during the past two years be exempt from this year's subscription to the Society."

The Society's finances flourished until its final year when a loss of 26/- on the year's operations caused the Society to decide that "rather than raise the subscription the branch should practice rigid economy." At this time the balance stood at about £20.

Few Balance Sheets are available for the Society, but a typical one for 1929, reads as follows:

Expenditure

Postage and stationery	16.0
Advertisements	6.6
Refreshments	2. 0.6
Balance 1929	13.14.5
	£16.17.5

Income

Balance 1928	8. 6.4
Subscriptions	7.10.0
Entrance Fees	5.0
Interest	16.1
	£16.17.5

The Society's membership of 26 in 1926 rose to 34 the following year, remaining at about this figure for the rest of its life. As in more recent times attendances at meetings caused disappointment to the Committee. The 1927 Annual Report expresses regret that "barely half . . . have attended meetings during the past year." Similar comments were made in 1927 and 1928 and in the latter year "or have paid their subscriptions" was added. The difficulties of Secretaries and Treasurers have not changed over the years!

The 1930 Annual Report shows an improvement when it states, "As a result of a circular sent to members in arrears 29 subscriptions we obtained from 18 members and the balance after the year's operations is £19.8.2."

Social Activities

The first Annual Report includes the following "The 'Chemical Teas' which have followed the meetings have been much appreciated and we are indebted to the President for his hospitality in providing these most essential aids to the social life of the Society."

The custom of the President providing refreshments did not last long however, and they were later provided out of Society funds. But the institution of 'Chemical teas' remained, and I can well remember the indignation of several older members when, as an economy measure, they were reduced to tea and biscuits. The replacement of 'chemical teas' by pre-meeting refreshments in recent years has removed a long-standing tradition.

The Annual Dinner was inaugurated in 1928, being held at the Hotel Auckland. Over the years this dinner has had a chequered career but seems to be firmly established again.

Formation of the New Zealand Institute of Chemistry

From the early days of the Auckland Chemical Society the matters of the Registration of Professional Chemists and the formation of a national Chemical Society formed a major part of the business of the Society.

At a dinner held on 12 November, 1928, a discussion was held on the matter of registration. The opportunity was taken during the Conference of the New Zealand Institute (now the Royal Society of New Zealand) being held in Auckland in January 1929 to discuss the matter with chemists from outside Auckland. This meeting, thought to be the largest meeting of Chemists ever held in New Zealand up to that time, adopted two resolutions:

(1) That it would be to the advantage of the manufacturing industries in N.Z., to Chemical Science, to the status of the Chemical Profession, and would be a protection to the public, if some form of registration of professional Chemists were effected.

(2) That it is desirable as soon as possible to form a New Zealand Chemical Society.

The Society was asked to communicate with representative chemists in other centres with a view to facilitate the foundation of Chemical Societies in the chief centres and ultimately the formation of a New Zealand Chemical Society. This instruction was carried out on 12 July, 1929, when

to 4½ hours (metal oxides) or increase it to over 2 years (beta-naphthol).

A meeting of the Society was called for November 5th, 1931, but as the Minutes record "owing to the small attendance due to the evening being Wellington Chemical Society had become a Section of the Wellington Philosophical Society some years previously. Both letters expressed interest in the formation of national society.

At the 1930 Annual General Meeting a Committee consisting of Drs Shepherd and Lynch, Prof. Worley, Messrs Frieberg and Griffin was set up to draft a constitution for the proposed N.Z. Chemical Society. The meeting was also of the opinion that Prof. W. P. Evans (Otago) should be the first President.

Before the Auckland Committee could report a letter was received from Prof. Denham (Canterbury) on the formation of a N.Z. Chemical Society and enclosing a draft Constitution. A report was also received from Otago. It was decided that:

(1) Copies of the draft be sent to regular members of the Auckland Chemical Society, and to other Chemists in Auckland.

(2) That the Committee appointed at the A.G.M. be asked to prepare a criticism of the scheme, and to call a meeting of Auckland Chemists.

The presence in Wellington of Mr. K. M. Griffin on 30 June 1930, enabled him to attend a meeting of Wellington Chemists called to discuss the formation of a N.Z. Chemical Society. From this meeting came two resolutions:

(1) That the time is now ripe for the formation of a New Zealand Organisation to embrace in its ranks all duly qualified Chemists.

(2) That Chemists in New Zealand seek registration and that a Committee of five be set up to confer with Dr. Denham.

The Auckland Committee reported back to the Auckland Chemical Society on 23 July, 1930, that they had met twice to consider the draft Constitution and proposed a number of amendments. They recommended that a N.Z. Institute be set up on the lines of the Australian Chemical Institute.

At the suggestion of the Auckland Chemical Society the opportunity was taken of the presence in Wellington of three Chemistry Professors, for a meeting of the Academic Board of the University of New Zealand, to hold a further meeting (7 Nov., 1930) on the formation of a N.Z. Chemical Institute. I have not been able to trace any reason why the name was changed from N.Z. Chemical Society to N.Z. Institute of Chemistry.

Present at this meeting were: Prof. W. P. Evans in the Chair, Mr. W. Donovan as Secretary, Profs. Denham, Easterfield, Inglis and Worley, Messrs B. C. Aston, G. A. Lawrence, A. D. Monro and P. R. Parr. Apologies were received from Dr H. E. Annett and W. R. Mummery.

Well attended meetings in all four centres had been overwhelmingly in favour of the formation of a Society that would include in its membership all well-trained chemical workers in New Zealand. The meeting unanimously resolved that:

"A New Zealand Institute of Chemistry be formed and that those present constitute themselves a provisional committee of the Institute."

So the N.Z.I.C. was formed and November, 1930, is taken as the date of its inauguration. But it had its teething troubles. The Auckland Chemical Society felt that all of its Members should automatically become Members of the N.Z.I.C., but the Council of the N.Z.I.C. set firm qualification requirements which not all Auckland members could meet. It was several years before this matter was finally resolved.

At the 1931 A.G.M. of the Auckland Chemical Society it was decided that the Society henceforth be known as "The Auckland Chemical Society and Auckland Branch of the New Zealand Institute of Chemistry." This title was retained until 1934 when at the A.G.M. the words "Auckland Chemical Society" was deleted from the title. In speaking to the motion Dr. Briggs said that the Society had now served its purpose and deserved a decent burial.

But the Auckland Chemical Society was not quite dead for in 1949 we find a move to reinstate the name in the title of the branch as a protest at the methods used by the Council in the election of some of its Officers. The motion was lost, but the meeting expressed the view that it was "laudable but inopportune." And so the Auckland Chemical Society was finally laid to rest.

Listed below are:
Presidents of the Auckland Chemical Society 1925-30;
Chairmen of the Auckland Branch, N.Z.I.C. and of the Auckland Chemical Society, 1931-1933;
Chairmen of the Auckland Branch, N.Z.I.C. 1934-

Note: The year given is the year of election.

1925	Prof. F. P. Worley
1926	Prof. F. P. Worley
1927	Prof. F. P. Worley
1928	Prof. F. P. Worley
1929	Dr. F. G. Shepheard
1930	Dr. F. G. Shepheard
1931	Prof. F. P. Worley
1932	Prof. F. P. Worley
1933	Mr. S. I. Crookes
1934	Mr. A. J. Parker
1935	Dr. J. C. Andrews
1936	Dr. J. C. Andrews
1937	Mr. P. R. Parr
1938	Mr. P. R. Parr
1939	Mr. F. H. Y. Fielder
1940	Mr. F. H. V. Fielder
1941	Dr. L. H. Briggs
1942	Dr. L. H. Briggs
1943	Mr. K. M. Griffin
1944	Mr. K. M. Griffin
1945	Mr. R. H. J. Stansfield
1946	Mr. R. H. J. Stansfield
1947	Mr. S. G. Brooker
1948	Mr. S. G. Brooker

1949 Mr. P. R. Parr
1950 Mr. A. W. Mackney
1951 Mr. G. S. Lambert
1952 Mr. G. S. Lambert
1953 Mr. J. Ricketts
1954 Mr. J. Ricketts
1955 Mr. W. E. Russell
1956 Mr. W. E. Russell
1957 Dr A. L. Odell
1959 Dr. H. Bloom
1960 Prof. D. R. Llewellyn
1961 Prof. D. R. Llewellyn
1962 Mr. P. J. Gallaher
1963 Mr. P. J. Gallaher
1964 Dr. G. A. Nicholls
1965 Dr. G. A. Nicholls/Mr. K. E. Seal
1966 Mr. K. E. Seal
1967 Dr. D. F. Nelson
1968 Prof. P. B. D. de la Mare
1969 Dr. J. Rogers
1970 Mr. J. C. Hawthorn
1971 Ass. Prof. G. A. Wright
1972 Mr. R. H. Hopgood
1973 Mr. G. J. Fletcher
1974 Mr. A. C. Kennett

Dr. Nicholls resigned in Jan., 1966, to take up an overseas appointment.

Conclusions Drawn From NZIC Manpower Surveys

By W. S. Simpson and Ward T. Robinson Report prepared for NZIC Council

During 1970, under the chairmanship of the Instituet President Professor J. Vaughan, a committee was set up to collect information on the likely needs in New Zealand for graduates in chemistry, biochemistry and chemical engineering, and to compare these with the anticipated production of graduates in those fields. Accordingly a questionnaire was sent to all organisations likely to employ chemists. The returns were analysed by one of the authors (W. R.), and a short summary of his report was presented to Council in August 1971. It was felt that this pilot survey was likely to be incomplete in coverage, so a second one was planned in September, 1972, by the Manpower Survey Committee convened by Dr P. Foster. Institute branches were to circulate the questionnaire, collate and follow up the returns so as to produce as complete coverage as possible. In the event the returns covered 1204 chemists compared to 1249 in the earlier survey. The questions in the second survey were much more detailed than the first, which focused entirely on supply versus demand considerations. Its objective was to determine the characteristics of the existing population of chemists rather than an attempt to measure supply and demand. Therefore the second survey allowed calculation of many statistical tables by the Manpower Committee, and in September 1974, these were passed back to Dr. Robinson for comments. Several others have also examined the tables, and a preliminary report was prepared by the present authors for the Council meeting in June, 1975. Branch Committees and others have been invited to comment before preparing the present paper.

In view of the actual numbers revealed in the surveys, a general comment on accuracy, or lack of it, is appropriate. The earlier one was filled in by employers, not individual chemists, so we rely on the accuracy of their records, and some employers may not have been contacted. The later survey is probably thorough in the case of universities, schools and major laboratories (as was the first), but will not include those abroad during the time of the survey, and its major deficiency is likely to be in returns from chemists working in industry.

Graduate Supply and Demand

Cumulative statistics have recently become available from N.Z. universities for the years 1970-74 which show that there has been a marked decline in the rate of graduation of chemists.[1] Total first year university enrolments have varied only 4% over the past four years and are currently at 1971 levels, while first year science enrolments (which exclude intermediates for professional degrees) have dropped 19% over the period. These figures differ greatly from the upper and lower limit projections of cumulative supply made in the 1971 report, shown in Figure 1, which assumed continuing growth of University Departments following the pattern of the 1960's.

The second survey did not provide any new information regarding future demand, and to illustrate the difficulties of prediction in this area we quote a pasage from the 1971 report;

". . . of 980 graduates supplied in the five year period 1966-1970 only 449 have been accounted for in our survey. There seems to have been a 43% loss to employment with no chemical connection. This high figure should, of itself, cause concern in the profession. Though many young graduates may emigrate temporarily or permanently, we feel it is more likely these trained chemists are moving in large numbers to other jobs within New Zealand. Such movements may become very necessary to close the very large gaps evident between supply and demand. Indeed it would take application of this 43% correction factor across the board, together with an unpredicted very large increase in demand in the secondary

Fig. 1

Totals for all graduates

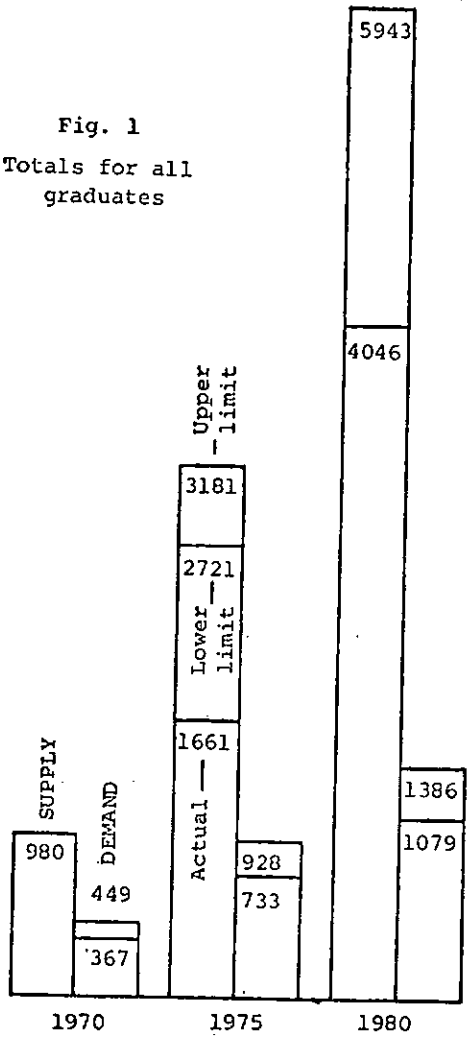


Fig. 2

Pass degrees or equivalent

The lower demand figures on the top graphs exclude the secondary teaching profession.

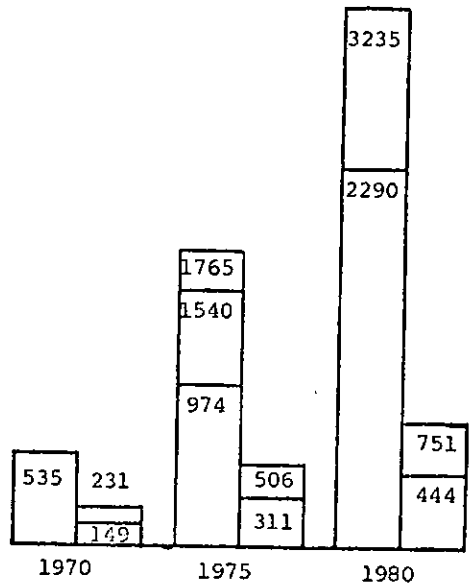


Fig. 3

Masters and Honours degrees

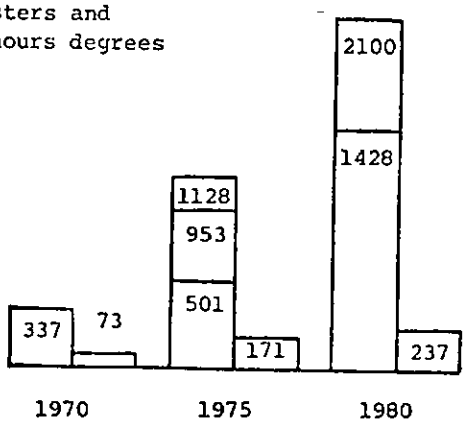
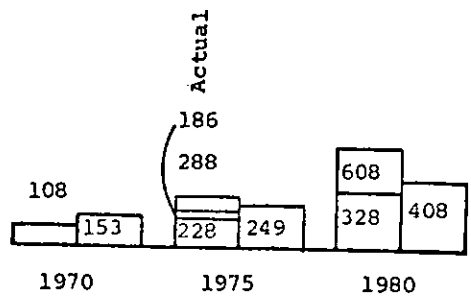


Fig. 4

Ph.D. degrees



Cumulative supply (left) and demand (right) estimates at 5-yearly intervals for chemists graduating from all New Zealand universities since 1965. All graphs are on the same scale

cluded in the survey it can fairly be said they are teaching profession to make our survey figures even look like balancing."

Since the second survey produced an unexpectedly small number of completed returns, it is reasonable to assume that at least 43% of recently graduated chemists continue to find employment outside recognised scientific areas.

A survey carried out on Leeds graduates and referred to in a recent U.K. Manpower Paper[2] showed that between 1964 and 1969 the proportion of first degree graduates in chemistry taking "unrelated" jobs increased from 26.6 to 39.4%, and continuance of this trend into the mid '70s would result in a current figure of the order of 43% as well.

Other sources[3] show the Technical Institutes are producing 50 to 60 N.Z.C.S. graduates in chemistry each year, or a cumulative 275 in the five year period up to the end of 1975, and many of these are now competing with B.Sc. Pass graduates for the same jobs.[4] Again the U.K. report is relevant, and it suggests that employers have neither prejudice against nor preference for those obtaining a polytechnic qualification, e.g., U.K. personnel officers when polled believed there is little difference between C.N.A.A. and University science and engineering qualifications. The trends showed an increasing preference by employers for the C.N.A.A. graduates, so that by 1971 their starting pay equalled that for graduates. In New Zealand, N.Z.C.S. graduates in Government employment currently enjoy a salary advantage over B.Sc. Pass graduates, but whether this fact has had a bearing on employers' recent recruitment patterns in New Zealand is not known.

Inferences from the 1972 Manpower Survey

1. Age distributions and year first employed.

Of those surveyed, approximately 220 graduates, of all classes, entered the profession in each of the three quinquennia preceding this survey. For comparison, the 1970 survey showed 289 and 419 for the two previous quinquennia and predicted a further 409 by 1975. During the latter quinquennium the universities produced 1661 male chemistry graduates. No matter which survey is the more reliable, the large loss of chemists to other employment or emigration is clearly established.

2. Highest qualification

75% of the highest qualification of N.Z. chemists are obtained in this country, a further 17.4% obtained theirs in the U.K. and 3.3% in Australia. The overall ratio of Pass: Masters or Honours: Ph.D. is 11:7:6 and has not changed much for 40 years. In the opinion of the authors the proportion of Ph.D's may be falling at the present time because of a world-wide lack of suitable employment opportunities.

Degree Specialisation and Job Specialisation

The data suggest considerable diversification of interests, particularly shown by graduates in Organic and Physical Chemistry later describing their special fields as Biochemistry and Chemical Engineering respectively. It appears that New Zealand imports a significant number of Ph.D. biochemists from the U.K. and U.S.A. In the light of this fact there would appear to be opportunity for reasonable numbers of home grown biochemistry graduates at this level.

Twice as many people describe themselves as Chemical Engineers as are formally qualified in this discipline. A recent independent survey[5] concluded "the estimates made for future requirements for chemical engineers were virtually correct" in forecasting the demand over the period 1970-73. More information is needed to illuminate the respective role of B.E. (Chem) and Chemistry graduates and competition between them for some classes of employment, but it is plain that many chemists by choice or necessity adapt successfully to a career in chemical engineering and complement the supply of graduates in that discipline.

Major Function

The great majority of chemists teach, administer or carry out research. Half our B.Sc. graduates go into teaching and most of the remainder take jobs in industry. Ph.D. graduates are concentrated in universities, government departments, and research associations.

Sex

12% of female chemists hold a Ph.D. degree compared to 25% of males. Over half the females are employed as teachers, and the age group distribution shows the expected losses associated with motherhood. There is significant evidence of a return to employment in the 40-45 age group, and this modern trend should be maintained in the 1970's and increased in the 1980's for both social and demographic reasons. The U.K. Manpower Paper found similar trends, which led them to predict a 29% increase in academically qualified females over 1971-76 compared with only 21% for males.

Age Structure in the Profession

The only conspicuous feature of the age structure is the rapid decrease in the number of practising chemists in each successive age group over 40 years. In the next 20 years only 5.4% of the survey sample may reach retirement age.

Summary and Conclusions

Perhaps the major shortcoming of the Manpower Survey is the difficulty in assessing the number of chemists who have not been included. Nevertheless the major laboratories, universities and school-teachers appear to have been well covered,

in addition to the Institute membership in industry, and a small scattering of others found by the enterprise of Branch Committees. Of those not in- either employed in ones and twos in small industrial chemistry laboratories and not located by survey officers, or they have emigrated in numbers far exceeding compensating imports, or they no longer practise chemistry.

The U.K. survey shows many general similarities to this one with respect to unaccounted numbers lost to non-chemical employment, the increase in work activity of female chemists after child-rearing, and competition with Technical Institute certificate holders for jobs, which suggests these trends are general. More particularly, the predictions of greatly increased numbers of employment opportunities *and* even more rapid escalation in numbers graduating, such as were made around 1970, both in the U.K. and here, have not materialised. Declining employment prospects have clearly curbed the output of graduate chemists and possibly slightly increased the already large proportion going to "unrelated" employment; this proportion probably exceeds 40%.

The Institute Salary Surveys provide some complementary information on the characteristics of the population of chemists. From the most recent such Survey[6] the proportion of chemists nearing retiring age is somewhat higher than was found in the Manpower Survey. However, the sample size in the latter is considerably larger (1204 *vs* 750) and the three years interval between the surveys would significantly alter the age distribution.

A lack of some types of graduates may be inferred from the survey, although some reservations must exist about the accuracy of job descriptions particularly for biochemists and chemical engineers.

In retrospect it would appear that as a means of predictive planning, the forms of Manpower Survey attempted so far have severe limitations. The current job market undoubtedly will continue to have a major influence on the number of students studying chemistry.

The authors are only too well aware of these limitations, and also of the fact that such a Survey could, itself, exert too strong an influence on the career considerations of students and their advisors.

Footnote: The authors have approximately 60 statistical tables derived from the original data. These are available on request to anyone interested.

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Review on Toxic Incidents

By I. R. C. McDonald

As an organic chemist who pipetted acetic acid as a student, commonly used benzene as an exraction solvent, benzidine as a spray reagent for pinosylvin, and 40 percent phenol solutions as a chromatographic solvent for amino acid separations, I am perhaps not the most suitable person to discuss the dangers of chemical spillages. I do not claim to be a toxicologist and I have the greatest difficulty in assessing the acute dangers that may exist between those chemical concentrations thought to be safe and the concentrations known to be dangerous. This paper will consider this intermediate situation which is likely to occur at a spillage site.

The safe concentrations are exemplified by the latest threshold limit values published by the American Conference of Governmental Industrial Hygienists, but even these are being constantly reviewed, and I am sure no chemist would now accept the revised 1971 value for vinyl chloride monomer of 200 ppm. At the other extreme many compounds have known LD_{50} values or the considered lethal dose for 50 percent of the population.

To illustrate my dilemma I would like first to consider two quite different compounds, carbon monoxide and styrene monomer.

The following effects of carbon monoxide inhalation are well documented[1]:

Blood Saturation	CO concentration in air	Effects
70%	4000 ppm	rapidly fatal
60-90%	1000 ppm	unconscious in 1 hour—fatal 4 hours
20%	500 ppm	minimal symptoms after 1 hour
	100 ppm	TLV (1961)
	50 ppm	TLV (1971)

Assuming an average inhalation of 20 litres per minute these concentrations and times can be expressed as mg CO inhaled as follows:—

1000 ppm	unconscious 1374 mg, fatal 5496 mg
500 ppm	minimal 687 mg
100 ppm	safe 1099 mg
50 ppm	safe 550 mg

Thus the body is apparently unaffected by 1100 mg of CO breathed over an 8-hour period but will become unconscious after inhaling 1374 mg CO in 1 hour. This is not surprising as the mechanism for CO poisoning is well understood and symptoms are only found at blood saturation levels above 40 percent. Clearly carboxyhemoglobin converts rapidly to oxyhemoglobin and CO could therefore be considered to have a short half-life in the body. Thus chronic poisoning in the sense of an irreversible accumulation of carbon monoxide in the body does not occur.

Styrene monomer[2] is another chemical that may be commonly encountered which has a TVL of 100 ppm in 1961 and is unchanged in 1971.

Styrene concentrations in air

10,000 ppm	Dangerous to animals 30-60 mins.
2,500 ppm	Dangerous to animals 8 hours.
1,300 ppm	No serious effect in 8 hours.
100 ppm	TLV (1971)

The actual weight of styrene inhaled during these periods at the concentrations are:

10,000 ppm	Dangerous 25,500 mg-51,000 mg
2,500 ppm	Dangerous 102,000 mg
1,300 ppm	No serious effect 53,040 mg
100 ppm	Safe 4,000 mg

The estimated fatal dose of styrene is 50,000 mg which is in apparent agreement with the 10,000 ppm effect calculated above but not with 1,300 ppm effect. Thus even though the same apparent amount was inhaled, the true absorption or the difference between inhalation and excretion rates must be quite different. I have mentioned these two compounds to illustrate the point that although the two TLV's were similar, the toxic levels are quite different. Also in both cases a toxic amount could be inhaled over a reasonably short time period (8 hours) without a noticeable effect.

I have used the word "toxic"; the expressive word "hazard" is frequently used; what is really meant by these words? E. A. Pfitzer[3] gives a very reasonable definition as follows:—

> **Toxicity** is an inherent property of a chemical to produce an unwanted effect when that chemical has reached a sufficient concentration at a certain site within the body, and **Hazard** is simply the probability that this unwanted effect will occur.

These definitions imply that a toxic effect is usually controlled by the chemical's ability to enter the body and then to be transported within the body to establish the necessary concentration in the critical area. Thus a chemical must be in a form in which it can enter the body by inhalation, ingestion, or skin absorption, and the rate of entry must exceed the rate of detoxification or excretion

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Chemistry Division, DSIR. Paper given at Auckland Symposium on Toxic Incidents 1975

by the body. This implies that every chemical is inherently toxic if given in sufficient quantity by the appropriate route of administration and in a suitable physical form. Thus, to describe any chemical as non-toxic is fallacious, although for all practical purposes the majority of chemicals are not toxic. It is probably better to describe chemicals as possessing an inherent potential for toxicity, and this fact must be appreciated when a chemical is encountered in an unusual circumstance or in an unexpected form. Just as the fact that every chemical is toxic is a basic principle of toxicology, so is the assumption that the majority of chemicals can be handled safely because the body can tolerate some level of exposure without any observable unwanted effect. This assumption implies knowledge that the half life of most chemicals in the body is so short that a cumulative effect does not occur. In the case of toxic metals the half life may be many days, or even years, so the tolerable level may be so low that the only practical attitude is to ban the chemical. This is one form of zero tolerance.

There are some chemicals that are thought to be capable of a non-reversible reaction at a critical site within the body. In a sense the body has no threshold tolerance for these compounds at the reaction site, although the body as a whole may have an elimination or protection mechanism. This may be true for carcinogenic compounds to which the body generally may be exposed, but which under certain circumstances could be highly toxic. In these circumstances it may be possible to define an actual threshold relative to practical exposure conditions, even though an individual molecular interaction may cause the adverse effect. The vinyl chloride monomer (VCM) controversy is a case in point[4].

Some forty years after the industrial production of VCM commenced, 12 cases of a rare liver cancer have been discovered in the U.S.A., 1 case in the U.K. and about 5 cases in Continental Europe. Of the 18 cases, 7 occurred in one U.S.A. plant and 3 in another plant of the same company. The average exposure time of the known cases approaches 20 years, and the atmospheric levels to which the workers were exposed is thought to be at least 1000 ppm. It is estimated that the average atmospheric concentration of VCM in U.K. factories was 1000 ppm in the 1945-1955 period, 4-500 ppm in 1955-1960, 3-400 ppm between 1960-1970, 180 ppm in mid-1973, and in mid-1974, 80 ppm. Major improvements during 1974 have come mainly from the elimination of procedures which **permitted** VCM to escape into the plant atmosphere within the prescribed limit of 200 ppm. Incidently, VCM presents a fire and explosion risk very similar to butane and there have been more deaths from fires and explosions of such materials than from industrial disease. On a world-wide basis more people have died from fire and explosions with VCM than with cancer over the past 10 years. However, permissible VCM levels of 1 ppm are now being seriously considered.

I have emphasised this point to illustrate the problem. VCM has clearly been shown to be a causative agent for this rare form of liver cancer. The known cases related to exposures over a 20-year period to between 200 and 1000 ppm. Now the TLV will certainly be reduced from 200 ppm to a figure such as 1 ppm, but I leave it to you to decide the toxic danger that a spillage of VCM would offer when the fire danger is also considered. Incidentally, if the ACGIH criteria are followed, there is provision for a permissible excursion above the TLV limit of 1.5 to 2 times in the case of VCM.

Thus, in the case of carcinogenic agents the basis for establishing a safe level of exposure is that as the result of exposure to a finite concentration of the chemical the likelihood that a molecule will reach a critical site is so remote as to be not measureable.

However, more acceptable bases for establishing TLV are the assumptions that

(1) The body can easily detoxify the dose through normal physiological mechanisms;
(2) That the lesions produced are easily repaired by body mechanisms with no resultant unwanted effect; and
(3) That the lesions are so inconsequential that they do not influence the reserve capacity for the maintenance of normal bodily functions.

Together with Threshold Limit Values and LD_{50}s you may also be aware of the limits that are placed upon those pesticides used in commerce that may give residual levels in foodstuffs.

These residue levels may not reflect the LD_{50}s of the compounds concerned, but rather the level that can be achieved under conditions of good agricultural practice consistent with the chemical achieving the desired effect upon the target organism. Thus, compound A which may have a lower permitted residue level than compound B could be less toxic (i.e., a greater LD_{50}) than compound B. This situation could be found if in practice compound A degraded more rapidly than compound B after application. A lower permitted residue could thus be considered necessary to ensure that the holding period was strictly enforced and unauthorised practices were not introduced.

I have attempted to describe the various types of information that are readily available to a chemist and to indicate the limitations to the information, but I have only suggested the fact that the true danger of any chemical to man can only be based upon, unfortunately, human experience. There are several outstanding examples of this and while I have mentioned VCM, I am sure you will be aware of asbestos, paraquat, phenol, and aniline. Phenol has been mentioned by Dr Bierre but many older reference books do not emphasise the extreme speed with which skin absorption occurs[5]. It may well be asked do we really appreciate the dangers of the chemicals we have used for many years both in the laboratory and in industry.

I continually remind myself that although I think I have some knowledge of the dangers of a pure laboratory chemical, this knowledge may not apply to an industrial drum labelled with the same chemical name. Thus I think chemists should not immediately concern themselves with the precise chemical involved in a spillage incident but should follow general procedures that apply to whole classes of chemicals.

Once a spillage has occurred someone will inform the emergency services and even at this stage there will be sketchy information of smell, fumes, liquid or powder. I would expect the Technical Liaison Committee personnel to be then alerted and my first reaction is to ask is there a smell or sign of fumes? In general solvents have characteristic smells and if the smell is described as present, I suggest that the spill should first be treated as a toxic hazard. If there is any suggested name for the chemical, I endeavour to relate the flash point to that of a common petroleum fraction, but if in doubt I say treat it as a petrol spill. Clearly there should be a warning to retreat to a position where the smell is not apparent, and to stay up-wind. The presence of a smell is also valuable information that should transcend even a chemical name. I need not remind this audience of the Parnell emergency, but the presence of a smell with lead naphthenate clearly indicated that this material was dissolved in a solvent as you would expect.

The presence of fumes is also characteristic information suggesting to me a possible corrosive hazard from hydrochloric acid, sulphur trioxide, nitric acid etc. If the colour is also mentioned this is valuable information. I dealt at a distance with a small brown fume incident said by those on the spot to be bromine, but later shown to be nitric acid. The majority of compounds that fume should not be approached under any circumstances until a technical assessment can be made on the spot.

Liquid or powder spills with no other apparent properties should be first treated as if they are toxic chemicals unless there is unequivocal information to the contrary. In general, time is not a problem with this type of incident, and I would prefer the emergency services, who after all are at greatest risk, to stand by until a more positive identification can be made at the site.

If the incident appears to involve a considerable quantity of chemical, or presents previously unencountered problems, I think the various officers associated with the Liaison Committee should attend to advise on the site. The subsequent steps to be taken will depend upon the agreed assessment of the problem. Personally, I would prefer to treat each incident initially as a potential danger and only relax precautions as the situation develops. Those of you who have been involved in incidents of this type will appreciate the need to contact the owner of the chemical, to sample and positively identify the material if there is any lingering doubt. Again, I suggest prudence and caution be your guide, because the decontaminating process may be equally hazardous, particularly if adequate protective clothing is not available.

You will note that I have not emphasised the need to approach the spillage to determine the label name. It is my opinion that a drum or container should have some distinctive label indicating the nature of the possible danger, fire, explosion, or poison, together with some action advice. A chemical description is useful for the storeman who receives the consignment, but I think any full identification should be contained in the documentation accompanying the cargo. I do not agree that a chemical name on the drum, which probably applies only to the major constituent, is a necessary prerequisite to a successful handling of a chemical spillage.

In conclusion, I suggest that all chemists who consider that they may be involved in chemical spillages should read the Quarterly Safety Summaries published by the Association of British Chemical Manufacturers and should ensure that all reference books on this subject are the latest editions.

References:

1 Robert H. Dreisbach, Handbook of Poisoning, 6th Edition. Lange Medical Publications 1969.
2 N. Irving Sax, Dangerous Properties of Industrial Materials 3rd Edition, Van Nostrand Reinhold Company. 1968.
3 Metallic Contaminants and Human Health, Academic Press, New York, 1972.
4 European Chemical News, p. 24, May 24, 1974.
5 Quarterly Safety Summary, p. 47, Vol. 37, No. 148, 1966.

New Zealand Institute of Chemistry (Inc.)

PRIZE-WINNERS FOR 1975

Associate Professor Charmain J. O'Connor of the Department of Chemistry at Auckland University, has been awarded the I.C.I. Prize for 1975. Dr O'Connor's work has been mainly concerned with the behaviour of compounds which are dissolved in water. Rates of reactions which are increased by the addition of acids are often dramatically enhanced by addition of trace amounts of detergents.

Miss T. C. Smith-Palmer, Department of Chemistry at Auckland University, won the award for the best student paper presented at the N.Z.I.C. Annual Conference.

HONORARY FELLOWS

During 1975 the Council elected three Honorary Fellows. Messrs M. S. Carrie and O. H. Keys, and Professor S. N. Slater.

Maxwell Stuart Carrie, M.Sc.(N.Z., C.Eng., M.I.Chem., M.N.Z.I.E., F.R.I.C., recently retired from the post of Research and Development Manager with the Canterbury Frozen Meat Company. An Otago graduate, Mr Carrie gained experience in the war time dehydration plants and took the classical route into chemical engineering via the I.Chem.E. examination.

Long experience and authority in the meat industry has led to his becoming virtually a father figure for younger chemists working in the field. His expertise has been sought in various capacities—membership of the Pollution Advisory and Water Resources Councils, the Leather and Shoe Research Association Committee, and the Wheat Research Institute Committee.

Mr Carrie is a former chairman of the Canterbury Branch. Many years service to the Institute culminated in his election as President in 1967.

Oswald Hilton Keys, J.P., M.Sc.(N.Z.), A.R.I.C. is a Victoria graduate. Apart from a post graduate scholarship held at Massey College, and a few years in industry, Mr Keys has spent his career with the D.S.I.R.

When he retired earlier in the year it marked the completion of thirty years service as a Government Analyst, firstly in Dunedin, then for many years in Auckland. Mr Keys holds an equally long record of scientific service to outside organisations. It includes chairmanship of the Interdepartmental Committee for Paint Investigation, Federal Presidency of the Australasian Corrosion Association, Chairmanship of the Auckland Air Pollution Research Committee, Presidency of the New Zealand Association of Scientists, Presidency of the Otago Branch of the Royal Society of N.Z., and membership of the N.Z. Committee of the R.I.C.

Mr Key's activities within the Institute have included a term as Journal Editor, Chairmanship of the Examinations Committee, membership of the Council, and Chairmanship of the Otago Branch during both 1947 and 1953.

Stanley Nelson Slater, M.Sc., D.Phil.(Oxon), F.R.I.C., did his masterate at Otago University and then studied under Sir Robert Robertson at the Dyson Perrins Laboratory.

He returned to New Zealand in 1938 to commence a university career which led to his appointment as Head of Department of Chemistry at Victoria University in 1950. Research interests have ranged from the "bitter principles" of plants such as the New Zealand Tutu through to the New Zealand iron sands. This encouragement of Martin's work led to the eventual setting up of the New Zealand steel industry.

Professor Slater served his university in various capacities and in 1965 was appointed Assistant Vice-Chancellor. He held this top administrative post until his retirement in 1975. His work for the university, particularly in planning and co-ordinating the construction of the Easterfield Boulding, is commemorated in the Slater Laboratory.

Since his return in 1938 Professor Slater has taken an active part in Institute affairs, chief among them being the Presidency in 1952-53.

INTERNATIONAL NEWS

—REPORT ON 5TH INTERNATIONAL CONFERENCE ON ATOMIC SPECTROSCOPY, MONASH UNIVERSITY, MELBOURNE, 25-29 AUGUST 1975

This conference was sponsored by the Australian Academy of Science and was attended by 260 participants from 17 countries, including F. J. Aggett, J. Pybus (Auckland), O. E. Clinton, M. M. Sutton (Hamilton), R. D. Reeves (Palmerston North), Mrs. D. Hinton (Christchurch), Mrs. B. E. Guthrie, J. L. Bahr, W. J. Sandle (Dunedin).

Professor D. P. Craig, Vice President of the Australian Academy of Science officially opened the conference. Dr. Alan Walsh, Assistant Chief C.S.I.R.O. Division of Chemical Physics, then presented the Conference Chairman's address on "Spectrochemistry since Kirchoff and Bunsen." Dr. Walsh, who is considered to be the "father" of atomic absorption spectroscopy, gave a most illuminating description of the developments which led to the production of the atomic absorption spectrophotometer, which has been hailed as the greatest invention since the bed! He also discussed some recent advances in the spectrochemical field.

Eight Plenary Lectures, all of a very high standard, were given by participants who had not acted in this capacity at previous International Conferences on Atomic Spectroscopy. The lecturers and their subjects were D. A. Segar — "Flameless atomic spectroscopy—a quantum jump in investigating the environment;" K. Laqua—"Glow discharges—a means to complete and universal spectro-chemical analyses"; N. H. Tolk—"The emission of optical radiation arising from low-energy ion-atom and ion-surface collisions"; A. G. Gaydon —"Spectroscopic studies on the state of equilibrium of flame gas"; G. M. Hieftje—"Atom formation processes in analytical flames"; N. Omenetto —"The possibility of local sensing of physical parameters in flames"; P. Hannaford—"The influence of spectral line profiles in atomic absorption spectroscopy"; and K. Yasuda—"Application of the Zeeman effect to atomic absorption spectroscopy".

Ninety contributed papers were presented in three concurrent sessions on Furnaces, Instrumentation, General Methods of Atomisation, Flame Interferences, Flame Molecular Spectroscopy, Light Sources, Biological Studies, Hydride Generation, Fundamentals of Analytical Spectroscopy, Plasmas, Metal Analysis and Spectrography, and Fundamental Atomic Spectroscopy. In addition there were Plenary Discussions on "Non-flame Methods" and "Absorption, Fluorescence, or Emission?" under the leadership of a panel of scientists distinguished in these fields of activity. An Exhibitors' Session was also held, in which brief summaries of items on display at the Conference Exhibition were given.

In general the contributed papers stimulated a lot of interesting and informative discussion. A growing interest in nonflame methods of atomisation was indicated by the fact that one third of the contributed papers dealt with furnace atomisation systems. The problems associated with atomisation in furnaces, particularly chemical interferences and non-atomic background absorption, were discussed in several papers. In the plenary discussion on "Non-flame Methods" it was noted that furnace techniques are being used successfully by a number of skilled workers who are able to perform analyses which are not practicable by any other method. However, it was observed that furnaces, because of their novelty, are being used in some cases when it would be more realistic to use the flame. A number of novel methods of atomisation were described which involved the use of lasers, cathodic sputtering, exploding wires, sparks and glow discharges. It was apparent that new and improved methods of sample atomisation are being actively sought, especially for situations where the quantity of sample is limited or the element concentration is very low.

The exhibitors' talks were followed by a lively discussion on the relative merits of the different analytical systems. Manufacturers' comments on the advantages and disadvantages of double beam and single beam atomic absorption systems were of particular interest, but no clear advantage of one over the other emerged from the discussion.

In the plenary discussion on "Absorption, Fluorescence or Emission?" it became apparent that no significant new developments were envisaged in the near future. Most people seemed to be reasonably content with the analytical techniques now being employed. It was considered that, because of its simplicity, atomic absorption will continue to be used extensively for elemental analyses.

The organisers are to be heartily congratulated on the smooth running of the conference, both from the scientific and social point of view. The evening visits to Varian Techtron Pty Ltd and the CSIRO Division of Chemical Physics, together with the Mixer and Banquet, were all memorable occasions. Attendance at this conference provided a unique opportunity for many scientists in Australia and New Zealand to hear papers presented by some of the world's leading atomic spectroscopists.

Books of abstracts of all plenary and contributed papers accepted for presentation are available at a cost of Aust.$7.50 post free from:

The Australian Academy of Science,
P.O. Box 216,
Civic Square,
Canberra 2608, Australia.

M. M. Sutton
Ruakura Agricultural Research Centre
Hamilton.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Commission II.1 on Atomic Weights

At the XXVIII IUPAC Conference held in Madrid, 3-7 September, 1975, the following changes in recommended values for atomic weights were approved:

Fluorine	from 18.99840	to 18.998403
Silicon	from 28.086*	to 28.0855*
Potassium	from 39.098*	to 39.0983*
Molybdenum	from 95.94*	to 95.94
Cadmium	from 112.40	to 112.41
Barium	from 137.34*	to 137.33

These figures are considered reliable to ±1 in the last digit or ±3 when followed by an asterisk.

These changes together with important new annotations and listings will be in the Commission's full Report to be published in the Journal for Pure and Applied Chemistry. This Report will also contain the full Table of Atomic Weights 1975.

H. STEFFEN PEISER, Chief, Office of International Relations and Secretary of IUPAC Commission II.I National Bureau of Standards, Washington, D.C. 20234.

Letter to the Editor

The publication of the 1974 Salary Survey prompts me to re-open a topic which I first broached almost 10 years ago. In my presidential address to the Institute in 1967[1], I pointed out that whereas prior to about 1940, chemists in Industry received salaries higher than those received by chemists in the University or the Government, the 1965 Salary Survey showed that the University salaries had gone ahead of the Industry salaries and that the Government salaries were about on a par with Industry. I attributed the relative loss of ground of Industry salaries, at least in part, to the fact that the industrial chemist had no organisation to look after his interests, whereas the University and Government chemists had. I admitted that, considering the multiplicity of employers and the wide variations in the work, it was difficult to imagine what kind of organisation could be set up, but I suggested that if anybody could devise a workable scheme, he would get a great deal of support from chemists in Industry.

I hoped and even expected that this address would elicit a considerable reaction, especially from industrial chemists, either in support of my contention or disagreeing with it. To my surprise and disappointment, not one person wrote either to the Journal or to me personally on the subject. I could only conclude that chemists in Industry were content to see their relative position deteriorate or that they thought the problem to be insoluble. In view of this attitude, the Institute, even although about one-third of its members were employed in Industry, could hardly be blamed for not initating any moves to remedy the situation.

The 1974 Salary Survey shows that the relative position of the industrial chemist has deteriorated still further in the last 9 years. He now ranks significantly below his colleagues in the University and the Government and would appear to be approaching parity with School Teachers who have been historically the Cinderellas of the profession.

I have now retired and my interest in the salaries of industrial chemists is academic rather than practical. If industrial chemists are still as apathetic as they were 8 years ago, there is little that anyone can do for them and they can expect to see their status and salaries continue to decline relative to the rest of the profession. All I can do is to call their attention once again to the situation and hope that some of the younger members will be sufficiently concerned to move towards setting up some sort of an organisation to protect their interests. This could be either under the aegis of the Institute or as an independent venture.

Max Carrie

(1) *J. of N.Z. Inst. of Chem. 31,* 123.

THE AUSTRALIAN AND NEW ZEALAND SOCIETY FOR MASS SPECTROMETRY

FOURTH BIENNIAL CONFERENCE: 25-28 January, 1977
Victoria University, Wellington

Planning is well under way for the above conference. The organising committee will consider papers in any area of mass spectrometry. Topics which the committee hopes to feature at the conference are: use of mass spectrometry in chemical medicine, mass spectrometry and environmental monitoring, instrumental techniques and geochemistry. Full registration details and titles of papers will be called for in June. Return the form below to ANZSMS secretary to ensure receipt of a conference newsletter which will be mailed in June.

Dr Evan Horning, Director, Institute for Lipid Research, Baylor College of Medicine, will be one of the guest speakers. Dr Horning's work involves the extraction, derivatization and quantitation of steroids, drugs and their metabolites. He has a broad interest in many aspects of gas phase analytical techniques including gas chromatography, mass spectrometry and the combination of these two analytical methods.

Negotiations are under way to have other well known mass spectroscopists at the conference to discuss topics such as respiratory gas analysis, geochemistry and environmental monitoring.

If you want to receive the next newsletter regarding the 1977 conference fill in the form below and send to:

Dr P. C. Rankin, Secretary ANZSMS,
C/o Soil Bureau, Private Bag,
Lower Hutt, New Zealand.

NAME: ..... TITLE: .....

ADDRESS: .....

.....

.....

I hope to attend the 1977 ANZSMS Conference.

My chances of attending are good/fair/poor*.

I shall/shall not* be giving a paper.

I shall/shall not* require accommodation (state number ( ).

*strike out whichever is not applicable.

International Newsletter on Chemical Education, No. 3, December 1975.

(Highlights of Newsletter No. 3)

The *Newsletter* is initiating a regular column on 'Research in Chemical Education' to establish a link between practising educators and those engaged in research in chemical education. Prof. M. J. Frazer (University of East Anglia, Norwhich, UK) will be in charge of this feature.

Articles in this issue deal with—a Television Course in Chemistry for the General Public in Netherlands; Chemical Education at University of Glasgow (UK); Chemistry and Society Course for Non-Science Majors at University of Windsor (Canada). Reports on the IUPAC Symposium on Educational Technology and European Seminar in Chemical Education both held in Madrid in September 1975 as well as a report on the Regional Laboratory Workshop in University General Chemistry held in Seoul (Republic of Korea) during August 1975 are included. There is an informative writeup on the Chemical Competition.

Available free of charge from the IUPAC Secretariat, Bank Court Chambers, 2-3 Pound Way, Cowley Centre, Oxford OX4 3YF, UK.

American Institute of Chemical Engineers

Asian Pacific and Western Hemisphere chemical-engineering societies will have their first joint meeting in history August 28-31, 1977, in Denver, Colorado, USA.

With the announcement of the meeting has come a particular invitation for technical papers from chemical engineers and scientists in New Zealand.

Prospective authors are invited to immediately contact Dean W. Robert Marshall, College of Engineering, University of Wisconsin, 1415 Johnson Drive, Madison, Wisconsin 53706, USA. Dean Marshall is vice program chairman, representing member societies of the Asian Pacific Confederation of Chemical Engineering.

The four-day meeting will be held at the Denver Hilton Hotel.

Correction

Chemistry in New Zealand Vol. 39, No. 4, November 1974, page 98, line 7; the name C. P. Mackie should real C. P. McBride.

Book Reviews

Ions in Solution 3 Inorganic Properties G. Pass, Oxford Chemistry Series, Clarendon Press, Oxford, 1973.

Inorganic Chemistry often involves the study of reactions in solution and in the first three sections of this book the author describes the nature of solute—solvent interactions, the process of solution and equilibrium reactions giving briefly the physical principles. The size and charge of the cation are seen to be important factors in these reactions. The acidity and basicity of acids in aqueous and non-aqueous media and a discussion on the acid—base clarification of oxides follows in the next section. The Chemistry of the elements in Groups I A, II A and III A, the metals of the B subgroup and the transition elements is generally discussed in sections five to eight in terms of electronic structures, ion sizes, standard electrode potentials, as well as the solubility, hydrolysis and complex ion formation of compounds of these elements. There is also a short section on the pattern of chemical behaviour of the non-metals.

No attempt (as indicated by the author) has been made to give a detailed account of the solution chemistry of the elements, instead the main features of the chemistry of each group are used to illustrate the trends in the periodic table. To this end the author has been reasonably successful though the depth and scope of treatment is felt to be lacking at times.

This book (101 pages) is mainly designed for first year students and is an interesting blend of physical and inorganic chemistry. There are problems (and solutions for some) for each section. The book is free of errors and at the price of $3.65 should be made available in University Libraries.

E. W. Ainscough.

Stereochemistry and Mechanism—D. Whittaker. Oxford University Press 1973, 96 pages $NZ3.65.

Stereochemistry and Mechanism is No. 5 in the Oxford University series and it comes up to the high standard expected of this series. It is a very readable account of the central role of stereochemistry in understanding reaction mechanisms.

In the first half of the book the author discusses the shapes of organic molecules including chirality and the relative stabilities of the conformations of acyclic systems. He covers all that is necessary to understand the stereochemical effects in addition, elimination and substitution reactions, which are the topics covered in the second half of the book. In these latter chapters the known shapes of molecules are used to understand the stereoelectronic requirements of the reactions, and then reactions of known stereoelectronic requirements are used to aid the understanding of the shape and flexibility of further molecules.

The reader is required to have an elementary knowledge of simple reaction mechanisms, but the aim of the book is to provide the necessary background of stereochemistry. In general the author achieves this aim except perhaps in the first chapter. This is an excellent summary of spatial arrangements of molecules, their representations on paper, and chirality, but would need some expanding for the novice. For example, although R- and S- terminology is used for the representation of absolute configuration, the D- and L-system creeps in without any explanation—a small point in this concise and highly logical approach by the author.

Five or six problems at the end of each chapter are also concise and to the point, and have been well chosen to test comprehension of each chapter.

This is an excellent book in both content and presentation and is good value as an introduction to stereochemistry. It could well be used as the basis for a short course at the third year undergraduate level, especially as the early chapters are really a summary of the stereochemistry often introduced in first and second year courses.

J. S. Ayers.

Keys to Chemistry Book I and *Teachers Guide*, by Graham Hill. Published by the English University Press Ltd., 1974. Pupils Book I, £1.15; Teachers Book, £1.50; Practical Book £6.50.

These books are aimed at 12-14 year-old children starting on chemistry. The language is simple, the many photos and historical and practical paragraphs are well chosen for this age group. Each chapter ends with a useful summary. However, definitions and explanations have suffered from the attempt to keep everything simple.

The teachers' book seems to be unnecessary for those with a chemical background, but does not give enough help to those without. Some answers to questions or references to other chapters are given, but the questions on the whole ask for more background than either teacher or children would normally have; and the book does not provide the possibility of finding the answers. Many questions are very factual but with minimal relevance to what the children are supposed to have learnt.

The book however has many good ideas and could well be valuable to the teacher of Form 1-4 science.

D. Suuring

Radiation Chemistry by Gordon Hughes. Clarendon Press, Oxford, 1973. 89pp. (£2.10 U.K.).

This small book is No. 6 in the well known Oxford Chemistry Series. Radiation Chemistry underwent such rapid development in the 1950s and 1960s that it is now perhaps losing its identity as a subject and in specific areas is becoming an integral part of other various branches of chemistry. This book starts with a brief historical introduction; then follow sections on sources of radiation, its interaction with matter, ions, solvated and trapped electrons, excited states, and free radicals —all basic material essential to understanding any more specific area of radiation chemistry. The penultimate chapter, "Studies of Selected Systems", gives a very brief introduction to areas which are subjects of individual books in their own right, while the final chapter outlines practical applications.

Its brevity and clarity make it ideal for anyone wanting a quick introduction to the field, and this reviewer has found it an excellent book for stage III honours students to read prior to a more detailed course on aqueous radiation chemistry. The inclusion of a few questions with worked answers at the end of each chapter is most useful for the

student reader. For those wishing to explore the subject further there is a well chosen bibliography for each chapter.

This book is good value.

J. E. Packer

UK Chemical Industry Statistics Handbook, 1975.

The 7th revised edition of this statistics handbook was published in July, 1975.

The familiar pattern and format of the book have been maintained and, as in previous years, all tables have been brought up to date, and simplified where appropriate. The contents are again arranged in the following main sections:—

Part I —Major economic indicators of the U.K. Chemical Industry.
Part II —Production and sales information about sectors of the U.K. Chemical Industry.
Part III—Production and consumption of fuel, energy and certain raw materials in the U.K.
Part IV—Selected major statistics of the EEC countries.
Part VI—Comparison of the chemical industries of the OECD countries in terms of major economic indicators.
Appendices— Definitions of the industry on the bases of the Standard Industrial Classification and of the Standard International Trade Classification (Revised).
Snbject Index—Extensively cross-referenced for easy access to information.

Copies will be available at £10.00 each, including postage to U.K. destinations, from Publications Department, CIA Ltd., Alembic House, 93 Albert Embankment, London S.E.1 7TU, remittance to accompany order.

Elements of Organometallic Chemistry by R. F. Hartley. The Chemical Society (London), Monographs for Teachers, No. 26, 1974, 103 pages (Price £1.20).

Organometallic chemistry, one of the most rapidly growing branches of chemistry, has wide application in industrial processes and bridges the traditional branches of chemistry. It is therefore pleasing to find a brief introductory monograph on the subject for teachers of chemistry. Teachers of 6th and 7th Form chemistry and chemistry teachers in Technical Institutes and Universities will benefit from reading this particular monograph. The author has attempted to cover the subject in a brief, but simple manner with an emphasis on reaction chemistry, particularly those with current industry applications.

The introductory chapter outlines the nomenclature and framework of organometallic chemistry. In an endeavour to classify the various types of organometallic compounds the author distinguishes between covalent organometallic compounds of the main-group elements and compounds of the transition metal compounds are also covalent. The division should be in terms of the mode of bonding rather than "covalent" and "transition metal" types.

The long list of methods of preparing organometallic compounds given in Chapter 2 is somewhat bewildering on a first reading, and readers would benefit from a re-read after covering the chapters on structure and bonding. It is a pity to note that dialkyl mercury compounds are mentioned as easy to handle and that they are commonly used as alkylating agents, without noting their extreme toxicity.

Both the structure and bonding chapters are written in a restrained manner and may be readily understood by people not familiar with modern molecular orbital theory.

The highlight of the monograph is the long section (27 pages) on the systematic chemistry of organometallic compounds. It would have ben useful to have emphasised and given more details on some of the common reactions such as oxidative addition, ligand insertion and elimination reactions. However, the chapter gives a good survey of the reaction chemistry of these compounds and in particular the reactions which are known to occur in industrial processes.

The last chapter outlines the details of experiments that could be carried out in schools. The details are given in full, are helpful, and the experiments should be successful provided one can afford expensive metals such as rhodium and palladium. The New Zealand landed price at the moment is approximately $42.00 for 1g of $RhCl_3.3H_2O$ and approximately $4.00 for 1g of $PdCl_2$. These high costs are in fact the main reason why such experiments are not common even at University undergraduate level.

The author has achieved the goal of presenting modern organometallic chemistry in a readable form for teachers of Chemistry. The monograph will stimulate readers to look further for more advanced reading, the number of which is much greater than given on p103 of the monograph.

J. E. Fergusson

Ionic Polymers, edited by L. Holliday, 1975. Applied Science £14.00.

The nomenclature ionic polymer would not have been as well known ten years ago as it is today since the Du Pont firm marketed a particular class of ionic polymers called ionomers.

Perhaps the metallic compounds in their polymerised form as silicates, phosphates and glasses have been taken for granted by people who were unaware of their complex chemistry and did not think of them particularly as types of ionic polymer.

Taking the publication as a whole Dr Holliday is to be congratulated on editing the first book entirely devoted to the subject of ionic polymers. The book includes information in thermoplastics, carboxylated elastomers and rigid materials, polyelectrolytes, silicates, phosphates and glass polymers. Dr Holliday has not only taken in the task of editing such a comprehensive work but provides an extensive chapter on the classification and general properties of ionic polymers. The remaining seven chapters, devoted to the ionic polymers, already mentioned, are so academic that one must agree with the editor that the publication is aimed at the post graduate and research worker. Unfortunately, there are not so many polymer chemists in New Zealand as would provide a great sale for this book.

Apart from the chapter in 'relaxation behaviour', which this chemist finds difficult to assess, the book is well written and illustrated.

Surely there must be a place for this book on the shelves of university libraries, government and research organisations using and researching into the many facets of ionic polymers.

A. C. Kennett

Developments in Thermosetting Plastics, Edited by A. Whelan and J. A. Brydson, 1975. Applied Science Publishers Ltd. Price £7.00. (198 pages).

This collection of eleven papers given to a symposium on recent developments in the field of thermosetting plastics is another of the well produced publications in a series taken from symposia held at the National College of Rubber Technology.

One must understand that the information collected is mainly for the use of the UK plastics industry and influenced by the UK economy. Nevertheles the plastics industry in New Zealand will be particularly interested in the sections on polyurethanes, powder processing, FRP low pressure processes and machinery.

The chemist (but not the analyst) is catered for in sections on amino resins, Friedel-Crafts resins and fixane resins, but, in the main the proceedings are aimed at the plastics technologist and engineer.

A minor criticism of editing (offset to some extent by explanation in the preface) is the decision to oscillate between SI and fps units, when in 1975 the SI unit should be given priority, with fps units used occasionally as a second alternative.

However, these adverse comments do not detract from the general excellence of the book which is written in an easy, flowing style with interesting information on improvements and developments in the thermosetting plastics field.

A. C. Kennett

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