U.D.C. 541.128 : 537.311.33

The "Memory" Effect in Semiconductor Adsorbents and Catalysts during Radiation†

F.F.Vol'kenshtein and V.G.Baru

CONTENTS

I. The "memory" effect under various forms of irradiation 724
II. "Memory" associated with a shift in the electronic equilibrium 725
III. "Memory" associated with a disturbance of the electronic equilibrium 726

I. THE "MEMORY" EFFECT UNDER VARIOUS FORMS OF IRRADIATION

This review is concerned exclusively with semiconductors, but all the statements to be made can be generalised to include dielectrics. There is no difference in principle between semiconductors and dielectrics other than the scale used to represent the energy spectrum. By expanding the spectrum we progress from semiconductors to dielectrics, whereas by compressing it we convert dielectrics into semiconductors.

The term irradiation will be used in the widest possible sense. It will refer to electromagnetic radiation, including visible and ultraviolet light, X-rays, and gamma rays. It will refer also to corpuscular radiation, including bombardment with neutrons, electrons, protons, and alpha particles. In every case, the material experiences a flux of energy from outside. Changes induced in solids by these various types of radiation often have a great deal in common.

Radiation is known to affect several of the properties of a semiconductor. First and foremost, it affects the electrical and optical properties of the material: the magnitude, temperature dependence, and sometimes even the type of the conductivity are affected; absorption bands are shifted; the spectrum, the intensity, and the decay rate of the luminescence are altered. The mechanisms underlying changes in all these properties, and involving the formation of radiation defects in the semiconductor, are fairly well understood (at least, qualitatively).

The mechanism of the influence of irradiation on the adsorption and catalytic properties of semiconductors, with which the present article is concerned, is very much less well understood. Irradiation often causes profound changes in the properties of a semiconductor. A semiconductor having little or no catalytic activity often emerges from this operation as an active catalyst. A semiconductor showing negligible adsorption is often converted into a good adsorbent by irradiation. In spite of numerous experimental investigations, the mechanism of these changes remains obscure. Some of the relevant problems will be discussed in this article.

Workers investigating the effect of irradiation on the adsorption and catalytic properties of semiconductors are faced with a two-fold problem. On the one hand, an understanding of the mechanism of the phenomenon is required, and on the other hand we must learn to control the properties of a semiconductor by modifying them to the required extent and in the appropriate direction by means of irradiation.

† Paper presented to the Miller conference on radiation chemistry (Warsaw, September, 1967).

As soon as the problem is formulated in terms of the use of irradiation as a tool for controlling the properties of a semiconductor, one is faced with the problem of the "memory" of the semiconductor: how long will the changes produced by irradiation persist in the semiconductor, or in other words, how long will the semiconductor "remember" the irradiation? The answer to this question varies from case to case. The problem of the memory of a semiconductor is the focal point of the present article.

A semiconductor sometimes forgets the irradiation instantaneously, immediately after the irradiation is removed. This is one extreme case. The opposite extreme is also possible, the "memory" of the irradiation remaining indefinitely in the semiconductor. But we are often faced with the intermediate, and more general, case of a semiconductor which remembers the irradiation for a finite time and gradually forgets it. We shall discuss all three cases.

The first case is encountered when the effect of irradiation is to produce ionisation directly, i.e. to generate non-equilibrium current carriers in the semiconductor. In this case the semiconductor remembers the irradiation only as long as it is exposed to it. The inner photoelectric effect produced by visible or u.v. light, by X-rays, or by gamma rays is a case in point. The irradiation gives rise to a disturbance of the electronic equilibrium in the semiconductor, and when the irradiation is interrupted the semiconductor usually reverts to its original equilibrium state very rapidly and almost instantaneously. Some exceptions to this rule will be discussed below.

The other limiting case (of a semiconductor which, once exposed to irradiation, remembers the event forever) is observed when the irradiation induces a nuclear reaction in the semiconductor. In this case the irradiation has the effect of increasing the impurity content of the semiconductor by converting normal lattice atoms into foreign atoms. This process is irreversible, and is accompanied by a shift in the electronic equilibrium. We note that both limiting cases can occur together when the products of the nuclear reaction are radioactive, and the semiconductor remains exposed to its own radiation.

Lastly, in the more general case, the memory of the irradiation remains in the semiconductor for a certain time and then gradually disappears. This case arises when the radiation, without actually changing the chemical composition of the semiconductor, leads to the appearance of structural defects, i.e. produces additional (radiation-induced) "disorder" in the lattice. This effect results in a shift of the Fermi level, i.e. in a displacement of the electronic equilibrium, which persists under these conditions. This effect is wholly equivalent to the introduction of impurities into the semiconductor, since the terms

"defect" and "impurity" are synonymous in the language of semiconductor physics. All structure-sensitive properties of the semiconductor must immediately find a new level as a result of the effect.

However, the radiation-induced disorder resulting from illumination is gradually re-absorbed when illumination is discontinued. The process can be accelerated by heating. In other words, by heating the semiconductor we compel it to forget the irradiation more quickly. The "impurities" created in the semiconductor by this process eventually disappear: this property distinguishes them from the impurities formed as products of a nuclear reaction.

Thus, by observing the "memory" of a semiconductor, i.e. by noting how quickly the semiconductor forgets its irradiation, we can identify to some extent the events taking place in the semiconductor during irradiation. In general, irradiation produces more or less reversible changes in the semiconductor. Sometimes, when the irradiation produces unfavourable changes in the semiconductor, we shall endeavour to make these changes easily reversible; conversely, when irradiation is applied in order to control the properties of the semiconductor, we shall be concerned with the stability of the changes.

Thus, irradiation affects the semiconductor in two ways. Firstly, it gives rise to structural defects and to chemically foreign impurities in the semiconductor. Secondly, it induces direct ionisation. In the first case we are dealing with a shift in the electronic equilibrium to what can be treated as a new equilibrium situation. In the second case we are dealing with a disturbance of the electronic equilibrium with generation of non-equilibrium carriers. In the first case the semiconductor remembers the irradiation forever, or for more or less extended periods. In the second case it forgets the irradiation almost immediately.

II. "MEMORY" ASSOCIATED WITH A SHIFT IN THE ELECTRONIC EQUILIBRIUM

We shall consider here the case of a shift in the electronic equilibrium as a result of irradiation.

We must stress, first of all, that the adsorption and catalytic properties of a semiconductor, which are our main concern, are usually related to properties of an entirely different kind: to the work function and electrical conductivity of the semiconductor. This statement is based on a large fund of experimental evidence. The adsorption capacity and catalytic activity of a semiconductor (on the one hand), and its work function and electrical conductivity (on the other hand), are linked by well defined correlations in most cases. The origin of this correlation is made clear by the electronic theory of chemisorption and catalysis [1].

A displacement of the electronic equilibrium (or in other words a shift of the Fermi level) results first of all in a change of the work function and carrier concentration of the semiconductor.

According to the electronic theory, an increase in work function (i.e. an increase in the concentration of free holes and a decrease in the concentration of free electrons, or in other words an increase in the contribution of holes and a decrease in the contribution of electrons to electrical conduction) is accompanied by an increase in the adsorption capacity of the surface towards donor molecules and, conversely, by a decrease in the adsorption capacity of the surface towards acceptor molecules.

As regards the catalytic activity, i.e. the rate of catalytic reactions taking place at the surface, all reactions can be divided into two classes from the standpoint of the electronic theory. One class includes the reactions which are accelerated by an increase in the work function. These reactions, called donor reactions, are accelerated by holes and retarded by electrons. Their rate varies in the same sense as the hole conduction, and in the opposite sense to the electronic conduction. The other class (acceptor reactions) includes those reactions whose rate is increased by lowering the work function. These reactions are accelerated by electrons and retarded by holes. In this case the catalytic activity varies in the same sense as the electronic conduction and in the opposite sense to the hole conduction.

Thus, changes in the electrical conductivity of a semiconductor give rise to changes in the adsorption capacity and in the catalytic activity, the changes being in the same sense or in the opposite sense depending on the nature of the semiconductor (p-type or n-type), on the nature of the adsorbed gas (donor or acceptor gas), and on the nature of the reaction (donor or acceptor reaction). The electronic theory is in no way concerned — and this must be stressed — with the cause of the conductivity changes. The correlation applies irrespective of the agency responsible for the shift of the electronic equilibrium. It could be an impurity added to the semiconductor: indeed, we know that changes in conductivity, accompanied by changes in adsorption capacity and in catalytic properties, can be brought about by doping the semiconductor. Alternatively, the agency could be irradiation. Hence, we are able to predict the effect of irradiation on the adsorption capacity and on the catalytic activity from the changes in electrical conductivity caused by the irradiation.

This general conclusion of the electronic theory can be illustrated by considering the decomposition of alcohols, for which two alternative mechanisms are known: dehydrogenation and dehydration. Let us consider first the dehydrogenation reaction. This, in the terminology of the electronic theory (see Section 6b in Ref. 1), is a typical acceptor reaction, accelerated by high concentrations of electrons and by low concentrations of holes in the semiconductor.

Evidence for the acceptor nature of this reaction comes from various sources. Thus, Zhabrova and coworkers [2], in their study of the dehydrogenation of isopropanol on zinc oxide, studied the changes in catalytic activity and in work function resulting from the addition of various impurities (both donors and acceptors) to the catalyst. A distinct correlation was observed: the lower work function, the greater was the activity. In an earlier investigation, Myasnikov and Pshezhetskii [3] examined the same reaction on a zinc oxide surface covered with chemisorbed oxygen, which behaved as a surface impurity in these experiments. Under the influence of oxygen, the electrical conductivity and the catalytic activity were found to decrease together. Since zinc oxide is an n-type semiconductor, conductivity and activity changes occurring in the same sense indicate that the dehydrogenation of an alcohol is an acceptor reaction.

Tsetskhladze and Kalandadze [4] made simultaneous observations of the effect of irradiation on the electrical conductivity and on the catalytic activity. The electrical conductivity of their specimens of cuprous oxide was increased by several orders of magnitude by gamma irradiation. The changes were relatively long-lived, and were probably caused by atomic displacements induced by the irradiation. The same samples were used as catalysts for the dehydrogenation of ethanol. Since cuprous oxide is a typical p-type semiconductor, and the dehydrogenation reaction (as indicated above) is a typical acceptor reaction, the activity could be expected to vary in a sense opposite to

that of the conductivity. This expectation was confirmed: according to the measurements of Tsetskhladze and Kalandadze, the reaction was strongly inhibited by previous irradiation.

Let us now turn to the dehydration reaction. It is usually assumed that this reaction takes place by an acid–base mechanism, which presupposes the presence of mobile hydrogen (Brønsted acid) on the surface. With oxide and hydroxide catalysts the mobile hydrogen is provided by OH groups, and the reaction ceases when these groups are removed from the surface. This mechanism, in every way analogous to the mechanism of homogeneous acid–base catalysis, is believed to exclude any correlation between the catalytic and the electronic properties of the catalyst. Yet, correlations have been observed by many workers and can hardly be dismissed as fortuitous.

Thus, Zhabrova and coworkers (see above[2]) doped their zinc oxide with sodium (donor) and sulphur (acceptor) impurities, and found that the work function was decreased by the former and increased by the latter. At the same time, they measured the catalytic activity towards the dehydration of isopropanol, and found that addition of sodium inhibited the reaction whereas addition of sulphur increased the reaction rate. Since the work function and the catalytic activity vary in the same sense, this reaction is of the donor type from the standpoint of the electronic theory.

Indeed, the dehydration of alcohols can be classified as a donor reaction in the terminology of the electronic theory both in the case of a purely electronic and in the case of an acid–base mechanism (as can be demonstrated). This is because the participation of positive holes is essentially implied in both the purely electronic mechanism (see Section 6b of Ref. 1) and in the acid–base mechanism, in which the catalyst and the reacting molecule exchange a proton with formation of an oxonium ion and subsequently of a carbonium ion as intermediates[5].

Spitsyn and coworkers[6] studied the dehydration of decanol $C_{10}H_{21}OH$ on tungsten disulphide WS_2. The samples had a stoichiometric defect of sulphur; as expected, they were found to be *n*-type by measurements of thermo-e.m.f. Special preliminary experiments confirmed the absence of hydrogen or hydroxyl groups on the surface. Thus, the acid–base mechanism (in the Brønsted sense) was excluded, and yet dehydration took place at appreciable rates.

The specimen was then placed in a nuclear reactor, where it was irradiated with slow neutrons. Radioactive isotopes of tungsten and sulphur were formed, so that the material remained exposed to internally generated and slowly decaying beta and gamma radiation after the neutron bombardment was stopped. The electrical conductivity of the sample was appreciably lowered by this treatment, and remained lower than the conductivity of the non-irradiated material over the whole of the experimental temperature range (from 20 to 350°). This fact alone is proof that the effect of the radiation in this case cannot be simple ionisation: were it not so, the radiation could only lead to an increase in conductivity.

The catalytic activity was measured at the same time as the electrical conductivity on the same specimens. In view of the donor nature of the reaction, a change in activity in the opposite sense to the change in conductivity could have been predicted (i.e., an increase in activity on irradiation). In fact, the irradiated specimen was found to be more active than the original material over the whole temperature range.

The basic cause of the effect of irradiation on activity is evidently to be found in the correlation between catalytic activity and electrical conductivity established by the electronic theory. Irradiation affects the electrical conductivity of a semiconductor, and changes in activity predictably follow the changes in conductivity as required by the electronic theory. The mechanism by which irradiation influences the electrical conductivity and the mechanism by which it influences the catalytic activity are not two independent problems, but a single problem. Because of the strict correlation between activity and conductivity, we can discount the second problem and concentrate on the first.

In this Section we have considered the case of a change in adsorption and catalytic properties resulting exclusively from a shift in electronic equilibrium brought about by irradiation. The radiation-induced defects which produce this shift do not themselves take part in the adsorption and catalytic acts. The memory associated with radiation-induced defects is retained for considerable times after irradiation is discontinued. As long as these defects persist, the electronic equilibrium remains displaced, the electrical conductivity retains a memory of the irradiation, and so also does the catalytic activity.

III. "MEMORY" ASSOCIATED WITH A DISTURBANCE OF THE ELECTRONIC EQUILIBRIUM

We shall now turn to the case where irradiation disturbs the electronic equilibrium in the semiconductor by generating non-equilibrium carriers without however giving rise to structural defects and impurities. We shall be considering, in other words, the ionising action of radiation. In particular, electromagnetic radiation such as visible and u.v. light, X-radiation, and gamma radiation shows this effect. (Note that gamma radiation can also produce structural disturbances as a secondary effect).

In these cases the semiconductor forgets the irradiation almost as soon as it is removed. This is the general rule. Noteworthy exceptions to this rule, in which the semiconductor retains a memory of the irradiation for an appreciable time even though no radiation defects have been produced, are far from uncommon. This Section is devoted to this anomalous memory, to its manifestations, and to attempts to elucidate its nature.

This memory consists in the following. If the semiconductor is irradiated with u.v. light and adsorption is measured some time after the end of the irradiation period, the dark adsorption capacity is sometimes found to be higher than before irradiation, and conversely the photoadsorption capacity is lower. The surface retains a memory of the irradiation after the irradiation has been removed, even though the production of radiation-induced defects in the sample by u.v. light is, of course, out of the question. This memory disappears very slowly, and can be completely erased only by heating the sample. A memory of this type has been observed by Solonitsyn[7] in his work on the adsorption of O_2 on ZnO.

This memory sometimes manifests itself in the kinetics of photosorption. If radiation is applied after the establishment of adsorption equilibrium, additional adsorption due to the radiation can be observed (photoadsorption). This continues by a kind of inertia for some time after the radiation is interrupted. This memory effect, which could also be termed the delayed action effect or "post-effect", has been observed by Coekelbergs and coworkers[8] during their investigation of the effect of X-radiation on the adsorption of O_2 and CO on Al_2O_3. As in the work of Solonitsyn, there is no possibility of radiation defects having been produced. Again, an increase in temperature tends

to eliminate the effect. At high enough temperatures the "post-effect" disappears completely.

Many experiments on the nature of the adsorption centres produced by irradiation and persisting on the surface for an appreciable time after the end of the irradiation period have been carried out in recent years: these experiments throw some light on the origin of this type of memory. The centres are shown to be non-equilibrium carriers generated by irradiation and captured by intrinsic defects of the surface, i.e. by defects not produced by the radiation.

Thus, the work of Kohn and Taylor [9,10] has shown that gamma irradiation of Al_2O_3 gives rise to adsorption centres for H_2 consisting of holes localised on Al atoms present in stoichiometric excess. Subsequently, Boreskov and coworkers [11] demonstrated that these centres are responsible for the catalytic activity towards the H_2–D_2 exchange reaction. Lunsdorf and Jayne [11,12] showed that u.v. irradiation of MgO produces colouration and an ESR signal due to an electron localised on an anion vacancy. Exposure to CO_2 caused bleaching of the colour and a change in the ESR signal, the new signal corresponding to the CO_2^- radical-ion. The same effect was found in the adsorption of the O_2 molecule, which was converted into the O_2^- radical-ion. Adsorption on F-centres produced by previous irradiation was involved also in the work of Bauer and Staude [13] on the adsorption of quinone on coloured AgBr crystals. Colourless crystals had no adsorption capacity at all. A similar effect was found by Rakityanskaya [14] in her work on the adsorption capacity of various alkali metal halide crystals before and after u.v. irradiation.

All these experiments suggest that irradiation can activate a surface by converting its natural structural defects into more or less long lived adsorption centres. Only thus can the memory exhibited by the surface in these systems be explained. We are dealing with adsorption at localised carriers which, from the standpoint of the electronic theory, play the role of localised unsaturated valencies. These centres are formed before adsorption, if irradiation is applied before adsorption, or alternatively they can be formed during the adsorption process if adsorption is taking place during irradiation. The problem of adsorption on a carrier trapped on a defect was treated quantum-mechanically by Bonch-Bruevich [15] in 1953, and later by Hauffe [16] from the point of view of the Boundary Layer Theory (Randschichttheorie), and by Kogan and Sandomirskii [17] and by one of us [1] from the standpoint of the electronic theory.

We have made a theoretical study [18] of the laws of adsorption on centres whose concentration is affected by irradiation. Ionisation followed by localisation of electrons (or holes) on defects leaves the system in a metastable state, i.e. in an excited state such that the system must overcome an activation barrier in order to pass into the stable state. It is because of this barrier that the centres created by the irradiation are relatively stable. As long as the concentration of centres remaining after irradiation has not decayed away, the surface shows an enhanced adsorption capacity. This was observed also by Solonitsyn, who exposed his specimens to preliminary irradiation. Under these conditions, however, the photoadsorption capacity can be shown to be less than before the preliminary irradiation. This is because the additional irradiation can only create a relatively small number of new centres, the bulk of the new centres having been produced during the preliminary irradiation. These phenomena have indeed been observed in practice.

At the same time, some peculiarities are observed in the kinetics of photoadsorption. If the rate of creation of adsorption centres exceeds the rate at which these centres are filled by gas molecules, the centres will continue to be filled by gas molecules even after the irradiation is stopped until an equilibrium between the surface and the gas phase is reached. Under these conditions we would expect to find a "post-effect" — the effect actually observed by Coekelbergs and coworkers but given a different interpretation in the interesting paper already quoted [8].

Having developed a theory of adsorption at a surface with a variable number of adsorption centres, we are led to the conclusion that photoadsorption is irreversible (or, more accurately, slowly reversible), that the activation energy of photoadsorption is negative, and to various other conclusions which are consistent with experimental results.

We have discussed some problems in the radiation chemistry of semiconductor surfaces. The central problem is that of the memory which the semiconductor retains after irradiation. We have considered the case of irradiation causing a shift in the electronic equilibrium, and the case of a disturbance in the electronic equilibrium. These two cases correspond, respectively, to a memory arising from radiation defects produced by the irradiation and lasting for an appreciable time and to a memory arising from the localisation of non-equilibrium carriers on structural defects, also for an appreciable time. Thus we have been concerned with two types of memory, of different origin.

The electronic mechanism of chemisorption and catalysis is particularly relevant to the influence of irradiation on the adsorption and catalytic properties of semiconductors. The electronic theory of chemisorption and catalysis is the key to an understanding of the phenomena observed during irradiation. At the same time, these phenomena are a basis for further development of the electronic theory.

REFERENCES

1. F.F.Vol'kenshtein, "Elektronnaya Teoriya Kataliza na Poluprovodnikakh" (Electronic Theory of Catalysis on Semiconductors), Fizmatgiz, 1960.
2. G.M.Zhabrova, V.I.Vladimirova, and O.M.Vinogradova, Dokl.Akad.Nauk SSSR, 133, 1375 (1960).
3. I.A.Myasnikov and S.Ya.Pshezhetskii, Symposium "Problemy Kinetiki i Kataliza" (Problems in Kinetics and Catalysis), 8, 175 (1955).
4. T.V.Tsetskhladze and G.Sh.Kalandadze, Trudy Inst.Fiz. Gruz.SSR, 6, 61 (1958–59).
5. M.E.Winfield, in "Catalysis in the Petrochemicals and Oil Refining Industry" (Translated into Russian), Gostoptekhizdat, Moscow, 1963, Vol.3, [possibly a reference to an article by this author in "Catalysis, Oxidation, Hydration, Dehydration, and Cracking Catalysts", Vol.7. (Edited by P.H.Emmett), Reinhold, 1960, Cf., Chem.Abs., 14501, 54. (Ed.of Translation)].
6. V.I.Spitsyn, F.F.Vol'kenshtein, I.E.Mikhailenko, and V.I.Pikaeva, Dokl.Akad.Nauk SSSR, in the press.
7. Yu.P.Solonitsyn, Thesis, Leningrad, 1965.
8. R.Coekelbergs, A.Crucq, J.Decot, L.Degols, M.Randoux, and L.Timmerman, J.Phys.and Chem.Solids, 26, 1983 (1965).
9. H.W.Kohn and E.H.Taylor, "Deuxiéme Congrès International de Catalyse", Paris, 1961.
10. H.W.Kohn, J.Chem.Phys., 33, 1588 (1960); J.Catalysis, 2, 208 (1963).
11. G.K.Boreskov, V.B.Kazanskii, Yu.A.Mishchenko, and G.B.Pariiskii, Dokl.Akad.Nauk SSSR, 157, 384 (1964).
12. J.H.Lunsford and J.P.Jayne, J.Phys.Chem., 69, 2189 (1965).

13. E.Bauer and H.Staude, "Berichte von Hauptjahrestagung (1958); Chemische Geseltschaft in der DDR", 1959, p.129.
14. O.F.Rakityanskaya, Thesis, Odessa, 1966.
15. V.L.Bonch-Bruevich, Zhur.Fiz.Khim., 27, 662, 960 (1953).
16. K.Hauffe, Bull.Soc.chim.Belges., 67, 417 (1958).
17. Sh.M.Kogan and V.B.Sandomirskii, Dokl.Akad.Nauk SSSR, 127, 377 (1959); Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1681 (1959).
18. F.F.Vol'kenshtein and V.G.Baru, Zhur.Fiz.Khim., 42, 1317 (1968) [Russ.J.Phys.Chem., 689 (1968)].

Institute of Physical Chemistry, USSR Academy of Sciences,
Institute of Radio Technology and Electronics, USSR Academy of Sciences, Moscow

U. D. C. 542.65 : 542.321.5

Countercurrent Fractional Crystallisation

Yu.A.Chikin and V.I.Lukhovitskii

Countercurrent fractional crystallisation (CFC) has been attracting increasing attention in recent years. The role of CFC among other methods of separation and purification based on crystallisation is described. Various specific arrangements for applying CFC are given. Different theories of CFC are examined, and the limitations of the process are discussed. 73 references.

CONTENTS

I. Introduction 728
II. Basic principles of CFC 729
III. Types of apparatus for the separation and purification of materials by CFC 729
IV. Theories of CFC 732
V. Fields of application of the CFC method 735

I. INTRODUCTION

Effective methods of separation and purification of materials involve repeated application of the elementary processes which constitute the basis of separation. These processes are: evaporation–condensation (in the case of distillation); sorption-desorption (in chromatographic separation); evaporation–crystallisation (in fractional sublimation); fusion–crystallisation (in countercurrent fractional crystallisation), etc. Thermodynamic partition coefficients, calculated from the chemical potentials of the various phases[1], can be defined for each elementary process.

As a rule, partition coefficients for the fusion–crystallisation process are high enough to ensure efficient separation and purification of materials. These high partition coefficients are due to the fact that in most systems of practical importance the impurities form eutectics with the main component. The thermodynamic partition coefficient of a mixture of a eutectic and a pure component tends to infinity. In some systems, however, mixed crystals, peritectics, or intermediate compounds are formed. Even more complicated systems exist, particularly in multicomponent mixtures. These mixtures are characterised by a finite partition coefficient, which makes their separation more difficult. Systems of this type can be used to evaluate the effectiveness of apparatus and to determine the parameters of the separation process. Most convenient for this purpose are the two-component systems which give rise to solid solutions (just as systems giving ideal solutions are used to study fractional distillation).

The present review will examine the theory and practice of only one of the methods of separation and purification based on crystallisation: countercurrent fractional crystallisation.

The theoretical aspects of the crystallisation process have already been adequately discussed in review articles[2,3].

Modern crystallisation methods of separation and purification can be classified into a number of groups, each of which has its own advantages and disadvantages.

The most widely known of these is the zone melting method[4], which gives products of the highest purity and is generally applied in the production of ultrapure metals, semiconductors, etc. However, in spite of later refinements to increase the number of zones per pass, to provide continuous operation, and to raise the efficiency[5], the purification process remains very slow, requiring many days or at least many hours, and its production capacity is therefore low. Furthermore, the separation of large amounts (tens per cent) of impurities is problematic. The same strictures apply to the directional crystallisation method.

The fractional crystallisation method, widely used in the past, is now hardly ever used as it is extremely laborious, and has been replaced by more satisfactory methods. Somewhat improved variants of the fractional crystallisation method are the continuous methods of fractional melting[6] and partial freezing[7], which can be used in laboratory practice but are hardly likely to find industrial applications because of the low efficiency of separation which they afford.

The method called chromatographic crystallisation by Findlay and McKay[8], proposed by Bowman[9] in 1947, consists in the following procedure: a temperature gradient is applied to a column filled with a filtration medium, and the mixture to be separated is applied at the top in the solid form. The mixture is brought into the liquid form by dissolution in a solvent which does not freeze at the separation temperature (or, alternatively, by fusion). The liquid is allowed to flow downwards, simultaneously moving the temperature gradient in the