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ABBREVIATIONS USED IN REFERENCES

Acta Physicochim. (U.R.S.S.).	Acta Physicochimica (U.S.S.R.).
A.E.C.D.	Atomic Energy Commission Declassified Document (U.S.A.).
Amer. J. Physics.	American Journal of Physics.
Anal. Chem.	Analytical Chemistry.
Analyst.	Analyst.
Ann. der Physik.	Annalen der Physik.
Ann. der Chem.	Annalen der Chemie.
Annales de Chim.	Annales de Chimie.
Ann. de Physique.	Annales de Physique.
Ann. Rep.	Annual Reports of the Chemical Society.
Ann. Soc. Sci. Brux.	Annales de la Société Scientifique de Bruxelles.
Arkiv f. Mat. Astr. o. Fysik.	Arkiv för Matematik, Astronomi och Fysik.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Biochem. J.	Biochemical Journal.
Brit. J. Radiology.	British Journal of Radiology.
Bull. Soc. Chim. France.	Bulletin de la Société Chimique de France.
Bull. Soc. Roy. Sci. Liège.	Bulletin de la Société Royale des Sciences, Liège.
Can. J. Res.	Canadian Journal of Research.
Chem. Eng. News.	Chemical Engineering News.
Chem. and Ind.	Chemistry and Industry.
Chem. Listy.	Chemické Listy pro vědu a průmysl.
Comment. Phys.-Math. Soc. Sci. Fennica.	Commentationes Physico-Mathematicae (Societas Scientiarum Fennica). Helsingfors.
Compt. rendu.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Disc. Farad. Soc.	Discussions of the Faraday Society.
Electronics.	Electronics.
Endocrinology.	Endocrinology.
Ges. Abhandl. z. Kenntnis d. Kohle.	Gesammelte Abhandlungen zur Kenntnis der Kohle.
Helv. Phys. Acta.	Helvetica Physica Acta.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.).	Industrial and Engineering Chemistry, Analytical Edition.
J.A.C.S.	Journal of the American Chemical Society.
J. Applied Physics.	Journal of Applied Physics.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Phys.	Journal of Chemical Physics.
J.C.S.	Journal of the Chemical Society.
J. Chim. Phys.	Journal de Chimie Physique.
J. Colloid Sci.	Journal of Colloid Science.
Jour. de Phys.	Journal de Physique.
Journal de Physique et de Radium.	Journal de Physique et de Radium.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Nat. Cancer Inst.	Journal of the National Cancer Institute.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Phys. Chem. (U.S.S.R.).	Journal of Physical Chemistry (U.S.S.R.).
J. Phys. Coll. Chem.	Journal of Physical and Colloid Chemistry.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Sci. Inst.	Journal of Scientific Instruments.
Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.	Det Kongelige Danske Videnskabernes Selskab, Matematisk-Fysiske Meddelelser.
Kolloidchem. Beihefte.	Kolloidchemische Beihefte.

Kolloid Zeit.	Kolloid Zeitschrift.
Leiden Communications.	Kammerlingh Onnes Laboratorium. Communica- tions, Leiden.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
M.D.D.C.	Atomic Energy Commission Declassified Docu- ment (U.S.A.).
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Nucleonics.	Nucleonics.
Phil. Mag.	Philosophical Magazine.
Philips Technical Review.	Philips Technical Review.
Physik. Z. Sowjetunion.	Physikalische Zeitschrift der Sowjetunion.
Phys. Rev.	Physical Review.
Physik. Zeit.	Physikalische Zeitschrift.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Cambridge Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Inst. Elec. Eng.	Proceedings of the Institute of Electrical Engineers.
Proc. Natl. Acad. Sci., U.S.	Proceedings of the National Academy of Sciences, Washington.
Proc. Phys.-Math. Soc. Japan.	Proceedings of the Physico-Mathematical Society of Japan.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Quarterly Reviews.	Quarterly Reviews of the Chemical Society.
Radio Rev.	Radio Review.
Rev. Mod. Phys.	Reviews of Modern Physics.
Rev. Sci. Inst.	Review of Scientific Instruments.
Research.	Research.
Roy. Inst. Chem. Monograph.	Royal Institute of Chemistry Monograph.
Science.	Science.
Soil Sci.	Soil Science.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Trans. Bose Res. Inst., Calcutta.	Transactions of the Bose Research Institute, Calcutta.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Farad. Soc.	Transactions of the Faraday Society.
Verh. d. Deutschen Phys. Ges.	Verhandlungen der Deutschen Physikalischen Gesellschaft.
Wienberichte.	Wienberichte.
Z. Angewandte Chem.	Zeitschrift für Angewandte Chemie.
Z. Anorg. Chem.	Zeitschrift für Anorganische Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. für Physik.	Zeitschrift für Physik.
Z. Naturforsch.	Zeitschrift für Naturforschung.
Z. Physikal. Chem.	Zeitschrift für Physikalische Chemie.

I

RADIOCHEMISTRY

1. INTRODUCTION

ALTHOUGH the use of radioactive isotopes has been extensively reported in recent years, it is by no means a new technique. By 1913 the work of separating and identifying the many isotopes of the naturally occurring radioactive elements had largely been completed and the earliest radiotracer experiments had been reported (4). Up to 1934 the use of radioactive techniques was entirely confined to the rather limited number of elements with suitable radioactive isotopes, such as thorium, bismuth, lead, and thallium, but the discovery by M. and Mme Joliot-Curie in 1934 that elements which are normally inactive could be made radioactive by bombardment with α -particles opened up a much wider field of study (5). Other workers, stimulated by this discovery, began seeking for alternative methods of obtaining radioactive material by artificial means. One of the most important was due to Fermi (6), who found that a wide range of elements became radioactive when bombarded with neutrons (which had previously been discovered by Chadwick in 1932 by the action of α -particles on beryllium). Concurrent with this work the rapid development of the cyclotron made available a much larger number of radioactive isotopes than could be obtained from other neutron sources or from the relatively low energy particle-accelerating machines such as that of Cockcroft and Walton. Although the use of radioactive isotopes continued to increase, however, many of the more important radio-isotopes (such as ^{14}C) could not be produced in sufficiently large amounts and not until 1945-6 did uranium pile reactors make such radio-isotopes generally available. The yields of isotopes produced by neutron capture reactions in a pile are considerably greater than those produced by use of other neutron sources, and these increased yields are one of the most important consequences of the practical utilization of atomic energy. Uranium reactors (piles) have also enabled a number of new isotopes to be obtained by nuclear fission (see Chap. V).

Radioactive tracer techniques are of very wide application and have been utilized considerably in medicine and biology, but in chemistry, physics, and metallurgy they have not yet been so extensively applied. Nevertheless, many of the problems which arise in these sciences can be studied by radiotracer methods and considerable advances are likely

by their use in the future. The technique has most often been applied using a radioactive isotope as a tracer for a stable isotope—both present together. Subject to some limitations, the chemical behaviour of such a system is then the same as that of the stable isotope, present in macro-amounts. As the weight of the radio-isotope necessary to give a measurable activity† is often less than 10^{-15} g. (far below that detectable by ordinary chemical means), the behaviour of ultramicro-quantities of material can also be studied. In this case no stable isotope of the radioactive element is added, and the concentration of material used (often referred to as 'radiotracer concentrations') is considerably lower than those normally called 'trace' amounts (say 10^{-6} g.). Radiotracer methods can thus be applied satisfactorily to study the behaviour of materials in macro-, trace-, or ultramicro-concentrations and the name 'radiochemistry' is used to describe chemical reactions in which such radioactive atoms are taking part, either in the presence or in the absence of stable isotopes of the same element. Radiochemistry should be carefully distinguished from 'radiation chemistry' which is the study of the chemical effects of nuclear particles and radiation on matter.

A fundamental assumption in tracer chemistry is that the radioactive and stable isotopes of the same element have identical chemical properties and are chemically inseparable. Experience has shown that this is generally true, but several apparent anomalies do exist. In some cases it is possible to mix a radiotracer with its stable isotope and then to separate the two by simple means. Such behaviour may be due to one of two causes.

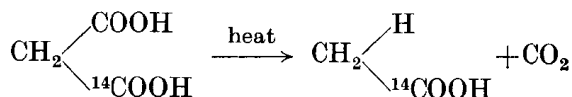
First, the tracer may not be in the same chemical state as its stable isotopes and care must always be taken to ensure that when more than one valency state is possible, active and inactive species exist in the same state. As an example, if sodium sulphite made from radioactive ^{35}S is added to a solution of sodium sulphate, the inactive sulphate may subsequently be completely separated from the active sulphite as long as the sulphite is not oxidized. On the other hand, if exchange were to occur between the two valency states, no separation would be possible. Thus, if radioactive ferrous iron is added to inactive ferric iron in hydrochloric acid solution, interchange between the Fe^{2+} and Fe^{3+} states occurs and the radioactive isotope becomes distributed

† When material has a detectable radioactive content it is common to say that it is 'active', and its measured disintegration rate is its 'activity'. In this sense activity should not be confused with thermodynamic activity, surface activity, etc.

homogeneously throughout both valency states (7). Even in apparently simple cases, difference of behaviour might occur. For instance, traces of ammonium ion may react with the platinum metals forming ammine complexes, the chemistry of which is considerably different from that of the element in a simple ionic form.

Other cases of incomplete mixing of inactive and active isotopes have been observed where the possibility of several valency states is excluded. This is due to the existence of the radioactive tracer in a colloidal, non-ionized form which does not readily exchange with the added ionized inactive isotope. It is frequently necessary to use vigorous reagents to convert the two to the same chemical state.

In some systems, however, a more fundamental difficulty occurs, namely the difference in zero point energy of the radioactive and stable isotopes. This arises from differences in mass of the two species and becomes apparent in changes in equilibrium constants, rates of reaction, bond strength, etc., as a result of isotopic replacement. Such effects are sufficiently great to enable separation of isotopes by chemical exchange on a large scale (8). Beeck *et al.* (9), who investigated the pyrolysis of 1- ^{13}C propane, found that the ^{12}C — ^{12}C bond ruptured 8 per cent. more frequently than the ^{12}C — ^{13}C bond and obtained a higher $^{13}\text{C}/^{12}\text{C}$ ratio in the first fractions of ethylene than present in the original propane. (If complete degradation were to occur, of course, the $^{13}\text{C}/^{12}\text{C}$ ratio must be unchanged.) Similarly, Yankwich and Calvin (10) have observed that when malonic acid, labelled with ^{14}C in one carboxyl group is partially decarboxylated, the carbon dioxide evolved is depleted in ^{14}C while the remaining acetic acid is enriched. Thus,



showing that the ^{12}C — ^{14}C bond is stronger than the ^{12}C — ^{12}C bond which is disrupted at a faster rate. Differences in the chemical properties of carbon isotopes were also observed in photosynthesis in plants grown in an atmosphere of $^{14}\text{CO}_2$ and $^{12}\text{CO}_2$, the residual carbon dioxide in the gas surrounding the plant becoming enriched in $^{14}\text{CO}_2$ (11).

In radiochemistry the possibility of isotopic separations even under equilibrium conditions should always be borne in mind. The effect may be particularly important in the case of the lighter elements, for which the relative isotopic mass differences are greatest. Thus, the large difference in mass of hydrogen and tritium (^3H) may result in

considerable divergences in chemical behaviour under some circumstances (12), but as the mass differences become smaller, the separation factors also decrease (13). The theoretical separation factors for such processes are seldom larger than 1.02, and this 2 per cent. separation is obtained only if the system is at equilibrium. Isotopic separation is only likely to be significant when there is isotopic exchange between two different molecular species containing the same element under conditions where the separated isotopes do not remix, and there is a chance of a multistage fractionation process occurring. Under these conditions considerable errors might result unless this possibility is kept in mind.

Remembering that the chemical identity of isotopes of the same element has been assumed, we may now proceed to the remainder of this chapter which is a discussion of tracer chemistry, with special reference to differences from normal behaviour, obtained in radiotracer concentrations. The last section illustrates the use of radiotracer techniques in chemical investigations (14).

2. SOME FACTORS AFFECTING RADIOCHEMICAL SEPARATIONS

When it is appreciated that the concentration of a radiotracer substance may be 10^{-6} – 10^{-15} times less than solutions of micro-gram quantities of material normally regarded as of extreme dilution, some modification of the normal behaviour is to be expected. Thus the presence of traces of impurities which can be neglected in ordinary chemical practice may be significant in radiochemical procedure. It is the purpose of this chapter to indicate the factors affecting the manipulation of radiochemical material and the practical procedures employed.

In order to obtain clean and efficient recovery of a radio-element it is necessary to use a method of separating it from other material which is as selective as possible. For instance, solvent extraction, precipitation, volatilization, electrochemical deposition, and adsorption have all been used widely.

Loss of activity by side reactions, adsorption on the surfaces of vessels, etc., must be avoided and it may be necessary to add a few milligrams of the same element to act as a 'carrier'—i.e. the active atoms are diluted with stable atoms, thus reducing the proportion of activity lost by side reactions. With the use of carriers it should be remembered that radioactive material produced by bombardment may, if it is multivalent, be present in more than one valency state. It is

necessary, therefore, to add the inactive carrier in all possible valencies, which may then be converted to the state necessary for separation. Alternatively the carrier may be added in one valency only and all valency conditions produced in turn by oxidation and reduction before separation is attempted. The possibility of the activity being present in an unexpected condition (due to the presence of trace impurities, etc.) should be kept in mind, particularly with elements forming co-ordination complexes and those which are readily hydrolysed.

A. Precipitation reactions

The regularities observed in the behaviour of micro-components with macro-precipitates were first formulated in 1913 by Fajans (15) and by Paneth (16) in 1914. The Fajans Precipitation Rule states that 'when a precipitate is formed in a solution containing micro-concentrations of a radioactive element, the lower the solubility of the compound between the anion of the precipitate and the radioactive element (cationic), the greater is the amount of radioactive element carried down with the precipitate'. A similar rule was proposed by Paneth to describe the behaviour of micro-components in solution when treated with insoluble compounds or preformed precipitates. These rules together are often referred to as the Fajans-Paneth Precipitation and Adsorption Rule. When a micro-component does not form an insoluble product with a precipitate, non-selective adsorption of the radioactive material on a solid substrate can be reduced by addition of an inactive analogue of the same element, referred to as a 'hold-back carrier'. If no stable species exists, a chemically similar element may be used either as carrier or hold-back carrier, e.g. rhenium for element 43 and zirconium for protoactinium. The use of hold-back carriers for micro-quantities of elements (such as niobium and tantalum) which are easily hydrolysed is sometimes inadvisable, however, since they precipitate under a wide variety of conditions. In such cases the use of carrier is more of an embarrassment than an advantage.

The Fajans-Paneth rule originated from observations such as the co-precipitation of small amounts of radium and lead with barium sulphate, and of radium, lead, and bismuth with barium carbonate; the absence of adsorption of small amounts of radium on silver chloride and of bismuth on barium sulphate in acid solution also supported the rule. As a more recent example, the existence of at least two valency states of neptunium (element 93) in solution was inferred from the absence of co-precipitation with lanthanum fluoride in strongly oxidizing

media, whereas complete co-precipitation occurred when the solutions were reduced (17).

As more data were accumulated, several examples which could not be reconciled with the Fajans-Paneth rule were observed (18-20). For example, the lead isotope, thorium B, is not co-precipitated with mercuric iodide or mercurous chloride although the corresponding lead compounds are sparingly soluble. Similarly, salts of radium with many organic acids such as fumaric and malonic have a low solubility in water and are carried down by the barium derivative, yet radium remains in solution when the copper, silver, and heavy metal salts are precipitated. Perhaps even more remarkable is the failure of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to carry down traces of radium, although radium sulphate is one of the least soluble compounds known (18).

These discrepancies showed that low solubility is not the sole criterion of co-precipitation, and it was suggested that true co-precipitation would be observed under all conditions only if the radio-element was incorporated isomorphously or at least uniformly in the precipitate (18). This is essentially Hahn's Precipitation Rule formulated to describe true co-precipitation reactions. In a number of precipitation reactions the separation of the micro-component depends on the precipitate and the manner in which it is produced, and such reactions are considered to be due to surface adsorption. In these cases the conditions for separation are given by Hahn's Adsorption Rule, which states that 'an ion at any desired dilution will be adsorbed by a precipitate if that precipitate has acquired a surface charge opposite in sign to the charge of the ion to be adsorbed and if the adsorbed compound is slightly soluble in the solvent involved' (18).

Hahn subdivided true co-precipitation with isomorphous replacement into two sub-groups:

- (1 a) precipitation or incorporation processes with true isomorphism or dimorphism of the components, and
- (1 b) incorporation into crystal systems in a manner suggesting isomorphism, when it is known not to exist if the components are present in macro-concentrations.

Precipitation by adsorption was also subdivided into:

- (2 a) adsorption processes where the precipitates have a large surface area, and
 - (2 b) incorporation into 'internal adsorption' systems.
- (1 a) Isomorphous replacement. Precipitation of a micro-component

which forms an isomorphous system with the precipitate is always observed with radium and barium salts. It would also be expected in the precipitation of, for instance, element 87 (actinium K) with caesium compounds.

Two rules expressing the behaviour of radium when barium salts are crystallized have been formulated. According to one, the distribution relationship in the crystal is logarithmic (21), whilst for the other it is homogeneous and follows the Berthelot–Nernst law of distribution (22). The logarithmic relationship may be expressed as

$$\log \frac{c_1^0}{c_1^0 - c_1} = S \log \frac{c_2^0}{c_2^0 - c_2}, \quad (1.1)$$

where c_1^0 and c_2^0 are the initial concentrations of radium and barium in solution respectively, $(c_1^0 - c_1)$ and $(c_2^0 - c_2)$ are the concentrations after separation of the crystals, c_1 and c_2 represent the amounts of radium and barium that have separated in the solid phase, and S is a constant. The homogeneous distribution may be expressed as

$$\frac{c_1^0}{c_1^0 - c_1} = Q \times \frac{c_2^0}{c_2^0 - c_2}, \quad (1.2)$$

where Q is also constant. If Q or S is greater than unity, radium concentrates in the crystal.

It has been found (23) that the logarithmic distribution applies when a precipitate is formed slowly from saturated but not supersaturated solutions. The distribution implies that each layer of crystal, as it is deposited, is in equilibrium with the solution and that there is no exchange between components in the interior of the crystal and the solution. Thus the composition of each layer is dependent only on the concentration of the components in solution at the instant of separation. In the case of a radium salt formed in the presence of the more soluble barium salt, for example, when crystallization starts the crystals form in the presence of the initial concentrations c_1^0 and c_2^0 of radium and barium respectively, whilst subsequently the concentrations are $(c_1^0 - c_1)$ and $(c_2^0 - c_2)$. As a result, the individual crystals contain a higher proportion of radium at the centre, decreasing exponentially outwards. This type of distribution has been confirmed by auto-radiographs.†

Although equilibrium conditions give a logarithmic distribution of activity, it has also been observed as a result of rapid crystallization from supersaturated solutions by vigorous stirring (24), for which the

† Photographs of crystals containing radium made by the influence of the emitted radiation on a photographic plate.

attainment of equilibrium is open to doubt. The homogeneous distribution has been found during slow crystallization of radium and barium salts from supersaturated solutions which are not stirred (25). It was assumed that under these conditions equilibrium was not maintained, and hence the logarithmic law was not obeyed. A more complete explanation, however, of the difference between this type of crystallization and that obtained in rapid precipitation from super-saturated solutions has yet to be given.

Although rapid crystallization from supersaturated solutions results in a logarithmic distribution, if the small crystals thus obtained are subsequently stirred in the solution for several hours, the radium becomes distributed homogeneously throughout the crystal and a Berthelot-Nernst distribution results (23). It is probable that this is due to recrystallization. A similar explanation, however, for slow crystallization from supersaturated solutions is not valid since it has been shown that the larger crystals obtained under these conditions do not recrystallize during the experiment (26).

(16) **Anomalous mixed crystals.** The homogeneous incorporation of a micro-component by crystals occurs in cases where it is not expected on chemical or crystallographic grounds. This is not a surface effect since inclusion is independent of the speed of formation of the precipitate and of excess of reagents, and the partition coefficient of the radioactive material between solution and precipitate is constant. Thus rhombic lead chloride is uniformly distributed in monoclinic barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). Similarly, lead (ThB) is homogeneously incorporated in crystals belonging to the sodium chloride lattice type such as sodium and potassium chloride and potassium bromide (27), but not in crystals of the caesium chloride lattice type such as the dihydrates of sodium chloride and bromide. Later experiments, however, have shown that detectable amounts of inactive lead can be accommodated in crystals which incorporate thorium B. It is probable that there is a limited replacement of host cations by lead, but the maximum solubility of the lead in the crystal is very low.

(2a) **Adsorption.** Apart from solubility effects the Hahn Adsorption Rule stresses the importance of the charge of the ion of the micro-component and that of the precipitate (caused by adsorbed macro-components). Many examples could be quoted to illustrate this rule (see Hahn (1)), but the case of silver and lead iodides will be mentioned as one which is particularly interesting (18). When silver iodide is precipitated by potassium iodide in the presence of thorium B (lead),

the amount of the latter carried down depends on the method of precipitation. If insufficient potassium iodide is added to precipitate all the silver ions, the latter are adsorbed by the precipitate, which repels the lead ions. Under these circumstances only 2–5 per cent. of the thorium B is adsorbed. Using an excess of potassium iodide, however, iodide ions are preferentially adsorbed and the precipitate attracts the lead ions, leading to about 75 per cent. adsorption in the presence of 50–100 per cent. excess of potassium iodide. As the excess is increased further, the adsorption of thorium B decreases, until in the presence of a 2,400-fold excess, the lead cation is converted to the anion PbI_4^- , and only 1.9 per cent. of the lead is carried down.

The explanation of surface adsorption based on the effects of charge and low solubility alone is, however, not always satisfactory since adsorption is sometimes observed when the precipitate and the ion are similarly charged (particularly when the adsorbent has a large surface area). In such cases the relative sizes and deformability of the ions and the concentration of the adsorbed ion, as well as considerations of solubility, are all factors which must be considered (28, 29).

(2b) **Internal adsorption.** The fourth type of co-precipitation, often called 'internal adsorption', can best be distinguished by the autoradiographic method. The crystals are often large (and therefore with small surface development) and show a non-uniform distribution of the radioactive material which is often concentrated along certain internal surfaces or areas of the crystal. Different elements concentrate at different surfaces, but the behaviour of a given element is consistent. The partition coefficient of the micro-component between the crystals and solution is in some cases reasonably constant, but is larger and in favour of the precipitate if precipitation is rapid. If the precipitate is redissolved and recrystallized more slowly, less radioactive material is included in the crystal. In the majority of cases the micro-component is associated with an ion with which it forms an insoluble compound in macro-concentrations or under conditions which favour hydrolysis; in this there is a close similarity to radio-colloidal behaviour (see p. 21). Polonium, which is readily hydrolysed, has a marked tendency to this form of precipitation. Similarly radium and lead also exhibit this phenomenon during the crystallization of ammonium and alkali sulphates and dichromates (1). Internal adsorption should be distinguished from mere inclusion of mother liquors in the crystal, for which no regularities are observed.

Cations which form compounds of low solubility with adsorbed anions