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# THE SECOND MILE

by

W. E. Wickenden

A digest of a paper read by the late Dr. Wickenden before the Annual Meeting of the Engineering Institute of Canada in 1941. It is reprinted from the "Engineering Journal," December, 1949, by courtesy of the Engineering Institute of Canada.

Every ealling has its mile of compulsion, its daily round of tasks and duties, its standard of honest craftsmanship, its code of man-to-man relations, which one must cover if he is to survive. Beyond that lies the mile of voluntary effort, where men strive for excellence, give unrequited service to the common good, and seek to invest their work with a wide and enduring significance. It is only in this second mile that a calling may attain to the dignity and the distinction of a profession.

Of professions there are many kinds; open professions like music, to which any man may aspire within the bounds of his talents, and closed professions like medicine which may be entered only through a legally prescribed process; individual professions like painting and group professions like law, whose members constitute " the bar," a special class in society; private professions like authorship and public professions like journalism, artistic professions like sculpture and technical professions like surgery; ameliorative professions like the ministry and social work, and professions which safeguard social institutions through a technique of destruction, like the army and navy. Despite all these differences of pattern, certain characteristic threads run like a common warp beneath the varying woof of every type of professional life and endeavour.

If one searches the authorities for definitions of a profession he will probably find four kinds.

One is likely to hold that the determining quality is an attitude of mind, that an altruistic motive can lift any honourable calling to the professional level. A second may say that it is a certain kind of work, one requiring special skill on a high intellectual plane. A third may state that it is a special order in society, as the bar, the bench or the clergy. Still others insist that no work can be professional without a confidential relationship between a client and his agent, as that of patient to physician, litigant to lawyer, etc. None of these definitions is ' Taken together, like the legs self-sufficient. of a table, they give a profession a stable base of support.

What is the distinctive mark of the professional man? First, we may say that it is a type of activity which carries high individual responsibility and which applies special skill to problems on a distinctly intellectual plane. Second, we may say that it is a motive of service, associated with limited rewards as distinct from profit. Third, is the motive of self-expression, which implies joy and pride in one's work and a self-imposed standard of excellence. And fourth, is a conscious recognition of social duty to be fulfilled among other means by guarding the ideals and standards of one's profession, by advancing it in public understanding and esteem, by sharing advances in technical knowledge, and by rendering gratuitous public service, in addition to that for ordinary compensation, as a return to society for special advantages of education and status.

Next, what attributes distinguish the corporate life of a group of persons as professional in character? We may place first a hody of knowledge (science) and of art (skill) held as a common possession and to be extended by united effort. Next is an educational process based on this body of knowledge and art, in ordering which the professional group has a recognized responsibility. Third is a standard of personal qualifications for admission to the professional group, based on character, training and proved competence. Next follows a standard of conduct based on courtesy, honour, and ethics, which guides the practitioner in his relations with clients, colleagues and the public. Fifth, we may place a more or less formal recognition of status, either by one's colleagues or by the state, as a basis for good standing. And finally, there is usually an organization of the professional group, devoted to its common advancement and its social duty, rather than to the maintenance of an economic monopoly,

The traditional professions of law, medicine and divinity had a common fountainhead in the priestcraft of antiquity. What is professional in modern technical callings such as engineering can be traced back only as far as the mediæval craft and merchant guilds, which arose out of the breakdown of feudalism.

There being no other effective authority, the guilds took over the regulation of the hours of labour, the observance of holidays, the length and content of apprenticeship, the wage system, the standards of workmanship and the quality of goods. The guilds also tested the progress of novices, apprentices and journeymen, and finally admitted them to the ranks of the masters with imposing ceremonies, of which college commencements and inaugurals are the most picturesque survivors in our modern day.

The guilds naturally took unto themselves considerable monopolies and privileges. As the cities gradually grew strong they usually recognized the guilds and gave them a considerable share of civic responsibility.

Many features of this distinctive type of citizenship are perpetuated in our modern professional bodies. The public grants to a profession more or less tangible monopolies and self-governing privileges, in consideration of which the profession engages to admit to its circle only men of proved competence, to guarantee their trustworthiness, to insist on the observance of ethical relations and practices, and to protect the public against bungling and extortion.

When a layman comes face to face with the complex and often terrifying specialization of professional skill and knowledge, he is likely to be baffled or easily misled. If you have a problem of mental illness in your family, how can you be sure you are dealing with a qualified psychiatrist and not with a plausible but unscrupulous quack? To protect you in these emergencies the public wisely puts the burden of guaranteeing at least minimum standards of competence and ethics on the profession itself. The physician you can trust is the one who is recognized as well qualified and reputable by his brother physicians of good standing; the same with lawyers, dentists, architects and engineers.

The state may implement the obligation of a profession to guarantee competence by designating a group of its members to conduct professional examinations and to issue public licences to those who pass them successfully, or it may leave professional bodies free to issue their own credentials. Both of these practices may exist side by side, as in the realm of medicine, where the state licenses general practitioners through a board of examiners, while the various groups of specialists have voluntary organizations which examine and certify physicians seeking recognition in their respective fields. In the end, it comes down to the same principle-a profession must guarantee to the public the trustworthiness of its practitioners, In return, the public protects the profession from the incompetent judgment of the layman by a privileged position before the law.

Professional status is therefore an implied contract to serve society, over and beyond all specific duty to client or employer, in consideration of the privileges and protection society extends to the profession. To possess and to practise a special skill, even of a high order, does not in itself make an individual a professional man. Mere technical training, at any level, is vocational rather than professional in nature. The difference between technical training and professional education is no simple matter of length—any difference of two years, or four, or six; nor is it a mere matter of intellectual difficulty. It is rather a matter of spirit and scope. More specifically, it can be described as an overplus beyond the knowledge, however intricate, a man needs to master his daily tasks.

The overplus in professional education, in short, is that which enables a professional man to view his work not only as a skilled service to a client but also in terms of its consequences for society. An engineer, for example, develops a labour-saving process and recommends its adoption; does he see in this act only an immediate saving in the cost of production, and assume that this is adequate justification in itself? Or can he perceive the sequence of effects which will be felt in the lives of individual workers, of the organization which employs them, of the community in which it functions, of the markets which it supplies, and of the wider sector of society which it ultimately serves ? In the answer to these questions there is wrapped up much of the difference between a high-grade technician and an engineer of true professional stature. Every professional body counts on its rosters many men who are little more than technicians, and it is well that they are included, since professional development comes so largely through association and indoctrination. But no professional body can be strong and effective unless it contains a substantial nucleus whose intellectual attainments far exceed in depth and breadth the technical demands of its practice.

The ethical obligations of a profession are often embodied in codes and enforced by police powers. Even when no written canons exist, as in the artistic professions, unwritten usages and standards exercise a powerful guiding and restraining influence. The physician and the lawyer are bound by explicit obligations. As engineers, our codes are less tangible and the means of enforcement less explicit, in proportion as our duties are less definable, but our ethical obligations are no less binding morally.

No professional man can evade the obligation to contribute to the advancement of his group. His skill he rightly holds as a personal possession and when he imparts it to another he justly expects a due reward in money or in service. His knowledge, however, is to be regarded as part of a common fund built up over the generations, an inheritance which he freely shares and to which he is obligated to add; hence the duty to publish freely the fruits of research and to share the advances in professional technique. If the individual lacks the ability to make such contributions personally, the least he can do to pay his debt is to join with others in creating common agencies to increase, disseminate and preserve professional knowledge and to contribute regularly to their support. That is the purpose to which a large share of the membership dues of our professional societies is devoted.

Too many engineers exhibit an unenlightened and petty attitude on these matters; mature men who complain that the direct returns to them of the researches and publications of a professional society are not worth the annual fee, and young men who grumble because membership does not lead to direct preferment in rank and salary. Shame on us ! Do we look with envy on the high prestige of medicine or surgery? Then let us not forget that this prestige has been won not merely through personal skill and service, but by magnificent contributions to human knowledge without profit to the seekers and with incalculable benefits to all mankind.

Measured by standards such as these, many men who call themselves engineers and who have proved themselves competent in accepted technical practices, have not attained a real professional stature. Some are victims of a deficient education, not in the sense that school and college failed to teach them all they would ever need to know, but rather failed to inculcate a taste and a capacity for continued learning under self-direction. They are usually the men who have let their scientific training slip away after they have mastered a specific job, who have been unable to surmount the routine of early experience and have gradually grown content with mediocrity. Some of the difficulty may be inherent in the operating routine so often associated with an engineer's work. If these deficiencies exist, they are not solely a reflection on the individuals involved, but also on the professional body. One of its obligations to its younger members is to give effective stimulus and guidance to their growth.

There is a school of thought which has two quick and ready remedies for all the ills and shortcomings of the engineering profession. One is to keep the boys longer in college and to compel them to cover courses in both liberal arts and engineering. The second is to limit strictly the use of the title "engineer" to men who have obtained a public licence. One need not quarrel with either the aims or the means; so far as they go both are good, but they cover only the first mile.

Registration will probably always be a qualifying standard rather than a par standard for the engineering profession. By its nature, it cannot be a standard of distinction. It will go far toward keeping the wrong men out of the profession, but it will serve only indirectly to get the right men in. Beyond it lies a second mile of growth and advancement for which effective guidance, incentives and rewards can be provided only within the profession itself.

The proposal to compel all engineering students to remain six years or more in college in order to complete combined courses in liberal arts and in engineering is attractive in theory but unworkable in practice. Some young men should do so, but the majority will not. Those who do are likely to find that the advantage gained comes quite as much, or even more, from sharing the life and spirit of two divisions of education with differing ideals and traditions, as from a more extended range of studies.

The engineer needs his profession for his personal advancement. That is the purpose which brought it into being.\* He needs it most at the beginning of his career. Young men need for their advancement wider sources of information, more varied personal associations, broader stimulation to achievement and less formal contacts with their seniors than they usually find in their daily jobs. As men mature they come to value professional rewards friendships, recognition, responsibility, pride in belonging, evidences of distinction, etc.—no less and often more than money rewards. These are the durable satisfactions of life.

The engineer, in a society based largely on group relations, needs his profession to safeguard his occupational and economic welfare. He needs protection against unethical competition, against indiscriminate use of the title " engineer," and against all influences which might undermine public confidence in his integrity and competence. He needs protection against those who assume that he is " just another employee " and against sub-professional groups seeking to act for engineers in the process of collective bargaining. He needs protection against the levelling influences of unionism and of civil service. He needs his profession because of his stake in the advancement of knowledge and technical skill.

Few engineers can do much about it alone. Collectively their capacity to advance knowledge is beyond calculation.

Millions of individual, unrelated efforts will not add up to the future that invites our profession. This is no time for engineers to wrap themselves in the mantle of isolation; let us get together and be about our common business.

There are undoubtedly some who feel that the cultural and spiritual interests of society are menaced by a greater dominance of technological education. I am unable to share these fears. We of the engineering schools have no quarrel with liberal education.

We are not indifferent to culture, save that of the dilettante type. Culture is to us not a form of professional interest, nor the fruit of any form of pose or academic exposure, but the fruit of spontaneous activity which all may share on an amateur basis in that second mile which lies beyond the compulsions of one's economic occupation. Expressional activities -sport, music, writing, speaking, dramatics, and the arts of design-also the reading of books, are flourishing on many an engineering campus to-day quite as vigorously as in many a so-called liberal college. If destiny is to make our technological institutions responsible in the future for a major stem of higher education, and not merely for some of its specialized phases, I have faith that we shall give a good account of our stewardship.

<sup>\*</sup> The first professional society, The Institution of Civil Engineers, was organized in London. The official account of its founding begins, "It was toward the end of the year 1817 that a few gentlemen, then beginning life, impressed by what they themselves felt were the difficulties young men had to contend with in gaining knowledge requisite for the diversified practice of engineering, resolved to form themselves into a society."

# MEMBERS OF THE TECHNICAL COMMITTEE

Arthur James Tyrrell was born in London in September, 1908. During the period 1924-1939 he studied at the London Polytechnics and obtained the Associate Membership Examination of the



Institution of Electrical Engineers in addition to securing certificates of the City and Guilds of London Institute inRadio Engineering and allied subjects.

After his initial training Mr. Tyrrell was employed by H. W. Sullivan, Ltd., as a research engineer from 1937-1942. Early that year he left to take up an appointment with

the Posts and Telegraphs Department, Singapore. This appointment was interrupted by the Japanese invasion, and Mr. Tyrrell was one of the few survivors to escape capture. He then joined Mullard Electronic Products, Ltd., and to-day he is chief development engineer of the magnet department.

Mr. Tyrrell was elected an Associate Member of the Institution in November 1942, and transferred to full Membership in October 1947. He has been a member of the Technical Committee since October 1948, and of the Papers Committee since October 1949.

The Institution has published three of Mr. Tyrrell's papers; the latest is contained in this issue.

Harry Edward Drew was born in Gillingham, Kent, on January 18th, 1909. He received his technical education at the Electrical and Wireless School, Flowerdown, whilst an Aircraft Apprentice in the R.A.F. On leaving the R.A.F. in 1938 he joined the Air Ministry Experimental Station at Bawdsey and was one of the team of scientists responsible for the design and development of the first Army Radar Transmitter.

In 1943 he was appointed works manager of the Radio Production Unit, Woolwich, and in January, 1946, was promoted to Principal Scientific Officer and appointed Officer in Charge of the Research Prototype Unit, West Howe, Bournemouth. In November 1946 he was appointed Principal Production Officer in the Directorate of Radio Production, Ministry of Supply.

He was elected an Associate Member of the Institution in 1943 and transferred to Full Membership in 1948. He served on the General Council from 1946 to 1948



and has been a member of the Membership and Technical Committee since 1946. He also represents the Institution on the Council of the World Engineering Conference.

Maurice Moise Levy was born at Alexandria, Egypt, in March, 1908. He was educated at the College Chaptal (Paris), obtaining his Bachelier-ès-Science. Subsequently he studied at the University

of Paris and the Ecole Supérieure d'Electricité, obtaining his Licencieès-Sciences and Ingénieur E.S.E. He then carried out research work at the Collège de France and completed a thesis for the degree Docteur-ès Science when the war started.



In 1935, he joined the International Standard Electric Corporation as

a research engineer in Telecommunications. Since 1945, he has been a member of the Staff of the Research Laboratories of the G.E.C., Ltd.

Mr. Levy has done a considerable amount of original research work and has written many papers which have been published in France and England, seven in the Institution's Journal.

Elected an Associate Member in November, 1942, Mr. Levy transferred to Full Membership in October, 1946. He served as a member of the Papers Committee from 1943-48, and of the General Council from 1944-45. He joined the Technical Committee in January, 1948.

# THE PERFORMANCE AND STABILITY OF PERMANENT MAGNETS\*

by

A. J. Tyrrell<sup>+</sup> (*Member*)

A paper read before the South Midlands Section on October 27th, 1949, the Merseyside Section on November 2nd, 1949, the London Section on January 19th, 1950, the West Midlands Section on January 25th, 1950, the Scottish Section on February 2nd, 1950, and the North-Eastern Section on April 19th, 1950.

### SUMMARY

Very little data is available on the stability of permanent magnets. This paper collates information of practical or empirical nature useful to the user of permanent magnets. The desirable characteristics which materially contribute to the long-term magnetic stability of a permanent magnet alloy are given.

The latest developments in permanent magnet alloys are discussed and an indication is given of present trends in production.

### 1.0. Introduction

In the early days of electrical engineering, quenched carbon steel was used to construct permanent magnets, but the magnetic properties of this steel are not only poor, but are very susceptible to vibration and temperature and the magnets appear to age continuously at normal room temperature.

Tungsten and chrome steels were developed about 1900, followed by cobalt steels some 20 years later. These were the first magnet steels which could be used in apparatus where a precision field was required. The magnetic properties of these steels are also susceptible to temperature, vibration and time, but experience has shown that when processed and handled correctly, magnets made from these materials are capable of meeting very stringent requirements by way of long-term magnetic stability, provided they are used under correctly specified and controlled conditions.

The next development in permanent magnets was the nickel-aluminium series based on the work of Mishima in Japan and introduced into this country in about 1933. The addition of other metals including cobalt followed, and a series of ferrous alloys in which Ni, Al and Co are the main alloying constituents is now available. Of these Alnico is a familiar example. The most recent and significant development is the "Ticonal" magnet, which is anisotropic or directional. The composition of "Ticonal" magnets is approximately 8 per cent Al, 14 per cent Ni, 3 per cent Cu, 24 per cent Co, balance Fe, and, when manufactured by a special process produces magnets with strongly directional properties giving over three times the performance of the best earlier materials. The amount of material required to produce a given magnetic effect is therefore reduced correspondingly. The performance of these materials is shown by the normal graphical representation in Fig. 1.

Fig. 2 shows the directional properties of the modern anisotropic magnet.

# 2.0. Technical Requirements of Magnetic Stability

The question of absolute stability of performance is of considerable importance in instrumentation, since the final products obviously cannot be better than the least stable component employed.

To quote a single example, the indication of a watt hour meter depends upon the square of the flux maintained by the brake magnet and, since the watt-hour meter is expected to give a very accurate indication under extremes of climatic temperature over a period of ten years or more, this type of meter presents one of the most exacting demands for stability of magnets.

<sup>\*</sup> Manuscript originally received April 4th, 1949. U.D.C. No. 621.318.2.

<sup>†</sup> Mullard Electronic Products, Ltd.



Fig. 1—Published characteristics of commercially available magnets alloys. Note: "Ticonal" GX and "Ticonal" K can at present only be manufactured in certain shapes and sizes.

Drift in the magnetic performance of a magnet may be caused either by the magnet being metallurgically unstable or by a reduction in flux due to external influences. To ensure stable performance, therefore, the first requirement is that the magnet itself shall be metallurgically stable. In quench hardened magnets, the degree of metallurgical stability is not high enough unless the material is given subsequent heat treatment at slightly elevated temperatures or is stored for a period of years in order to



Fig. 2.—The change in magnetic characteristics of "Ticonal G" as the operating flux deviates from the predetermined magnetic axis.

establish metallurgical stability through the effect of time alone.

In magnet alloys which receive a final heat treatment or tempering process at a high temperature the metallurgical stability is usually of a very high order.

The second requirement for stability is that the performance of the magnet shall be unaffected by any external influences encountered under normal operating conditions. This requirement is met by applying a demagnetizing effect estimated to be in excess of any external influence likely to occur in normal use, and by reducing the performance of the magnet to a slightly lower value than it would ultimately reach if left in an unstabilized condition.

#### 3.0. General Characteristics of Permanent Magnets

Permanent magnets may be roughly classified into two groups :----

- (a) The relatively tough quench-hardened machinable types.
- (b) The dispersion-hardened non-machinable types.

Carbon, tungsten, chrome and low percentage

## TABLE. 1. PERFORMANCE OF BRITISH COMMERCIAL PERMANENT MAGNET ALLOYS

Material	(BH) max	Br gauss	H <sub>c</sub> oer-	B work-	H work-	Recomm Satura Valu	nended ation es*	Approximate Composition*	Approximate heat	
Material	× 10 <sup>6</sup>			gauss	oer- sted	B <sub>sat</sub> gauss	s gauss		treatment*	
Ticonal GX†	7.5	13,500	720	12,000	625	17,000	3,000	8 Al, 14 Ni, 24 Co, 3 Cu	Heat approx.	
Ticonal G	5.7	13,480	583	11,000	520	17,000	3,000	8 Al, 14 Ni, 24 Co, 3 Cu	1250°C.	
Ticonal F (44/44)	4.8	12,400	600	10,000	480	17,000	3,000	8 Al, 14 Ni, 24 Co, 3 Cu, 0.5 Ti	Cool in 2-15	
Alcomax III	4.75	12,200	650	9,500	500	17,000	3,000	8 Al, 13 Ni, 24 Co, 3 Cu, 1 Cb	600°C in mag-	
Alcomax IV	4.3	11,200	750	8,000	537	17,000	3,000	8 Al, 11-5 Ni, 24 Co, 6 Cu, 2 Cb	Temper. ap-	
Alcomax II	4.3	12,400	575	9,570	450	17,000	3,000	8 Al, 11.7 Ni, 24 Co, 6 Cu	prox.550-650°C between 4-50	
Ticonal E (42/50)	4.1	11,070	740	7,500	550	16,000	3,000	8 Al, 14 Ni, 24 Co, 3 Cu, 1 ·5 Ti	upon type.	
Ticonal D (3.8)	3.8	12,000	600	9,000	420	16,000	3,000	8 Al, 14 Ni, 24 Co, 3 Cu, 1 0 Ti		
Ticonal K†	3.6	8,500	1,150	465	775	15,000	6,000	—		
Alcomax I	3.5	12,000	475	9,500	370	16,000	2,000	8 Al, 11 7 Ni, 24 Co, 3 Cu		
Hycomax	2.8	8,500	790	5.5	500	15,000	3,000	8.5 AI, 21 Ni, 20 Co. 15 Cu, 1.5 Ti		
Reco 2A	1 .92	5,500	1,000	3,300	600	13,000	4,000	7 Al, 20 Ni, 20 Co, 7 Cu, 6·5 Ti	1	
Reco 3A	1.7	7,200	645	4,350	390	13,500	3,000			
Alnico (High Br)	1.7	8,000	500	5,200	327	13,500	3,000			
Alnico	1.7	7,250	560	4,700	362	13,500	3,000	10 Al, 17 Ni, 12 Co, 6 Cu	Heat 1200- 1250°C.	
Alnico (High H <sub>c</sub> )	1.7	6,500	620	4,250	400	13,500	3,000	_	Force cool to	
Hynico	1.63	7,250	628	4,660	350	12,500	3,000	10 Al, 20 Ni, 13·5 Co, 6 Cu	1-4 minutes de-	
Alni (High B <sub>r</sub> )	1.25	6,200	490	4,000	312	12,000	2,000		type.	
Alni	1.25	5,800	550	3,650	340	12,000	2,000	12 Al, 24 Ni		
Alni (High H <sub>c</sub> )	1.25	4,700	700	2,840	440	11,500	3,000	_		
Hynical	1.15	5,250	674	3,290	350	11,500	3,000	12 A1, 32 Ni	1	
35% Cobalt stee	1 0.95	9,000	250	5,930	160	15,500	1,000	_		
15% Cobalt stee	1 0.62	8,200	180	5,250	118	15,000	600	_	Multiple heat-	
9% Cobalt steel	0.5	7,800	160	5,000	100	15,000	600	_	treatment usually involv-	
6% Cobalt steel	0.44	7,500	145	4,680	94	15,000	500		quench.	
3% Cobalt steel	0.35	7,200	130	4.220	83	15.000	500		)	
6%Tungstenstee	1 0.30	10 500	65	6 980	43	14,500	300		Nister or -it	
3% Chrome stee	10.285	9,800	70	6,200	46	13,500	300		quench from approx. 850°C.	

Columns 1-6 are based on manufacturers' published data. \*Approximate figures not taken from manufacturers' data. † These materials can only be supplied in certain shapes.

## A. J. TYRRELL

# TABLE 2. PERFORMANCE OF AMERICAN COMMERCIAL PERMANENT MAGNET ALLOYS

Material	(BH) max	Br gauss	He oer-	B work-	H work-	Recommended Saturation Values		Nominal Composition (balance Fe)
	× 10 <sup>6</sup>		5104	gauss	oer- sted	B <sub>sat</sub> gauss	H <sub>sat</sub> gauss	
Alnico V (orange)	4.5	12,500	600	9,680	465	16,500	3,000	8 Ai, 14 Ni, 24 Co, 3 Cu
Modified Alnico V	4.25	11,200	660	8,500	500	16,000	3,000	8 Al, 14 Ni, 24 Co, 3 Cu
Alnico VI	3.5	10,000	750	7,000	475	14,300	3,000	8 Al, 15 Ni, 24 Co, 3 Cu, 1 · 25 Ti
New KS	2.03	7,150	785	4,150	490	13,000	3,000	3·7 Al, 17·7 Ni, 27·2 Co, 6·7 Ti
Honda Metal	2.0	7,100	780	4,250	470	13,000	3,000	3·3 Al, 18 Ni, 27 Co, 6·7 Ti
Cunife	1.75	5,700	600	4,500	390	8,400	2,400	20 Ni, 60 Cu
Alnico XII	1.75	5,800	950	3,100	565	13,200	4,000	6 Al, 18 Ni, 35 Co, 8 Ti
Alnico II (red)	1.55	7,300	530	4,620	335	12,900	2,000	10 Al, 17 Ni, 12.5 Co, 6 Cu
Modified Alnico 11	1.55	7,000	600	4,200	370	12,900	2,000	10 Al, 17 Ni, 12·5 Co, 6 Cu
Alnico I (blue)	1.4	7,100	450	4,600	305	12,500	2,000	12 Al, 20 Ni, 5 Co
Alnico III (green)	1.4	7,000	470	4,300	325	12,000	2,000	12 Al, 25 Ni
Modified Alnico III	1.4	6,700	555	3,800	370	12,000	3,000	12 Al, 25 Ni
Mishima Metal	1.4	6,000	550	3,900	360	12,000	3,000	13 Al, 29 Ni
Modified Alnico IV	1.35	6,000	620	3,800	360	11,600	3,000	12 Al, 28 Ni, 5 Co
Alnico IV	1.25	5,200	750	3,000	415	11,600	3,000	12 Al, 28 Ni, 5 Co
Vicalloy	1.02	9,000	300	5,530	185	15,000	1,000	52 Co., 10 V
Remailoy	*							
Comol	1.0	9,330	243	5,900	170	17,000	1,000	12 Co, 15 Mo
Cunico	0.85	3,400	710	2,020	420	8,000	3,200	45 Cu., 25 Ni, 30 Co
Simanal	0.08	595	575			20,830	20,000	86·5 Ag, 8·8 Mn, 4·7 Al
Cunife II	0.78	7,300	260	4,680	167	9,500	2,400	50 Cu, 20 Ni, 2 · 5 Co
Kato's Oxide	0.5	1 600	000	011	530	4 800	3 000	30 Fe <sub>2</sub> O <sub>2</sub> , 44Fe <sub>3</sub> O <sub>4</sub> ,
Vectalite Sintered Oxide	0.2	1,000	900	944	530	4,000	5,000	$26 \operatorname{Co}_2 \operatorname{O}_2$
36% Cobalt Steel	0.95	9,600	240	6,150	155	15,500	1,000	_ ·
17% Cobalt Steel	0.62	9,000	165	5,900	105	15,000	1,000	
5% Tungsten Steel	0.32	10,300	70	6,900	46	14,500	300	
3½% Chrome Steel	0.29	9,200	65	6,400	45	13,500	300	
Manganese Steel	0.18	10,000	43	6,250	29	15,000	300	
Carbon Steel	0.18	8,600	48	5,625	32	14,800	300	-

This table is based on manufacturers' published data and is an extended version of the table which appeared in J.Brit.I.R.E., Vol. 6, No. 5.

#### World Radio History

cobalt steels fall into the first group. They can be drilled, tapped, forged and fabricated, and therefore meet applications where machining is necessary. Their coercive force and performance, however, are relatively low.

The aluminium-nickel series and the anisotropic magnets ("Ticonal") fall into the second group. They are hard, relatively brittle, and can only be cast to shape and ground; but they have a high coercive force and high performance.

The physical properties and magnetic characteristics of 35 per cent cobalt steel lie between these two main groups; it can be drilled, tapped and machined with some difficulty, and its performance compares well with that of the lower performance aluminium nickel alloys.

Tables 1 and 2 show, respectively, British and American manufacturers' published data on the commercially available permanent magnet alloys, but information on their behaviour under rigorous conditions of service is not generally available.

## 4.0. Effect of Mechanical Vibration on Permanent Magnets

Experimental work on the magnetic stability of various permanent magnet materials indicates that severe mechanical vibration virtually demagnetizes carbon steel. The effect of severe and prolonged vibration on tungsten, chrome, and the low percentage cobalt steel magnets is to cause a reduction of flux following an approximately exponential law, the final loss being of the order of 20 per cent. For 35 per cent cobalt steel, the drift is stated to be only approximately 10 per cent under the same conditions. Materials in the aluminium-nickel group are affected to a much lesser degree, the loss being only 2 per cent or 3 per cent under similar conditions. The effect of vibration on "Ticonal" magnets is suspected to produce a very small drift, but no decrease in flux was observed with the measuring apparatus used, even though in these tests vibration was continued until mechanical failure of the assembly or the fracture of the magnet resulted.

Experimental work indicates that, if a magnet is artificially aged to a slightly lower value of flux than that to which it would be reduced by prolonged vibration, it will not drift further when subsequently subject to vibration. There is, however, some controversy on this point, at least one observer reporting that, with the early types of magnet steels, a further small drift can be produced by vibration even after artificially ageing.

Various reports indicate that if, for the purpose of calibration or adjustment, a magnet is artificially aged more than is necessary to achieve stability, there is a tendency to recover (i.e. performance increases after a lapse of time).

This is found to be quite definitely the case with some aluminium-nickel magnets if aged by more than approximately 10 per cent.

The author has not been able to obtain sufficient reliable experimental data for materials other than "Ticonal" alloy. Very careful tests which have been made with this material, however, indicate that it is quite stable regardless of the degree of artificial ageing.

# 5.0. Effects of Temperature on Permanent Magnets

The effect of heat on a permanent magnet tends to produce a change of metallurgical state which may result in a change in the magnetic performance of the magnet. An alloy whose final heat treatment or tempering took place at a relatively high temperature would be expected to be more stable metallurgically at normal ambient temperatures than a quenched steel or a steel tempered at a lower temperature.

Carbon steel is known to age at normal ambient temperatures due to metallurgical changes which, in turn, cause changes of magnetic performance.

The drift in magnetic performance of metallurgically unaged tungsten chrome and cobalt steel magnets is fairly small at room temperatures but continues over a period of many years, and may become very serious at slightly elevated temperatures.

It has been found, however, that with this type of magnet one hour at 100 deg. C gives approximately the same metallurgical ageing effect as one year at normal room temperature, and this effect is responsible for the many and varied methods adopted to improve magnetic stability, such as boiling in water or oil for many hours or storing for a period of years before use.

The effect of temperature on a metallurgically aged magnet is found to be similar to that of mechanical vibration, i.e. regardless of whether the agitation is thermal or mechanical, the initial magnetic performance is reduced according to an approximately exponential law.

The aluminium-nickel alloys are very resistant to change of magnetic performance with temperature and are not seriously affected up to approximately 300 deg. C. Above this temperature serious drift has been reported to occur reaching approximately 10 per cent at 500 deg. C, and 25 per cent at 600 deg. C.

"Ticonal" magnets have been found to be reasonably stable at 500 deg. C, but drift commences at 600 deg. C.

Temperature has two effects on the performance of a correctly aged or stabilized permanent magnet. One is to produce a cyclic change in magnetic flux due to the negative temperature coefficient of magnetic performance (i.e. an increase in temperature produces a decrease in flux) stated to be -.02 per cent per deg. C, and the other is to produce cyclic changes due to thermo-mechanical effects in the magnetic circuit due to thermal expansion. This change of magnetic performance due to thermo-mechanical effects bears a close relation to the slope of the recoil curve of the alloy used, and since the slope of the recoil curve is reasonably parallel with the demagnetization curve at  $B_r$ , it follows that an alloy with a high fullness factor where the demagnetization curve at B<sub>r</sub> is practically horizontal, would produce a correspondingly small change of magnetic performance due to temperature changes.

#### 6.0. Effects of Stray or Alternating Fields on Permanent Magnets

The extent to which a magnetized permanent magnet is affected by stray or alternating fields is dependent not only upon the shape, dimensions and design of the magnet but also upon the coercive force and fullness factor of the alloy used.

Fullness factor is expressed as 
$$\frac{(BH)_{max}}{B_r H_c}$$

Its dependence on coercive force is more or less obvious, since a material with a high coercive force needs a correspondingly high demagnetizing effort to reduce its flux to zero, and it is therefore reasonable to suppose that its resistance to partial demagnetization would be more or less proportional to its coercive force. Experimental results prove this to be so.

Its dependence on fullness factor is not so obvious but may be explained as follows :----

If the demagnetizing characteristic of an alloy is a fairly straight line for B plotted against H (see Fig 3), it would indicate that if a demagnetizing force equal to say 1/10 of the H<sub>c</sub> is applied, a reduction of approximately 1/10 of the flux would result The reduction would be less under practical conditions for two reasons; firstly, the demagnetizing characteristic of a magnet is normally curved, and secondly, there would be an appreciable recovery when the demagnetizing force is removed; but nevertheless there would be a net loss of flux.

This loss can be attributed only to the fact that the magnet may be considered as a mass of extremely small elementary magnets or domains which are not all identical, some being easily disturbed by a small reverse M.M.F. (demagnetizing force), while the remainder are not influenced. If the reverse M.M.F. is increased, more and more domains are disturbed until a reverse M.M.F. equal to  $H_c$  is applied when the last of the domains are upset.



Fig. 3.—The demagnetization characteristic of a theoretical permanent magnet where the domains are uniformly graded.

If, however, all the domains had similar magnetic characteristics, the application of any reverse M.M.F. or demagnetizing force less than the H<sub>c</sub> value would fail to disturb any of them and, when a reverse M.M.F. equal to H<sub>c</sub> is applied, they would all give way at once. This state of affairs would be represented when the measured demagnetizing characteristic of the alloy is rectangular in shape, as illustrated in Fig. 4.

Now, since the fullness factor is a convenient method of indicating the degree to which the demagnetizing characteristic is rectangular, it would appear reasonable to expect an alloy with a large fullness factor to be more resistant to demagnetizing fields than an alloy with a smaller fullness factor providing, of course, that the  $H_c$ values of both are similar. Experimental data indicates that this is so.



# 7.0. Effects of Time on the Performance of Permanent Magnets

The effect of time on the performance of magnets has received a very considerable amount of attention, but since room temperature is of necessity associated with time, the effect of time alone is not known nor would it be of any practical value if it were. Observations indicate that a magnet is relatively stable with respect to time when maintained below a certain critical temperature; at this temperature observable deterioration of performance takes place, and at higher temperatures the deterioration rapidly increases. This implies, and experimental results confirm, that the higher this critical temperature is above room temperature, the more stable is the magnet with respect to time, and conversely the lower the critical temperature (i.e. the nearer to room temperature), the greater the amount of artificial ageing which is required to give the magnet a reasonable degree of stability.

## 8.0. Method of Stabilizing a Magnet

The first requirement of magnetic stability is metallurgical stability. In the case of dispersionhardened magnets with a final heat treatment or tempering at approximately 600 deg. C, the magnets should require no further thermal treatment.

In quench-hardened steels, the practice of storing for a period of years may be abandoned in favour of a simple heat treatment consisting of holding the magnets at 100 deg. C for eight to ten hours, during which the metallurgical changes corresponding to approximately the first ten years of storage will take place. Any subsequent small changes are usually negligible.

Next, the metallurgically stable magnet must be magnetized to complete saturation. The method of magnetization should be such that the flux produced by the magnetizer is sensibly similar in direction to the direction of the flux required in the operating magnet. Therefore, if the magnet comprises only part of the magnetic circuit, the final assembly should be completed before any attempt is made to magnetize the magnet. Information and advice on magnetization should be obtained from the magnet manufacturer, and the magnetizing impulse should always err on the generous side since inadequate magnetization is liable to produce instability.

Finally, the magnet should be magnetically stabilized by reducing its flux to a predetermined percentage of its maximum value. This reduction should be such that the remaining flux is a little lower than the value to which it would have fallen during the most adverse conditions of use over the entire estimated working life of the apparatus in which the magnet is to operate.

The best method of reducing the flux is the subject of considerable controversy. The method recommended by the author for approximately circular magnets, which are magnetized by a current-carrying conductor passing through the centre of the magnet, is to pass through the same conductor an alternating current of sufficient magnitude to produce the required reduction of flux; but this alternating current must be slowly increased from a very small value to a maximum and then be reduced practically to zero equally slowly.

Magnets which are not magnetized in this way should be placed in a reasonably large and uniform alternating field (such as inside a large open coil) and the field should be either slowly increased to a maximum and again slowly decreased, or the magnet moved slowly into and out of the field produced by the coil. In this case, it is recommended that the direction of the field be parallel to the lines of force in the gap of the magnet.

## 9.0. Handling Stabilized Magnets

The importance of care in handling a stabilized magnet is not always recognized. The most

#### **Ouench Hardened\*** Dispersion Hardened Ticonal Tungsten 3% Chrome 35% Alnico (Direc-Steel Steel Cobalt Cobalt tional) Minimum Reduction Where the magnet is 15% 15% 15% 5% 3% 1% relatively undisturbed **Recommended Reduction** Where the magnet is subjected to the effects of 30% 30% 30% 10% 3% 6% vibration, wide ranges of temperature and stray fields. **Maximum Reduction** If this value is exceeded the magnet may effect 10% 100% some recovery of performance.

# TABLE 3

# DEGREE OF REDUCTION OF MAGNETIC PERFORMANCE NECESSARY TO PRODUCE MAXIMUM MAGNETIC STABILITY

\* These figures apply only to metallurgically aged magnets.

important point is to avoid any alteration in the distribution of its flux. This means that the magnet must be kept away from ferrous objects such as tools, etc., or other magnets. The inadvertent contact of the magnet with a ferrous object such as a screw-driver, for example, will considerably upset the distribution of its flux, and the beneficial effects of stabilization will be to a certain extent lost. It is therefore preferable that the magnet be magnetized and stabilized in the complete instrument and the covers immediately fitted.

Meter designers do not always appear to take seriously the fact that a redistribution of flux in the magnet renders the stabilizing treatment to a certain extent ineffective, and that the use of a magnetic shunt may be detrimental to the overall stability of the magnet. Fortunately, the instability caused by the use of a shunt represents only a percentage of the flux disturbed by the shunt, and, since this flux is generally only a small percentage of the whole, the instability caused is usually of negligible proportions. For example, in watt-hour meters, the only method of achieving the highest possible stability while allowing some degree of adjustment of braking effect is to arrange that the magnet, as a whole, can be moved so that its braking effect may be varied while its flux is allowed to remain constant and undisturbed.

A further point which should be carefully watched is that magnets should be adequately protected from accidental contact with tools used by operators during the test and adjustment of the meter; otherwise instabilities may be introduced which could reflect on the performance of the meter as a whole.

Keepers should never be used with modern high-performance magnets, since they disturb the flux distribution in the vicinity of the pole faces, thereby nullifying any attempt at stabilizing the field at a precise value. Keepers are also liable seriously to impair the performance of the magnet if allowed to come into contact with parts of the magnet other than the pole faces. The inflexible rule should be that if a stabilized magnet is touched by any magnetic object, it should be re-saturated and re-stabilized.

#### 10.0. Effects of Modern High-performance Permanent Alloys on the Design of Instruments

The early types of magnet steels, with their low coercive force and consequent high lengthto-section ratio, necessitated most instrumenttype magnets taking the form of long loops with, of course, an unavoidably high magnetic leakage. The new high-performance materials, requiring only a relatively small block of alloy to meet the same magnetic specification, have allowed the design of the magnetic circuits to be considerably modified, resulting in very much smaller and more compact systems with a correspondingly reduced magnetic leakage.

A further reduction in size and cost is obtained, since the reduction of magnetic performance, in order to achieve stability, is much less with the high-performance permanent magnet alloys than with the earlier types (see Table 3). Therefore, when comparison is made between various magnetic materials, these factors should always be taken into account.



Fig. 5.—A typical eddy current damping or braking imagnet.

Watt-hour meters have been affected in a rather different manner by the improvements in permanent magnet alloys. The early types of magnet steel with their high length-to-section ratio were particularly suitable for the construction of long single-piece magnets extending from one side of the rotating disc to the other.

With the improvements in magnetic materials, whereby less alloy is required to meet a given magnetic specification, increasing difficulty has been experienced in utilizing the alloy economically, the magnet frequently having to be made longer than the magnetic requirements demanded in order to clear the edge of the disc.

The latest very high-performance anisotropic magnets require such a small volume of material to meet the magnetic specification that it would prove both wasteful and costly to manufacture a magnet consisting wholly of magnet alloy extending from one side of the disc to the other. This problem has received considerable attention and various experimental constructions have been tested whereby a piece of magnet alloy forms part of a composite construction employing mild steel to carry the flux to the required areas of the disc. (See Fig. 5.)





Fig. 6.—(a) The "Ticonal" magnet. (b) The magnet with its protective covering. (c) The complete adjustable eddy-current braking assembly.

Meter manufacturers are generally apprehensive of any mechanical joints in so critical a part as the braking magnet, with the result that these composite assemblies have not been favourably received.

The problem appears to have been satisfactorily solved by using a magnet as illustrated in Fig. 6, designed so that the flux passes through the disc to an iron yoke and, at a short distance along the yoke, back through the disc to the magnet, thus utilizing the very high coercive force of the latest magnet alloys to drive the flux twice through the disc, so obtaining a double braking effect.

In this design the method of adjusting the braking effect is not by shunting or otherwise interfering with the stabilized performance of the magnet, but by rotating the magnet so that the rectangular areas of braking flux may present their wide or narrow faces to the direction of motion of the disc. (See Fig. 6 (c).)

Meters using this new type of braking system have been on test for over five years, and there is no indication of change or drift in the performance of the magnet.

#### 11.0. Conclusions .

1. It appears reasonable to deduce that the desirable characteristics which materially contribute to the long-term magnetic stability of a permanent magnet alloy are :---

- (a) A high degree of metallurgical stability.
- (b) A high temperature at which the magnetic performance commences to deteriorate.
- (c) Maximum resistance to the effects of mechanical vibration.
- (d) A high coercive force.
- (e) A high fullness factor.

2. The latest developments in permanent magnet alloys (anisotropic alloys) represent improvements in all the characteristics which promote good long-term stability, and "Ticonal" anisotropic magnets, now in their tenth year of manufacture, and after extensive tests throughout this period, have been proved to be more stable than previously obtainable materials.

3. Watt-hour meters (which probably make the most exacting demands on stability) have been designed to take advantage of the characteristics of "Ticonal" magnets, have proved thoroughly satisfactory, and have been for some years in full-scale production.

#### 12.0. Acknowledgments

The author is indebted to many engineers for the considerable amount of unpublished information made available to him during the preparation of this paper. He also wishes to express his thanks to the management of Mullard Electronic Products, Ltd., for permission to publish this paper.

#### 13.0. Bibliography

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# TRANSFERS AND ELECTIONS TO MEMBERSHIP

Subsequent to the publication of elections to membership which appeared in the April issue of the Journal, a meeting of the Membership Committee was held on April 25th, 1950. Eleven proposals for direct election to Graduateship or higher grade of membership were considered, and twenty-two proposals for transfer to Graduate or higher grade of membership.

The following list of elections was approved by the General Council : Twelve for direct election to Graduate or higher grade of membership, and eighteen for transfer to Graduate or higher grade of membership.

Direct Election to Full Member

Simmonds, John Charles,	London,
M.Sc.(Eng.), Ph.D.	N.W.10
Simpson, Jack William Newby, M.Sc., B.E. (Hons.)	Wellington, N. Zealand
, , ,	-

Direct Election to Associate Member

Denham, Thomas William	Sevenoaks,
	Kent
Hazell, Robert Charles, Sqd./Ldr.	Horseheath, Cambs.
Picksley, George Hugh	Richmond, Surrey

#### Direct Election to Companion

Godfrey, George William	West Horsley,
	Surrey

#### Direct Election to Associate

Castell, Reginald Thomas	London,
Castell	S.W.2
Inder, Walter Willcocks	Aberdeen, Scotland
Mathews, James William	Cuffley, Herts.
Phillips, Graham	Godstone Green, Surrey

#### Direct Election to Graduate

Fitch, Stanley William Martin,	Woodford
B.Sc.(Eng.)	Green, Essex
Hodgkinson, Cyril Duncan,	Porchester,
Lieut.(L)	Hants

Transfer from	Associate	Member	to	Full	Member

Swann, I	Eric	Dennis	Maidstone,	
			Ken	it

#### Transfer from Associate to Associate Member

Amor, Mervyn	•	Bombay, India
Davis, Norman		Sleaford, Lincs.
Jones, John Elfed, B.Sc.		Roath, Cardiff
Lobb, Kenneth, Lieut.(L)		Lee-on-Solent, Hants
Telfer, James Connell Welsh		Glasgow, W.4
Wentworth, William Henry		Greenford, Middlesex

#### Transfer from Graduate to Associate

Lockley, Noel Arthur Bridgnorth,

Salop.

#### Transfer from Student to Associate

Dobson, William John	Manitoba,
	Canada
Etter, Alwyn Charles	Dartford, Kent
Sharpe, Kenneth Allan	Niton, Isle of
	Wight

#### Transfer from Student to Graduate

Ali, Ahmad, B.Sc.	Dacca,
	E. Pakistan
Boyce, Desmond Archibald	Oxford
Conlon, James	London, S.W.2
Hicks, Charles Ernest	London, E.13
Hubbard, John Valentine, B.Sc.	Godalming,
	Surrey
O'Hagan, Michael	London, N.W.9
Robertson, Albert William	Edgware,

Middlesex

# NOTICES

#### **Radio Component Specification**

The Radio Industry Council (of Great Britain), which last year published specifications for climatic and durability tests of components and for choice of materials, has now published the first of a series of specifications covering class, category and quality of components. This specification, No. RIC/122—Resistors Rotary Variable, Composition Track (With or Without Switches), is significant of the careful and detailed technical work now being undertaken jointly by all sections of the British radio industry under the auspices of the R.I.C. The intention is that all components in general use in the radio and electronic industries will eventually be covered in the series.

The new specification represents many months of work by the technical representatives of both manufacturers and users of components. It was finally approved by the Technical Directive Board of the R.I.C. on which all four constituent associations are represented (the fourth being the British Radio Valve Manufacturers' Association).

The specification, in standard loose-leaf form, measuring 8 in.  $\times$  10 in., is in three sections as follows :—

- I. Performance requirements.
- 2. Production tests.
- 3. Schedule of types, values, sizes.

Section 3 so far contains preliminary dimensional data only, but will eventually contain full details of dimensions, ratings and values.

For the time being the specification is meant for use internally within the industry, but it is intended to submit it eventually to B.S.I., by which time it may be found possible to co-ordinate the requirements of the industry and of the Services in one comprehensive national standard.

The Radio Industry Council is urging its members to make the fullest use of the specification.

The complete specification is obtainable from the Radio Industry Council, 59 Russell Square, London, W.C.1, price 3s. 6d., and the sections are available separately at 2s. 6d., 9d. and 3d. respectively. Amendments will be sent to those asking for them on buying the original specification.

#### **Technical State Scholarships**

The Ministry of Education has announced that the number of Technical State Scholarships available this year is to be increased from 100 to 120.

Eighty of the scholarships will be available to candidates under the age of 20 on July 31st next, and up to 40 scholarships available for candidates aged 20 or over at that date. There is no upper age limit for the latter awards.

These scholarships will be offered to students to enable them to pursue full-time degree courses normally leading to an honours degree—or courses of equivalent standard at Universities, University Colleges or Establishments of Further Education.

Candidates must have completed a course leading to an Ordinary National Certificate or Diploma or course of equivalent standard, and normally have been in full-time or part-time attendance at an Establishment for Further Education for not less than two years immediately preceding August 1st next. All applications must carry a recommendation from the Principal of the Establishment which the candidate has been attending.

The award of a Technical State Scholarship will not exempt the holder from the normal admission requirement of a University. Successful candidates must make their own arrangements for acceptance by a University, University College or Technical College. Candidates are strongly advised to secure provisional acceptance by the institution they choose, making it clear that they are candidates for a Technical State Scholarship.

Explanatory leaflets and application forms may be obtained from Principals of Further Education Establishments or from the Ministry of Education, Curzon Street, London, W.1. Applications must be submitted through Principals to reach the Ministry not later than June 30th next.

#### C.B.S. Television Papers

Owing to unforeseen printing difficulties it has not been found possible to include the two papers by Dr. P. Goldmark of C.B.S. Inc., in this issue of the Journal as anticipated.

It is intended to include one or both of these papers in the June issue of the Journal.

# ELECTRONIC INSTRUMENTATION FOR CHEMICAL LABORATORIES\*

by

Felix Gutmann, Ph.D.†

## **SUMMARY**

Electronic technique, i.e. the employment of electron tubes and other electronic devices in amplifying and in measuring circuits has, during the last decade or so, pervaded a number of fields which are somewhat remote from that realm of communications in which these techniques first arose. One of these newer fields of application which is probably less familiar to Radio Engineers is the use of electronic instruments in chemical laboratories, where such apparatus leads not only to greater accuracy and greater speed, but also to considerable savings in time and manpower employed. While the present short survey cannot lay claim to any exhaustive treatment of so vast a subject, the attempt will be made to present to Radio Engineers some of the most commonly used electronic instruments which find a wider application in chemical laboratories.

#### 1.0. pH Meters

The reaction of an aqueous medium is either acidic, basic or neutral. This property is of paramount importance in a wide range of chemical processes (e.g. electro-plating, canned foodstuffs, ore flotation, dairying industry, wool scourers and dyers, tiles and china manufacture, wineries, paper mills, synthetic plastics, flour mills, etc.). It depends on the relative concentration of hydrogen-ions, (H+), and of hydroxyl-ions, (OH -), in the medium. The acid or basic behaviour of a solution is measured in so-called pH units,<sup>1</sup> pH being defined as the negative logarithm of the hydrogen-ion concentration in the solution. Pure water is exactly neutral and has a pH of 7. A fairly concentrated (1N) solution of a strong acid, say hydrochloric acid, has a pH of 0 and a 1N solution of a strong base, say caustic soda, a pH of 14. It is seen that an acidic solution will have a pH below 7 and an alkaline solution a pH above 7. The lower the pH, the more acid, and the higher the pH, the more basic is the solution.

The pH of a solution can be measured by employing the unknown medium as the electrolyte in an electrolytic cell having one inert and one pH sensitive electrode, and measuring the electric potential appearing between these two

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electrodes. The most convenient pH sensitive electrode is the so-called glass electrode,<sup>2,8</sup> which consists of a small, thin-walled bulb of special glass containing a solution of known pH.

When immersed into the liquid to be tested for its pH, the potential difference set up is proportional to the difference in pH of the solutions inside and outside the glass electrode. It can be shown from thermodynamics that one pH unit difference generates a potential difference of 59.1 millivolts at 25 deg C. However, the measurement of these potentials is by no means easy, since the internal resistance of the glass electrode is very high, usually of the order of 300-900 megohms. Since a direct potential is generated and an accuracy of 0.05 pH is required, a voltmeter is needed with about 840 mV d.c. full-scale sensitivity, accurate to 0.3 per cent. and having an input resistance of at least 300 times the electrode resistance, i.e. an input resistance of 10<sup>12</sup> ohm or better.

Vacuum tube voltmeters filling these requirements have been developed overseas<sup>3</sup> as well as in Australia. While great care must be taken to ensure sufficient insulation and proper shielding of all input circuits, reduction of the grid current to extremely minute values is necessary, since a grid current of as little as 10<sup>-11</sup>A produces a voltage drop of about 5 mV in the internal resistance of the electrode. This amounts to about 0.1 pH unit and cannot be tolerated. The problem has been tackled from a number of angles. Firstly, by the use of electrometer tubes.<sup>4</sup> These are special tubes,

<sup>\*</sup> Reprinted from the Proc.I.R.E., Australia. September, 1949. U.D.C. No. 541.1:621.389.

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usually of very low, if not fractional, gain, often with quartz insulation and specially designed for extremely low grid current. They operate at very low operating voltages, have wide interelectrode spacing-and are rather expensive. However, the use of such a tube as an impedance transformer followed either by a highly sensitive galvanometer or by another conventional stage and an ordinary moving coil meter, has permitted the design of a number of overseas commercial pH meters which have given satisfactory performance. Leeds and Northrup, Marconi and others operate on these lines. Two typical circuits are shown in Fig. 1. The quiescent plate current through the meter is seen to be balanced out. The circuits shown, which have been developed by Barth and modified by Pennick,<sup>5</sup> are independent of small changes in the operating voltages, which are derived from dry batteries.



Figs. 1a & 1b.—Electrometer-Tube Circuits according to Barth and Pennick.

Another avenue of approach to the problem is represented by the impulse type, or ballistic amplifier,<sup>6</sup> which is shown in its essentials in Fig. 2.



Fig. 2.—Goodhue's Ballistic Amplifier.

The condenser C is charged by the voltage under test, in series opposition with a known voltage derived from the potentiometer P. During this time, the grid of  $V_1$  is maintained at earth potential. When the key  $S_1$  is depressed, C shares its charge with the input capacity of  $V_1$ , which can be made much smaller than C. The grid, therefore, becomes charged to a potential only little less than the original potential of C, which in turn has been charged up to a potential equal to the algebraic sum of the electrode potential and the known output of P. If the latter is equal in magnitude to the electrode potential, this sum will be zero, no charge will flow into C and no change in the grid potential and therefore in the r ading of a meter MA inserted in the plate circuit of the amplifier will ensue when  $\hat{S}_1$  is pressed. The operation of this type of instrument therefore consists in adjusting P so that no deflection of MA is obtained on pressing the key S<sub>1</sub>. The unknown voltage is then read off the potentiometer P, which can be directly calibrated in pH units. The amplifier may be a conventional R-C coupled audio amplifier.

A number of direct-coupled amplifiers, using standard radio tubes, have been developed for



Fig. 3.—Typical Direct Coupled Current Amplifier.

use as pH meters. In general, the tubes have to be specially selected for stability and low grid current. Dry batteries are employed as coupling elements, as shown in a typical circuit illustrated in Fig. 3.

A slide-back valve voltmeter suitable fo. pH meters and using standard 1K5G valves, which need not be specially selected, has been developed by the author<sup>7</sup> and is shown in Fig. 4. The grid current is reduced to about  $10^{-13}$  A by reducing the filament voltage to 1.5 V, reducing the plate current to a very small value and operating the 1st stage under a high negative grid bias with a large degree of inverse current feedback. No coupling batteries are necessary and the degeneration present leads to good stability. A similar circuit has been developed, independently, by Shepard.<sup>9</sup>



Fig. 4.—Electronic pH Meter Circuit, according to Gutmann.

All the circuits shown so far are battery operated. A very simple mains-operated pH meter, the first of its class developed in this country, has been designed by the author and its fundamental circuit is shown in Fig. 5. A 6B6, which again need not be specially selected, serves as input stage, cathode coupled to a 6SN7 also operated as a cathode follower. Again the 1st stage operates under a much reduced plate current and a high negative bias, as well as reduced heater voltage. While the instrument, due to the 100 per cent. degeneration present, is largely independent of variations in the plate supply voltages, regulation of the heater supply is essential. Dr. G. Builder has designed a special purpose constant voltage transformer of the saturable reactor type, which keeps all supply voltages sufficiently constant for mains voltages varying between 190 and



Fig. 5.—High Gain Mains Operated Current Amplifier according to Gutmann.

#### 2.0. Current Amplifiers in General

It will be recognized that the pH meter circuit last described is a special case of a kind of amplifier rarely encountered in radio work, viz. a current amplifier. Thus, in the abovementioned circuit (Fig. 5), a current of the order of  $3 \times 10^{-9}$  A flowing in the input circuit gives a full scale deflection of  $250 \,\mu$ A. The instrument therefore has a current gain of about  $10,^5$  but only a fractional voltage gain.

Besides the measurement of pH, current amplifiers find application in chemistry in colorimeters, vacuum gauges, null point indicators for titrations and for electrolytic conductivity determinations, in polarography, gas analysis and in a host of other cases. In certain of these applications, particularly where a recorder has to be operated, the gain has to be even higher.

The most straightforward way to obtain high current amplification is the combination of a mirror galvanometer of the required sensitivity with an amplifier photo-electrically coupled to the galvanometer. Many such arrangements have been published.<sup>10</sup> Light is reflected from the galvanometer mirror, spread out into a band by means of an optical arrangement and allowed to fall on to the cathodes of two photo cells mounted side by side. Their position is so arranged that, for zero galvanometer deflection, the same amount of light is incident on both cathodes. If the galvanometer is deflected, this equilibrium is disturbed and the resulting unbalance current, generated by the photo cells, is amplified and operates a meter or recorder. The Tinsley Direct Current Amplifier is a commercial version of such an instrument.

The recently released "Zeus" circuit,<sup>11</sup> an American wartime development, should find many uses apart from the amplification of ionization chamber pulses for which it was originally developed. The circuit is shown in Fig. 6 and should be self-explanatory.



Fig. 6.—Typical Electrometer Circuit (Zeus).

Extremely low grid current is a pre-requisite to high current-amplification. Apart from the 1K5 and the 6B6, the 6AK5, 6AU6, 38, 959, 954, 6C6, 6C8, 12BE6, 9001 are standard radio tubes suitable for operation involving low grid currents. Nielson<sup>12</sup> has investigated a number of American valve types for suitability as electrometer valves, and Crawford<sup>13</sup> has done the same for some English valves. The miniature and sub-miniature tubes developed during the war all show great promise in this respect and their use may allow the designer even higher figures of current gain. One important consideration in the design of current amplifiers is the relaxation time, or the effective time constant of the circuit. In effect, a capacitance, even if it may consist only of the grid and input lead capacitance, is charged through a very high resistance. It will therefore take a finite time, and this time may become uncomfortably large, to produce a response to changes in the potential under test. Ballistic amplifiers are the worst offenders in this respect, due to the large additional capacitance introduced, while a cathode-follower input leads to an appreciable reduction in the relaxation time of the circuit.<sup>14</sup>

Current amplifiers of high input impedance are also prone to show parasitic oscillations. There is no panacea against this annoying property, but liberal by-passing and earthing of the heaters, in the case of indirectly heated tubes, is often found to be of value.

In order to circumvent the difficulties inherent in the design of multi-stage direct-coupled amplifiers, a number of current amplifiers have been designed involving the conversion of the d.c. signal into a.c. Electronic conversion,<sup>15</sup> mechanical transducers,<sup>16</sup> and vibrating capacitors<sup>17</sup> charged by the signal have all been > employed, but none of these types of circuitry has found any appreciable use in chemical laboratories, due to the high cost and complication of the apparatus involved. Recently, magnetic amplifiers<sup>18</sup> have been used as directcurrent amplifiers and it may well be that in many applications these will supersede circuits employing vacuum tubes. Furthermore, it is of interest to note that the magnetron also can be used as a current amplifier.<sup>19</sup>

## 3.0. Colorimeters

Under this heading, it is intended to summarize a rather wide variety of instruments which rely on the measurement of light incident on a photo-electric cell. Colorimeters proper are instruments which compare, against a standard, the variations in the absorption of light produced by a colour change in a liquid undergoing a chemical reaction. Spectrophotometers employ a monochromatic beam of light of adjustable wavelength and thereby permit a better degree of discrimination. Photo-Fluorometers illuminate the solution with—usually ultra-violet—light and measure the fluorescence which it excites by means of a photo-electric cell mounted at right angles to the exciting beam of light. All these instruments employ either photo-voltaic cells (usually selenium) or photoelectric tubes (usually with caesium cathodes).

The photo-voltaic cell consists of a layer of selenium or cuprous oxide grown on a metallic Upon illumination, electrons are support. emitted from the metal into the semi-conductor or vice versa, depending on the type of cell. A potential difference is thereby generated and a current flows through the external circuit. While this current is strictly proportional to the intensity of light incident on the cell, the voltage follows an approximately logarithmic law. Failure to realize this has cast undeserved doubt on the reliability of the photo-voltaic cell. These cells are essentially current generators of low internal resistance. If connected to a measuring device of appreciable resistance, it will be their voltage rather than their current output which will be measured and nonlinearities result. Since the currents obtained are comparatively large, while the potential generated is small, a straightforward connection to a meter or galvanometer of very low internal resistance represents the easiest way out.



Fig. 7.—Feedback Circuit according to Rittner, maintaining Zero Voltage across the Photocell.

However, even the best galvanometer presents an appreciable resistance to the cell and electronic circuits must be employed if strict linearity is desired. A circuit which offers virtually zero resistance has been developed by Rittner<sup>20</sup> and is shown in Fig. 7. The flow of photo current causes a voltage to appear across the load  $R_2$  and a corresponding change in voltage across the cell. This latter voltage, amplified by the tube, appears across  $R_1$  in series opposition to the photo-electric potential across the cell. The circuit parameters can be arranged so as to virtually eliminate the total change in potential across the cell.

One advantage which photo-voltaic cells have over other photo-cells is that they do not require

an external power supply. While having a light sensitivity which is orders of magnitude larger than the sensitivity which may be achieved with photo-voltaic cells, photo-electric cells need an external plate voltage supply. If the cell, as is usual, is operated under conditions of voltage saturation, this potential need not be very constant and for many applications may even be alternating. A photo-electric cell, however, can also be operated without any auxiliary voltage whatever by simply connecting it between grid and cathode of a suitable tube, as shown in Fig. 8. The plate current then follows Koechel's equation<sup>21</sup> and is proportional to the logarithm of the light intensity. Russell,<sup>22</sup> who developed the circuit in Fig. 8, has also given a theoretical foundation for this empirical relationship, based upon Richardson's equation<sup>23</sup> for the thermionic grid-current. Such a logarithmic colorimeter should be of particular value, since absorption of light follows the Beer-Lambert law, which also is of a logarithmic form.



While the current generated by a photoelectric vacuum cell under voltage saturation is strictly proportional to the intensity of illumination, it is very much smaller than the currents generated by photo-voltaic cells, since the photoelectric cell represents a source of very high internal resistance. In order to obtain an appreciable voltage output, the cell has to work into a rather large load resistance, which then also functions as the grid leak of the input tube.

The sensitivity which can ultimately be achieved with photo-electric instruments is truly enormous. An instrument which has been developed for astronomical work has been said to be capable of measuring the light received in London from a single candle burning in California.<sup>24</sup> Such apparatus employs multiplier types of photo-tubes, where secondary electron emission serves as a means of obtaining such enormous figures of gain. The cell and input stages are refrigerated to reduce the noise level. While such high sensitivities are quite unnecessary in apparatus destined for chemical laboratories, the modern trend nevertheless is towards instruments which have a higher sensitivity than can be achieved with photo-voltaic cells. The latter always require a rather strong illumination of the sample under test, and, in many cases, undesired chemical reactions are set up in the sample by the strong light. Another drawback is the comparatively large area which has to be employed in photo-voltaic cells in order to obtain an appreciable current output. This again requires rather large quantities of solution, which often is a great inconvenience, particularly in biological work.

A large number of circuits for photo-electric cells have been described elsewhere.<sup>25</sup> The author has adapted the current amplifier shown in Fig. 5 for a completely mains-operated colorimeter where the illuminating lamp is supplied from the built-in constant voltage transformer. The high current gain allows the use of filters with only a low intensity of light falling on the sample. The instrument, by virtue of its high sensitivity, can also readily be adapted to serve as a photo-fluorometer, simply by the addition of an external mercury vapour lamp. Provision has been made for the insertion of polaroid filters, thus further extending the use of this rather versatile instrument.

An interesting application of a photo-electric cell is the Dewpoint Meter for Condensable Vapours developed by Puck.<sup>26</sup> Very small concentrations of such vapours can be determined photo-electrically by measuring the decrease in reflectivity of a cooled surface on which the vapours condense.

Photo-electric methods are of particular advantage in high polymer research, e.g. in the field of synthetic plastics, since Debye<sup>27</sup> has developed a method which permits the determination of the molecular weight and of the size of particles from light-scattering measurements. Debye<sup>28</sup> has designed a special photo-electric instrument for such measurements.

Colorimeters find a wide variety of applications in chemical laboratories. Quantitative analysis can be carried out with their aid whenever the presence of the substance, which is to be determined, changes the absorption of light. Often the analysis can be carried out by the addition of a reagent which produces a reaction and thereby influences the absorption. In this way, the colorimeter can be applied for pH measurements by adding to the solution so-called colour indicators.



Fig. 9.—Polarographic Current-Voltage Curves.

#### 4.0. Polarographs<sup>29</sup>

Polarography is a method of electrochemical analysis, devised by Heyrovsky,<sup>30</sup> which is based on the interpretation of the characteristic current vs. voltage curves obtained in the electrolysis of solutions. In order to avoid electrode contamination by the products of electrolysis, and for other reasons, a dropping mercury electrode is used in conjunction with a second electrode of an effective area very much larger than the area of the mercury drops. The potential applied to the system is continuously increased and the current flowing determined as a function of the potential. Curves such as shown in Fig. 9 are obtained. When a certain critical voltage is reached, electrolytic discharge commences and the current starts to rise. Later, a region of saturation current is reached and it can be shown that this saturation current is directly proportional to the concentration of the substance which is being discharged, while the discharge potential depends on the nature of this substance. The mid-point of the discharge curve, called the half-step potential, serves to identify the substance. The whole curve is termed a polarographic "step" or "wave." These halfstep potentials have been tabulated<sup>29</sup> for a large number of ions and other substances which can be reduced or oxidized at a mercury electrode. A quantitative analysis of the substance being electrolysed is thereby possible.

The current-voltage curves can be obtained either by means of a calibrated potentiometer and a mirror galvanometer (the currents involved are of the order of microamperes or fractions of microamperes) followed by manual plotting, or from an automatic recorder like the Leeds and Northrup Micromax. The latter measures the current by means of a self-balancing potentiometer employing a current amplifier in older to amplify the out-of-balance current. Of course, any suitable current amplifier which does not introduce too high a resistance into the polarographic circuit may be used. This last limitation is sometimes a serious one, but the author has used a converter type of d.c. amplifier with



Fig. 10.—Roberts' Electrometer Circuit.

some success and, for all industrial purposes, an adapter has been designed by R. Millership, of Davis Gelatine, Ltd., Sydney, to allow the use of any pH meter for polarographic determinations.



Fig. 11.—Matheson and Nichol's Circuit for the Oscillographic Display of Polarographic Curves.

A polarograph employing a current amplifier has been designed by Schulman and co-workers.<sup>31</sup> Using a degenerative electrometer circuit first given by Roberts<sup>32</sup> and shown in Fig. 10, a compact instrument of good sensitivity has been developed by these authors.

The periodicity of the dropping mercury electrode suggested the synchronization of the drops with the sweep circuit of a cathode ray oscillograph, with the result that the whole polarographic curve is displayed on the screen. Matheson and Nichols,<sup>33</sup> by synchronizing a voltage sweep of 30 c/s with a dropping electrode of 1/30-second drop-time, displayed the whole curve stationary on the screen. Their circuit is shown in Fig. 11. The potential applied to the electrolysis cell is derived not from a potentiometer but from the 40  $\mu$ F condenser C, which is charged and discharged in synchronism with the dropping time by means of the motor-driven switch S.



Fig. 12.—Breyer and Gutmann's a.c. Polarograph. Alternating Current Plotted against Direct Voltage, showing Cadmium and Zinc Steps.

The difficulties inherent in low-level d.c. amplification can be completel *j* overcome by a new method of polarographic analysis, developed by Dr. B. Breyer and the present author at the University of Sydney. This method, which is the outcome of some purely theoretical work on Electrode Reactions in Alternating Fields,<sup>34</sup> superimposes a small alternating potential upon the direct voltage. The alternating current flowing through the system is then amplified by means of a conventional amplifier (a commercial microphone amplifier has been used with success). The magnitude of this current is a function of the applied direct potential and becomes a maximum at the half-step potential. At this point its magnitude depends on the concentration of the substance being electrolysed. A theoretical foundation and equations describing these effects have been given by Dr. Breyer and the author in a series of publications.<sup>34</sup> A plot of these direct voltage/alternating current curves is shown in Fig. 12 for a solution containing cadmium and zinc. However, in practice it is not necessary to obtain the whole plot, since a single current reading at the point where the current reaches its maximum yields all the information desired. The amplifier involved, as mentioned before, is quite conventional. A gain of a few thousand and a power output sufficient to operate a meter, plus very good stability and freedom from hum, is all that is required.

ment has been simplified to the point where results can be obtained in a matter of minutes.

#### 5.0. Gas-Analysers

Photo-electric as well as polarographic methods are applicable only to solutions. Often, however, the composition of gases has to be controlled or determined. Sometimes this can be done by dissolving the gas in a liquid and then measuring the change in some physical property of the medium, say the conductivity, or polarographically.

Two electrical methods<sup>35</sup> have been developed for direct gas analysis, one based upon the thermal conductivity of a gas mixture and the other on the heat of a catalytic chemical reaction.



Fig. 13.—Alternating Current Polarograph Circuit according to Breyer and Gutmann.

The dropping mercury electrode, employed in polarography, leads to current oscillations in synchronism with the drop-time. This can be very annoying and, for some analyses, introduces severe limitations. Electronic amplification allows the use of a peak-reading vacuum tube voltmeter and thereby completely overcomes these fluctuations. This is made particularly easy in a.c. polarography, where a peak reading device is interposed between the last stage of voltage amplification and the power amplifier driving the indicating meter or recorder. The circuit simply consists of a condenser-resistor combination, of an adjustable time constant, usually somewhat larger than the dropping time of the electrode, where the potential across the condenser is measured by means of a tube. The complete circuit of an a.c. polarograph is shown in Fig 13. Analysis with this new instru-

Electrically, both employ the simple Wheatstone bridge circuit. A given current flows through the bridge, which comprises two arms of a fine wire of high temperature coefficient of resistance, usually a platinum alloy. One arm is immersed in the gas mixture under test, and the other arm is in an atmosphere of a standard reference gas, which might be air. These two arms are heated by the current to a temperature of the order of 100 deg. C. However, the rate at which these filaments lose heat depends on the thermal conductivity of the surrounding gas. Both filaments will reach thermal equilibrium at different temperatures, depending on the nature of the unknown gas mixture. This temperature difference unbalances the bridge and the out-ofbalance current is indicated by a meter. The method is at its best in binary or ternary mixtures where one constituent of different thermal conductivity has to be estimated. The meter then can be calibrated directly in percentages of this constituent: carbon dioxide in air and hydrogen or methane in flue gases are examples where the method has been used with success.

Employment of an alternating current with subsequent amplification of the bridge output permits very high sensitivities to be reached. In an instrument for the determination of traces of  $CO_2$ , in the course of development at Sydney University, there is at present good reason to hope that a sensitivity of one part in 10,000 will be surpassed. Again, quite conventional a.f. amplifiers can be used. As the method stands, the respiration of a single housefly can be measured.



Fig. 14.—Garman and Droz's Direct Reading Electronic Potentiometer Bridge.

R <sub>1</sub>	1,000 $\Omega$ uniform volume control.	S1	S.P.D.T. switch.
R,	2,000Ω, 0.5W resistor.	M	0-50 mA.
R,	2,500Ω, 0-5·W or 5,000Ω semi-	R <sub>1</sub>	1.5-V dry cell.
-	variable resistor.	R,	45-V battery.
R4	50,000 $\Omega$ volume control with switch	1, 2	unknown e.m.f.
-	cover plate for S <sub>1</sub> .		

Many chemical reactions between gases take place only in the presence of a suitable catalyst, often platinum, and the heat of the reaction can be utilized to actuate an indicator. Again the same simple bridge circuit is used, one filament being now the catalyst, say a platinum wire, which generally need not be externally heated. Chemical reaction takes place on its surface; the quantity of heat evolved, and therefore the equilibrium temperature of the filament, depending on the amount of reacting gas present. This change in resistance again unbalances the bridge and can be read on a meter. As before, an alternating voltage followed by electronic amplification extends the sensitivity of the method and allows remote indication and recording. Carbon monoxide in air can be estimated with such instruments to as little as 1 part in 100,000. Ammonia, many organic vapours like alcohol or benzene, methane, hydrogen and other gases can be determined by this method.

### 6.0. Potentiometers and Potentiometric Titrations<sup>36</sup>

Many chemical reactions involve the simultaneous oxidation of one substance and reduction of another, i.e. the transfer of electrons from one substance to another. Electrical methods are available for the determination of the quantity of either oxidant or reductant present. The potential difference between a reference electrode and a piece of bright platinum immersed in the reactant solution can be shown to depend on the ratio between the concentrations of oxidant and reductant.

At the endpoint of the titration there is a sudden change in potential. The sensitivity of the method, particularly with the aid of an electronic null indicator, is very high. The potential difference, which is of the order of a few hundred millivolts, must be measured without drawing any appreciable current from the system, because otherwise polarization sets in and the reaction no longer proceeds in a perfectly reversible manner. While d.c. vacuum tube voltmeters of input resistance in excess of 20 megohms or so can be used to obtain a direct indication, this is usually too insensitive and a potentiometric method is preferable. As a nullpoint indicator either a highly sensitive mirror galvanometer is used, or, with great advantage, a current amplifier.

Often these "RedOx" potentials are measured by means of a pH meter, which can be calibrated to read millivolts. Goode<sup>37</sup> was the first to apply electronic methods to potentiometric titrations. More recently, a special purpose direct-reading electronic bridge has been designed for such measurements by Garman and Droz.38 The circuit, which is of interest from the purely electronic point of view, is shown in Fig. 14. A 1A7/G converter tube is employed in a Wheatstone bridge circuit, made up of (1) the cathodeplate resistance, (2) the plate load  $R_3$ , (3) the cathode-grid resistance, and (4) the load resistance R<sub>2</sub>. The meter reading is linearly proportional to the unknown e.m.f. introduced between the cathode and No. 4 grid. For routine determinations, the sensitivity of the instrument is adjusted so that the meter reads exactly full scale at the endpoint of the titration. Another special purpose instrument developed for potentiometric titrations is the Sarfass Titrimeter.<sup>39</sup> Employing an electron-ray indicator it is the basis of a number of commercial instruments. A titration instrument incorporating a photo-electric cell has been designed by Mueller.<sup>40</sup>



Fig. 15.—Rich and Gardner's Self-Balancing Electronic Potentiometer.

A self-balancing electronic potentiometer has been developed by Rich and Gardner.<sup>41</sup> Its principle is illustrated in Fig. 15. The galvanometer mirror reflects light on to a special mirror which splits the beam into two exactly equal components which fall upon two photo-cells. Their output is amplified in a push-pull balanced amplifier arrangement. Deflection of the galvanometer causes one photo-tube to receive more light than the other. The resulting amplified unbalance current flows through a resistor which is in series with the input. Thus a voltage drop is produced in the input circuit equal and in opposition to the input voltage. The galvanometer therefore will always balance itself to zero and a true potentiometric circuit with virtually no current drain from the source of e.m.f. is the result. The magnitude of the unbalance current necessary to keep the system in equilibrium is a measure of the input voltage and can be read on a meter or applied to a recorder.

Any reaction which can be made the basis of a conventional titration can be followed by potentiometric methods, always provided that a suitable indicator electrode is available. Not only oxidation-reduction reactions, but also precipitation reactions and many others can be thus titrated. In cases of coloured media, where no visual indicator can be applied, the electrical method is of particular advantage.

#### 7.0. Electrolytic Conductance Bridges

The determination of the electrolytic conductivity<sup>42</sup> of solutions is often of great importance and, in many cases, titrations can be carried out by plotting the conductivity of a solution as a function of the quantity of reagent added. Many end and equivalence points are indicated by pronounced changes in the conductivity. Basically, conductimetric titrations rely on the fact that all ions in a solution contribute to its conductivity. If, during the course of a chemical reaction, ions are either liberated or taken out of the solution, the conductivity accordingly changes.

Alternating voltages of audio-frequency, of the order of 10-100 V or so, are generally employed in order to avoid polarization effects. A bridge is used with a suitable null-point detector. Special cells with two platinum electrodes and very careful temperature control are essential for accurate results, since the conductivity changes about 2 per cent. per deg C. Quite conventional single- or double-tube a.f. oscillators, giving a reasonably pure wave-form, are sufficient for this kind of work. Vibration galvanometers, dry rectifier microammeters and the simple pair of headphones are often used as detectors. The modern trend, however, is towards electronic detectors which offer higher sensitivity combined with greater ruggedness. Since the bridge circuit involved usually presents a low impedance to the detector, step-up transformers are interposed for impedance matching. While any vacuum tube voltmeter of sufficient sensitivity can be employed, specialized null-point detectors have been developed by a number of authors.<sup>43, 44</sup> It is common practice to use an electron-ray tube as visual indicator. Garman<sup>44</sup> uses two such tubes, one to indicate a rough and one the final balance. For a sharp null point it is essential to keep hum to a very low level.

In a bridge the voltage output is a parabolic function of the resistance of the arm containing the unknown. A rather remarkable direct-reading electronic conductivity bridge having a linear scale has been developed by Garman.<sup>45</sup>

Its circuit is shown in Fig. 16. One half of a 6A6, or 6SN7, functions as oscillator, energizing the bridge. The voltage output thereof is applied to the second half of the tube, via an impedance matching transformer, amplified and read on a meter. Since this vacuum tube voltmeter part of



Fig. 16.-Vacuum-tube Circuit for Conductivity Determination according to Garman.

the circuit is arranged so as to operate as a square law voltmeter, the current indicated by the meter becomes a linear function of the unknown resistance and the meter therefore can be linearly calibrated in terms of the resistance of the conductivity cell.

An entirely new method of conductimetric analysis at radio frequencies has been developed at the University of Sydney by G. G. Blake.<sup>46</sup> The principle of the arrangement is shown in Fig. 17. The method relies upon the change in the Q of an oscillatory circuit which is shunted by a resistance consisting of a conductivity cell of special form and design, which unlike conventional cells, should have a high impedance. While the method is extremely sensitive, it measures admittance rather than conductance. Much experimental work remains to be done on its operation with liquids which have a pronounced Debye-Falkenhagen effect<sup>47</sup> (variation of conductance with frequency) and also on the influence of the dielectric constant of the solvent. Combination of Blake's method with the use of a commercial Q-meter should prove particularly convenient.

### 8.0. Dielectric Constant and Dielectric Loss **Measuring Equipment**

A comparatively recent application of a physical method to chemistry is the measurement of the dielectric properties of a substance. Since the introduction of the concept of polar molecules\* into science by Debye,<sup>48</sup> a great deal

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L<sub>1</sub> Choke, 30H. L<sub>2</sub> Choke, 30H, 200Ω.  $\mu A 0 \rightarrow 500$  microammeter

 $R_1$  5 to 7 M $\Omega$ , 1W. R, 1-M $\Omega$  volume control.

- R, 50,000 Q volume control.
- R. Voltage divider, 1,000 Ω,
- 25W R, Voltage divider, 20,000 Ω,
- 25W R. Volume control, 15,000 Ω.
- radio R, General potentiometer, 1,000 s.
- R<sub>A</sub> General radio potentiometer, 100Ω. R, 15Ω, 100W. R<sub>10</sub> 140Ω, 100W. C: Conde-

- $C_1$  Condenser, 0.01 mfd, mica.  $C_2$ ,  $C_3$ ,  $C_4$  Condensers, paper, 0.5 mfd, 200V.
- C. Electrolytic condenser, 8
- mfd. C. Electrolytic condenser, 4
- mfd. T<sub>1</sub> Low ratio audio trans-
- former. T. Single-button carbon mic-
- rophone transformer.

of work has been done on the relation between the electric moment of a molecule and its structure. The dielectric constants and loss angles of many compounds were measured at various frequencies. The general course of the dielectric constant against frequency relation is illustrated in Fig. 18. At low frequencies, a polar molecule can align itself in the field and is capable of following the changes in the field. At these frequencies, the total electric polarization of the molecule is made up of 3 components : its molecular polarization arising from the electric moment of the molecule as a whole, its atomic polarization caused by the electric moments of its constituent atoms and finally the electronic polarization due to the displacement of the electrons within the molecule caused by the action of the field. As the frequency is increased, a point is reached where a natural resonance frequency of the oscillating molecule coincides



Fig. 17.—Blake's Conductivity Method. Circuit and Measuring Cell.

A polar molecule is one which exhibits an electric dipole moment while being electrically neutral as a whole.

with the period of the external field. At this point an absorption maximum, i.e. a maximum of dielectric loss, is observed and at higher frequencies the dielectric constant commences to drop sharply, due to the increasing inability of the molecule to align itself in the field. A similar process takes place at still higher frequencies with respect to the atomic polarization until, at very short wavelengths, the electronic polarization is the only contributing factor to the dielectric constant. Determination of the dielectric constant of a compound therefore throws much light on its constitution and has become a standard method in chemical research.49 Methods capable of very high accuracies have been developed for such measurements.<sup>49, 50</sup> They employ capacitance bridges for audio and the lower radio frequencies and, sometimes very elaborate, heterodyne or resonance methods for the higher radio frequencies.



Fig. 18.—Dependence of the Total Polarization of a Polar Substance on the Field. According to Le Fevre.

Frequency Regions						
Ultra radio -	- up to $5 \times 10^{10}$					
Infra red	5 × 10 <sup>10</sup> -4 × 10 <sup>14</sup>					
Visible 1	$4 \times 10^{14} - 8 \times 10^{14}$					
Ultra violet	8×1014-1014					
Then X-rays						

High quality standard condensers, sometimes equipped with an extended pointer and a measuring microscope, are employed in parallel with special cells, filled first with dry air and then with the unknown. The dielectric constant is calculated from the change in capacitance. One oscillator is usually crystal controlled and elaborate mixer circuits prevent the reference and the measuring oscillators from "pulling-in." The audio beat-frequency is amplified and sometimes again heterodyned against a 1,000 c/s signal from an a.f. oscillator controlled by an electrically maintained tuning fork. The resonance point is determined either visually or aurally by means of the zero beat method. The whole apparatus is thermostatically controlled and the temperature of the unknown controlled. Resonance methods,<sup>51</sup> based upon a very accurate measurement of the frequency of an oscillator which employs the unknown as the dielectric in its tank circuit capacitance, are also capable of a high degree of accuracy but appear to be less favoured than the heterodyne method.

At ultra-high frequencies quite different arrangements have to be employed. The simplest is the well-known Drude<sup>52</sup> method of measuring the wavelength along a set of parallel wires first in air and then with the unknown as medium. The dielectric constant is then given by the square root of the ratio of the two wavelengths thus obtained. This method has been simplified and modernized by King.53 Coaxial conductors are used for wavelengths down to 10 cm, wave guides serve for still higher frequencies and in each case the dielectric is physically part of the transmission line. Such methods have been applied to dielectric research, e.g. by Englund.<sup>54</sup> A re-entrant resonant cavity has been used by Works, Dakin and Boggs<sup>55</sup> for dielectric measurements up to 600 Mc/s, the reading being taken from a micrometer vernier acting on a movable electrode connected through a Sylphon bellows. Since the Q of the cavity is extremely high (>2,000), the method can be applied also to dielectrics of poor resistivity, where many other methods fail. Measurements in the 3-cm band have been carried out by Roberts and von Hippel.<sup>56</sup> These authors employ a magnetron with an open anode which radiates directly into a wave guide without the intervention of a transmission line. The guide, in the form of a long tube, is filled with the liquid under test and the resonance position is determined by means of a bolometer or crystal detector travelling along the axis of the tube. Most of these authors employ the frequency variation technique developed by Hartshorn and Ward,57 which is very convenient also for the lower radio frequencies, since it practically eliminates the effect of series resistance and inductance of the leads and electrodes. It consists essentially of taking response readings at

resonance and again at a frequency where the response is exactly one half of the value at resonance.

While such precision apparatus finds its place in research laboratories of universities and large chemical industries, where the molecular constitution and arrangement of compounds is being investigated, dielectric measurements are being increasingly used as an analytical tool in smaller laboratories of a wide range of industries. The analytical use of these methods is largely due to Ebert.<sup>58</sup> Essentially, these techniques are all empirical. They are based upon a previously obtained calibration curve showing the resultant dielectric constant and/or loss values for a certain range of concentration and composition of a mixture, which is usually binary or ternary.



Fig. 19.-Alexander's Dielectric Constant Meter.

A number of simple and rugged instruments designed for industrial use have been developed. The Dielcometer, designed by Ebert and described by Jupe,59 employs a heterodyne method in a simplified three-tube circuit, operating at 1 Mc/s and using a crystal-controlled oscillator. A remarkably simple industrial dielectric constant meter, employing only one 6E5, has been developed by Alexander<sup>60</sup> and is illustrated in Fig. 19. It is based upon the sudden change in the plate current of a crystal oscillator when it is tuned through resonance, an effect which was first applied to dielectric constant determinations by Henriquez<sup>61</sup> It operates on 7 Mc/s, is independent of supply voltage fluctuations and gives results to within better than 1 per cent. The present author has built a similar apparatus for the determination of butterfat in milk for a large Sydney industrial undertaking.

Several authors have reported<sup>62</sup> adaptations of the familiar Q-meter to dielectric determinations, connecting the test condenser containing the dielectric under investigation across the tuning condenser of the instrument. This allows measurements up to 50 Mc/s without any auxiliary apparatus.

All r.f. methods of measurement become difficult once the conductivity of the dielectric becomes appreciable, since it depresses the Q of the oscillatory circuits employed and eventually stops oscillation altogether. Apart from some of the ultra-high frequency methods mentioned before, there are only a few other methods at present available for determining the dielectric constant of solutions having appreciable conductivity. One measures the torque experienced by a metal ellipsoid<sup>63</sup> (a so-called Fuerth<sup>64</sup> ellipsoid) in a test condenser filled with the liquid under test.

Another very elegant method has been described by Wyman.<sup>65</sup> He immerses very small resonators completely into the conducting liquid and measures the resulting resonance frequency. The method works in as little as 15-20 cc of liquid and is accurate to about 0.2 per cent. It is applicable if the product of the period of the applied r.f. field and the conductivity of the solution is small. At frequencies of the order of 1,000 Mc/s a conductivity a hundred times greater than that of water is still permissible.

An absolute method for such determinations has been developed by Hellman.<sup>66</sup> He measures the intensity of the stationary waves set up in a Lecher wire system which has one end immersed in the conducting liquid under test. This yields the reflection coefficient of the liquid surface, from which its dielectric constant can be calculated.

More recently, Cole<sup>67</sup> has developed a method which consists of a circuit containing the unknown and a standard capacity in series, the potential difference across them being applied directly to the vertical and horizontal deflectionplates of a cathode ray oscillograph. The principle is illustrated in Fig. 20. If the dielectric



Fig. 20.—Basic Circuit for the Determination of the Dielectric Constant of Conducting Liquids, according to Cole.

under test has no conductivity, and assuming that the standard condenser is loss-free, the trace on the screen will be a straight line. Otherwise, an ellipse will result, the opening of which is a function of the conductivity. However, the angle between the ellipse and the abscissæ, as shown in Fig. 20b, is independent of any conductivity present and allows the calculation of the dielectric constant.

Another, quite different, method for dielectric research could be found in the so-called dipole rotation effect. When a liquid containing polar molecules is subjected to a rotating electric field, the liquid tends to follow the field, the rotation lagging behind the field by a certain phase angle. The effect is quite complex. At low frequencies a similar rotation is observed, produced by the conductivity of the liquid and superimposed upon the dipole rotation effect proper. This conductivity effect has a maximum at a critical frequency which depends on the dielectric constant and on the conductivity of the solution. At high frequencies it is negligibly small. This subject was first studied by Lampa.<sup>68</sup> Born<sup>69</sup> has proposed an equation for the dipole rotation effect, which subsequently has been verified by Lertes<sup>70</sup> working in the 4-metre band. The existence of a similar effect for solids has been predicted by Debye<sup>71</sup> and confirmed experimentally by Hartmann and Stuermer<sup>72</sup> for a number of solids, working in the 1-2 metre band. A solid dielectric body, suspended in a rotating electric field, experiences a torque if the frequency of the field is in the region of a dispersion frequency of the body. All this work needs further development.

#### 9.0. Moisture Meters

One important and widely used application of conductivity and/or dielectric constant determinations is found in the measurement of the moisture content of various media.

The standard chemical method for the determination of water content consists of a titration with the so-called Karl Fischer reagent.\* McKinney and Hall<sup>73</sup> used an interesting electronic technique for this kind of analysis. They first add an excess of reagent and then back-titrate with a standard solution of water in methanol. Two platinum electrodes are immersed

\* This reaction is based upon a quantitative reaction between iodine SO<sub>2</sub> which proceeds only in the presence of water. into the solution under test and a direct potential of about 10 mV applied. Current flows during the titration, but ceases abruptly at the endpoint. The authors employ a 6F5 as current amplifier followed by a 6E5 electron ray indicator.



Fig. 21.—Hartshorn and Wilson's Moisture Meter with Phase-Selective Indicator.

D.C. indicating instrument : sensitive range, 0-200  $\mu$ A ; normal range, 0-1 mA.

C <sub>1</sub> C <sub>1</sub> C <sub>3</sub> Ch <sub>1</sub>	   2 μF 0·3 μF 0·01 μF 50H	$\begin{array}{c} Cn_2 \\ R_1, R_2, R_3 \\ R_4 \\ Valves \end{array}$	25H 5,000Ω 0·5 MΩ EBC33 (CV1055)
			(CV1055)

In general the presence of moisture affects the electric conductivity as well as the dielectric constant. It depends on the nature of the medium whether it is more convenient to measure one or the other of these quantities as an indication of the moisture content-sometimes a combination of both is found to yield the most sensitive and accurate test. Special purpose moisture meters have been developed, inter alia, by Jones<sup>74</sup> for textiles, by Davies<sup>75</sup> for seeds, by Coleman<sup>76</sup> and by Cook, Hopkins and Geddes<sup>77</sup> for grain, and many others. Hartshorn and Wilson<sup>78</sup> have designed a remarkably simple universal moisture meter which operates on any desired combination of conductivity and permittivity variation in the sample. The circuit is shown in Fig. 21. A constant alternating voltage is impressed upon the sample which constitutes the dielectric in a test condenser. The total current passing, having a conductive as well as a capacitive component, flows through a fixed resistor. The potential across this resistor is applied to a phaseselective vacuum tube voltmeter, which measures that component of the total voltage input which bears a definite, pre-set, relationship to the mains

supply or to some other extraneous auxiliary source. It can be made to respond therefore to the in-phase or to the out-of-phase component only or to such a combination of these two vectors which has been found empirically in any particular case to bear a convenient relationship to the moisture content of the sample. The phase selective voltmeter consists essentially of a pair of cathode loaded triodes, the anode circuits of which are energized in phase opposition from a tapped transformer. The grids are tied together and connected to the input. The indicating meter, by-passed against a.c., is connected between the cathodes, and measures that component of the input voltage which is in-phase with the plate supply. A phase shifting network consisting of a condenser-resistor-choke combination as a voltage divider, is included in the input circuit and preset for any particular dielectric. Moisture in grain, egg powder, flax, straw, ceramics and moulding powders can thereby be determined.



Fig. 22.—Control Circuit according to Rudy and Fugassi.

- R1
- R,
- 50,000Ω potentiometer. 2,000Ω resistor, 2W. 2 mfd condenser. Cold cathode, gas-filled triode, Type OA4G. Regulator contacts. Ĉ,
- ŘC.
- Relay, Utah, Type RAC-110.

#### 10.0 Supersonic Apparatus<sup>79</sup>

Supersonic soundwaves in liquids find application in chemical laboratories mainly for the preparation of colloidal solutions and emulsions and as an analytical tool. The emulsifying action of supersonics was first observed by Wood and Loomis.<sup>80</sup> Immiscible liquids, like mercury and water, or water and oil, can be transformed, under appropriate conditions, into very stable emulsions. Electrolysis in a supersonic soundfield allows the preparation of truly colloidal suspensions of metals in water.<sup>81</sup> It is of interest

to note that the action of supersonics on gaseous media is the opposite, aerosols being precipitated.<sup>82</sup> The analytical use of supersonics relies on the different acoustic impedances and velocities of propagation of sound in divers media. A large number of compounds have been investigated by Parthasarathy.83 The wavelength of a supersonic vibration in a liquid can be measured to a high order of accuracy by means of the interferometer.<sup>84, 85</sup> This employs an accurately adjustable reflection plate, which is shifted for one half wavelength, corresponding to two subsequent nodes. The sound field is usually produced by means of a magnetostrictive transducer for the lower frequencies and by a vibrating quartz or tourmalin crystal for higher frequencies. Irradiation of conductive liquids is sometimes difficult, since the liquid tends to short circuit the vibrating crystal, but the author<sup>86</sup> has designed a crystal holder which allows the direct irradiation of such fluids. Supersonic interferometry also permits the measurement of molecular weights,<sup>87</sup> particularly of high polymers like plastics.

The quartz or magnetostrictive transducer is powered from a conventional oscillator.<sup>88</sup> Apart from the design of the crystal holder, the main problem is one of impedance matching. The liquid imposes very heavy damping on the vibrating quartz, a damping which also depends on the acoustic impedance of the fluid, and therefore on its temperature, density, composition and quantity. The author has noticed that the resonant frequency of the electro-acoustic system changes with any chemical reaction taking place in the medium as a consequence of the irradiation itself. Constant retuning, therefore, might become necessary.

## 11.0, Electronic Control Circuits

Electronic chemical control consists essentially of the operation of a relay by small changes in an electrical parameter which is in turn produced by a chemical process. Gas triodes and thyratrons are coming more and more to the fore in a wide variety of such control mechanisms. Applications are too numerous to be dealt with in any detail. A bibliography on this subject has been published by Waddle and Saeman<sup>89</sup> covering the years up to 1940. A typical circuit is shown in Fig. 22, which has been developed by Rudy and Fugassi.<sup>90</sup> The 2  $\mu$ F condenser prevents relay chattering. A gas triode OA4G is employed, its output actuating a 32-110 V/25 mA relay.

A good example of what can be done by utilizing electronic aids to the full, can be found in the automatic titrator developed by Slenk and Fenwick.<sup>91</sup> This instrument carries out and stops an electrometric titration automatically, ringing a bell and calling the chemist as soon as the titration endpoint has been reached. Its operation is based upon the sudden change in potential between two dissimilar electrodes which occurs at the endpoint. A change in e.m.f. of 5 mV fires a thyratron and actuates a relay which closes a stopcock. A similar instrument has been developed by Mueller and Partridge,<sup>92</sup> using a photo-electric indicator. The circuits involved are quite conventional.



Fig. 23.—Principle of Ionization Gauge.

# 12.0. Radiometric Methods. The Ionization Gauge

Under this heading it is intended to summarize that wide variety of rather recent methods based upon applications of methods utilizing atomic or subatomic particles and ionizing radiations. This comprises the various X-ray techniques, electron diffraction, the electron microscope, the mass spectrograph, work with tracer elements, and allied methods, each of which would warrant an entire monograph of its own. At present, these advanced and complex instruments are to be found in very few chemical laboratories indeed and here it is proposed to mention only one of the more common applications of these techniques, viz. the ionization gauge,93 often used as a vacuum indicator for vacuum distillations and the like.

The principle of this gauge is illustrated in Fig. 23. Electrons are accelerated between cathode and grid, but fail to reach the negatively charged plate. Some electrons, however, will penetrate through the meshes of the grid and ionize those of the gas molecules with which they collide. The resulting positive ions go to the plate and the plate current therefore is a measure of the number of such ions. The number of molecules ionised is proportional to the grid current and to the pressure of the gas, over a rather wide range of low pressures, from about 0.5 mm down to about  $10^{-8} \text{ mm}$  Hg. A meter in the plate circuit, therefore, can be calibrated directly in pressure units if the grid current is maintained constant. Pure tungsten cathodes are commonly used, with the grid some 200 V positive and the plate 20 V negative with respect to the cathode. A wide-mesh grid is essential to avoid, as far as possible, ionization in the space between grid and cathode, since any ions formed there would bombard the cathode. Water vapour and appreciable amounts of oxygen must be excluded, or else thoriated or oxide coated cathodes must be used. These, however, need rather frequent replacement due to positive ion bombardment.



Fig. 24.—Ridenour and Lampson's Current Control Circuit.

In ionization gauges it is essential to keep the grid current constant. A simple and elegant method to accomplish this has been developed by Ridenour and Lampson.<sup>94</sup> The principle of the method, which should be adaptable to the control of power or voltage in a number of other fields, is shown in Fig. 24.  $T_1$  supplies power to the load R, in this case the heater of the ionization gauge. Control is exercised by change of  $E_g$ , which here consists of the voltage drop produced by the gauge tube grid current flowing

through an adjustable resistor. An elaboration of this circuit, resulting in an ionization gauge which can be made to indicate the attainment of a pre-set degree of vacuum has been developed by Ridenour.<sup>95</sup> It employs a standard receiving type of valve as a gauge-tube.

# 13.0. Other Electronic Aids. The Electronic Balance

There exists a wide field where other electronic aids have been employed with advantage in chemical laboratories. High Voltage Supplies for Electrophoresis, High Current Supplies for Electrolytic Processes, many kinds of Electric Thermometers (resistance, thermoelectric and photo-electric instruments) and many other applications have been reported. However, only one more instrument will be outlined here, since it is a very recent and rather unique development.



Fig. 25. : (a) Clark's Electronic Balance. Block-diagram (b) Clark's Electronic Balance. Magnetic Circuit and Lay-out.

The electronic balance, developed recently by  $Clark^{96}$  is shown in Fig. 25. The instrument weighs small objects with a precision equal to that of a chemical beam balance, is fully direct reading and capable of operation by semi-skilled

labour. It operates as follows : The tray system of the balance is supported by an electromagnet (see the magnetic circuit shown in Fig. 25). A vane attached to the tray partially intercepts a beam of light falling upon a photo-cell. The output of this is amplified and connected to the electromagnet so as to oppose any motion of the suspended system. The tray and its suspension therefore hang freely in space touching neither the magnet nor the limiting stop provided. The object then is placed upon the tray and the current necessary to restore the previous equilibrium position of the suspended system is read off a meter.

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