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Cubic Decimetre or Litre?

Attempts now being made to ‘tidy up’ the metric system of volume measurement were reviewed in the November issue of BSI News. The early definition of the litre (= 1 dm³) was dropped in 1901 because it was easier to measure weight than volume. The new definition made the litre to be the volume occupied by 1 kg of pure water under specified conditions, and in 1910 it was accepted that 1 litre = 1·000027 dm³ (corrected to 1·000028 in 1927). At that time, the difference of 28 parts per million was regarded as insignificant for practical purposes, but with the ever-increasing precision of measurement in science and technology such a discrepancy can no longer be overlooked. In October 1964 the 12th Conférence Générale des Poids et Mesures abrogated the 1901 definition, declared that ‘litre’ could be used as a special name for the dm³ and recommended that ‘litre’ should not be used to express volumes measured with high precision.

This clearly had implications for the U.K., where the movement towards metric units is continually gaining momentum. The British Standards Institution therefore organized a conference representative of scientific, educational and industrial interests in April 1965 at which these implications were discussed with members of the BSI committees directly concerned. There was unanimous agreement that ‘all educational authorities should be urged to adopt the International System (SI) of units (BS 3763) throughout the educational system for purposes of teaching, textbooks and examination papers (this adoption entailing also the abolition of the use of the ml and the litre)’. The BSI committees dealing with subjects in these fields were encouraged to use the cm³ and dm³ in their standards wherever this did not contravene existing legislation.

This conference thus accepted that the litre and ml would ultimately be replaced in science and technology by the dm³ and cm³, respectively. Opinion varied as to the speed at which the changes might be expected to take place, especially in industries where it could give rise to commercial problems, e.g. in the petroleum industry. Subsequent consultations have shown that the problem should be approached under two headings: action needed forthwith, and the situation as it may develop over a longer period.

Since the conference, strong representations have been made that the abbreviations dm³, cm³ and mm³ are ‘unsuitable’ for medical and pharmaceutical purposes. Only comparatively recently the medical and the scientific world was persuaded to adopt ml in place of c.c., and the recommendation to drop ml completely would now cause confusion out of all proportion to the likely benefit. (Having used both on occasion for some years without trouble, we find it difficult to understand this point of view.) More important is the fact that during recent months it has transpired that litre and ml are likely to continue in general use in several ‘metric’ countries—France, India, Italy, the Netherlands and the USSR. Thus it is likely that the term ‘litre’ will be retained by the International Standards Organization, but it will be used in all cases as equivalent to the dm³.

The laboratory apparatus manufacturers are dealing with the problem rapidly. Since 1 January, 1965, the NPL has issued certificates for volumetric glassware in which the test results are expressed in cm³, whether or not the apparatus is inscribed in this way. The BSI decided last year that both ml and cm³ will be permitted in future, and that the appropriate Standards will be amended accordingly.

The ISO’s technical committee on laboratory glassware has also examined the problem and has recommended that, in all ISO work, the terms litre, millilitre and microlitre should be regarded as special names for dm³, cm³ and mm³, respectively. For the time being, both cm³ and ml will be used in various countries, and it has been agreed that both cm³ and ml should be permitted as inscriptions. For articles of the highest precision, where 28 parts per million may be significant, the only permitted inscription should be cm³.
Mr Dennis G. Chisman, FRIC, Education Officer of the Royal Institute of Chemistry, has been appointed to a new post of Science Education Officer at the London Headquarters of the British Council. During his eight years at the Institute, he has helped to pioneer and develop various activities in the field of chemical education as well as assisting in the work of several of the Institute's Committees, especially those concerned with technical education and Grad. R.I.C. courses. More recently, as Secretary to the British Committee on Chemical Education and as a member of both the Consultative Committee for the Nuffield Chemistry Project and the Physical Science Committee of the Association for Science Education, he has been closely concerned with the study of the problems of school science teaching in Britain and has also been involved with overseas problems as a consultant to OECD and UNESCO.

Mr Chisman, in his new appointment, will keep the British Council's overseas officers in touch with current British trends and supply them with information on new equipment, textbooks and audio-visual aids, as well as on new teaching methods.

Dr A. L. Buley, ARIC, has been appointed to succeed Mr Chisman as from 1 January. He was educated at Epsom College and St John's College, Oxford, where he worked on the application of electron spin resonance spectroscopy to free radicals under Dr (now Professor) R. O. C. Norman. In 1964 he became an assistant chemistry master at Eton College.

IN-SERVICE TRAINING FOR SCHOOL TEACHERS

The British Committee on Chemical Education and the corresponding committees in physics, biology and mathematics brought to the attention of the Council of the Royal Society the importance of refresher courses for school teachers of science and mathematics. Following discussions with the Department of Education and Science and the Schools Council, the Council of the Royal Society convened a conference to discuss arrangements for in-service training in the light of current developments and to consider ways in which scientific societies and institutions and other bodies might assist in their increase and improvement. It was recognized that many different organizations were concerned with this question in various ways and for that reason invitations to attend the conference were sent to a wide cross-section of individuals and organizations.

A report of this conference held on 16 September, 1965, has been published. The main conclusions and recommendation were:

It was agreed that there is an urgent need for a very considerable increase in in-service training for teachers of science and mathematics and this must go together with curriculum development and must be regarded as an essential and continuing part of the educational system. The Department of Education and Science and the Local Education Authorities were urged to provide the funds required for this increase, it being noted that they represented only a very small fraction of the national bill for education. It was suggested that the Schools Council might provide co-ordination for this curriculum reform and provision of in-service training since many different organizations are already involved in these. It was recommended that the learned societies and professional institutes concerned with science should foster their links with school teachers of science in order to strengthen the teachers' sense of community with their specialized professions and it was strongly urged that Local Education Authorities should act with the utmost generosity in supporting teachers who wish to attend appropriate courses of in-service training. It was recommended that the Council of the Royal Society should commend the report of this meeting to the Department of Education and Science, to Local Education Authorities, to universities and to other bodies concerned with the questions under discussion.
SOME USES OF THE EPOXY RING IN INDUSTRY

By L. W. Chubb, B.Sc.

Shell Chemical Company Ltd, Egham, Surrey

HISTORICAL

The preparation of the simplest organic compound containing an epoxy ring,
\(-\text{HC}--\text{CH} \cdot \text{O}--\text{CH} = \text{CH}_2\), was described by Wurtz in 1859. Ethylene (ethene, IUPAC) was made to react with hypochlorous acid and by distilling the resulting chlorohydrin with caustic potash he obtained the epoxy compound which he named ethylene oxide (epoxyethane, IUPAC). He also described its reaction with water to give a product he called ethylene glycol (ethanediol, IUPAC).

\[
\text{CH}_2=\text{CH}_2 \rightarrow \text{HO}-\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{H}_2\text{C}--\text{CH}_2
\]

\[
\text{HO}-\text{CH}_2\text{CH}_2\text{OH}
\]

Wurtz considered that ethylene oxide could not be prepared by the direct interaction of ethylene and oxygen.

INDUSTRIAL DEVELOPMENT

This series of reactions was used in commercial manufacture during the period 1925–30 by the then Carbide & Carbon Chemical Corporation, U.S.A.—now Union Carbide Corporation. Lefort, of this Company, subsequently discovered that ethylene and oxygen would combine directly to give ethylene oxide in the presence of a silver catalyst, despite Wurtz’s views to the contrary.

Today, for commercial manufacture, the ‘direct oxidation’ process has largely superseded the ‘chlorohydration’ process.

Epoxy rings are chemically reactive, and will readily attack compounds containing active hydrogen atoms by the general reaction:

\[
\text{-HC}--\text{CH}_2 + \text{H-R} \rightarrow \text{-CH-CH}_2\text{R}
\]

\[
\text{OH}
\]

Thus compounds containing an epoxy ring can be important chemical intermediates and, at the present time, ethylene oxide is the most important. World production of ethylene oxide is around 14–13 m. tons per annum and its most important derivative is ethylene glycol.

ETHYLENE OXIDE AS A CHEMICAL INTERMEDIATE

1. Reaction with water

Ethylene oxide reacts with water at temperatures of 50–100°C and at atmospheric pressure. An acid catalyst is sometimes used. The main product is ethylene glycol. However, di- and tri-ethylene glycols are produced at the same time, as co-products, by the reaction of ethylene oxide with the hydroxyl-groups of the main product, ethylene glycol, since the oxide and the glycol must be in contact at some instant in the continuous reactor. A high water : ethylene oxide molar ratio minimizes the production of co-products but cannot eliminate it.

\[
\text{H}_2\text{C}--\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{HO}-\text{CH}_2\text{CH}_2\text{OH}
\]

ethylene glycol and co-products

\[
\text{HO}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{OH}
\]

diethylene glycol

\[
\text{HO}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{OH}
\]

triethylene glycol

2. Reaction with alcohols

Ethylene oxide reacts with aliphatic alcohols in a way analogous to its reaction with water. The resulting products, containing an hydroxyl group and an ether link, are known in industry as glycol ethers. The reaction with ethanol, for example, is carried out hot (170–190°C) and under pressure (ca 15 atm) with a catalyst such as caustic soda. A high alcohol to oxide ratio is used to minimize the formation of di- and tri-co-products but small quantities of the latter are nevertheless produced.

\[
\text{H}_2\text{C}--\text{CH}_2 + \text{R-OH} \rightarrow \text{HO}-\text{CH}_2\text{CH}_2\text{O-R}
\]

glycol ether and co-products

\[
\text{HO}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{O-R}
\]

di-glycol ether

\[
\text{HO}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{O-R}
\]

tri-glycol ether
The glycol ethers of commerce are usually based on methyl, ethyl, isopropyl and butyl alcohols. The systematic name (IUPAC) for that derived from ethyl alcohol is 2-ethoxyethanol but it is generally known in industry as ethylene glycol monoethyl ether (ethyl glycol is an alternative name used in parts of Europe). The glycol ethers are usually sold by the manufacturers under trade names.

3. Reaction with ammonia

Ethylene oxide and ammonia react at moderate temperatures and pressures to produce a mixture of the mono-, di- and tri-ethanolamines (MEA, DEA and TEA). The systematic names (IUPAC) are, respectively, 2-aminoethanol, N-(2-hydroxyethyl)aminoethanol and NN-bis(2-hydroxyethyl)aminoethanol.

\[ \text{H}_2\text{C}=\text{CH}_2 + \text{NH}_3 \rightarrow (\text{HO-CH}_2\text{CH}_2)\text{NH} \]

\[ \rightarrow (\text{HO-CH}_2\text{CH}_2)_2\text{N} \]

The temperature, pressure and molar ratio of the reactants determine the proportions of the three ethanolamines produced, for example:

at 30-40°C, and 1.5 atm

Ammonia : ethylene oxide MEA : DEA : TEA

10 : 1   75 : 25 : 4
1 : 1    12 : 23 : 65

This allows considerable flexibility in manufacturing in order to meet changing market demands for the three products without producing an excess of any one.

Properties and uses of these products

GLYCOLS are moderately viscous liquids, soluble in water, alcohols and low-boiling-point ketones but not miscible with hydrocarbons, esters, chlorinated hydrocarbons or animal and vegetable oils. They have high boiling points and are relatively non-volatile. They are hygroscopic and can therefore act as humectants (i.e. maintain a constant water content when there are large fluctuations in humidity).

Industrial uses include: chemical intermediates in manufacture of polyester resins, plasticizers and explosives; automotive antifreeze and de-icing fluids; components in hydraulic-brake fluids; plasticizers for regenerated-cellulose packing film; solvents and humectants in certain pharmaceutical, toilet and cosmetic preparations. Ethylene glycol is an intermediate in the manufacture of 'Terylene' polyester fibre (polyethyleneglycol terephthalate).

GLYCOL ETHERS are miscible with water and with many organic liquids and have moderately high boiling points. They are powerful solvents for many organic materials, especially many natural and synthetic resins used in paints, varnishes and lacquers.

Industrial uses include: solvents in a wide range of paints, varnishes, lacquers, printing inks; components in hydraulic-brake and shock-absorber fluids; solvents for certain textile dyestuffs; intermediates for manufacture of esters used as solvents and plasticizers.

ETHANOLAMINES are soluble in water and alcohols but are sparingly soluble in many organic liquids. Being substituted amines, they are relatively strong bases.

Industrial uses include: cations, as alternative to sodium, potassium and ammonia, in soaps and synthetic detergents and in emulsifiers (especially for pharmaceutical and cosmetic products); intermediates in manufacture of foam stabilizers for detergents, dyestuffs, anti-corrosion agents, agricultural weed-killers; absorbants for acidic impurities during the purification of industrial gases, e.g. synthesis gas (carbon monoxide and hydrogen).

Parallel series of products can be manufactured from propylene oxide, \( \text{H}_2\text{C}^{\cdot}\text{HC}^{\cdot}\text{CH}_2 \) and butylene oxide, \( \text{H}_3\text{CH}_2\text{C}^{\cdot}\text{HC}^{\cdot}\text{CH}_2 \), but not all the products have been developed commercially.

SOME POLYMERIC PRODUCTS

1. Polyoxyalkylene glycols

A molecule of ethylene oxide will react with the terminal hydroxyl group of a molecule of a glycol, adding on and giving a molecule characterized by two terminal hydroxyl groups and an ether linkage.
Further molecules of ethylene oxide can be progressively added by the same mechanism to give products known as polyoxyethylene glycols.

\[
\text{HO-CH}_2\text{CH}_2\text{-OH} + \text{H}_2\text{C-CH}_2 \rightarrow \text{HO-CH}_2\text{CH}_2\text{-OH}
\]

Similarly, propylene oxide can be used to produce polyoxypropylene glycols.

\[
\text{HO-CH}_2\text{CH}_2\text{-OH} \rightarrow \text{HO}\left[\text{CH}_3\text{CH-O-}\right]_n\text{CH}_2\text{CH}_2\text{-OH}
\]

The reaction proceeds readily at elevated pressure and temperatures, with an alkaline catalyst, e.g. caustic soda.

Commercial products of molecular weights ranging from 200 to 6000 are made.

**Polyoxyethylene Glycols** range from mobile liquids to hard wax-like solids and are soluble in water and many organic liquids. They are good solvents for many materials, including pharmaceuticals, dyes, and resins. They possess hygroscopic properties.

*Industrial uses include:* ingredients in cosmetics and pharmaceutical products (especially ointments); water-soluble textile lubricants; components in hydraulic-brake fluids; intermediates for the manufacture of emulsifiers and plasticizers; plasticizers for regenerated-cellulose film and adhesive tape.

**Polyoxypropylene Glycols** in contrast are not soluble in water and do not possess hygroscopic properties.

*Their industrial uses include:* intermediates for manufacture of surface-active agents, plasticizers and polyurethanes; components in hydraulic-brake fluids; lubricants for many purposes.

**2. Copolymers**

Increments of ethylene oxide and propylene oxide can be condensed step by step on to a glycol by the same mechanism as that by which the individual oxides condense. The resultant product contains 'blocks' of polyoxyethylene and polyoxypropylene and terminal hydroxyl groups. These products are called block copolymers, e.g.:

\[
\text{HO-CH}_2\text{CH}_2\text{OH} + \frac{(a+c)\text{H}_2\text{C-CH}_2 + b\text{H}_2\text{C-HC-CH}_2}{\text{O-}} \rightarrow \text{HO}\left[\text{CH}_3\text{CH-O-}\right]_n\text{CH}_2\text{CH}_2\text{OH}
\]

As the polyoxyethylene part of the molecule is hydrophilic and the polyoxypropylene part is hydrophobic, products can be 'tailor-made' to possess varying solubility in water and oil by varying the proportions of ethylene oxide and propylene oxide incorporated.

*The main industrial use of these copolymers* is as lubricants, especially water-soluble lubricants, e.g. for textiles and leather. They are also important components in hydraulic-brake fluids and mould-release agents in the rubber and plastics industries.

**Detergents**

The condensation of ethylene oxide at the hydroxyl groups of higher aliphatic alcohols, higher fatty acids and alkyl phenols to give polyoxyethylene chains terminating in hydroxyl groups yields a range of synthetic detergents. The length of the polyoxyethylene chain (the hydrophilic part of the molecule, the hydrophobic part being supplied by the hydrocarbon portion of the phenol, alcohol or acid) must be carefully chosen so
that the hydrophilic–hydrophobic balance of the product enables it to function as a detergent.

The phenol and alcohol condensates are more important than the fatty-acid condensates. They do not ionize in aqueous solution, as do the sodium alkyl sulphates and the sodium alkylbenzene sulphonates, and are usually referred to as non-ionic detergents.

They are widely used as processing materials in the textile industry, and large quantities are used in various domestic detergent products.

HIGH POLYMERS

1. Polyurethanes

Polyether polyols are manufactured by condensing propylene oxide on to the hydroxyl groups of a polyhydric alcohol such as glycerol, thereby building up polyoxypropylene chains which themselves terminate in hydroxyl groups.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{O} \cdot \left[ \text{CH}_3\text{CH}_2\text{OH} \right]_n \cdot \text{H} \\
\text{CH}_3\text{OH} & \quad \text{CH}_3\text{O} \cdot \left[ \text{CH}_3\text{CH}_2\text{OH} \right]_n \cdot \text{H} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{O} \cdot \left[ \text{CH}_3\text{CH}_2\text{OH} \right]_n \cdot \text{H}
\end{align*}
\]

Polyether polyols of molecular-weight range 300 to 5000 \((a + b + c \approx 6-155)\) are manufactured.

An isocyanate group will react with a hydroxyl group to give a urethane linkage.

\[
\text{R-NCO} + \text{HO-R}' \rightarrow \text{R-NH-C'O-R'}
\]

Thus, reaction of a polyl containing three (or more) functional hydroxyl groups with a difunctional isocyanate, e.g. tolylene diisocyanate, will produce a very large three-dimensional cross-linked molecule. Such polyurethanes are rubber-like materials, whose physical properties can be varied over a wide range according to the structures and molecular weights of the polyols and isocyanates incorporated.

These materials are used as jointing and sealing compounds for gaskets and the like.

Polyurethanes can be 'expanded' by several techniques (as can other polymers) to produce cellular materials. Just as the polyurethanes can range from hard and rigid to soft and flexible elastomers, so can the expanded urethanes. To obtain the expanded material, gas bubbles must be generated in the growing polymer at just the right moment—when the polymer is sufficiently viscous to retain the dispersed bubbles but has not developed so much cross-linked structure that it cannot be expanded. The two main techniques are (a) the use of a blowing agent such as a fluoro-chloro-methane or (b) the deliberate introduction of a small amount of water and excess of isocyanate; water and isocyanate react to produce an unstable intermediate which breaks down into an amine and carbon dioxide gas. The amine reacts with isocyanate through its active hydrogen atoms and becomes built into the polymer.

\[
\text{OCN-R-NCO} + 2\text{H}_2\text{O} \quad \text{[HOOC-NH-R-NH-COOH]} \\
\downarrow \quad \downarrow \\
\text{H}_2\text{N-R-NH}_2 + 2\text{CO}_2
\]

\[
\text{OCN-R-NCO} + \text{H}_2\text{N-R-NH}_2 \rightarrow \text{OCN-R-NH-CO-NH-R-NH}_2
\]

(The \(-\text{NCO} \text{ groups can then react with the \(-\text{OH group of a polyl or the active amino hydrogen.})\)

Separate catalysts are needed for the polymerization and for the generation of \(\text{CO}_2\) so that the reactions can be kept in step.

Expanded polyurethanes are used in thermal insulation materials (rigid types), cushioning (furniture, transport and so on) and packaging (flexible types).
2. Epoxy resins

If chlorine and propylene are mixed at high temperature and under pressure (ca 500°C and 2 atm) a substitution and not an addition reaction takes place, giving allyl chloride. Reaction of the allyl chloride with hypochlorous acid gives the corresponding di-chlorohydrin which on treatment with alkali (e.g. milk of lime) gives the epichlorohydrin.

\[
\text{CH}_2\text{CH} = \text{CH}_2 \rightarrow \text{Cl·CH}_2 \text{CH} = \text{CH}_2
\]

\[
\text{ClCH}_2\text{HC} \rightarrow \text{CH}_2 \rightarrow \text{Cl·CH}_2\text{CH(OH)}\text{CH}_2\text{Cl}
\]

Condensation of the epichlorohydrin with a diol such as diphenylol propane gives rise to a range of epoxy resins of differing molecular weights.

The commercial resins range in weight from liquid to hard brittle solids, depending on the value of \( n \), with molecular weights ranging from about 340 to 3,750.

To be of use industrially, the resins must be built up into much larger cross-linked structures by reaction of their terminal functional epoxy groups with some other polyfunctional molecule, for example a diamine or triamine (the 'curing agent' or 'hardener'). The type of reaction which takes place is shown below.

This example shows how the ends of four molecules of epoxy resin are joined together by a molecule of diamine. By a series of such reactions very large three-dimensional cross-linked molecules are built up.

\[
\text{CH}_2\text{CH} = \text{CH}_2\rightarrow \text{Cl·CH}_2 \text{CH} = \text{CH}_2
\]

\[
\text{ClCH}_2\text{HC} \rightarrow \text{CH}_2 \rightarrow \text{Cl·CH}_2\text{CH(OH)}\text{CH}_2\text{Cl}
\]

The many industrial applications of epoxy resins include: use in paints, varnishes, as part of the film-forming composition resulting in improvements in the adhesion, flexibility and chemical resistance of the dried coating; in the electrical and electronics industries for encapsulation of components; as adhesives; reinforced with fibrous materials (e.g. glass fibre) as pipe and as laminated construction material; as binders for aggregate in chemically resistant floorings and some specialized road surfacings.
LABORATORY COURSE IN PHYSICAL-ORGANIC CHEMISTRY

By Neil S. Isaacs, B.SC., Ph.D.

Assistant Professor of Chemistry, University of Victoria, British Columbia, Canada

We would suggest that many of the concepts on which physical-organic chemistry depends may be conveniently illustrated by laboratory experiments. At the University of Victoria we now include one term of practical physical-organic chemistry in the final year for chemistry honours students, comprising seven or eight of the experiments listed below.

Most of the experiments are modified procedures from well-known sources in the literature and can be completed in one laboratory period (four hours) or less. This is achieved by the use of permanently set up apparatus, ready-prepared starting materials and standardized solutions; instrumental methods are used wherever practical for making rapid measurements and analyses—in itself an advantage since it provides good opportunities for instruction on instruments such as the u.v. and i.r. spectrophotometers, gas chromatograph, pH meter and polarimeter as means of solving definite problems, rather than 'black boxes' whose true function in relation to chemistry is obscure.

For rate measurements, first-order kinetics are chosen where possible so that rate constants may be evaluated simply from the half-lives of the reactions. This is sufficiently accurate in most experiments, since the emphasis is on relative measurements on different compounds rather than precise values. The experiments are partly physical measurements and partly preparative in nature, bringing variety to a term's work. Outline procedures of satisfactorily tested experiments are given below.

1. To Investigate the Electronic Effects of Substituent Groups and Demonstrate a Linear Free-Energy Relationship

The Hammett relationship\(^1,2\) for practical reasons is more easily tested by acid-base equilibria than kinetic measurements. Two parallel series of aromatic acids are supplied: benzoic, \(p\)-toluic, \(m\)-toluic, \(p\)-chlorobenzoic, \(m\)-chlorobenzoic, \(p\)-hydroxybenzoic and \(p\)-nitrobenzoic acids, together with the analogously substituted anilinium chlorides. Approximately 50–100 mg of each (it is not necessary to weigh) is separately and completely dissolved, the anilinium chlorides in 50 ml water, the less soluble benzoic acids in 50 ml 10 per cent aqueous ethanol. Each solution is titrated against approximately \(\frac{\text{s}}{100}\) sodium hydroxide using magnetic stirring and a direct-reading pH meter\(^3\); the titration-curve of \(\text{pH}\) against titre is plotted for each compound, at least as far as the neutralization point. From the curve, the \(\text{pH}\) of the solution when half the quantity of base necessary for neutralization has been added is obtained, this value being numerically equal to the apparent acid dissociation constant, \(pK'\), for the acid.

\[
\begin{align*}
\text{HX} + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^- \\
K &= \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} \\
\end{align*}
\]

At half neutralization, \([\text{HX}] = [\text{X}^-]\) and, assuming the activity coefficients equal unity (the original of the 'apparent' \(K\)), \(pK' = \text{pH}\).

Now, applying the usual Hammett equation:

\[
\log \left( \frac{K'}{K_0} \right) = \rho \sigma \quad \cdots \quad (2)
\]

where \(K'\) refers to one of the substituted acids and \(K_0\) to the appropriate 'reference' acid, i.e. either benzoic acid or anilinium chloride. A graph is plotted of \(\log \left( \frac{K'}{K_0} \right)\) for the benzoic acids against the same function for the corresponding anilinium chlorides to give a straight line of slope \(\rho\). From the position of each point, values of \(\sigma\) for each substituent are obtained and the values interpreted in terms of electronic theory.

2. A Kinetic Isotope Effect

The mutarotation of glucose in water and in \(\text{D}_2\text{O}\) provides a convenient demonstration of a primary kinetic isotope effect, readily observed by polarimetry\(^4-7\).

The mutarotation of a molar solution of pure \(\alpha\)-d-glucose in distilled water is observed
in the usual way, the rotation being plotted as a function of time, over a period of two to three hours as a pseudo first-order reaction. A semimicro polarimeter tube is constructed from a 10-cm length of 4 mm i.d. glass tubing equipped with a side arm for filling and plane glass ends glued to the tube with epoxy cement. The total volume is about 1·3 ml. Into this tube is placed a freshly prepared molar solution of α-D-glucose in D₂O, made up in a flask calibrated to 1·5 ml. The tube is best filled by a hypodermic syringe with very fine polythene tubing attached to the needle. The mutarotation of this solution is observed as before and the ratio of half-lives of the two reactions, \( K_{\text{H₂O}}/K_{\text{D₂O}} \), obtained.

The observed magnitude of the isotope effect, \( K_{\text{H}}/K_{\text{D}} = 2·5 - 2·6 \), is consistent with the rate-determining step being the removal of the anomeric proton from protonated glucose (II). The argument is that, since all the hydroxyl groups will rapidly exchange with D₂O, a 'normal' isotope effect of \( \approx 7 \) would be observed, but this is reduced (by a factor of about 3) by the greater concentration of the conjugate acid (II) in D₂O than in H₂O because \( \text{D}_3\text{O}^+ \) is a stronger acid than \( \text{H}_3\text{O}^+ \), i.e. \( K_1(\text{D}_2\text{O}) > K_1(\text{H}_2\text{O}) \).

The D₂O may be recovered, only slightly diluted with H₂O, for re-use in this experiment.

3. **Kinetic and Thermodynamic Control of Reaction Products**

Different products are sometimes obtained, depending on whether the reaction conditions are those which yield the product formed the more rapidly (kinetic control) or that which is more stable (thermodynamic control); this may readily be illustrated by the hydrochlorination of isoprene to give initially the 1,2- (III) and finally, the 1,4- (IV) adducts.

\[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{HCl}} \text{CH}_3 \\
\text{H}_2\text{C} = \text{C}-\text{CH} = \text{CH}_2 & \xrightarrow{-20^\circ} \text{H}_3\text{C}-\text{C}-\text{CH} = \text{CH}_2 \\
& \xrightarrow{\text{Base}} \text{H}_3\text{C} = \text{C}-\text{CH} - \text{CH}_2\text{Cl}
\end{align*}
\]

(a) Approximately 10 g freshly distilled isoprene, dissolved in an equal volume of ether, is placed in a two-necked flask fitted with a gas-delivery tube reaching to the bottom and a calcium-chloride tube. The apparatus is weighed and cooled to between \(-20^\circ\) and \(-30^\circ\) in a bath of acetone/dry ice. HCl gas is passed in until approximately 0·8 mole is absorbed. The mixture is then divided into two equal portions: one is allowed to stand at about \(-10^\circ\) for one to two hours to complete the reaction, then
solid potassium carbonate and calcium chloride are added, the solution filtered and the filtrate distilled to yield the kinetic product, 3-chloro-3-methylbut-1-ene, b.p. 80°/760 mm. The second portion is saturated with HCl at −10° and allowed to stand overnight at low temperature before working up as before. This yields the thermodynamic product, 1-chloro-3-methylbut-2-ene, b.p. 110°/760 mm. The terminal or non-terminal double bonds in the respective products are apparent from the i.r. spectra.

(b) As an alternative experiment, 5α-6β-dibromocholanone (V), readily prepared from cholesterol by the method of Fieser,11 is made available to the student. This may be brominated according to Corey12 in the 4-position to give the kinetically favoured 4-α-bromo compound (VI) which under acid conditions epimerizes to the 4-β-bromo compound (VII), thermodynamically favoured because of reduced steric interactions with the angular methyl group. The preparations give good yields and distinct products.

4. The molecularity of Substitution Reactions

The slow, clean second-order hydrolysis of n-butyl bromide contrasts strikingly with the rapid first-order reaction of the t-butyl halide to give both alcohol and alkene. A kinetic experiment provides a good illustration of S$_{N}2$ and S$_{N}1$-E$_1$ mechanisms.13

n-Butylbromide (0.05 moles) is added to a 50-ml volumetric flask followed by approximately 40 ml solvent—80 per cent ethanol, 20 per cent water by weight. The flask is placed in a thermostat at 60°; when thermal equilibrium is established, 1.0 ml 1.0N sodium hydroxide is added and a clock is started simultaneously. Aliquot parts (5 ml) are taken at intervals over 2 hours, water added and the residual base titrated against standard HCl. The experiment is repeated with the t-butyl bromide at 25°, taking samples for an hour.

The results are plotted both according to unimolecular and bimolecular rate equations, by plotting 1/x and 1/(a − x) against time where a = initial concentration and x = concentration at time t of hydroxide ion. The normal compound exhibits a linear dependence on 1/(a − x) and the tertiary bromide upon 1/x from which specific rate constants may be calculated. Gas chromatography of the residue from the tertiary bromide reveals a low-boiling peak due to isobutene, whereas no such product is evident from the normal isomer.

5. Trapping of Reactive Intermediates

The following preparations exemplify a useful technique where certain transient species are involved.

(a) Dichlorocarbene.14a Dichlorocarbene is readily generated by the action of a strong base on chloroform and is rapidly captured by an olefin to form a cyclopropane derivative, e.g. the preparation of 7,7-dichloronorcarane by the action of potassium t-butoxide on chloroform in a large excess of cyclohexene. Dry cyclohexene (40 ml) and potassium t-butoxide (5.6 g) or the equivalent quantity of potassium dissolved in dry t-butanol is placed in a 250-ml three-necked flask fitted with stirrer, calcium-chloride trap and dropping funnel and cooled in a dry-ice bath. Dry chloroform (6.0 ml) is added with stirring over 30 min, also low-boiling petrol if the mixture becomes too viscous. After a further 30 min stirring, the mixture is poured into water, extracted with petrol, dried and distilled, and the 7,7-dichloronorcarane collected at 75–80°/15 mm.
Monovalent nitrogen analogues, nitrenes, could be used in a similar experiment, e.g. the thermal decomposition of benzenesulphonazide to benzenesulphonalide.

\[
\text{Heat} \quad \text{PhSO}_2\text{N}_4 \quad \longrightarrow \quad (\text{PhSO}_2\text{N}^+); \quad \quad \text{PhSO}_2\text{NPh}
\]

(b) Benzyne. Numerous facile methods of generating benzyne are now available: a reliable preparation of triptycene involves the decomposition of diazotized anthranilic acid in the presence of anthracene as trapping agent.\(^{15a}\) In Fieser's\(^ {15b}\) modification of the procedure, the temperature of reaction is raised to permit a more rapid decomposition. Thus, 2 g anthracene and 2 ml amyl nitrite\(^ {29}\) are gently refluxed in 20 ml ethylene glycol dimethyl ether, and 2·6 g anthranilic acid in 20 ml of the same solvent is slowly added. A further 2 ml amyl nitrite is added and 2·6 g anthranilic acid in the solvent is added slowly. After a further 20 min refluxing, ethanolic sodium hydroxide is added and the insoluble mixture of triptycene and excess anthracene filtered. The latter is removed by adduct formation with maleic anhydride in boiling triglyme and solution in alkali to yield pure triptycene, m.p. 255°.

\[
\text{COOH} \quad \longrightarrow \quad \text{COOH}
\]

(c) o-Benzquinone.\(^ {18}\) It is sometimes possible to add a nucleophile to a benzenoid system containing two hydroxyl groups, ortho or para, in the presence of an oxidizing agent. The intermediate quinone (or the radical-ion) is not isolated although sometimes it is apparent from the presence of transient colours.

To a solution containing potassium ferri cyanide (6·5 g) and sodium acetate (10 g) in 25 ml water, a solution of catechol (1·3 g) and thiourea (2·6 g) in 10 ml water is added with stirring during 15 min. After addition of a further 10 g sodium acetate, the white precipitate of \(S-(3,4\text{-dihydroxyphenyl})\text{thiourea, m.p. 180° (dec.) is filtered.}

6. Cryoscopic Evidence for a Carbonium Ion

The dissociation of weak bases such as tertiary alcohols in 100 per cent sulphuric acid to yield carbonium ions may be inferred from the enhancement of the freezing-point depression by the factor \(i\) above that expected for the undissociated molecule.\(^ {17,18}\) Sulphuric acid (100 per cent) is prepared by addition of the appropriate amount of oleum to 98 per cent sulphuric acid, adjusting the quantities to give a product melting at 8–10°. Approximately 5 g of the 100 per cent acid is weighed into the flask (Fig. 1)
fitted with a Beckman thermometer attached by a rubber sleeve and side-arm for addition of reagents. The acid is frozen in dry ice and then allowed to warm up slowly in a stirred cold-water bath, agitating the acid with the thermometer. The temperature at which the last crystal melts is recorded. The freezing-point constant of sulphuric acid is obtained by adding successive small portions of potassium hydrogen sulphate, dissolving by gentle warming and measuring the freezing point. Successive portions (ca 0.1 g) of triphenylcarbinol are then added to give a yellow solution of the carbonium ion and the freezing points measured. The depression of freezing point, \( \Delta T \), is plotted against mole concentration of Ph₃COH, and from the slope the apparent molecular weight of triphenyl carbinol calculated. The true molecular weight of the alcohol is greater than this figure by a factor of 4 (i.e. \( i=4 \)) on account of the almost complete dissociation into four ions. \[ \text{Ph}_3\text{COH} + 2\text{H}_2\text{SO}_4 \rightarrow \text{Ph}_3\text{C}^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+ \]

7. Measurement of Relative Reactivities by a Competition Technique

The relative reactivities to substitution of benzene and the three positions of toluene may be demonstrated by allowing a known mixture of benzene and toluene to compete for reagent; the reactivities are then in the ratios of the quantities of products obtained. Two precautions must be observed: the benzene and toluene must be in great excess with regard to the reagent or the proportions of each will change significantly during reaction; also, the quantities of products must be corrected statistically for the fact that there are six available positions in benzene, but only five in toluene—two ortho, two meta and one para.

Reactivities to Electrophilic Nitration. To a mixture of 1 mole benzene and 1 mole toluene is added 4 g concentrated nitric acid in 20 ml acetic anhydride. After standing for 30 min, the solution is washed with sodium carbonate solution until neutral, dried over solid sodium carbonate, and the benzene and toluene almost completely removed by distillation or on a rotary evaporator. The residual mixture of nitrobenzene and the nitrotoluenes is analysed by gas chromatography on a 6-ft silicone column at 150°C. The peaks are eluted in the order nitrobenzene, \( m \)-nitrotoluene, \( o \)-nitrotoluene, \( p \)-nitrotoluene. The areas under the peaks are, to a good approximation, in the ratio of the weights of products.

It is instructive to compare the above results with those obtained when chlorobenzene is substituted for toluene, and also the experiment may be extended to free-radical substitution, e.g. phenylation by decomposing dibenzoyl peroxide. Analysis of the diphenyls is best achieved with a Golay capillary column.

8. Constitutional Effects on the Course of Elimination Reactions

The veracity of the Hofmann and Saytzeff rules for elimination can be simply examined with the appropriate \( t \)-butyl derivatives, analysing the mixture of olefins produced for each by gas chromatography.

\[
\text{CH}_3\text{CH}_2\text{CHBr} \quad \text{OH}^- \quad \text{CH}_3
\]

\[
\text{CH}_3\text{CH}^{-}\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{CH}^{-}\text{CH}_2 \quad \text{70%}
\]

\[
\text{OH}^- \quad \text{CH}_3\text{CH}_2\text{CH}^{-}\text{NMe}_3 \quad \text{25%}
\]

\[
\text{t-Butyl bromide (5 g)} \quad \text{is conveniently dehydrobrominated by refluxing with excess 25 per cent ethanolic potassium hydroxide in an efficient fractionating column and collecting the material which distils below 80°C in an ice-cooled receiver.}
\]

\[
\text{t-Butyltrimethylammonium iodide (5 g) is converted to the hydroxide by an equivalent of silver oxide. After filtration, excess sodium hydroxide is added making an approximately 10 per cent solution, which is distilled through the fractionating column as above. Sufficient olefin for analysis is obtained after 2 hr although considerably more time is required for complete reaction.}
\]
Gas-chromatographic separation of the isomeric pentenes may be achieved with a Golay column or AgNO₃–ethylene glycol (15 per cent) on firebrick. In both reactions a mixture of the products is obtained showing that the above rules are a guide only to the product in major yield.

9. To Examine a Primary Salt Effect

The reaction between crystal violet (VIII) and hydroxide ion to give the colourless carbinol (IX) involves a recombination of ions of opposite charge, yet is slow enough to permit rate measurements.

\[
\begin{align*}
\text{Ph}_2\text{N} & \quad \text{C}^+ + \text{OH}^- \\
\text{Me}_2\text{N} & \quad \text{C}^- \text{OH} \\
\text{(VIII)} & \quad \text{(IX)}
\end{align*}
\]

13 resonance forms

The rate of such a reaction is highly sensitive to the ionic strength of the medium, exhibiting a negative primary salt effect, i.e. the rate is depressed by addition of inert ions, e.g. lithium sulphate, according to the Brönsted equation:

\[
\log \frac{K}{K_0} = 2S_{Z_A} \cdot Z_B \cdot F(I) \quad \ldots \quad (4)
\]

where \(K_0\) refers to the rate at zero ionic strength and \(K\) that at ionic strength \(I\), \(S\) is a constant (0·50 g for water at 25°), \(Z_A, Z_B = 1\), and are the charge on the ions and \(F(I)\) to a first approximation may be taken as \(\sqrt{I}\) or better, according to Debye-Hückel theory, as

\[
\frac{\sqrt{I}}{1 + 1.56 \sqrt{I}}
\]

Solutions of 1·5 \(\times 10^{-4}\) \(\text{M}\) crystal violet, 0·5 \(\text{M}\) sodium hydroxide and 0·5 \(\text{M}\) lithium sulphate are prepared. The dye solution (5 ml) is placed in a volumetric flask and made up to 49·8 ml. The solution is placed in a thermostat bath at 25°C, 0·2 ml sodium hydroxide solution added and a clock started. The absorbance of the solution is measured at 464 m\(\mu\) with a spectrophotometer and aliquot parts taken at 5-min intervals for ca 40 min, rinsing the cell between samples with ethanol. The latter precaution removes dye absorbed on the glass and, for the same reason, the dye solution should be stored in a polythene bottle. The experiment is repeated, adding 5, 15, 25, 35 ml of lithium sulphate solution to the crystal violet before making up to the mark. The Brönsted expression is tested by plotting \(\log K/K_0\) against \(F(I)\), noting to what ionic strength the relationship is linear.\(^{25,26}\)

10. To Test the Brönsted Catalysis Law

An early type of linear free-energy relationship, the Brönsted catalysis law,\(^4\) expresses the relationship between the catalytic constant \(K_a\) for a weak acid, HA, in a general acid-catalysed reaction and its dissociation constant \(K_{HA}\). The expression\(^{27}\) is usually given the form

\[
\log K_{HA} = a \log K_a + b
\]

where \(a\) and \(b\) are constants.

This relationship may be examined by measuring polarimetrically\(^{28}\) the pseudo first-order rates of mutarotation of \(\alpha\)-D-glucose in the presence of a series of weak acids. In this reaction, the kinetic expression is

\[
\frac{\text{d}[\text{glucose}]}{\text{dt}} = [\text{glucose}] \left( K_0 + K_{H\text{O}^+} + K_{HA}[\text{HA}] \right) \quad \ldots \quad (5)
\]

where \(K_0\) and \(K_{H\text{O}^+}\) are catalytic constants for the neutral water reaction and for catalysis by \(\text{H}_2\text{O}^+\). These constants must first be evaluated from the half-life or a first-order rate plot of the mutarotation of 1·0 \(\text{M}\) \(\alpha\)-D-glucose in pure water (in equilibrium with atmospheric \(\text{CO}_2\)) in which rate = [glucose] \(K_0\) and then in 0·01 \(\text{M}\) HCl, in which rate = [glucose] \(K_0 + K_{H\text{O}^+}[\text{H}_2\text{O}^+]\) \ldots (6)

The experiment is then repeated with 1·0 \(\text{M}\) glucose in water made 0·01 \(\text{M}\) with respect to each of the following acids: acetic, formic, chloroacetic, dichloroacetic. Substitution in eqn 5, obtaining \([\text{H}_2\text{O}^+]\) for each solution by a \(\text{pH}\) meter, permits evaluation of each \(K_{HA}\) value. Finally, a plot of \(\log K_a\) against the appropriate \(\log K_{HA}\) values is made which is linear and of slope \(a\), a factor analogous.
to the Hammett term, \( \rho \). The experimental work thus consists only of following the change in rotation of six solutions, several of which may be observed simultaneously if a number of polarimeter tubes are available.

11. **Stereochemistry of Displacement Reactions**

The following sequence of reactions may be carried out with high yields with quantities of 1–2 g, providing examples of inversion, retention and racemization of configuration at a centre undergoing nucleophilic substitution.

\[
\text{D-Oct-OH} \xrightarrow{\text{SOCl}_2} \text{D-Oct-O-SOCl} \xrightarrow{\text{Heat}} \text{D-Oct-Cl} \xrightarrow{\text{SNi, retention NH}_3} \text{S}_{\text{Ni}}, \text{inversion} \]

\[
\text{DL-Oct-OH} \xrightarrow{\text{NaN}_2} \text{L-Oct-NH}_2 \xrightarrow{\text{HCl}} \text{S}_{\text{N1}}, \text{racemization}
\]

**Oct = 2-octyl**

D- (or L-) 2-Octanol is provided, being readily prepared by resolution of DL-2-octanol as described by Vogel.\(^{29}\) This is converted into the chlorosulphite and the chloride by an \( S_{\text{Ni}} \) process according to Lewis.\(^{30}\) The chloride undergoes a Walden inversion when treated with ammonia in non-polar solvents, giving the inverted amine which suffers deamination via a carbonium ion with nitrous acid to yield the DL-octanol. The rotations of the chloride, amine and alcohol are measured and compared with the known signs and values of each stereoisomer (Table I). Since the sequence may require more than one afternoon, it is convenient to assign the experiment to two students on successive periods.

|--------------|----------|-------------|----------|-------------------|----------------------|

**TABLE I**

<table>
<thead>
<tr>
<th>Substance</th>
<th>[( \alpha )]</th>
<th>[( \alpha )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-2-octanol</td>
<td>+9.9°</td>
<td></td>
</tr>
<tr>
<td>D-2-octyl chloride</td>
<td>-20.40°</td>
<td></td>
</tr>
<tr>
<td>D-2-aminet</td>
<td>-8.53°</td>
<td></td>
</tr>
</tbody>
</table>

12. **Measurement of Solvent Effects**\(^{31}\)

Solvent effects, being complex phenomena, are rather difficult to display by simple experiments. The following procedure has given fairly good results, however.\(^{32}\)

Solutions of triethylamine and benzyl bromide (1.0 M; 5.0 ml each) in 100 per cent ethanol are placed in a thermostat bath at 25°. Aliquot parts (5 ml) are withdrawn at 5-min intervals for 40 min, each being run into a separation funnel containing water and benzene. The ionic bromine is extracted and titrated against standard silver nitrate. The kinetic run is repeated with increasing quantities (up to 70 per cent) of benzene in the solvent, longer times being required for these reactions. For each run, the second-order rate constant, \( K_2 \), is evaluated from the slope of a plot \( 1/(\alpha - x) \) against time, and values of \( K_2 \) plotted against the Kirkwood\(^{32}\) dielectric constant function, \( (\varepsilon - 1)/(2\varepsilon + 1) \), values of the dielectric constant of each solvent mixture being available from the literature.

13. **Woodward's Rules**

The additive nature of substituents on the ultraviolet spectrum of organic compounds, which is summed up in Woodward's tables,\(^{34}\) may be used to adduce structural information. The student is given a series of substances in solutions of known concentration. The u.v. spectrum of each is measured, \( \lambda_{\text{max}} \) and \( \varepsilon \) values tabulated and, from this information, suitable chromophores suggested. Finally, the identities of the compounds are revealed to be matched to the spectra. Suitable compounds, readily available in small sample quantities,\(^{35}\) are listed in Table II.

14. **Detection of Charge-Transfer Spectra**

One of the most easily examined charge-transfer systems is that between the powerful \( \pi \)-acid tetracyanoethylene and aromatic compounds;\(^{36}\) the charge-transfer bands occur
in the visible or near-u.v. region, the positions of $\lambda_{\text{max}}$ being related to the donor ability of the aromatic system. This effect may be used to demonstrate relative electron donor or acceptor properties of various substituents (cf. Expt 1).

\[
\text{NC} \quad \text{C} = \text{C} \quad \text{CN} \quad + \quad \text{(TCNE)}
\]

Solutions (0-006M) of tetracyanoethylene and of various aromatic compounds (Table III) in methylene chloride are separately mixed in equal volume and u.v.-visible spectra between about 350 and 500 m\(\mu\) recorded by a spectrophotometer. The absorption maxima are recorded and related to the electronic effects of substituent groups.

Further, it may be shown that

\[
\frac{[\text{TCNE}]}{D} = \frac{1}{K\epsilon[B]} - \frac{1}{\epsilon}
\]

where $l = \text{cell length, } D = \text{absorbance (optical density), and } \epsilon = \text{extinction coefficient of the } \pi\text{-complex. A plot of } [\text{TCNE}] / D \text{ against } 1/[B] \text{ is linear, with slope } = 1/K\epsilon \text{ and intercept } \epsilon$. By measuring the absorbance of a series of solutions at constant TCNE concentration but with increasing $\pi$-base concentration, the association constant, $K$, and $\epsilon$ for any complex can be readily obtained. The student should do this for one example.

15. Structural Assignments from Dipole Moments

With an accurate capacitance bridge, e.g. of the heterodyne-beat oscillator type, it is a fairly routine matter to measure dipole moments of compounds in dilute solution from dielectric-constant measurements, i.e. the ratio of capacitance of a cell, usually of an annular cylindrical design filled with solution as dielectric, to that with air. A typical experiment enables the student to differentiate between isomeric polysubstituted benzenes, e.g. o- and m-dichlorobenzenes or the o- and p-nitrotoluenes isolated in expt 7. The dielectric constants of a series of four or five solutions in benzene of either compound are measured over the concentration range 0-01-0-05M. The computation of dipole moments from such data is discussed at length in ref. 38.

16. Preparation of Representative Stable Carbon Ions and Radicals

The ability of phenyl groups to delocalize and stabilize a positive or negative charge,
an odd electron or a carbon atom may be shown by preparations of the triphenyl methyl carbonium ion, carbanion and radical.

(a) Triphenylmethyl Chlorate. Triphenylmethyl chloride (5 g) prepared from the carbinol by the method of Hughes is dissolved in 60 ml carbon tetrachloride and 9 g silver chloride is added. The mixture is stoppered and placed on a shaker for at least 12 hr. After decantation of silver chloride, the solvent is evaporated under vacuum to yield the trityl salt as an orange solid.

\[ \text{Ph}_3\text{C}-\text{Cl} + \text{Ag}^+\text{ClO}_4^- \rightarrow \text{Ph}_3\text{C}^+\text{ClO}_4^- + \text{AgCl} \]

(b) Sodium Triphenylmethyl. Triphenylmethyl chloride (0.01 mole) is dissolved in benzene, cooled in ice and shaken under nitrogen with 26 g of 1 per cent sodium amalgam. On standing, a clear red solution of the carbanion remains whose spectrum may be measured, taking care to transfer an aliquot portion of solution to a stopped cell while excluding oxygen. Excess of methylene dichloride is added and the colour discharged instantly with the formation of 2,2,2-triphenylethyl chloride (m.p. 97°) which is isolated by evaporation of the solvent, showing the carbanion to be an extremely powerful nucleophile.

\[ \text{Na} \rightarrow \text{Ph}_3\text{C}-\text{Na}^+ + \text{NaCl} \]

(c) Triphenylmethyl Radical. Triphenylmethyl chloride in benzene solution kept under nitrogen is shaken with zinc dust until the solution obtains a yellow colour which intensifies on warming. The visible spectrum of the radical is measured, taking care to avoid contact with oxygen. The e.s.r. signal of the solution may also be measured, confirming the radical nature of the absorbing species, and the radical may be allowed to add to isoprene to give \( \text{1,1,1,6,6,6-hexaphenyl-3-methylhex-3-ene} \).

Non-Benzenoid Aromatic Compounds. The electronic similarity between benzene and compounds with different sized rings but the same number of \( \pi \)-electrons delocalized all round the ring, may be demonstrated by the synthesis of the cyclopentadienyl anion and the tropylium cation. By comparing the u.v. spectra with that of benzene the aromatic bands around 260 mp are apparent, whereas those of the parent polyenes, cyclopentadiene and cycloheptatriene, show no aromatic character and absorb at shorter wavelengths.

(a) Cyclopentadienyl Sodium. Cyclopentadiene is readily prepared by distilling the dimer, dicyclopentadiene, with rapid boiling and collecting the monomer, b.p. 41°, at the top of a fractionating column. The cyclopentadienide is prepared by addition of this to an equimolar suspension of finely dispersed sodium in xylene, stirring at room temperature until all the sodium is dissolved. The resulting solution may be converted to ferrocene by refluxing with anhydrous ferrous chloride in tetrahydrofuran.

(b) Tropylium Fluoroborate. A convenient preparation from cycloheptatriene and phosphorus pentachloride initially forms the double salt, tropylium chloride-hexachlorophosphate, which is treated with fluoroboric acid to give the desired product, tropylium fluoroborate.

\[ 2 \overset{\text{Cl}}{\text{PCl}_3} \rightarrow \text{Cl}^- \overset{\text{PCl}_4^-}{\text{Cl}} + 2\text{HCl} \]

Spectra may be run in ethanol.

In addition to the experiments described, others suitable for inclusion in a course of
this type are constantly being evaluated and developed. These include the measurement of resonance energies, cyclization under high dilution, the investigation of keto–enol tautomeration, the use of the V. Auwers–Skita rule, a Baker–Nathan reaction-order effect, reactions involving non-classical ions, copolymerization and inter- and intra-molecular rearrangements; many others are possible. Each experiment is presented in a manual, with all relevant theory and practical information which must be read before starting the work.

The adoption of some examples of this type of experiment into a senior organic course cannot fail to bring to the student an appreciation of many fundamental principles, born of experience.

REFERENCES

3. A pH-meter with unit-expanded scale, such as the Corning Model 12 or Beckman Model 76, is particularly convenient.
21. A dual-column chromatograph with flame ionization detector was used (Perkin–Elmer Model 810).
(b) K. B. Wiberg, ref. 4, p. 253 et seq.
28. A research-quality polarimeter measuring to 0·02° or better should be used.
31. K. B. Wiberg, ref. 4, p. 374 et seq.
35. From Aldrich Chemical Co., Milwaukee, Wis., or Eastman Kodak, Rochester, N.Y.
37. A reliable but simplified design will appear elsewhere.
The traditional method of teaching elementary organic chemistry has largely involved a didactic presentation of the preparation and properties of the various classes of organic compounds. This method, which is still the most common initial approach to the subject, places before the pupil some of the wealth of factual material which organic chemists have known for many years. All too frequently, however, in schools, little attempt is made to introduce the underlying physico-chemical principles of organic reactions which are so vital to the modern chemist. Some mention of the phenomena which are the impetus for reactions to take place and the intermediate stages whereby reactants yield products must be included, I believe, in any satisfactory introduction to organic chemistry if real understanding, as against parrot-fashion learning, is to be imparted. Taught by the traditional method, the average pupil is left somewhat bewildered by the vast number of apparently unrelated reactions which he has to commit to memory and the important question for the more inquiring pupil, 'Why should it be that A and B react to give C and D?' is left unanswered.

**UNIFYING FACTORS**

Organic reactions can be rationalized under remarkably few headings. There are essentially only four basic reaction types—substitution, addition, elimination and the less well-known rearrangement reactions. There are but two ways in which a covalent electron-pair bond can break—heterolytically to form ions or homolytically to form free radicals; and there are but three types of reagent species—positively polarized electrophiles, negatively polarized nucleophiles and, less commonly, free radicals. There should be room in our teaching at school to emphasize these unifying features and their governing principles upon which the factual network of the subject can be slowly grafted in a logical reasoned manner.

**EXPLAINING REACTIONS**

The refined theories of organic reactions, which have been developed over the last 40 years under the initial impetus of Ingold in the U.K., have, of course, followed on from the longer known facts of definite reactions. It is surely an error for us to continue to teach historically—facts now, theories and explanations later. We must surely use established theory where possible as an aid to our teaching. The more we can encourage our pupils to use logical reasoned thinking towards organic reactions the better will be their understanding of the essential nature of organic materials.

The post 'O'-level pupil should from the outset be presented with new reactions with explanations (and demonstrations) wherever possible. This does not mean that there has to be a lengthy introductory series of lessons on the theory of reaction mechanism and principles, for these can be introduced gradually as required by the reactions as they occur during the course of a conventional syllabus for 'A'- and 'S'-level. As structure is a prime consideration, the only essential prerequisite is that the pupils should have a working knowledge of atomic theory and molecular structure, including an elementary treatment of orbital theory. This must therefore precede the organic work in the syllabus.

Table I indicates one way in which concepts and principles of reaction theory can be introduced during a school course based upon the present syllabuses of the examining boards.

Throughout this approach emphasis is laid upon the electron distribution and three-dimensional nature of organic molecules. The movement and redistribution of electrons during reactions are followed closely, and recourse to the physical measurements upon which reaction theories are based (e.g. rates...
of reaction, dipole moments, optical activity, pK values, isotopic tracer studies) is made continuously.

**DIFFICULTIES**

In the initial stages of this method of approach to organic reactions, school pupils are liable to encounter more difficulties than in the traditional method. They have to learn to use a new vocabulary, to look at molecular species in a different light, and, of course, to wrestle with that educatively essential, but often painful problem, of learning how to think—probably for the first time where chemical reactions are concerned. However, it is rewarding to battle on through these initial difficulties, for once pupils grasp something of this new way of examining reacting molecules, they find themselves able to predict reactions of unfamiliar substances. Here they taste something of one of the goals of chemical science—that of predicting by logical reasoning the paths of the interconversion of matter.

Not all elementary organic reactions are, of course, explicable in simple terms. Reaction theory, though highly developed in many areas, still cannot supply the answers to many relatively ‘elementary’ phenomena (e.g. the acidity of acetylenic hydrogen atoms and the inductive push of electrons by alkyl groups). This is not a real difficulty, for pupils should be continually made aware that there are still many unsolved chemical problems.

Introduction of many of the named ‘effects’ in the theory of reaction mechanism can be confusing for the school pupil and should be avoided as far as possible. The concepts implied by ‘inductive effect’ and ‘resonance effect’ render these terms useful exceptions.

Nomenclature of organic compounds is forever a problem. It will be a welcome day when the examining boards introduce the logical Geneva names at least as alternatives to the trivial ones so commonly used.

There would appear to be no easy way of systematizing reaction conditions. General statements such as ‘higher temperatures favour elimination over substitution reactions’ can help, but practical experience of a reaction is probably the best aid here, though, of course, this is rarely possible except for a handful of reactions.

**CHANGING OUR APPROACH**

There can be no doubt that many pupils find much of chemistry a genuine burden upon their memories. A mechanistic approach

**TABLE I**

<table>
<thead>
<tr>
<th>Topic or reaction</th>
<th>Principle of concept introduced or applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin hydrocarbons</td>
<td>Bond energy; molecular shape and flexibility (conformation mentioned).</td>
</tr>
<tr>
<td>Chlorination; cracking</td>
<td>Bond fission; free-radical reactions.</td>
</tr>
<tr>
<td>Alcohols</td>
<td>Lewis acids and bases; electrophiles and nucleophiles; electron-pair shifts; nucleophilic substitution at saturated carbon atoms. Elimination reactions.</td>
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<td>Olefin formation</td>
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<td>Alkyl halides</td>
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<td>Olefins and acetylenes</td>
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<td>Carbonyl compounds</td>
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<td>Hofmann reaction</td>
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<td>Benzene and its derivatives</td>
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<td>Cumene–hydroperoxide process</td>
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<tr>
<td>Primary amines treated with nitrous acid</td>
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to organic reactions of the type outlined here, can I believe, help a great deal towards this problem of factual recall, and in addition give pupils a firmer understanding of the nature of organic chemistry. There may be many teachers who will fight shy of such an approach for at least two very understandable reasons. Firstly, there has been a tendency for 'reaction mechanism' to become a discredited term, having associated with it pictures of complex rate expressions, energy profiles and curly arrows jostling about by the score! As one to whom organic chemistry was all toil, sweat and tears until the revealing light of reaction mechanics illuminated it, may I encourage those who feel this to look again at the essential principles of reaction mechanisms which are really remarkably simple? Secondly, the examining boards have yet to incorporate any mention of the principles governing organic reactions in their syllabuses and this inevitably mitigates against a change in teaching method in schools. Organic questions at 'A' level are invariably of the factual recall type and fail to test real understanding of the nature of organic materials, and, moreover, there is little likelihood of credit being given to pupils who do explain reaction processes.

Change must come, however, if we are to produce intelligent inquiring chemists who are interested in their subject and have been taught to see it as more than an everlasting shopping list of reactions.

G.C.E. 'A'-LEVEL ENTRIES

Statistics relating to G.C.E. 'A'-level entries in various subjects over the last five years show trends which are disturbing to those concerned with the supply of future scientists. The following table gives the total number of entries in the eight most popular subjects at G.C.E. 'A' level for the years 1961–64 and the final column indicates the percentage increase in the entries over those five years.

It will be noticed that the increase in the entries for chemistry was less than for the other subjects; indeed the actual number of chemistry entries dropped slightly in 1963 compared with the previous year. Moreover the percentage increase in entries for science subjects was considerably less than for the 'arts' subjects. A significant trend is the remarkable popularity of economics as a school subject.

Entries for the 1965 G.C.E. 'A'-level examination are not yet published but statistics have been obtained from six of the nine examining boards responsible for about 76 per cent of the students. These show (Table II) that there has been a considerable increase in the number of candidates at G.C.E. 'A' level in all subjects but again the percentage increase for 'arts' subjects, compared with 1964 for the same Boards, is greater than for the science subjects.

D. G. C.

<table>
<thead>
<tr>
<th>TABLE II PER CENT INCREASE 1964-65 FOR SIX BOARDS</th>
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<tr>
<td>Chemistry</td>
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<th>TABLE I ENTRIES TO G.C.E. 'A'-LEVEL EXAMINATIONS (ENGLAND AND WALES) IN SELECTED SUBJECTS DURING 1960–64</th>
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<tr>
<td>Chemistry</td>
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<td>11,630</td>
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<td>15,685</td>
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DEMONSTRATION OF LATTICE DISLOCATIONS IN THE TEACHING LABORATORY

The considerable difficulty of demonstrating the presence and properties of lattice defects in crystals, with ordinary laboratory apparatus, is almost certainly the main reason why this important topic has tended to be neglected in undergraduate chemistry courses. Accordingly, the introduction of a relatively inexpensive kit, by means of which the presence and behaviour of dislocations in LiF crystals can be observed, is greatly to be welcomed. Although intended primarily for metallurgists, the kit (marketed by Metallurgical Services of Reliant Works, Betchworth, Surrey) appears to be well suited to the requirements of chemists; an appreciation of the significance of the experiments listed and an understanding of the simple dislocation theory described in the accompanying booklet should not prove difficult to students already familiar with the principles of crystal structure.

The kit, conveniently supplied in a well-made wooden case, comprises 12 LiF crystals having dimensions of 2.5 \( \times \) 4.0 \( \times \) 12.0 mm, each so cut that all the block faces expose the 100 crystal plane. In addition, there is a purpose-made jig for compressing a crystal under a microscope, an atomic model of the LiF crystal structure, a pair of tweezers and a 40-page instruction booklet. The complete kit is priced at £19 10s. 6d., with extra LiF crystals available at £6 19s. 6d. per dozen.

However, in order to carry out the experiments described, it is necessary to have in the laboratory (i) a reflexion microscope giving a magnification of \( \times 50 \) up to about \( \times 500 \), with provision for oblique illumination of the specimen, and (ii) a low-power transmission polarizing microscope, preferably with a rotating stage and having a magnification of about \( \times 30 \). I found that these two items could readily be borrowed from the metallurgy and geology departments respectively, where they are regarded as standard equipment. However, the cost of purchasing these microscopes for sole use by a chemistry department might prove difficult to justify.

The accompanying instruction booklet is written by Drs C. W. A. Newey and R. W. Davidge, of the Department of Metallurgy, Imperial College; the authors must be congratulated on their clear and concise treatment, particularly with regard to the first 12 pages dealing with dislocation theory. The subsequent section describes some of the techniques used in the study of dislocations, including crystal etching and stress birefringence; finally, 16 pages are devoted to describing experiments which can be performed with the kit and interpretation of the results obtained.

I have had the opportunity of seeing a demonstration of the kit (at the Portsmouth College of Technology) and also of carrying out some of the experiments described; the accompanying photograph (taken by the College photographer) gives an indication of the results which can be obtained.

It should perhaps be pointed out that the LiF crystals can only be used for one or two experiments, after which they are discarded. Nevertheless, at the price quoted, this kit appears to represent good value for money.

M. I. Pope

Etch pit distribution in a 'rosette' produced by indentation with a steel needle and subsequent etching with hydrogen peroxide. Cleavage steps (running diagonally) can also be seen.
TEACHING THERMODYNAMICS TO SIXTH-FORMERS

By J. E. SPICE, B.Sc., M.A., D.Phil., F.R.I.C.
Senior Chemistry Master, Winchester College

Should an introduction to the ideas of thermodynamics form part of school chemistry? Few would argue that the subject should be developed far, but I believe there is a strong case for giving a simple treatment of some of the leading ideas. It is most important that a clear distinction should be drawn between equilibria and kinetics, and I think a real appreciation of the interplay of the total energy, free energy and entropy factors can be acquired in the sixth form. Indeed, two 'A'-level syllabuses* already include an implicit or explicit mention of free energy, and this concept forms an important part of the Nuffield approach to chemistry at 'O' level.

One or two recently published 'A'-level textbooks of physical chemistry have included brief sections on thermodynamics, but these have been compressed versions of the treatments found in degree texts and, I suggest, are likely to do more harm than good. I believe that an introductory treatment of thermodynamics suitable for the sixth form should fulfil the following conditions:

1. It should take as its starting-point facts and ideas with which the pupils are already familiar.

2. Without making any attempt at complete rigour, it should include a very careful discussion of the key ideas of thermodynamics. Although pupils who subsequently study the subject at a higher level will need to augment a sixth-form treatment, they should not have to unlearn any part of it.

3. It should lead to results which are clearly of practical importance.

1. Like many chemists, I believe that the traditional introduction to thermodynamics via the Carnot cycle is the one best calculated to frighten the beginner, and I take as starting-points:

(a) the ideas and nomenclature of thermoch­emistry;

(b) the discussion of phase equilibria in terms of vapour pressures;

(c) simple ideas about redox potentials.

Sixth-form chemistry has included (a) and (b) for a long time, and the 'Δ' convention is now often used in 'A'-level textbooks and teaching, even if it is not always properly explained. Redox potentials did not appear explicitly in 'A'-level syllabuses until the recent revisions, but are now included in several.

(2) Certain important thermodynamic ideas will have to be explained very carefully. One such concept is the notion of a reversible process. Another is the idea of a system as distinct from its surroundings. Another is the fact that functions like energy and entropy have definite values for a system, depending on the pressure and temperature, and hence that changes in the values of these functions are independent of the method of passing from one state of a system to another. But the central idea of modern chemical thermodynamics is, perhaps, the statistical basis of macroscopic phenomena. Purists may rightly say that thermodynamics has no necessary concern with atoms and molecules and hence with statistics, but most chemists feel it is essential to introduce the statistical basis for entropy as soon as possible.

Two atoms form a stable molecule if there is a sufficiently deep minimum in the appropriate potential energy curve; that is, the only relevant factor here is the energy of the system. But with very large numbers of atoms and molecules the statistical or entropy factor becomes all-important, and with it the idea of free energy. This

* Oxford and Cambridge, and Cambridge Alternative T.
distinction between the treatment of single atoms and molecules, and that of very large numbers of atoms and molecules cannot be over-stressed. The discussion of energy is different at the two levels, and quantities like entropy, free energy and temperature only have a meaning at the macroscopic level. In this article, statistical arguments are used to give a physical meaning to entropy, in a more or less conventional treatment of chemical thermodynamics. In another article, I shall attempt a more thoroughgoing statistical approach which, although falling short of the standard treatment, should nevertheless convey its essential ideas.

(3) The main practical results are summed up in the equations: \( \Delta G = \Delta H - T\Delta S \) and \( \Delta G = -RT\ln K \), which make it possible to discuss how atomic and molecular properties, through their effect on the energy and entropy factors, influence chemical and physical equilibria.

**SUMMARY OF THE PROPOSED DEVELOPMENT**

The development I propose may be summarized as follows:

A consideration of mechanical systems shows that the important factor in determining the direction of spontaneous change is the possibility of the system doing work. The accompanying conversion of potential and kinetic energy into heat does not contradict the law of conservation of energy (the first law of thermodynamics), but it corresponds to a degradation of energy which can be understood in terms of the unorganized nature of thermal energy.

If the ‘work’ criterion holds for mechanical systems, it is at least possible that it is also relevant for chemical and physical systems. Discussion shows that this is so for cell reactions and for phase changes. Such processes occur spontaneously if they can, in principle, be made to yield work. Conversely, in order to reverse the spontaneous change, it is necessary to do work on the system. All this is without reference to the total energy change; indeed, some spontaneous processes are endothermic.

Nevertheless, there must be some connexion between the capacity of a process for doing work and the accompanying total energy change. It seems unlikely that just as much heat should be evolved when an exothermic process is made to perform work, as when it occurs in such a way that no work is produced, and the relationship between the energy and work terms must presumably express the idea of a degradation of energy. Discussion of the phase transformations of pure substances shows that this ‘degradation’ term becomes more important as the temperature increases. The relationship \( \Delta G = \Delta H - T\Delta S \) is now assumed; \( \Delta G \) has not yet been properly discussed, but is taken to be an index of the work which can be obtained from the process, and \( \Delta S \) is a quantity whose dimensions are those of energy divided by temperature.

If \( \Delta G \) is to express the capacity of a process for doing work, its value must not depend on the way in which the change is actually carried out, and this implies that \( \Delta G \) is the difference between the values of some function, \( G \), which the system has in its initial and its final states. The maximum amount of work is actually obtained when the change is carried out in such a way that the forces opposing it are always infinitesimally less than the driving force of the change. An infinitesimal alteration in the opposing force can thus bring the change to a standstill or reverse it.

The statistical nature of the entropy function is illustrated by considering the isothermal expansion of an ideal gas, and the same example indicates the connexion between heat absorbed and entropy increase for a reversible change, which has already been noticed for cell reactions.

The distinction is now made between chemical or physical processes which occur in isolated systems and those for which an interchange of energy with the surroundings is possible. For the first type, the condition for a spontaneous change is simply that the entropy of the system should increase. For the second type, the total entropy of system plus surroundings still increases for a spontaneous change, but the entropy of the system itself may now decrease. The useful criterion here is that the free energy of the system must decrease.
With reversible reactions, the free-energy changes for the forward and reverse reactions clearly depend on the concentrations of the reactants, and this happens essentially because of the variation of entropy with concentration. In this way it is possible to derive the van't Hoff isotherm for chemical equilibria.

Finally, the connexion between heat absorbed and entropy increase makes it possible to determine entropy changes by purely thermal measurements, and thus to evaluate $\Delta G$ for chemical reactions.

DEVELOPMENT FOR PRESENTATION TO SIXTH-FORMERS

Introduction

Two questions need to be answered about every chemical reaction: how far does it go? how fast does it go? That is, where does its equilibrium lie, and how long does it take for this equilibrium position to be reached? If these questions can be answered, it may be possible to see why some chemical reactions do take place and why others do not. The aim of modern chemistry is to answer both questions from a knowledge of the reactant and resultant molecules, perhaps without actually carrying out the reaction. The present discussion is concerned only with the first question, and to this a complete answer is, in principle, possible.

In the late nineteenth century some physical chemists thought there was a direct connexion between the 'affinity' of a reaction (given by its equilibrium constant) and its heat change, now known as $\Delta H$, since strongly exothermic reactions often go virtually to completion. This would have been a very satisfactory answer, since the heat of any reaction can be found from directly measurable heats of reaction by an application of Hess's law. It was eventually recognized that the heat of a reaction cannot be a measure of its affinity, but not before chemists had been stimulated to carry out much useful thermochemical work. A moment's reflection shows that $\Delta H$ cannot determine chemical affinity. For instance, most thermal decompositions are endothermic, yet take place readily at sufficiently high temperatures, and many salts (e.g. ammonium nitrate) dissolve spontaneously but endothermically in water. Moreover, any state of chemical equilibrium can be approached from either side. If the forward reaction is exothermic, then the reverse reaction must be endothermic, but it too can occur spontaneously.

Changes in Mechanical Systems

It is natural to suppose that the decrease in the energy of a system is a criterion of spontaneity, for this is the case with mechanical changes. When an iron weight is dropped, it falls spontaneously to the ground and loses energy. The energy (potential at first and then kinetic) does not disappear, but is converted into thermal energy at the moment of impact.

The term thermal energy is misleading, for in the last resort there are only two kinds of energy—kinetic due to motion, and potential due to position—and both contribute to thermal energy. As the temperature of a piece of iron rises, the average vibrational energy of each atom increases and is, in fact, a measure of the temperature. Vibrational energy is partly potential and partly kinetic. At a given temperature, all the atoms do not have the same amount of vibrational energy; there is a constant interchange from one to another, some atoms having very little energy at a given time and others having a great deal more than the average. In spite of the large fluctuations in energy of any one atom from one moment to another, the fact that extremely large numbers of atoms are present means that the proportion of atoms having any particular energy is constant, at a given temperature. From the point of view of individual atoms, though, there is a randomness of distribution of this energy. In addition, the vibrations themselves are randomly directed in space. The atoms do not vibrate uniformly in phase with one another; they vibrate in varying directions and with varying amplitudes as they gain and lose energy. As well as vibrational energy, atoms possess both electronic and nuclear energy. At ordinary temperatures there is little interchange between these different kinds of energy, but at high temperatures the
interchange is considerable. All things considered, then, thermal energy is a very random quantity. Indeed, a better name for it might be ‘unorganized energy’.

When a weight is dropped, a common (and increasing) velocity component is superimposed on all the random motions of the atoms. At the moment of impact, this organized kinetic energy is dissipated as thermal or unorganized energy. If the weight suddenly rose into the air, becoming colder, no violence would be done to the law of conservation of energy, but considerable violence would be done to common sense, for it is inconceivable that the random motions of an extremely large number of atoms would suddenly co-operate to provide a common velocity component in one particular direction.

The falling weight could be made to turn a wheel, and thus produce work; conversely, in order to lift it, work would certainly have to be done on it. A little thought now shows that in all spontaneous mechanical processes, potential energy is lost and work can in principle be obtained from the system. Conversely, the reversal of such spontaneous processes requires the performance of work on the system. Coupled with this work criterion is the idea of a degradation of energy: not its disappearance, but its conversion into a less available, a less organized form. The total energy (mechanical plus ‘thermal’) of the weight and the surface on which it falls remains constant, but the ‘work potential’ of the whole system decreases.

Spontaneity in Chemical and Physical Changes

It seems unlikely that chemical systems are entirely different from mechanical ones. The spontaneity or otherwise of chemical and phase changes may therefore be closely connected, first with the capacity of the system for doing work, and second with its passage towards a more unorganized state. Two types of spontaneous process will now be examined, in which it can readily be seen how the occurrence of the process could lead to the performance of work.

First, the guiding principle for phase changes is that the stable form of a substance at any temperature is the one with the lowest vapour pressure. This is readily justified by imagining samples of two phases of a substance in two bulbs of an evacuated apparatus. As an example, rhombic and monoclinic sulphur may be considered, see Fig. 1. In each bulb there is an equilibrium between sulphur vapour and the particular solid form present, and hence a constant pressure of sulphur vapour—namely, its equilibrium vapour pressure at that temperature. Below 96°C the vapour pressure of monoclinic sulphur is greater than that of rhombic sulphur, and above 96°C it is less. Below 96°C then, the pressure difference causes sulphur vapour to move from one bulb to the other when the tap is opened, upsetting the equilibrium in each bulb and causing the continued vaporization of monoclinic sulphur and the continued condensation of sulphur vapour to rhombic sulphur, i.e. monoclinic sulphur distils over to form rhombic sulphur. Above 96°C the reverse process occurs. Only at 96°C, the transition point, are the vapour pressures equal, and only at this temperature can the two forms of sulphur be in equilibrium with each other. At any particular temperature the spontaneous change is the one which could, in principle, be made to yield external work. For instance, a small turbine could be placed in the connecting tube, and this would be turned by the vapour as it distilled from one bulb to the other. On the other hand, the turbine would behave as a pump if it were turned in the other direction by an external motor. Some of the vapour would be drawn off the form with the lower vapour pressure and forced into the bulb containing the form with the higher vapour pressure.

![Fig. 1](image-url)
Thus, the non-spontaneous change could in principle be made to take place, but only by performing work on the system. At any temperature the total energy content of monoclinic sulphur is greater than that of rhombic sulphur, but this does not affect the above argument. The spontaneous change from monoclinic to rhombic sulphur below 96\degree C is, in fact, exothermic, but the spontaneous change from rhombic to monoclinic sulphur above 96\degree C is endothermic.

Second, differences in electrical potential determine the direction of electrochemical changes. When an e.m.f. which is smaller than the difference between the electrode potentials of copper and zinc is applied to a Daniel cell (movable contact at X in Fig. 2) the cell produces a flow of current in such a direction that the reaction: \( \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \) occurs. This is the spontaneous reaction which takes place when zinc is simply added to a solution of copper sulphate. In the sulphur example, the driving force of the spontaneous change is the pressure difference of sulphur vapour. Here, the driving force is the pressure difference of electrons in the two metals. The more electropositive metal, zinc, has the larger electron pressure (the more negative potential) so that the electron flow takes place from the zinc to the copper in the spontaneous change. It could drive a motor placed in the circuit. For equilibrium, the applied e.m.f. must be exactly equal to the difference of the electrode potentials (movable contact at Y). But when the contact is at Z, the external e.m.f. forces electrons round the circuit in the opposite direction to the one just discussed. This could also happen through a motor in the circuit being driven externally in the reverse direction. It would then function as a dynamo, and electrolysis would occur with the copper anode dissolving and zinc being deposited on the cathode: \( \text{Cu} + \text{Zn}^{2+} \rightarrow \text{Cu}^{2+} + \text{Zn} \). Once again, performance of work on the system is necessary if the non-spontaneous reaction is to occur. The reaction for the Daniel cell is exothermic, but some cell reactions are endothermic. For instance, the reaction

\[
2\text{Ag} + \text{Hg}_2\text{Cl}_2(s) \rightarrow 2\text{Hg} + 2\text{AgCl}(s)
\]

has \( \Delta H = +2.55 \) kcal, but it occurs spontaneously as a cell reaction with an e.m.f. of 0.05 volts.

Changes in Total Energy, Free Energy and Entropy

As discussed later, it is possible to define a quantity \( \Delta G \), which represents the work potential of a reaction and is an index of spontaneity. The increase in \( G \) (Gibbs free energy) for a system as a result of the change under discussion is \( \Delta G \), just as \( \Delta H \) is the increase in \( H \), the heat content. The term 'system' means the collection of elements and compounds, enclosed in some vessel, on which the attention is concentrated during a physical or chemical change. It may be necessary to draw a sharp distinction between a system defined in this way and its surroundings.

For a reaction to be spontaneous, it must be capable of doing work. That is, the free energy of the system must decrease as a result of the reaction, and \( \Delta G \) must be negative. Conversely, a non-spontaneous reaction has a positive value for \( \Delta G \).

Like \( \Delta H \), \( \Delta G \) is an energy quantity and, because of the first law of thermodynamics, the two quantities must be related. Spontaneous endothermic processes like the solution of a crystal or the decomposition of a solid to gases, involve a passage from a
more to a less ordered state. From this, and from what has been said about the degradation of energy when a weight hits the ground, it may be guessed that the difference between $\Delta G$ and $\Delta H$ will be an energy term which expresses this degradation of energy. Furthermore, by considering the phase relationships of a pure compound, it is clear that this 'degradation' term must involve the temperature. For any compound, the change from liquid to solid at any temperature is invariably exothermic, as is the change from gas to liquid. At a low enough temperature, every gas liquefies and every liquid solidifies; that is, at a low enough temperature the direction of spontaneous change is dictated by the requirement that the total energy should be a minimum. On the other hand, at sufficiently high temperatures the randomness factor becomes dominant, for the most stable phase is now first liquid and then gas (progressively less ordered), in spite of the fact that the changes from solid to liquid and liquid to gas are always endothermic.

If the randomness term is to become more important as the temperature increases, the simplest thing is for it to be proportional to the absolute temperature—that is, $T$ multiplied by the change in some quantity might express the disorder of the system. This quantity has come to be called entropy, $S$, and it has the dimensions of energy temperature$^{-1}$. Various expressions of the form $X\Delta Y$ have the dimensions of energy; for example, $P\Delta V$, where $P$ is pressure and $V$ is volume; $E\Delta Q$, where $E$ is potential difference and $Q$ is charge; $\sigma\Delta A$, where $\sigma$ is surface energy and $A$ is area; $\rho\Delta l$, where $\rho$ is the tension in a string and $l$ is its length, and so on. In all these expressions, $X$ is a kind of potential—a quantity whose value determines the direction in which something moves. Sometimes $X$ is described as an intensive quantity or intensive factor; if the amount of a system changes, the value of $X$ need not change. On the other hand, $Y$ is an extensive quantity or capacity factor, and its value is directly related to the amount of the system. In particular this must be so for entropy. It seems, then, that every system under stated conditions of temperature and pressure has a definite value for the quantity $S$, which is related to the degree of order of the system.

**Measurement of $\Delta G$**

The heat-content change, $\Delta H$, of a reaction is a definite quantity; it is the difference between the energy content of the system in its final state and that in its initial state, when the change occurs at constant pressure (the physical forms of the various substances concerned, and their temperature, must naturally be specified). The value of $\Delta H$ is readily obtained—by direct calorimetry, or by Hess's law. If $\Delta G$ is to be a useful criterion of spontaneity, it must similarly have a definite value for a reaction, depending only on the initial and the final states. From the analogy with mechanical potential energy this may very well be possible. The actual measurement of $\Delta G$ is, however, rather a different matter, because the work obtained from any process depends on the method adopted to extract the work. A waterfall has a maximum potential for work, but unless a turbine is installed, no work is actually obtained.

For a chemical system it is easiest to consider a cell reaction. No work is obtained when zinc is added to copper sulphate solution; for the extraction of work, the reaction must be made to occur in a cell, connected to an electric motor. Just as $\Delta H$ for the reaction:

\[
\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}
\]

is the change in heat content when one mole of zinc reacts with one mole of cupric ions, so $\Delta G$ is the change in free energy when one mole of zinc reacts—that is, when two moles of electrons or $2F$ coulombs of electricity pass round the external circuit. If the motor has a back e.m.f. of $E$ volts, the work actually obtained for the passage of this quantity of electricity is $2EF$ joules or $2EF/J$ calories. Clearly, $E$ may have any value from zero (when the motor is short-circuited) up to $E^\circ$, the e.m.f. of the Daniel cell on open circuit. If $E < E^\circ$, the cell reaction takes place at a finite rate, but produces less than the maximum possible amount of work. The only amount of work which can be said to have a definite value, independent of the
actual working conditions, is $2E^\circ F$. This is the maximum work, and is equal to $-\Delta G$, the free-energy decrease for the reaction. The maximum work is in principle obtained when the opposing e.m.f., $E$, is only infinitesimally less than the e.m.f. of the cell; in fact, the current would pass infinitely slowly under these conditions. But from the point of view of finding $\Delta G$ this does not matter, for the accurate measurement of the e.m.f. of a cell on open circuit is a routine matter. In general, for cell reactions $\Delta G = -nE^\circ F$, where $E^\circ$ is the e.m.f. of the cell on open circuit and $n$ is the number of electrons transferred.

When the force which opposes any change is only infinitesimally less than the driving force of the change ($E$ and $E^\circ$ for a cell reaction), the change is said to take place reversibly, since by an infinitesimal change in the opposing force, the change can be halted (i.e. brought to equilibrium) and then reversed. Any change yields its maximum work $-\Delta G$ if, and only if, it is carried out reversibly.

$\Delta G$, $\Delta H$ and $\Delta S$ for Cell Reactions

In the Clark cell the reaction is:

\[ \text{Zn (amalgam)} + \text{Hg}_2\text{SO}_4 \rightarrow 2\text{Hg} + \text{ZnSO}_4 \]

$\Delta G = -66.1$ kcal, $\Delta H = -81.9$ kcal

Thus, 81.9 kcal of heat is evolved when the reaction is carried out in a single vessel. If it takes place in a cell, it will not be possible to draw up to 66.1 kcal as work from the external electrical circuit and 81.9 kcal as heat. The heat evolution will vary from 81.9 kcal, when the cell is short-circuited and no work is obtained, to 15.8 kcal, the difference between $\Delta H$ and $\Delta G$, when the reaction is carried out reversibly. This difference is, of course, equal to $T\Delta S$, i.e. $T\Delta S = -15.8$ kcal. The entropy of the system decreases as a result of the reaction. The system passes to a state of less disorder and, as a result of this, heat is evolved. Alternatively, not all of the total $\Delta H$ is available as electrical energy; some ($T\Delta S$) is unavoidably lost. The quantity $T\Delta S$ is sometimes called the 'unavailable' energy; it may be considered to be used up in decreasing the disorder of the system.

On the other hand, for the reaction between cadmium amalgam and mercuric iodide:

\[ \text{Cd (amalgam)} + \text{HgI}_2 \rightarrow \text{CdI}_2 + \text{Hg} \]

$\Delta G = -19.9$ kcal, $\Delta H = -13.6$ kcal

and consequently, $T\Delta S = +6.3$ kcal. Here, the maximum electrical work is greater than the heat evolved when the reaction occurs in a single vessel, the difference being made up by heat absorbed by the cell from its surroundings, while it is producing electrical energy. This absorption of heat is accompanied by an increase in the disorder of the system.

The above discussion indicates an important relationship between entropy changes and quantities of heat passing between a system and its surroundings, viz.

\[ q_{\text{rev}} = T\Delta S \]

or

\[ q_{\text{rev}}/T = \Delta S \]

where $q_{\text{rev}}$ is the heat absorbed by the system during a reversible process, $\Delta S$ is its entropy increase and $T$ is the absolute temperature. It is most important to note that this is true only if the change is reversible. If it is not carried out reversibly, less work than the maximum will be done, and consequently less heat will be absorbed from the surroundings. The value of $\Delta S$ depends only on the initial and final stages, and is independent of the way in which the change is effected. Thus, for an irreversible process, $\Delta S > q_{\text{rev}}/T$. These relationships will be discussed in more detail in a later section.

$\Delta G$ and Chemical Equilibrium

The sign of the change in free energy of a reaction indicates whether or not it is spontaneous, and considering $\Delta G$ as the difference of $\Delta H$ and $T\Delta S$, four sets of conditions can be distinguished.

1. $\Delta H$ negative, $\Delta S$ positive. Here $\Delta G$ must be negative and the reaction occurs spontaneously. The combustion of carbon to carbon monoxide: $C + \frac{1}{2}O_2 \rightarrow CO$, comes into this category. This reaction is exothermic.

* These figures have no exact meaning, since the physical states of reactants and products are not specified; the same is true of the reactions for the Clark cell. This imprecision does not, however, affect the argument.
and the change from one mole of solid carbon and half a mole of gaseous oxygen to one mole of gaseous carbon monoxide corresponds to a considerable increase of disorder and hence of entropy.

2. $\Delta H$ positive, $\Delta S$ negative. Here $\Delta G$ must be positive, and the process will not occur spontaneously. It may be possible to bring it about by coupling it to some other reaction, in which there is a larger negative $\Delta G$. It is in this way that many of the highly organized molecules in living organisms are built up from much simpler molecules.

3 and 4. $\Delta H$ and $\Delta S$ both positive, or $\Delta H$ and $\Delta S$ both negative. The two terms in the expression for $\Delta G$ now work in opposite directions, and the sign of $\Delta G$ depends on their relative magnitudes. This category includes endothermic reactions which are spontaneous because of a large entropy increase (e.g. thermal decompositions), and exothermic reactions which are not spontaneous because of a large entropy decrease (many would-be precipitations).

When equilibrium processes are considered, it is fairly clear that $\Delta G$ must depend on the concentrations of the substances involved, since for a reversible reaction, either the forward or the reverse reaction may be made to take place, by an appropriate choice of concentrations. As will be seen later, this effect of concentration on $\Delta G$ is due to its influence on the term $\Delta S$. Most reactions which give readily attainable equilibrium states belong to cases 3 and 4. $\Delta G$ has a small numerical value and can be made either positive or negative by altering the concentrations.

**Isothermal Expansion of an Ideal Gas**

Another example of a reversible process is provided by the isothermal expansion of an ideal gas. Suppose one mole of the gas is confined in a cylinder closed by a piston (Fig. 3) at a constant temperature $T^\circ K$, and suppose the initial and final pressures and volumes to be $P_1$, $V_1$ and $P_2$, $V_2$. If the gas is ideal, then (a) its total energy, $U$, is independent of $P$ and $V$; (b) it obeys Boyle’s law, $P_1V_1 = P_2V_2$; (c) its heat content or enthalpy, $H = U + PV$, is also independent of pressure and volume. If $V_2 > V_1$, then the change will be spontaneous and can yield work. The piston may be coupled to an engine which offers a ‘back’ pressure, $P'$, and for an increase in volume of $\delta V$, the work done by the gas is $P'\delta V$. As with the cell reaction, the work done can range from zero, when there is no force to oppose the expansion of the gas, up to a maximum of $P'\delta V$, when the opposing pressure is infinitesimally less than the pressure of the gas at each stage of the expansion. As with the cell reaction, the reversible expansion of the gas, although yielding the maximum amount of work, would take place infinitely slowly. By an infinitesimal increase in the pressure, the expansion could be halted or reversed. In order to calculate the total work done by the gas during a reversible expansion, $P'\delta V$ has to be integrated between the limits $V_1$ and $V_2$:

$$w_{\text{max}} = -\Delta G = \int_{V_1}^{V_2} P\,dV = RT\int_{V_1}^{V_2} \frac{dV}{V} = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}$$

Accordingly, when one mole of an ideal gas passes from the state $(P_1, V_1, T)$ to the state $(P_2, V_2, T)$, the following relationships hold:

(i) $\Delta H = 0$; (ii) $\Delta G = -RT \ln (P_1/P_2)$; and (iii) since $\Delta G = \Delta H - T\Delta S$, it follows that $\Delta S = R \ln (P_1/P_2)$.

**Statistical Interpretation of the Entropy Change for the Expansion of an Ideal Gas**

When the gas expands from a smaller to a larger volume its disorder evidently increases, since in the initial state the molecules are more confined than in the final state. Since $P_1$ is greater than $P_2$, $\Delta S$ is positive, which it must be if $S$ is a measure of the degree of disorder.

Suppose now that the ‘probability’ for each molecule of the gas is proportional to the volume in which it moves; that is, a
molecule in a volume $2V$ is twice as "de-localized" as one in a volume $V$. The probabilities for two molecules in volumes $V$ and $2V$ are, respectively, $V^2$ and $(2V)^2$, and for $n$ molecules, $V^n$ and $(2V)^n$. This is because the probability for a multiple event is the product of the probabilities for the individual events. The chance of throwing two heads simultaneously is not 1/2 but 1/4, and of throwing three heads, 1/8.

Entropy has been seen to be an additive quantity. If the entropy of a volume, $V$, of gas is $S$, then the total entropy of two such volumes of gas is $2S$. If the probability for volume $V$ is $W$, then on adding another volume $V$, the total probability will be not $2W$, but $W^2$. This is because any one of the $W$ arrangements of molecules in the first volume of gas, can occur alongside any one of the $W$ arrangements in the second volume.

Assuming that there is a functional relationship between entropy, $S$, and probability, $W$, and that entropy is additive whereas probabilities must be multiplied, it is not difficult to see that the relationship must be of the form $S = C \ln W$, where $C$ is a constant.

On this basis, the entropy increase when the gas expands is:

$$S = C \ln \left( \frac{W_2}{W_1} \right)$$

But $W_2/W_1 = (V_2/V_1)^N$, since the probability for one molecule has been assumed proportional to $V$, and the total number of molecules in one mole is $N$, Avogadro's number.

That is,

$$S = C \ln \left( \frac{V_2}{V_1} \right)^N = NC \ln \left( \frac{V_2}{V_1} \right)$$

Comparison with the previous result for $\Delta S$, shows the constant $C$ to be equal to $R/N$, the gas constant per molecule. This constant is called the Boltzmann constant, $k$. Thus, the relationship between entropy and probability is: $S = k \ln W$.

$\Delta G$ and $\Delta S$ for the Isothermal Expansion of an Ideal Gas

When the gas expands spontaneously from volume $V_1$ to the larger volume $V_2$ it can do work, and the necessary energy is absorbed from the surroundings, since the energy of the gas itself is independent of $P$ and $V$. The heat absorbed, like the work done, can vary from zero (when nothing opposes the expansion) to $RT \ln(P_1/P_2)$, when the expansion is done reversibly. As for the cell reaction, absorption of heat thus accompanies an increase in the entropy of the system. Conversely, an isothermal compression of the gas would need work to be done on it; heat would then be lost to the surroundings and the entropy would decrease.

For the expansion of the gas, carried out in any way, $\Delta G = -RT \ln(P_1/P_2)$. This is a constant quantity which depends only on the initial and final pressures. If, and only if, the expansion is reversible, there is the further relationship:

$$w_{\text{max}} = -\Delta G = RT \ln(P_1/P_2)$$

For irreversible expansions the work done is less than the maximum:

$$w < -\Delta G$$

Further, for any expansion of the gas, $\Delta S = R \ln(P_1/P_2)$, which is also constant, depending only on the initial and final pressures. If, and only if, the expansion is reversible, then

$$q_{\text{rev}}/T = \Delta S = R \ln(P_1/P_2)$$

where $q$ is the heat absorbed by the gas. For any other expansion

$$q_{\text{irrev}}/T < \Delta S$$

These equalities and inequalities involving $\Delta G$, $\Delta S$, heat absorbed and work done have been illustrated for cell reactions and for the expansion of an ideal gas, but a more detailed analysis shows that they are generally valid. Their importance is that they make it possible to calculate $\Delta G$ and $\Delta S$ for a process purely from knowledge of the properties of the initial and final states, even though the derivation of the necessary formulae has involved a hypothetical reversible process.

Entropy Changes and Spontaneity

Many spontaneous processes are clearly accompanied by an increased disorder, and it is natural to ask under what conditions the passage from order to chaos provides a criterion of spontaneity. The natural order is quickly lost and never likely to be recovered when playing cards are shuffled. Random molecular movements rapidly equalize the
pressure when the tap is opened in the apparatus of Fig. 4, and all the gas will never again be in the globe from which it started, Fig. 4.

unless it is pumped back. When a layer of alcohol is placed carefully on top of a layer of water, the two liquids gradually mix by diffusion, but do not unmix again.

All these spontaneous processes correspond to an increase in randomness or disorder—or entropy—and the shuffling or randomizing tendency may well seem a natural index of spontaneous change. But the previous discussion has indicated the general relevance of the work or free-energy criterion and, indeed, spontaneous changes like crystallization obviously involve a decrease in entropy for the compound which crystallizes.

In order to resolve this difficulty, the conclusions of the last section about the entropy increase of irreversible processes will be applied to the transfer of the heat.

In the thermodynamic sense, a 'system' is a collection of elements or compounds which undergoes some transformation. Such a 'system' is never completely isolated from its surroundings; even if the containing vessel is closed so that none of the reactants or products can escape, heat is usually gained or lost by the system depending on its temperature in relation to that of the surroundings. If, now, a quantity of heat, q, is transferred reversibly from the system to its surroundings, the temperature of the latter being only infinitesimally less than that of the system, T:

\[
\text{decrease in entropy of system} = \frac{q}{T}
\]

\[
\text{increase in entropy of surroundings} = \frac{q}{T}
\]

\[
\text{net increase in entropy of system + surroundings} = \frac{q}{T}
\]

That is, the total entropy of system and surroundings is unchanged by a reversible transfer of heat.

Suppose, now, the same quantity of heat is transferred, but with the temperature, \(T_1\), of the system greater by a finite amount than the temperature, \(T_2\), of the surroundings. In order to retain the reversible nature of the transfer as far as system and surroundings individually are concerned, the system can be assumed to lose the heat to a large reservoir whose temperature is only infinitesimally less than \(T_1\). The temperature of the reservoir is then lowered to a temperature infinitesimally greater than \(T_2\), and the same amount of heat is transferred to the surroundings.

Then,

\[
\text{decrease in entropy of system} = \frac{q}{T_1}
\]

\[
\text{increase in entropy of surroundings} = \frac{q}{T_2}
\]

\[
\text{net increase in entropy of system + surroundings} = \frac{q}{T_2} - \frac{q}{T_1}
\]

and since \(T_2 < T_1\), this is positive.

That is, for the system and its surroundings, an irreversible transfer of heat corresponds to a net increase of entropy, and for the particular example discussed, this must happen during the fall in temperature of the intermediate reservoir.

These conclusions apply not only to the transfer of heat but to all processes. They may be summarized:

In any isolated system (e.g. a non-isolated system plus its surroundings) the entropy is constant for reversible processes, but increases for irreversible processes.

This is one of the ways of stating the second law of thermodynamics. Since spontaneous processes occur at a finite rate they are necessarily irreversible, and are therefore always accompanied by an increase in entropy.

A randomizing tendency inexorably operates in nature; for an isolated system, atoms and molecules mix themselves up rather than arrange themselves in ordered patterns and temperature differences even themselves out. All forms of energy ultimately appear as heat, so that there is a continuous conversion or degradation of energy into less available forms. Left to itself, the universe will eventually run down.

In practice, however, a chemical or physical system is never isolated; there is always the possibility of energy transfer between it and its surroundings. A spontaneous change in
a system at constant temperature always involves a decrease in free energy, but may also involve a decrease in entropy. If such a decrease occurs, it is at the expense of a larger increase in the entropy of the surroundings.

It is interesting to consider another apparent paradox; a supercooled liquid is completely isolated from its surroundings, but eventually crystallizes. This is a spontaneous change in an isolated system, which apparently involves a decrease in disorder for the compound! In fact, the change is exothermic and, since the system is isolated, both its temperature and its total entropy will increase.

It is often useful to distinguish 'configurational' entropy, given by the geometric order of the system, from 'thermal' entropy, which is determined by the randomness of thermal energy and always increases as the temperature increases. In the example just discussed, the increase in the thermal entropy more than balances the decrease in the configurational entropy, so that the total entropy of the system does increase.

A more detailed analysis than has been given here shows that the condition for a spontaneous change in a system, kept at constant temperature by exchanges of energy with the surroundings, is actually that at constant pressure the free energy, $G$, must decrease. Since most chemical measurements are carried out at constant pressure and temperature, this is the most useful practical criterion.

For spontaneous changes at constant temperature and constant volume, the Helmholtz free energy, $F$, must decrease. $F$ is defined as $U - TS$, and thus bears to $G$ the same relationship as $U$ does to $H$.

**Chemical Equilibrium**

Any spontaneous process within a system whose temperature and pressure are constant must involve a decrease in Gibbs free energy, $G$. Accordingly, the equilibrium state for such a system is the state for which $G$ is a minimum. The mechanical analogy of Fig. 5 will make this clear. How does this work for chemical reactions?

An equimolecular mixture of hydrogen and iodine vapour reacts until a definite proportion of hydrogen iodide has been formed, after which there is no further change in the composition of the mixture; also, hydrogen iodide decomposes at the same temperature to give the same equilibrium mixture. The total free energy of the equilibrium mixture must be smaller than that of the hydrogen and iodine, or of the hydrogen iodide, separately. If more iodine vapour is introduced, there is a further reaction to give hydrogen iodide, until the free energy again reaches a minimum value. From all this it is clear that the free energy of a gas depends on its concentration or pressure.

Only changes in heat content and free energy can be measured, so that it is necessary to define a standard state for each element and compound, and a corresponding standard molar heat content and free energy, $H^\circ$ and $G^\circ$. For this purpose the physical state of the element or compound at room temperature is chosen and, for gases, a pressure of one atmosphere. The standard entropy, $S^\circ$, is similarly defined. Thus, $G^\circ = H^\circ - TS^\circ$ at any temperature, although standard values are usually tabulated at $T = 298·1$°K.† Attention may now be restricted to ideal gases for which $H^\circ$ is independent of pressure. Since the entropy change for an expansion is $S = R \ln(P_1/P_2)$, it follows that the

![Fig. 5. B and D are positions of unstable equilibrium; the slightest disturbance of the ball causes it to move irreversibly and spontaneously to one of the positions of stable equilibrium, A, C or E. Any small disturbance of the ball in these latter positions is immediately followed by a return to its equilibrium position.](image)

*† I have assumed that pupils will have been told about the difference between $\Delta U$ and $\Delta H$. I think it best, in an introduction of this kind, to deal only with $\Delta G$ and $\Delta H$.

† These standard states are not quite as usually defined, but I do not think this matters in the present context.
entropy of one mole of an ideal gas at pressure $P$ is $S = S^\circ - R \ln P$. Consequently, $G = G^\circ + RT \ln P$. From a purely qualitative point of view, this latter expression is seen to be of the correct form; the higher the pressure and the higher the temperature, the more work can a given quantity of gas perform. The use of vapour pressure as an index of spontaneity for phase changes will now be recalled. The stable form of a pure compound at any temperature is, of course, that with the lowest free energy, since free energy could otherwise decrease as a result of a phase change; and the lower the partial pressure, the lower is the free energy.

At temperature $T$ the resulting mixture of gases:

(a) It may be an equilibrium mixture, when the partial pressures will not change with time. Since $G$ has a minimum value for such a mixture, the reaction of one mole of $A$ at partial pressure $P_A$ to give two moles of $B$ at partial pressure $P_B$ will thus have $\Delta G = 0$.

(b) It may be such that the reaction $A \rightarrow 2B$ occurs spontaneously. In this case $\Delta G$, calculated for the transformation of one mole of $A$ at partial pressure $P_A$ to two moles of $B$ at partial pressure $P_B$, will be negative.

(c) It may be such that the reverse reaction is spontaneous, when $\Delta G$, calculated for the forward reaction, will be positive.

From the expression $G = G^\circ + RT \ln P$,

$$\Delta G = 2G_B - G_A = (2G_B^\circ - G_A^\circ) + RT(2 \ln P_B - \ln P_A) = \Delta G^\circ + RT \ln (P_B^\circ/P_A^\circ)$$

If the pressures are equilibrium pressures, $P_{A,e}$ and $P_{B,e}$, then $\Delta G = 0$, as in (a) above, and

$$\Delta G^\circ = -RT \ln (P_{B,e}/P_{A,e}) = -RT \ln K_e$$

The free-energy change, $\Delta G^\circ$, would accompany the conversion of one mole of $A$ to two moles of $B$, with both compounds at unit pressure. It is clearly constant at a given temperature, and is called the standard free-energy change for the reaction. Consequently, the expression $P_{B,e}^2/P_{A,e}$ is also constant at a given temperature. It is, of course, the equilibrium constant $K_p$, and the equation is known as the van't Hoff Isotherm.

This reasoning is readily generalized for a chemical reaction involving any number of molecules on either side, and forms the theoretical justification for the constancy of the equilibrium constant, $K_p$. Similar reasoning shows that for an equilibrium between ideal gases in which the concentrations are measured in moles per litre rather than as partial pressures, $\Delta F^\circ = -RT \ln K_p$. Although $K_e$ and $K_p$ are, strictly speaking, constant only for ideal gases, deviations are small for real gases except at high pressures. A straightforward argument leads to an analogous expression for the equilibrium constant of reactions in solution. In sufficiently dilute solutions of non-electrolytes $K$, written in terms of molar concentrations, is essentially constant, but in more concentrated solutions, and particularly for reactions between ions, it is strictly necessary to use 'activities' instead of concentrations. The difference between $\Delta G^\circ$ and $\Delta F^\circ$ for reactions in solution is so small that it is usually ignored. Thus, for most calculations the following expressions are used:

$$\Delta G^\circ = -RT \ln K_e$$ for gaseous equilibria

$$\Delta G^\circ = -RT \ln K$$ for reactions in solution

$K$ being in terms of either molar concentrations or activities.

The free-energy change for a reaction may be expressed in the following imprecise but convenient form:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{conens of products}]}{[\text{conens of reactants}]}$$

Application of this equation to a cell reaction ($\Delta G^\circ = -nFE$) leads easily to the equation for the variation of redox potential with the concentrations of the oxidized and reduced forms.

It is also of interest to consider the free-energy change for a heterogeneous reaction, e.g.:

$$3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$$
The essential assumption is that the free energy of a pure condensed phase is constant at a constant temperature. (The only exception is that the free energy of a finely-divided solid or of very small drops of a liquid may be slightly greater than that of the compound in its normal solid or liquid state).

Then:

\[ \Delta G = G_{f_0} + 4G_{H_2} - 3G_{f_0} - 4G_{H_2O} \]

\[ = (G_{f_0} + 4G_{H_2} - 3G_{f_0} - 4G_{H_2O}) \]

\[ + 4RT \ln P_{H_2} - 4RT \ln P_{H_2O} \]

\[ = \Delta G^o + RT \ln (P_{H_2}^o/P_{H_2O}^o) \]

and

\[ \Delta G^o = -RT \ln K_p \]

where \( K_p = (P_{H_2O}^o/P_{H_2}^o) \), and is thus written in terms of the gaseous components only.

The importance of all this is that \( \Delta G^o \) can be determined, for reactions which have never been carried out, from the standard free energies of formation of the reactant and resultant compounds. The procedure is exactly the same as for finding heat-content changes from heats of formation by Hess’s law. If \( \Delta G^o \) is positive and large (more than about 2 kcal), \( K \) is extremely small. The positive value for \( \Delta G^o \) means that the reaction is not spontaneous when reactants and products are all at unit concentration or unit pressure. Nor will normally obtainable pressures or concentrations be able to make it spontaneous. For example, \( \Delta G = \Delta G^o + RT \ln (P_{H_2}^o/P_A) \) in the reaction \( A \rightleftharpoons 2B \), where \( P_A \) and \( P_B \) are the actual pressures (neither 1 atmosphere nor the equilibrium pressures) to which \( \Delta G \) relates. If, for instance, \( \Delta G^o = +5 \) kcal, then \( RT \ln (P_{H_2}^o/P_A) \) would have to equal \(-5 \) kcal before the reaction could become spontaneous. At 300°K this implies \( P_A = 10^4 P_{H_2}^o \), which would only begin to be feasible if some means were available for removing the product B as soon as it was formed.*

Thus, a reaction with a large positive \( \Delta G^o \) is one which will not occur spontaneously, whereas a reaction with a large negative \( \Delta G^o \) has a very high equilibrium constant, and is likely to take place spontaneously, at almost any pressures or concentrations. If \( \Delta G^o \) lies between about \( \pm2 \) kcal, it will usually be possible to obtain a negative \( \Delta G \) by a suitable choice of pressures or concentrations, and this is the normal type of equilibrium reaction.

Here a proviso about rates and equilibria must be made. All the above relates to the final equilibrium position, and gives no information at all about the rate at which this position can be reached.

**Determination of Entropy Changes from Thermal Measurements**

The absorption of heat by a system has been seen to involve an increase in entropy, but this increase is given by \( q/T \) only if the transfer is reversible with an infinitesimally small temperature difference between the system and its surroundings. For phase changes this is readily arranged, since the equilibrium temperature for two phases of a pure compound is constant so long as some of each phase is present, and absorption of heat alters the proportion of the two phases without changing the temperature. So for the conversion of one mole of the substance from one phase to another at constant pressure:

\[ \Delta S = \Delta H/T \]

where \( \Delta H \) is the heat-content change for the transformation and \( T \) is its equilibrium temperature.

Apart from phase changes, a compound can absorb heat reversibly if the temperature rise, \( \delta T \), is infinitesimally small. For one mole of the compound, \( \delta S = \delta q/T \), and \( \delta q = C_p \delta T \), where \( C_p \) is the molar heat capacity at constant pressure. Thus, \( \delta S = (C_p/T) \delta T \), and in the limit \( dS = (C_p/T) dT \). The entropy increase when one mole of a compound is heated from \( T_1 \) to \( T_2 \) may therefore be obtained by integration:

\[ \Delta S = \int_{T_1}^{T_2} C_p \cdot dT = \int_{T_1}^{T_2} C_p d \ln (T) \]

If the entropy of a pure compound is \( S_0 \) at the absolute zero of temperature, its entropy at any other temperature is thus

* Ionic reactions with a large positive \( \Delta G^o \) may, indeed, take place in solution, since the formation of extremely insoluble precipitates or extremely stable complex ions may produce a very high ratio of ionic concentrations.
So + X, where X involves a number of terms of the types \( \Delta H/T \) and \( \int C_p \, d(ln T) \), and can be determined by purely thermal measurements. According to the third law of thermodynamics, \( \Delta S^0 \) is zero for reactions between most compounds, so that \( \Delta S^0 \) for a reaction is usually given by \( \Delta X \), whose evaluation is essentially a routine matter. \( \Delta H^\circ \) for the reaction can usually be found from tabulated heats of reaction, and it is then possible to calculate \( \Delta G^\circ \).

\( \Delta G^\circ \) may also be found:

(i) from the van't Hoff isotherm;
(ii) for cell reactions, from the equation \( \Delta G^\circ = -nFE \);
(iii) for reactions of known \( \Delta H^\circ \) which involve only gases, from molecular energy levels.†

By these methods, singly or in combination, \( \Delta G^\circ \) has been found for a great many reactions, and it has been possible to draw up tables of free energies of formation of compounds from their elements. With the help of such tables, \( \Delta G^\circ \) can be found for many reactions, and their thermodynamic feasibility assessed before any experimental work has been done.

EXTENSIONS TO THE MAIN DEVELOPMENT

I should confine sixth-form thermodynamics mainly to the argument summarized at the beginning of this article and then developed in some detail. It involves very little mathematics but it deals with what are probably the most central and most important ideas of chemical thermodynamics, and all sixth-formers should be able to grasp at least the main threads of the argument. The ideas would, of course, be illustrated as widely as possible with actual examples and calculations. In particular, pupils should become very familiar with the use of tables of \( \Delta H^\circ \) and \( \Delta G^\circ \).

Some of the processes which it is particularly fruitful to discuss qualitatively in terms of the total energy and entropy factors are:

(a) reactions of ions, such as acid–base and complex-forming reactions; (b) processes involving metals and ionic crystals, such as solubility equilibria, redox equilibria and the reactions of extraction metallurgy; (c) phase changes. All this can be done with no more background than has been given in this article, although it would also be useful to be able to quote the equations: 

\[
S = -dG/dT \quad \text{and} \quad \Delta S = -d\Delta G/dT.
\]

For the more able pupils the treatment might be slightly extended. Thus, the equation \( \Delta S = q/T \) makes it possible to discuss the efficiency of heat engines and refrigerators. This is not of direct chemical interest, but the result:

\[
\text{work done in cycle/heat absorbed at higher temperature} = (T_2 - T_1)/T_2
\]

can be used to derive the Gibbs–Helmholtz and Clapeyron equations. Alternatively, the following argument might be used; it is more in line with the quasi-functional approach of this article, and it does not involve the explicit use of partial differentiation.

For a small change in any system, the energy increase is equal to the heat absorbed by the system minus the work done by it:

\[
\delta U = \delta q - \delta w
\]

When the change is reversible,

\[
\delta q = T\delta S \quad \text{and} \quad \delta w = P\delta V,
\]

so that

\[
\delta U = T\delta S - P\delta V
\]

This is, in fact, always true, since both \( S \) and \( V \) have definite values for a given state of the system, and the values of \( \delta S \) and \( \delta V \) therefore do not depend on how the change is effected. (When it is done irreversibly, \( \delta q < T\delta S \) and \( \delta w < P\delta V \)).

Since \( H = U + PV \), for a small change in the system at constant pressure,

\[
\delta H = \delta U + P\delta V
\]

i.e., at constant pressure \( \delta H = T\delta S \)

and in the limit,

\[
dH/dT = T (dS/dT)
\]

Differentiating the equation \( G = H - TS \)

* This will be discussed briefly from the point of view of sixth-formers, in my second paper.

† I shall discuss how the principles of this kind of calculation might be explained to sixth-formers in my second paper.
with respect to $T$ at constant pressure gives:

$$\frac{dG}{dT} = \frac{dH}{dT} - T\left(\frac{dS}{dT}\right) - S = -S$$

In order to emphasize that this only applies at constant pressure, it is usually written:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Similarly, for any change in a system at constant pressure:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

This last expression is useful in the discussion of phase changes and of the effect of temperature on chemical reactions.

Substitution in the equation

$$\Delta G = \Delta H - T\Delta S$$

gives the Gibbs–Helmholtz equation:

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_p$$

which when applied to cell reactions becomes:

$$\Delta H = -nEF + nF T\left(\frac{\partial E}{\partial T}\right)_p$$

An alternative form of the Gibbs–Helmholtz equation is obtained by differentiating $\Delta G/T$ with respect to $T$ at constant pressure:

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{1}{T} \frac{d\Delta G}{dT} - \frac{\Delta G}{T^2}$$

$$= \frac{1}{T^2} \left(T \cdot \frac{d\Delta G}{dT} - \Delta G\right)$$

$$= -\Delta H/T^2$$

When this is applied to a chemical reaction, for which $\Delta G^\circ = -RT \ln K$, the van’t Hoff isochore is obtained:

$$\frac{d}{dT}(\ln K) = \frac{\Delta H^\circ}{RT^2}$$

For the equilibrium between a solid or liquid and its vapour, the equilibrium constant is simply the vapour pressure $P$, so that for the vaporization of one mole, $\Delta G^\circ = -RT \ln P$. Applying the isochore, the Clausius–Clapeyron equation is obtained:

$$\frac{d}{dT}(\ln P) = \frac{\Delta H}{RT^2}$$

in which $\Delta H$ is the molar heat of vaporization.

This may also be written:

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta H}{RT^2}$$

and if the vapour is assumed to behave as an ideal gas, $P = RT/V$, so that

$$\frac{V}{RT} \frac{dP}{dT} = \frac{\Delta H}{RT^2} \text{ or } \frac{dP}{dT} = \frac{\Delta H}{VT}$$

This is practically the Clapeyron equation, $dP/dT = \Delta H/(T\Delta V)$, which may be shown by a completely rigorous argument to apply quite generally to the equilibrium between any two phases.

* This is seen to be true by applying the argument, used previously for a heterogeneous chemical reaction, to the equilibrium solid = vapour or liquid = vapour.

**PROJECT WORK IN CHEMISTRY**

With the introduction of new syllabuses in Chemistry at ‘O’ and ‘A’ level much more emphasis is likely to be placed on the importance of suitable project work. Unfortunately the organization of this type of practical work is time-consuming and concepts suitable for grammar school students are not easy to design. There is now a strong case for teachers to co-operate in sharing views and ideas and so make the work practicable.

This may be carried out by collecting ideas from teachers and publishing them at intervals. They can thus be made available to those who wish to evaluate new ideas and to those who, because of lack of time, may not be able to test their own ideas practically.

Initially it is proposed to produce a regular newsletter in which suitable projects will be outlined, and it is hoped that this may eventually form the basis of a book on project work.

Will all teachers interested in the scheme contact:

D. R. Browning,
Science Department,
The College of Technology and Art,
Queen Alexandra Road,
High Wycombe, Bucks.
The author of a recent textbook of organic chemistry\textsuperscript{1} states that the disturbing amount of incorrect and misleading information found in introductory texts had led him to add to the large number of existing elementary books.

Many 'A'-level syllabuses require a study of a relatively small number of specific compounds, although a more general approach, giving particular examples of each class of compound, is preferable. The latter approach leads to a more systematic presentation of the subject and avoids many of the widespread misconceptions in elementary organic chemistry. The purpose of this article is to draw attention to some of the more common misconceptions which are found at this level.

**DECARBOXYLATION OF CARBOXYLIC ACIDS**

This is sometimes given as a general method of preparation for paraffins by heating a mixture of the anhydrous sodium salt of the acid with soda-lime.

\[
\text{RCOO}^- + \text{OH}^- \rightarrow \text{RH} + \text{CO}_2^\text{2-}
\]

However, it has been shown\textsuperscript{2} that only sodium acetate decomposes according to this equation, giving a high yield of at least 97 per cent pure methane. In the other examples studied, including sodium propionate and butyrate, various products were obtained, \textit{e.g.} with sodium propionate:

\[
\text{C}_2\text{H}_5\text{COO}^- \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 + \text{H}_2 \\
(44\%) \quad (20\%) \quad (33\%)
\]

+ various unsaturated products

This reaction should not, therefore, be given as a general preparative method for simple paraffins since a low yield is generally obtained and it is difficult to separate the mixture of products.

A possible mechanism for the decarboxylation is:

\[
\text{RCOO}^- \quad \text{OH}^- \quad \text{CO}_2^\text{2-}
\]

\[
\text{RCO}^- \quad \text{C} = \text{O} \quad \text{R} + \text{H} \\
\text{carbonate ion (mesomeric)}
\]

The fact that at least an incipient carbanion is involved in this reaction explains why the presence of electron-attracting groups facilitates the loss of carbon dioxide, \textit{e.g.}, with sodium trichloroacetate:

\[
\text{Cl} - \text{C} = \text{O} \quad \text{Cl} - \text{C} = \text{O} \quad \text{Cl} - \text{C} = \text{O}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

**WURTZ REACTION**

An ethereal solution of an alkyl halide reacts with metallic sodium to form a paraffin:

\[
2\text{RHal} + 2\text{Na} \rightarrow \text{R-R} + 2\text{Na}^+ + 2\text{Hal}^- \\
\]

This is known as the Wurtz reaction and is sometimes given as a general preparative method for paraffins or as a general method for increasing the length of a carbon chain. However, unsaturated hydrocarbons are also obtained and it is difficult to isolate the individual paraffin from the resulting mixture. This reaction is, therefore, rarely used as a preparative method except for higher paraffins with an even number of carbon atoms, where the yields are often good.

A mechanism involving the formation of an alkylsodium is more likely in solution than the alternative radical mechanism which has also been suggested.\textsuperscript{3} The alkylsodium formed reacts with a second molecule of the alkyl halide to give the paraffin:
e.g. \( C_4H_4Br + 2Na \rightarrow C_4H_5Na^+ + Na^+ + Br^- \)
\( C_4H_4^- + C_4H_4Br \rightarrow H_4C_2-C_4H_5 + Br^- \)

The disproportionation which also occurs can be explained on the basis of the following mechanism:

\[
\begin{array}{c}
\text{Na}^+ \\
\text{CH}_3 \quad \text{CH}_2 \quad \text{Br} \\
\downarrow \\
\text{CH}_3 + \text{CH}_2=\text{CH}_2 + \text{Na}^+ + \text{Br}^- \\
\end{array}
\]

so that, in this example, ethane and ethylene are also present in the product.

The use of Grignard reagents is, therefore, preferable for this purpose since they are of great synthetic importance, giving pure paraffins in high yields.

**ACTION OF ALCOHOLIC POTASH ON ALKYL HALIDES**

This reaction is still sometimes given as a general preparative method for olefins, although the yield of the corresponding olefin from a primary alkyl halide is low (sometimes < 1 per cent). High yields of olefins are obtained only with secondary and particularly tertiary alkyl halides. It should, therefore, be emphasized that the course of the reaction depends on the nature of the alkyl halide and the conditions, so that an ethyl halide gives only 1 per cent ethylene even under the most favourable conditions, the main product being ether, while an isopropyl halide gives up to 80 per cent propylene, and t-butyl halide 100 per cent isobutylene.

Alcoholic potash contains a potassium alkoxide, e.g.

\( C_4H_4OH + OH^- \rightarrow C_4H_4O^- + HOH \)

so that the alkyl halide can undergo an \( E2 \) or an \( S_N2 \) reaction, e.g.

The alkoxide ion, \( C_4H_4O^- \), can act either as a base, i.e. donating a pair of electrons to hydrogen (\( E2 \) reaction), or as a nucleophile, i.e. donating a pair of electrons to carbon (\( S_N2 \) reaction). The proportion of elimination can be increased, for preparative purposes, by increasing the size of the base, e.g. \( (CH_3)_3CO^- \), so that attack on the \( \alpha \)-carbon atom is sterically inhibited and its nucleophilicity declines.

**PYROLYSIS OF THE CALCIUM SALTS OF CARBOXYLIC ACIDS**

The pyrolysis of the calcium salt of a carboxylic acid (other than formic acid) either alone or mixed with calcium formate is sometimes given as a general preparative method for ketones and aldehydes, respectively. However, side-reactions always occur and variable yields are obtained.

Simple and mixed ketones can be obtained by this method:

\[
(RCOO)\_2Ca \rightarrow R\cdot CO\cdot R + CaCO_3
\]

\[
(RCOO)\_2Ca + (R'\cdot COO)\_2Ca \rightarrow 2R\cdot CO\cdot R' + 2CaCO_3 + \text{corresponding simple ketones}
\]

The yield of mixed ketones is always low. The yield has been shown to vary considerably with the metallic salt used, though it is not clear how the metal exerts its specific effect. For instance, barium salts generally give better yields than calcium salts.

A free-radical mechanism has been suggested for this reaction, from the nature of the by-products and the strong heating required, on the basis of isotopic tracer studies:

\[
\begin{array}{c}
\text{R-COOM} \\
\downarrow \\
\text{\cdot R} + \text{C-OM} \\
\downarrow \\
\text{R-C} + \text{OM} \\
\end{array}
\]

(formation of aldehyde)
SOME COMMON MISCONCEPTIONS IN ORGANIC CHEMISTRY

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{·R} + \text{C-OM} & \rightarrow \text{R-C} + \text{·OM} \\
\text{O} & \quad \text{O} \\
\text{(formation of ketone)}
\end{align*} \]

\[ \begin{align*}
\text{·OM} + \text{R-COOM} & \rightarrow \text{·R} + \text{M}_2\text{CO}_3 \\
\text{·COOM} + \text{·M} & \rightarrow \text{M}_2\text{CO}_3
\end{align*} \]

\( \text{(chain termination)} \quad (M = \frac{1}{2} \text{Ca}, \text{etc.}) \)

This reaction is, therefore, of doubtful value as a general preparative method for aldehydes and ketones. Both simple and mixed ketones can be prepared in higher yields by the thoria method, e.g.

\[ \begin{align*}
2\text{CH}_3\text{COOH} \xrightarrow{\text{ThO}_4} & \text{CH}_3\text{CO-CH}_3 \\
& + \text{CO}_2 + \text{H}_2\text{O}
\end{align*} \]

Reasonably good yields (50–90 per cent) of simple ketones are obtained in this way.

**FORMATION OF ‘ALDEHYDE-AMMONIAS’**

When ammonia is passed into an ethereal solution of a lower aldehyde (excluding formaldehyde) at \(0^\circ\text{C}\) a crystalline precipitate of the corresponding ‘aldehyde-ammonia’ is formed. The initial addition product (I) is generally very unstable and undergoes polymerization to a complex cyclic compound. The reaction with ammonia is reversible and the aldehyde is reformed by hydrolysis:

\[ \begin{align*}
\text{O} \\
\text{H} \\
\text{CH}_3\text{C} \xrightarrow{\text{NH}_3} & \text{CH}_3\text{C-} + \text{NH}_3 \\
\text{H} & \text{H}
\end{align*} \]

\[ \text{CH}_3\text{C-} \xrightarrow{\text{OH}} \text{CH}_3\text{C-NH}_2 \\
\text{H} \]

The ‘aldehyde-ammonia’ then loses the elements of water to form an aldimine (II) (better known as a Schiff’s base):

\[ \text{acetalimine (II)} \]

\[ \begin{align*}
\text{CH}_3\text{C} & \xrightarrow{\text{N}} \text{CH}_3\text{C-NH} + \text{H}_2\text{O} \\
\text{H} & \text{H}
\end{align*} \]

The cyclic trimer (III) obtained from acetaldehyde can be isolated as an insoluble crystalline trihydrate. The formation of an ‘aldehyde-ammonia’ is therefore exceptional, being restricted to a small number of aldehydes, e.g. chloral, which forms a stable addition product (m.p. 73°C). This exceptional behaviour may be attributed to the powerful electron-withdrawing inductive effect of the three chlorine atoms.

**REDUCTION OF FEHLING’S SOLUTION**

The reduction of Fehling’s solution by chloroform was formerly attributed to the production of formate ions when the latter undergoes alkaline hydrolysis. However, it has been shown that while Fehling’s solution is in fact reduced by pure chloroform it is not reduced by formates.

A possible mechanism for the alkaline hydrolysis of chloroform involves the formation of dichlorocarbene as an intermediate. The formation of carbon monoxide in this reaction was first suggested in 1862. It arises from the dichlorocarbene formed as an intermediate:

\[ \begin{align*}
\text{CCl}_3 + \text{H}_2\text{O} & \xrightarrow{\text{several steps (}+\text{OH}^-\text{)}} \text{CO} + 2\text{Cl}^- \\
\end{align*} \]

Presumably the explanation of the reduction of Fehling’s solution by chloroform is to be found in this mechanism. Carbon monoxide is known to reduce Fehling’s solution to copper(t) oxide and it seems likely that its formation in the alkaline hydrolysis of chloroform accounts for the positive reaction of the latter with this reagent.
Action of Nitrous Acid on Primary Aliphatic Amines

This reaction has probably caused more confusion at sixth-form level than any of those so far discussed. The overall reaction, in which the yield of gas is quantitative, is:

\[ R-\text{NH}_2 + \text{HNO}_2 \rightarrow R-\text{OH} + \text{N}_2(g) + \text{H}_2\text{O} \]

The mechanism of this reaction involves the formation of a highly reactive carbonium ion which can undergo three main types of reaction:

(a) combination with a nucleophilic reagent, *e.g.* water (I);
(b) elimination of a proton to form an olefin (II);
(c) rearrangement, *e.g.* by migration of a hydride ion (III).

These processes are well illustrated by the behaviour of n-propylamine in this reaction.

The much higher yield of isopropanol compared with n-propanol reflects the greater stability of the isopropyl, as compared with the n-propyl, carbonium ion.

Similarly, ethylamine gives a 60 per cent yield of ethanol, but methylamine gives a low yield of methanol—methyl nitrite is the main product here. The methyl nitrite may arise in two ways:

Small amounts of alkyl chlorides (by reaction with \( \text{Cl}^- \) ions) and of ethers (by reaction with the alcohols produced) may also be obtained.

The wide variety of products obtained in all these reactions can thus be satisfactorily explained on the basis of the formation of an alkyl carbonium ion. It has been shown by kinetic studies that, in weakly acidic nitrite solutions, dinitrogen trioxide is formed and this then nitrosates the amine:

\[ \text{2HNO}_2 \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O} \]

\[ R-\text{NH}_2 + \text{N}_2\text{O}_3 \rightleftharpoons R-\text{N}^+ + \text{NO} \]

\[ R^+ + \text{N}_2 \rightleftharpoons R-\text{N}=\text{N} \rightleftharpoons R-\text{N}=\text{N}-\text{OH} \]
This is not, therefore, a satisfactory general method of preparation for an aliphatic primary alcohol from the corresponding primary amine. It should, however, still be given to sixth-form students, the low yield of the corresponding alcohol being emphasized. It is also important to emphasize the essential similarity of both aliphatic and aromatic primary amines in their reaction with nitrous acid, the aromatic diazonium ion (ArN₂⁺) being stabilized by resonance:

\[
\begin{align*}
\text{R-} & \quad \text{N} & \quad \text{N} \\
& \quad \downarrow & \quad \downarrow \\
& \quad \text{N} & \quad \text{N} \\
& \quad \text{N} & \quad \text{N}
\end{align*}
\]

**Reduction**

Many inorganic reducing agents have been used in organic chemistry, but the most widely used are:

(i) hydrogen with a catalyst such as nickel;

(ii) active metals, such as zinc and sodium, in conjunction with a suitable solvent;

(iii) metal hydrides, such as lithium aluminium hydride.

Catalytic hydrogenation (i) is a general method applicable to most types of unsaturation, including >C=C<, >C=O and -C≡N, and involves a surface reaction between molecular hydrogen and the unsaturated compound.

In (ii) it is the dissolving metal which is important, and this should be strongly emphasized since many elementary textbooks imply that different reductions require different metal-solvent combinations, a particular combination having to be memorized for each. It is extremely doubtful whether 'nascent hydrogen' plays any part, the reduction being effected by the metal itself, with the hydrogen evolved merely as a by-product. The metal transfers electrons to a ketone, for example, and the resulting negative charge is subsequently neutralized by the donation of protons by the solvent.

The most widely used solvents, water and alcohol, are, of course, Brönsted acids:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{H}^+ + \text{OC}_2\text{H}_5^- 
\end{align*}
\]

In the reduction of an aldehyde by sodium and alcohol, the sodium donates two electrons to the aldehyde and the resulting anion (I) liberates C₂H₅O⁻ from the alcohol forming an alkoxide (II) which gives a primary alcohol (III) on acidification:

\[
\begin{align*}
\text{2Na.} & \rightarrow \text{R}-\text{C}==\text{O} \rightarrow \text{R}-\text{C}^{-}\text{O}^- \rightarrow \text{R}-\text{C}^-\text{OH} \\
\text{H} & \uparrow \text{H} \downarrow \text{H} \\
\text{H} & \uparrow \text{H} \downarrow \text{H}
\end{align*}
\]

The use of lithium aluminium hydride as a reducing agent was first reported in 1947. It has been widely used subsequently and has largely displaced the classical reagents, such as sodium and alcohol, or metal amalgams. It is commonly used in anhydrous ether as solvent and is the only common reagent capable of reducing carboxylic acids. The recognition of the versatility of this reagent and similar complex hydrides in `A' -level courses is long overdue. Lithium aluminium hydride is particularly important where selective reduction is required as it does not normally attack >C=C< bonds. Sodium borohydride is a less vigorous reducing agent than lithium aluminium hydride and so is more selective, reducing the carbonyl group in aldehydes and ketones, but not in carboxylic acids or amides. It has the advantage that it may be used in water or alcohol as solvent.

The complex hydrides may be regarded as nucleophilic reagents, the AlH₄⁻ and BH₄⁻ ions acting as hydride-ion carriers, e.g. in the reduction of ketones:
CONCLUSION

The main purpose of this article has been to show that many elementary textbook 'facts' are misleading or even erroneous and that a considerable amount of material is neither practicable nor general. Organic chemistry can no longer be regarded merely as the learning of a large number of reactions in isolation from inorganic and physical chemistry. It is important that organic reactions should be presented in more general terms to illustrate the fundamental principles. In this connexion, it is desirable to explain some selected reactions in terms of the electronic theory, using a simplified treatment at the sixth-form level, this approach being adopted from the beginning of the sixth-form course. In this way, the student is encouraged to think for himself and he learns to interpret many of the reactions which he encounters in terms of a logical and systematic pattern of chemical behaviour.

REFERENCES


The following general reference works will also be found useful in uncovering further misconceptions:


SYMPOSIA AND A CONFERENCE FOR TEACHERS

The following one-day symposia have been arranged by Local Sections of the Royal Institute of Chemistry in collaboration with the Association for Science Education:

University of Southampton, Saturday, 26 March, 1966—'A Modern Approach to Chemistry'
Norwich City College, Saturday, 2 April, 1966—'Organic Mechanisms'
University of Liverpool, Saturday, 30 April, 1966—'Valency'

Leaflets will be distributed by direct mail to all schools in the areas concerned and to members of the Institute in the appropriate Local Sections. Additional leaflets may be obtained from the Education Officer, The Royal Institute of Chemistry, 30 Russell Square, London, W.C.1.

The Education Group of The Institute of Physics and The Physical Society is arranging a conference on 'The integration of physics and chemistry teaching' at the University of Sheffield on 13–15 April.

Residential accommodation will be available in the University Halls of Residence and advance registration is necessary. Further details and application forms are available from the Meetings Officer, The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S.W.1.
R.I.C. EDUCATIONAL MEETINGS

Bournemouth
R.I.C. Mid-Southern Counties Section Lectures, particularly for sixth-form students, at Bournemouth School for Boys.

Tuesday, 1 February, at 5 p.m. 'Chemistry in Everyday Life', by Prof. G. W. A. Fowles.

Wednesday, 2 March, at 4.30 p.m. 'The Preparation of Purified Water by Ion Exchange', by Elga Products.
(Hon. Sec., Mr T. F. McCombie, 50 Springdale Avenue, Broadstone, Dorset.)

Dundee
Friday, 28 January, at 7.15 p.m.
R.I.C. Dundee and District Section Educational Evening. Lecture, 'The New Chemistry in Scotland', by Mr A. H. Johnstone, in the Chemistry Department, College of Technology, Bell Street.
(Hon. Sec., Mr J. C. Smith, 41 Forfar Road, Maryfield, Dundee.)

Hull
Tuesday, 18 January, at 8 p.m.
R.I.C. Hull and District Section Lecture, 'Modern Trends in Higher Education', by Dr B. Jones, at Queens Hotel, George Street.
(Hon. Sec., Mr W. E. Bibby, The Distillers Co. Ltd, Development Department, Saltend, Hull.)

Liverpool
R.I.C. Liverpool and North-Western Section, Chemical Education Meetings for Teachers, in the Donnan Laboratories, The University, Vine Street.
Monday, 31 January, at 7 p.m. 'What are Acids and Bases?', by Dr D. Nicholls.
Monday, 21 February, at 7 p.m. 'Structure and Properties of Matter', by Dr J. E. Spice.
(Hon. Sec., Mr C. B. F. Rice, Department of Chemistry and Biology, College of Technology, Byrom Street, Liverpool.)

Manchester
R.I.C. Manchester and District Section, Lectures at the Renold Building, The College of Science and Technology, Manchester.

Saturday, 29 January, at 9.30 a.m. Education Lecture and Demonstration for Grammar School students, 'Chemistry and Light', by Professor J. C. Robb.

Friday, 18 February, at 6.30 p.m. Education Lecture, 'Energy factors in the Teaching of Chemistry', by Mr H. R. Jones.
(Hon. Sec., Mr L. Winestone, Ashburton Chemical Works Ltd, Tenax Road, Trafford Park, Manchester 17.)

Newport, Isle of Wight
Friday, 11 March, at 4.30 p.m.
R.I.C. Mid-Southern Counties Section Lecture, particularly for sixth-form students, 'Chemistry in Everyday Life', by Prof. G. W. A. Fowles, at Carisbrook Grammar School.
(Hon. Sec., Mr T. F. McCombie, 50 Springdale Avenue, Broadstone, Dorset.)

Preston
Friday, 21 January, at 10.30 a.m. and 3 p.m.
R.I.C. North Lancashire Section Young People's Lectures, 'Colour in Inorganic Chemistry', by Professor R. S. Nyholm, F.R.S., at Harris College.
(Hon. Sec., Mr A. C. Bushnell, Westway, Skip Lane, Hutton, Preston, Lancs.)

Stockton-on-Tees
Friday, 18 February, at 7.45 p.m.
R.I.C. Tees-Side Section Lecture, 'The Nuffield Chemistry Teaching Scheme', by Mr A. Jackson, at Black Lion Hotel, High Street.
(Hon. Sec., Dr T. C. Downie, 17 Westlands, Tynemouth, North Shields, Northumberland.)

Winchester
Friday, 4 February, at 4.30 p.m.
R.I.C. Mid-Southern Counties Section Lecture, particularly for sixth-form students, 'Thunderstorms', by Professor B. J. Mason, F.R.S., at Winchester College.
(Hon. Sec., Mr T. F. McCombie, 50 Springdale Avenue, Broadstone, Dorset.)
RECENT BOOKS

It is the customary fate of new truths to begin as heresies and to end as superstitions.

T. H. Huxley (1825–1895)


Many chemistry teachers must have been troubled by the apparent complexity of books about programmed learning. In the absence of a simple book the difficulty of evaluating commercially available books, and of beginning to write their own programmes, is very great. Susan Meyer Markle's book is a critical appraisal, in programmed form, of the two basic theories and how they can be put into practice. The first chapter discusses the basis of Skinner's linear programming method and demonstrates its advantages and drawbacks, with examples drawn from such diverse fields as elementary vector analysis and Lewis Carroll. There is then a rather protracted diversion into the definitions of prompting, some of which may be considered rather academic.

The second chapter deals with Crowder's theories and the branched or intrinsic programming technique. Here the book changes from linear to branching form, comparing the two methods and leading the reader through a short example on bridge playing. A short section on combinations and variations of the two methods follows, before the final chapter on 'Editing'. This section shows some of the pitfalls waiting for the unwary programmer and will be of great use to those chemistry teachers who wish to experiment with their own programmes. It will also be of use to teachers who cannot spare the time to write and who wish to find whether books on the market are good examples of the programming method.

The book is written in programmed form, changing from the linear to the intrinsic at the end of the first section but never rigidly bound into one form or the other. This form of writing, together with the wide range of examples, makes it particularly valuable as an introduction to the technique since many teachers find that programmes in their own subjects are pitched at such a low standard that they are hard to assess. Mrs Markle's book is written with humour, and it is refreshing to find that, occasionally, there is no specific answer to a frame. At the end of the book there is a section of detachable 'panels' containing examples of programmes, programmed writing systems and other information referred to in the text.

The price seems high, but for those who seek to be guided about programmed learning, it will be worth paying.

R. B. MOYES


As public examining bodies are becoming increasingly aware, the types of examination questions set under their jurisdiction exert a marked influence on the ways in which subjects are taught in schools and colleges. Chemistry is particularly vulnerable to this kind of pressure, so there is a need for careful appraisal of the types of question now being used for assessment purposes, and for experiment with new forms of question. This book assists the former task and makes some contribution to the latter one.

About half the 500 or so questions are taken from past public examination papers, mostly G.C.E. 'A' and 'S' levels, but some from National Certificate papers; the dates when these were set are not always stated. The remaining questions have been devised by the author. The questions are grouped mainly into organic chemistry (15 test papers, each containing 8 questions), physical and organic chemistry (15 papers with 4 physical and 4 organic questions in each), and general chemistry (20 papers). Then follow 112 miscellaneous questions and 46 of scholarship-
standard. Answers are given for all numerical problems. There is occasional evidence of casual proof reading, such as 'diazo benzene nitrate' (p. 46), 'hydrogenium' (p. 66) and 'Cribb's "Phase Rule"' (p. 105). On the whole, however, this is a fairly varied selection, ranging from 'straight recall' questions to those which demand a positive contribution by the candidate.

E. H. COULSON


The bulk of this book deals with inorganic qualitative analysis up to the standard of the 'A' and 'S' papers of G.C.E. and of University Entrance Scholarships. A small amount of material slightly beyond this level has been put in square brackets. By inclusion of this material, the book will be useful for first-year university courses and for the National Certificate courses at technical colleges. Throughout the book the author assumes that the student is undergoing a parallel course in inorganic and physical chemistry at the appropriate level and consequently only brief notes on theory have been given. The methods and operations described can be carried out without any item of equipment costing more than one or two shillings. It is possible, with the aid of this book, for a person who so desires to practise analytical chemistry by working at home, even under primitive conditions.

Traditional qualitative inorganic analysis was often slow and messy. With the advent of semi-micro methods, small tubes replaced large ones, filter funnels were replaced by centrifuges and transference of liquids was simplified by the use of teat-pipettes. However, there were many objections to the semi-micro techniques; students who used semi-micro methods found it harder to recognize smells, because the scale of operation was too small, adequate boiling was difficult in the small tubes, trace quantities precipitated in semi-micro analysis often failed to give good flame reactions and so on. Moreover, there is the great difficulty of cleaning and adequately draining a small tube, and time saved on the old filtrations may be lost here.

In the scheme proposed in his book, Dr Clark retains all the advantages of semi-micro analysis, since small quantities are used, but the newer techniques and readily available materials have made it possible to use the time-honoured test-tubes (1.75 x 12.5 cm), which possess advantages of ease of handling, boiling, cleansing and draining. It is proposed that filtration is conducted by suction through a filter pad, prepared from a tuft of cotton wool with, or without, the addition of a little ashless 'floc'. This process is more rapid than centrifugation and can be applied to liquids of all kinds encountered in analysis.

For the actual analysis scheme, the metals are separated into groups in the conventional ways. Teachers accustomed to other methods can easily make the necessary modifications. One widely used modification is that the alkaline earths (group V in the traditional scheme) are removed as sulphates before hydrogen sulphide is passed into the acidic solution; this scheme has been included in the book as an alternative and is described after the customary group I separation.

The book is attractively set out and printed; it contains an index and a useful appendix on reagents. The binding could probably be improved, since this is a book to be used in the laboratory, but this is a relatively minor point compared with its value to the students and teachers. It will certainly be welcomed by teachers of chemistry at the levels already mentioned.

DAVID ABBOTT


Although over 250 pages in length, this is intended as a revision book for students taking 'A'-level and O.N.C. examinations.

Mostly it is logically set out. Each chapter or section starts with a general consideration of the characteristics and properties of the
functional group concerned; this is followed
by descriptions of particular compounds. The
logical order occasionally breaks down; for
example, the primary, secondary and tertiary
alcohols are not considered at the beginning
of the chapter on alcohols but are slipped in
under their oxidation. There are numerous
comparative tables and 'flow sheets' sum­
marizing the reactions of the more important
groups, and there is much up-to-date
information about industrial processes. The
appendix contains tables of types of isomer­
ism, of the commoner named reactions and
of tests for some common functional groups.
The book contains no experimental
instructions.

Unfortunately, the authors seldom mention
the conditions required for the reactions they
describe. Thus they write 'the alkyl halides
are converted to amines by reaction with
ammonia' rather than by heating in alcoholic
solution with ammonia under pressure.

Much useful information seems to be
omitted. For instance, there is no mention,
under either the reactions of alcohols or the
preparation of halogen derivatives, of the
reaction of alcohols with halogen hydrides
or thionyl chloride, nor does there seem to
be any mention of the associated nature of
liquid alcohols.

The chief weakness of this book is that
while it is too condensed to be a satisfactory
textbook, it is too long to be a really useful
revision book.

Although it is quite well and clearly
printed it is bound in a rather dull cardboard
cover and seems rather expensive.

E. J. Vernon

Concise Inorganic Chemistry, by J. D. Lee.
Nostrand Co. Ltd, London and New
York, 1965. 50s. board; 27s. 6d. paper.

In the first edition of his book (reviewed in
Educ. Chem., 1964, 1(4), 226) Dr Lee's
aim was to provide students with a frame­
work into which fact could be fitted without
a great deal of memory work, and this was
certainly achieved.

In the second edition this attitude has
been maintained and it is pleasing to see
that such topics as stoichiometric and non­
stoichiometric defects have been included.
Particularly pleasing is the inclusion of
acid-base theory beyond Arrhenius, but
more space might have been devoted to the
theory of solvent systems to include some­
thing of the rapidly expanding work on
reactions in non-aqueous solvents.

The book is still intended for Part I of
the Grad.R.I.C. and similar examinations,
and students for this would do well to give
this work serious consideration.

Alan W. Mackaill

Elementary Electrochemistry, by A. R.
Denaro. Pp. vii + 221. Butterworths,
London, 1965. 22s. 6d.

This book is intended primarily for students
studying for the Part I examination of the
Royal Institute of Chemistry, and as an
introduction for the first and second years
of a Diploma of Technology or degree
courses. In the main, it should prove very
useful for such students. The author has set
out to expound the principles of the subject
in as simple a manner as is consistent with
clarity and exactness, and to forego the use
of the time-honoured 'it follows that',
'obviously' and so on, in connective pas­sages.
For this, the student will be grateful. In
particular, the chapters on electrolytic
conduction, ionic equilibria, applications of
conduc­tance measurements, applications of
emf. measurements and electrolysis are
excellent, extremely readable and very in­fon­
mative and make little or no demand that
the student have previous knowledge of the
topics.

There are, however, certain places where
greater clarity might have avoided possibly
false impressions. The concept of infinite
dilution is difficult enough for students with­
out their having to cope with a misleading
term. It is most unfortunate that Dr Denaro
uses the phrase zero concentration (for com­
parison with zero ionic strength?) which
could imply, for those not conversant with
the topic, that the quantity of solute present
in the given solution is zero. One can rightly
deduce that there consequently will be no
ion-ionic atmosphere interactions, but for the
wrong reason. For electrolytic conduction
surely, the term limiting conductance for $A_0$ is more precise and to the point than the term ‘ionic conductance at zero concentration’.

In the qualitative description (pp. 50–51) of the variation of activity coefficients with concentration, the increase in $f_{\pm}$ with concentration at high concentrations is given as due to non-ionic effects; this is misleading, especially as the next sentence states the variation to be more marked for polyvalent electrolytes.

The equation $a = f c$ (p. 50) is stated, where $f$ would appear to be a pure number and $c$ has the units of concentration (e.g. mole $1^{-1}$). Hence $a$, the activity, would also have the units of concentration. To then state (p. 57) that ‘thermodynamic activities are dimensionless’ and that in general ‘thermodynamic dissociation constants are also dimensionless’ is incorrect. Further, to state that a distinction between classical and thermodynamic dissociation constants is possible on these grounds is nonsense.

The concept of an ion-pair is only briefly mentioned, which may be the reason why the wrong meaning is conveyed, viz. all ion-pairs have zero charge (p. 26), ion-pairs are virtually unionized molecules (p. 84).

I have certain reservations regarding the value of including the units in a mathematical formulation, e.g. $c_{vc} F A C/sec$ (p. 31). Also, at times, the choice of symbols is rather confusing.

I was sadly disappointed with the chapter on reversible electrode potentials; it is not to be recommended as a clarification of other texts. The author has attempted to develop a logical and self-consistent procedure leading to the correct expression for the e.m.f. of a reversible chemical cell, seemingly without prior knowledge of the electrode processes or the chemical reaction. However, the structure rests on the ability of the student to formulate the expression for the individual electrode potentials (i.e. without first writing the cell reaction) and thence to calculate the e.m.f. of the cell from the difference between the more positive and less positive potentials. From the polarity, the cell process may be deduced, which seems circuitous. It is regrettable that all the arguments on e.m.f.’s of cells are not based on the procedure adopted on pp. 105–107, i.e. from the equation for the chemical process, the $\Delta G$ is computed which leads directly, via $\Delta G = -z F E$, to the expression for the e.m.f. of the cell.

The calculation of $\Delta S$ (misprinted as $S$) from e.m.f.’s of cells on p. 110 is clumsy. A simple use of the relation

$$\left( \frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S$$

leads immediately to the required equation.

Sign conventions are, admittedly, a stumbling block for students, but this seems to be an argument more in favour of their inclusion in the main text rather than their relegation to an appendix. There is an important omission on p. 212: the international electrode potentials are defined as equal to the potential of the electrode with respect to the hydrogen electrode with the hydrogen electrode written on the left-hand side (IUPAC convention). As this is the crux of the argument it should not be omitted.

Despite these and other shortcomings in points of detail, this book is a welcome addition to a student’s collection and can be recommended.

M. ROBSON WRIGHT


This book is one of a series of chemical science texts edited by Professor W. G. Overend. The authors of this volume have devised a total of 220 problems concerned with most aspects of inorganic chemistry; answers are provided at the end of the volume. The selection of questions is such that the book will be of use to students throughout the post-intermediate years, and should prove interesting to postgraduate students.

The majority of the problems are divided among the first nine chapters according to the element principally involved. This leads to some curious juxtapositions and I feel that it would have been more helpful to teachers of the subject if an index of the subject matter had been included.
The selection of questions is a good one. The range is wide and much emphasis has been given to thermodynamic principles and to structural chemistry (chapter 10 is devoted to structural types). Topics which one would have expected to be mentioned in a book of this kind, but which have been omitted, are radiochemistry, solvent-extraction techniques and the interpretation of X-ray powder photographs. Fault may be found with some of the answers proffered—a few are incorrect and others are incomplete; on the whole, however, they are quite satisfactory (occupying a total of 63 pages) and many references are made to the chemical literature as well as to standard texts.

A Periodic Table, a list of atomic weights, four-figure logarithm tables and some physical constants are included and enhance the value of this admirable book.

M. F. A. DOVE


This book has been written mainly for use in conjunction with Physical Inorganic Chemistry by M. J. Sienko and R. A. Plane in the same series, and it is therefore a survey of experimental inorganic chemistry by groups of elements.

The authors have made a praiseworthy attempt to incorporate the maximum amount of structural, thermodynamic and kinetic data in the volume, but within the space of 175 pages (if one excludes the index) it is impossible to consider many examples in the detail necessary if the study of inorganic chemistry is to be an educational, as distinct from a fact-accumulating, subject. Some of the authors' brief treatments are masterly summaries (e.g. that of proton magnetic resonance on pp. 2-4), but often one is left with a feeling that condensation has been carried much too far. The treatment of the chemistry of the metals of the first transition series, for example, occupies a mere 20 pages, and although it includes nine useful tables of data, the contents of the tables never receive adequate discussion. As a handbook for teachers up to honours-degree level, however, this book will be very useful, and a copy should certainly be available in every chemical library.

A. G. SHARPE


Any author writing a book with this title, 'Transitional Elements', in 183 pages is faced with a virtually impossible task, and it is interesting to see how Professor Larsen tries to solve the problem, especially since he includes the lanthanides and actinides within his definition.

The first chapter, entitled 'The Properties of Transitional Elements', follows the usual treatment of the structures of the atoms, the theories of bonding and the factors of importance thereto (e.g. ionic and covalent radii, ionization potentials) and then discusses those physical properties relevant to transition-metal compounds, e.g. magnetism and colour. This is a reasonably competent chapter and is treated simply enough to be understood and appreciated by the elementary student.

The second chapter attempts to discuss the chemistry of the metals and their binary compounds such as oxides and halides in 27 pages. Although easy to read, this chapter is of little use because of the compression that has been required and because the selection of topics is somewhat random. This type of information, treated in the classical way, which compares unfavourably with the modern approach adopted in the rest of the book, can be found in more detail in any of a number of textbooks.

The structures of the metals and their solid binary and ternary compounds are dealt with in the next chapter. The treatment, in terms of close packing of the largest component and occupancy of octahedral and tetrahedral holes in the structure by the smaller components, is most useful in demonstrating the relationship between idealized forms of apparently very different structures; most of the diagrams are very clearly drawn and
assist the visualization of these forms in three dimensions.

The rest of the book, dealing with solution chemistry (equilibria and mechanism) and co-ordination chemistry (why must people, in 1965, still look upon this as a separate small topic that is quite independent of the main stream of inorganic chemistry?) overlaps considerably with a previous book of this series, written by Basolo and Johnson who, incidentally, do a better job. This overlap indicates a slackness on the part of the editor and should not have been allowed to take place. The space would have been better spent on enlarging the second chapter.

The attractive feature of this book is the way in which the author has tabulated a wide range of useful data in the text and also in the appendixes, and has then proceeded to use these data in a semi-quantitative fashion to explain and rationalize certain of the chemical behaviour. The application of the Born-Haber cycle to topics such as the disproportionation reactions of transition-metal halides and to redox properties is especially welcome.

M. L. TOBE


This is a book in which oxidation mechanisms are summarized for an unusually large range of conditions. After a very brief introduction the next five chapters deal with ionic reactions in solution.

The kinetics of oxidation by such substances as chromic and periodic acid, where a pre-equilibrium esterification appears to take place, are given in the seventh chapter. Chapters eight and nine are, respectively, on some reactions of radicals in solution and the gas phase. The last chapter discusses oxidation, mostly by oxygen gas, of various solutions.

The author clearly has a wide knowledge of the subject, but this has not enabled him to present oxidation in a unified manner (which is a very difficult task). This book really presents an illustrated classification of oxidation mechanisms and as such may be of great use to students taking Ph.D. degrees on topics dealt with in the first seven chapters. Students studying for honours degrees might find the last three chapters useful but the book has, in my opinion, suffered rather than gained by their inclusion.

The treatment of the theory of reaction rates (p. 3) misses the point by failing to show how the theories differ in their predictions. However, such failings as the book has are due mainly to attempts to include too much material. In general the book is well written and the material clearly presented.

D. E. HOARE


Modern analytical chemistry is based on the same fundamental principles as classical analytical chemistry, but increasingly it uses the techniques and tools of the physical chemist. However, the basic objectives and the entire outlook of the analytical chemist are totally different from those of the physical chemist, and this is a frequent stumbling block for many.

In their preface, the authors of this monograph indicate that they have directed the text towards students who may be bewildered by the array of modern instruments and to older readers who received their training some time ago and now need an introduction to a particular technique. Accordingly, they have provided thumb-nail sketches of recent developments in titrimetric (inappropriately referred to as volumetric) analysis, in polarography, in u.v., visible- and i.r.-spectroscopy, in mass spectrometry and in radio-chemical techniques. Recognizing the importance of separation techniques, the authors conclude with an extensive chapter of this title, but dealing almost entirely with ion-exchange and chromatography in its many guises.

I do not feel that this text has been entirely successful in its object, though it has made a commendable attempt to fulfil the need for such a book. It does not, in my opinion, convey to its readers, except in
a few places, the basic outlook of the analytical chemist, and the treatment varies considerably from chapter to chapter. Each chapter is, of course, to be regarded as an introduction and, as such, some of them are indeed excellent. However, the scanty treatment of atomic absorption and spectrofluorimetry in the spectroscopy chapter, the absence of electrochemical techniques other than polarography and the absence of separation techniques other than those already mentioned presents a rather sporadic view of the analytical scene.

Many of the sections on techniques are completed by a short list of experiments for students which should be of considerable use to teachers who want to modernize their teaching syllabus. Obviously this book has considerable potential, and it is to be hoped that a further edition in the not too distant future will include some of the techniques omitted from this first edition.

T. S. West


The contents of this book are beautifully presented, and it provides an appropriate selection of evidence for the main conclusions and generalizations concerned with additions at carbon–carbon multiple bonds, nucleophilic substitutions, elimination reactions and electrophilic aliphatic substitutions. Very wisely, the author provides examples of the applications of these various types of reaction to important syntheses.

Unfortunately, the conclusions and generalizations are provided before the data which blaze the trail to them; while convenient and suitable, perhaps, for the teacher, this cart-before-the-horse approach robs the student of the exciting and invaluable experience of drawing his own conclusions by logical argument. The introduction, which outlines some basic concepts of chemical kinetics, is too condensed to be effective and the part concerned with activation energy and energy diagrams will probably mislead the student. The sentence on lines 8–11 of p. 5, with its ambiguous ‘extent of reaction’, will certainly be misinterpreted. The curves in Figs 1–3 on pp. 5 and 6, though in common use, are unsuitable for teaching purposes in that they imply that the curve has ends; the student with imagination should not be left wondering how the reactants and products are prevented from falling off the ends of the curve.

G. Baddeley


This book is the third in a series of monographs on reaction mechanisms in organic chemistry, formerly edited by the late Professor E. D. Hughes, F.R.S., and now by Professor C. Eaborn. In it, the principles of the electronic theory of organic chemistry, insofar as they are relevant to aromatic substitution, are first discussed and the reaction pathways available for electrophilic substitution are briefly surveyed. Then individual reactions are described in detail, starting with substitutions involving electrophilic nitrogen, sulphur, oxygen, halogen, carbon, mercury, thallium and lead. Hydrogen-exchange is then described, followed by a chapter on replacement of substituents by hydrogen and electrophilic interchange of substituents.

Chapters on recent developments, particularly those concerned with linear free-energy relationships, and on preparative procedures, conclude the book. Each chapter is well documented with references and there is an adequate subject index.

Professor Norman and Dr Taylor are to be congratulated on this excellent survey. It is up to date, as exhaustive as possible within the chosen bounds, and it gives a fair picture of the views of workers on the subject, without engaging in unnecessary controversy. The layout results in the discussions of the effect of substituents on reactivity sometimes seeming a little repetitive; and perhaps the
emphasis on the $S_{e2}$ mechanism and its elaborations could have been associated with more discussion of the less usual reaction paths in aromatic substitution. These are small faults, however, and there is no other book which gives such a complete picture of how wide are the applications of the qualitative electronic theory of organic chemistry to aromatic chemistry. It will be valuable to undergraduates and to research workers alike, and I warmly recommend it.

P. B. D. DE LA MARE


Since 1955 every student of these subjects must have consulted Nuclear and Radiochemistry—indeed, it was probably the first textbook on the subject that many students have bought. Recently, however, it has become somewhat out of date because of important advances in techniques and developments in theory. It is therefore of great interest to see the new edition. This time J. M. Miller is a joint author to deal particularly with the sections originally written by the late J. W. Kennedy.

The principal features of the new edition are that about 50 per cent of it is re-written and revised material, the chapters have been rearranged and two completely new ones have been added.

The rearrangement has resulted in a better division between the more practical aspects of radiochemistry and theoretical nuclear chemistry. The first seven chapters are entitled radiochemistry, atomic nuclei, equations of radioactive decay and growth, interaction of radiations with matter, detection and measurement, statistical considerations in radioactive measurements and tracer applications. Editing and rewriting has improved these chapters and the inclusion of new material, such as the section on solid-state detectors, has added to their value.

The chapters on radioactive decay processes and nuclear reactions are largely rewritten and, together with the new chapter on nuclear models, serve as a very adequate introduction to advanced aspects of nuclear chemistry.

The section on charged-particle accelerators in the chapter on sources of nuclear bombarding particles has been largely revised. Recent developments in linear accelerators, circular machines and the tandem Van de Graaff machine are described.

The chapter on techniques in nuclear chemistry has been enlarged to include useful material on reactor and accelerator targets, measurements of beam energies, coincidence methods, calibrated detectors and a bigger section on decay schemes.

One of the most important recent developments in the study of nuclear processes of interest to the chemist has been the discovery of several nuclear processes which are affected by their environment. These include the Mössbauer effect, positron annihilation, the angular correlations of cascade radiations, muon depolarization and muonium formation. These are briefly described in a new chapter.

The appendixes have been completely revised. Masses are based on the $^{12}$C atomic-mass scale throughout the book (in place of the $^{16}$O scale) and more recent values for cross-sections, half-lives and decay data are given.

This is an excellent book, and this edition will no doubt prove as popular as the previous ones. The rewriting is so well done that this, together with the new data, will make it of value not only to the person entering nuclear and radiochemistry, but to many more experienced workers.

G. R. HALL


The explosive advances in the study of nucleic acids, protein biosynthesis and the relevant genetic fields and their interpretation at the molecular level led to the development of 'molecular biology'. The introduction of the new knowledge into undergraduate and postgraduate courses has resulted in the need for special textbooks to cover this subject in a concise but nevertheless easily
readable manner. These requirements have been successfully met by the author of this book who is well known for his researches on polynucleotides. It gives a clear exposition of the wider aspects of the chemical foundation of this subject, ranging from the chemical structure of proteins to their spatial organization and their most important chemical functions—biosynthesis of the various types of nucleic acids, ribonucleic acids, the bacteriophages, the viruses, the relevant genetics and energy transformations; associated mutations as well as the subject of carbohydrates—and their biosynthesis—are also clearly expounded.

A reasonable number of useful references is given at the end of each chapter. There are appendixes on the primary structure of the B-chain of insulin, basic thermodynamic aspects, synthesis of polypeptides and biological oxidations and reductions. The last three could have justifiably been treated more extensively.

It is disappointing to see in such a good book the propagation of the mistaken labelling of an external hydrogen atom as nitrogen in the guanine component of the guanine-cytosine base pair in the structural drawing of DNA (p. 274). This error, originally present in the paper of Pauling and Corey (Archs Biochem. Biophys., 1956, 65, 179), has been repeatedly reproduced in a number of other articles and books; it is time this 'lethal mutation' was eliminated.

This book should be read by every aspiring molecular biologist.

S. Lewin

B.P. CONFERENCE

A conference on 'New Approaches to the Teaching of Chemistry and their effect on Independent Schools' was held in Cambridge from 24 to 26 November, 1965. This conference, which was sponsored by the British Petroleum Co. Ltd, was attended by about 50 chemistry masters and mistresses from independent and preparatory schools. The principal speakers included several members of the Nuffield School Chemistry Project and the Co-ordinator of the Nuffield Science Teaching Projects, Mr John Maddox. The chairman of the conference was Mr M. J. W. Rogers, Westminster School.

The main aim of the conference was to study some of the new approaches and new materials that are becoming available for the teaching of chemistry to pupils of 11-16 years and to learn something of the projects being developed for the 'A'-level students of science.
FILMS FOR TEACHERS
By J. H. Pryor, B.Sc., Ph.D., F.R.I.C.

For key to arrangement of data, see Index of Chemistry Films, 4th edn, 1965. This is published by the Royal Institute of Chemistry, price 7s. 6d. (members, 5s.).

THE CHEMISTRY OF THE CELL 1965
Col. Sd. 37 min. (total). 16 mm. Hire.
S: Council of Europe.
Part I. THE STRUCTURE OF PROTEINS AND NUCLEIC ACIDS (21 min.).
Part II. THE FUNCTIONS OF DNA AND RNA IN PROTEIN SYNTHESIS (16 min.).

FAST REACTOR DEVELOPMENT 1964
Col. Sd. 17 min. 16 mm. Free loan.
S: Argonne National Laboratory, U.S.A.
The history and development of sodium-cooled fast breeder reactors; features of their design; fuel and coolant handling; operation.

GETTING DOWN TO OIL 1964
Col. Sd. 41 min. (total). 16 & 35 mm. Free loan.
S: Shell Petroleum Co. Ltd.
D: Petroleum Films Bureau.
Part I. DISCOVERY (22 min.).
Part II. DRILLING (19 min.).

MINORITY CARRIERS IN SEMICONDUCTORS 1964
B/W. Sd. 26 min. 16 mm. Hire.
S: Educational Services Inc., U.S.A.
D: Central Film Library (V 672).
A modified reproduction of the Haynes-Shockley drift-mobility experiment to demonstrate the existence and behaviour of injected excess minority carriers in semiconductors.
Made for the American Semiconductor Electronics Education Committee.

NEUTRON ACTIVATION 1964
Col. Sd. 8 min. 16 mm. Free loan.
S: Argonne National Laboratory, U.S.A.
The principles and some applications of neutron activation analysis.

UNDER THE SUN 1965
Col. Sd. 10 min. 16 mm. Free loan.
S: Gas Council.
D: Gas Council Film Library.
The sun as a source of energy; storage of this energy as coal and oil; latitude and the seasons; maintenance of life on earth.

A NEW REALITY 1965
Col. Sd. 51 min. 16 mm. Hire.
S: O.E.C.D.
The evolution of the concept of atomic structure since the 1890's, with emphasis on the work of Neils Bohr and brief consideration of its philosophical implications.

THE PHYSICS AND CHEMISTRY OF WATER 1965
Col. Sd. 21 min. 16 & 35 mm. Free loan.
S: Unilever Ltd.
D: Unilever Film Library.
Structure of the water molecule; bonds between water molecules; relation of physical and chemical properties to structure. Produced in collaboration with Prof. J. D. Bernal, F.R.S.

PIMENTAL DISCUSSES CHEMICAL BONDING 1965
B/W. Sd. 27 min. 16 mm. Hire.
S: CHEM Study, U.S.A.
D: Sound-Services Ltd (4192/999).
The role of electrons in bond formation; derivation of the virial theorem; application to covalent, ionic and other types of bonding. A lecture for teachers.

PIMENTAL DISCUSSES THE HYDROGEN ATOM 1965
B/W. Sd. 27 min. 16 mm. Hire. 1965
S: CHEM Study, U.S.A.
D: Sound-Services Ltd (4191/999).
Shortcomings of the planetary model of the atom; significance of the Schrödinger equation; the desirability of teaching an up-to-date atomic model. A lecture for teachers.

RADIATION EFFECTS IN CHEMISTRY 1964
Col. Sd. 13 min. 16 mm. Free loan.
S: Argonne National Laboratory, U.S.A.
Techniques used to investigate the mechanism of chemical reactions which are initiated by radiation.

THE SEEKERS 1965
Col. Sd. 20 min. 16 mm. Free loan.
S: Anglo-American Corp. of Central Africa Ltd.
D: Sound-Services Ltd (1503/281E).
Prospecting for minerals in Central Africa.
A YEAR OF CHEM STUDY

Since the first Sputnik was successfully launched in 1957 a revolution in American science teaching has taken place. During the last two years two American chemistry courses, the Chemical Education Material Study\(^1\) (CHEM Study) and the Chemical Bond Approach Project\(^2\) (C.B.A.), have been made available in Britain.

Both these programmes, but particularly CHEM Study, have been praised by chemistry teachers in the U.K., but their applicability to teaching here, with our syllabuses and examination system, doubted. However, last year we decided to experiment with three applications of the CHEM Study course.

At first-form level, expts 1, 2 and 3, ‘The Observation and Description of a Burning Candle’, ‘The Behaviour of Solids on Warming’ and the ‘Melting Temperature of Pure Substances’ were used along with other experiments such as the semi-quantitative observation of the expansion of solids, liquids and gases and the diffusion of gases into air and into a vacuum, to build up the particulate idea of matter. Also, when combustion was being introduced, exp 4, ‘The Combustion of a Candle’ was invaluable as a training in the deduction of viable conclusions from observation. Exp 5, a determination of the heat involved during the melting and combustion of a candle, was a useful introduction to elementary thermochemistry and afforded a distinction between so-called ‘Physical and Chemical Changes’.

In examination questions and consequently in ‘A’-level textbooks and teaching, the effect of experimental conditions such as concentration, pressure and temperature on the position of equilibrium in a chemical reaction is emphasized but their effect on the rate of the reaction and the dependence of the position of equilibrium on \(\Delta H\) almost ignored. The second use of CHEM Study was directed towards the correction of this.

Exp 12 gives some brief evidence of the rate of reaction depending on temperature, concentration and catalysts and raises the question of whether reactions go to completion. Exp 13 allows Hess’s law to be deduced by simple ‘conical flask and thermometer experiments (a), (b) and (c).

\[
\begin{align*}
H_2O & \rightarrow Na^+ (aq) + OH^- (aq) + X_1 \text{ cal} \\
H_2O & \rightarrow Na^+ (aq) + OH^- (aq) + X_2 \text{ cal} \\
H_2O & \rightarrow Na^+ (aq) + OH^- (aq) + X_3 \text{ cal} \\
\end{align*}
\]

The effect of concentration and temperature on the rate of the ‘iodine-clock’ experiment:

\[
\begin{align*}
IO_3^- (aq) + 3HSO_3^- (aq) & \rightarrow I^- (aq) + 3SO_4^{2-} (aq) + 3H^+ (aq) \\
20Cl^- (aq) & \rightarrow O_2 (g) + 2Cl^- (aq) \\
\end{align*}
\]

and concentration, temperature and catalysts on the decomposition of household bleach

\[
\begin{align*}
20Cl^- (aq) & \rightarrow O_2 (g) + 2Cl^- (aq) \\
\end{align*}
\]

can be investigated in the simple quantitative expts, 14 and 14a.

The concept of dynamic equilibrium can be introduced by the use of demonstration 4 and further investigated by the students themselves trying exp 15. Both these experiments involve the thiocyanate equilibrium

\[
\begin{align*}
Fe^{3+} (aq) + SCN^- (aq) & \rightleftharpoons Fe(SCN)^{2+} (aq) \\
\end{align*}
\]

Leading on from here, solubility can be introduced and experiments can be tried, such as 16, a simple determination of the solubility product of silver acetate, and 19, an experiment investigating the effect of a common ion on the equilibrium

\[
\begin{align*}
BaCrO_4 (s) & \rightleftharpoons Ba^{2+} (aq) + CrO_4^{2-} (aq) \\
\end{align*}
\]

The third and major application of CHEM Study concerns the teaching of science to Arts sixth-formers. Some schools successfully run a History and Philosophy of Science course, others study for periods varying from a week to half a term each, a number of selected topics such as ‘The Origin of the Universe’, ‘Evolution’ and the ‘Structure of
Indeed, at Leeds Modern School both these courses are offered (three and two periods, respectively) in the first-year sixth, and the ‘topic’ course only (two periods) in the second-year sixth. However, at their best they both may fail to achieve what I consider to be the most important result of science teaching in schools. The subjects studied and the facts acquired are incidental: the student should be more mature scientifically at the end than he was at the beginning or half-way through the course. Thus the student should be better equipped to explore, at a later date, any scientific topic he feels is of interest or importance to him. This can best be done by following a carefully planned course where the student progresses to the more advanced concepts by a process of building up over a reasonable period of time on simpler concepts already grasped.

The CHEM Study course, five periods per week last year and four plus the occasional lunch-time this year, seemed to us to provide the answer.

About three-quarters of the course was completed and the material on Atomic Structure was supplemented by the use of the ‘G.B.’ film, Atomic Physics, Parts 1-5, visits to the University of Leeds to see demonstrations of a mass spectrograph and a Van der Graaf generator, and to the Nuclear Power Station at Trawsfynydd and its subsidiary hydroelectric station at Ffestiniog. Certainly the course seemed to achieve what we intended it to do. The experiments were excellent in their simplicity and the good results they yielded. The students, representing a fair cross-section of sixth-form ability, made good progress.

Perhaps, in conclusion, one might say that CHEM Study and C.B.A. satisfy a very real need of the chemistry teacher for textbooks reaching beyond ‘A’ and ‘S’ levels but not insisting on the rigorous mathematical treatment given in university textbooks. Certainly after ‘a year of CHEM Study’ the Chemistry Department at Leeds Modern School felt they were better chemists and chemistry teachers than before.

D. G. FISHER
Senior Science Master,
Leeds Modern School.

REFERENCES


THE HISTORICAL METHOD

How refreshing to read the praise of the Historical method by J. D. Dann (Educ. Chem., 1965, 2(6), 316), for while I believe in most of the aims of the ‘Nuffield’ scheme and am in fact throwing in my support of the investigations, I am also very perturbed by the excessive courtship of science teachers by industry.

A good teacher will neither exaggerate applied science nor pure science—he will teach science—the scientific method—as a means of inculcating both knowledge and understanding of man’s environment so that some of his pupils will become pure scientists interested in extending knowledge and others will become applied scientists interested in making use of existing and new knowledge, as their own inclinations and aptitudes lead them. Furthermore, the two should meet in their common understanding of the scientific method and common humanity.

As man proceeds more and more to take upon himself the role of God in the Universe, by bending the environment to his own purposes, let us be true scientists and thus humble enough to recognize that basing our aims on economics is not necessarily the only or the right way of guiding human destiny. It may be. It may not be. Thus, to assume over-confidently that it is, as is the fashion today, and to conclude that because under existing conditions of organization and finance, Great Britain, or ‘the World’ for that matter, needs more applied scientists and so the teaching of science must be biased in favour of turning out applied scientists
as quickly as possible, by cutting out any ‘history of science’ or any ‘wrong theories’ however interesting and revealing of human fallibility—seems to me short-sighted if not downright dishonest and unscientific!

How does one develop the ‘whole man’ who is the true scientist (pure or applied) unless one deals with the whole progress of science, its failures as well as its successes?

If many of the pleas for ‘cutting out the dead wood’ being made these days were honest to the point of admitting at the start that the mass of knowledge is getting too big for the human mind to encompass, or, less commendably, we must have more applied scientists to maintain and extend the existing conditions whatever happens to the ‘souls’ of men and so on, then at least everyone would know where they stood. Of course we require applied scientists, but as I explained in a letter published in the Bulletin of the Association for Science Education (February, 1965), even more does mankind need fully educated men who besides being brilliant scientists are at the same time whole men and human beings with their minds unfettered by the unavoidable ‘blackmail effect’ of a good job in a big industry.

No, teachers must not be coerced or misled into producing either pure or applied scientists alone. Their job is to produce good scientists and leave the choice to the individuals concerned.

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P.S.—May I thank you and congratulate the Institute on publishing Education in Chemistry. It was needed. I would like to thank all those who joined in the discussion on the ‘Law of Mass Action’ for it has resulted in my getting some points of doubt cleared up and I feel sure that my teaching of reversible reactions will be considerably better than it was.

AZEOTROPY

In a recent article Dr D. Jaques draws attention to the fact that azeotropy is most common in liquid mixtures for which the vapour pressures of the pure components are close. However, his diagrams have errors which I have had difficulty in removing from the work of students of this department and which I do not think should be encouraged.

Figs 1 and 2 do not conform to the Gibbs–Duhem equation. This requires that the expansion of $\ln \gamma_A$ in powers of $x_B$ starts with the second or higher power. Clearly the same restriction applies to the expansion of $(\gamma_A - 1)$. The restriction is not satisfied by Figs 1 and 2, both of which show a strong linear term in $x_B$.

Fig. 3 fails to satisfy one of the Gibbs–Konowalow laws for azeotropes, namely that

$$\left( \frac{\partial p^b}{\partial x} \right)_T = \left( \frac{\partial p^d}{\partial y} \right)_T = 0$$

where $p^b$ and $p^d$ are the bubble- and dew-point pressures. The second of these equations is satisfied by the figure, but not the first. What should be a smooth minimum in $p^b$ is drawn as a sharp cusp at which the derivative, so far from vanishing, has its greatest value.

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REFERENCES


OXFORD UNIVERSITY CONFERENCE FOR SCIENCE TEACHERS

A conference for school teachers of chemistry and physics will be held on 18–20 April in the Chemical Laboratories, Oxford. There will be lectures on current research in chemistry and chemical physics, accounts of the teaching of chemistry at Oxford and ample opportunity for visits to the research laboratories. Forms of application may be obtained from Professor R. E. Richards, F.R.S., Physical Chemistry Laboratory, Oxford, which must be returned not later than 1 February, 1966.