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THE USE OF RADIOACTIVE INERT GASES IN THE STUDY OF SOLIDS

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1. INTRODUCTION

The development of work on the study of solids requires the use of sensitive methods of various types for the study of phase transitions, chemical changes, the production of imperfections and defects in the crystal lattice, changes in the properties of a surface, etc.

In addition to physical methods of study, the use of radiochemical methods is of interest; in these methods, the liberation of radioactive inert gases makes it possible to follow continuously various types of change taking place during processes in a solid at the temperature of the experiment. The general term "emanation" is often used to denote the radioactive inert gases formed in nuclear reactions, and the methods of study based on the introduction of a radioactive inert gas into a solid and subsequent measurement of the fraction of emanation liberated or the emanating power of the substance are usually described as emanation methods.

The classical emanation method, using natural radioactive inert gases, was suggested by Kolovrat-Chervinskii[1] and subsequently developed and improved by Hahn[2], Zimens and Flügge[3,4], and Starik[5]. Various modifications of this method are now known[6-8], based on the use of radioactive isotopes of the inert gases.

Work on the theory and application of the emanation method in the study of reactions in solids has been reviewed in papers by Hahn[2,9] and in a monograph by Wahl and Bonner[10].

In recent years, in connection with the development of work on the peaceful uses of atomic energy and new problems in the physical chemistry of solids, a large number of papers have been published on the use of different versions of the emanation method in the study of solids. At the same time there has been a marked increase in the range of problems studied by emanation methods, and in many cases these methods are combined with X-ray diffraction, thermographic, dilatometric, and sorption methods; this makes possible a more unambiguous interpretation of the results obtained[11-13].

2. THEORETICAL PRINCIPLES OF EMANATION METHODS. METHODS OF INTRODUCING AND MEASURING RADIOACTIVE INERT GASES

The emanation method is fundamentally different from other radiochemical methods; the classical version of the method is based on the properties of various radioactive elements, such as radium, thorium-X, and actinium-X, which disintegrate with the liberation of radioactive noble gases or emanations, which may be quantitatively determined with a high accuracy from their α-radiation. Less frequently, the β-radiation of the active residue from the emanation is measured[2]:

$$^{228}\mathrm{Th\,(RdTh)} \xrightarrow[5.4\ \mathrm{MeV}]{\alpha} \mathrm{ThX} \xrightarrow[5.7\ \mathrm{MeV}]{\alpha} {}^{220}\mathrm{Em\,(Th)} \xrightarrow{\alpha} {}^{216}\mathrm{ThA} \xrightarrow{\beta} \ldots$$

The method involves the introduction, into the solid being studied, of a mother isotope (Ra, RdTh, AcX), which generates emanation continuously by radioactive disintegration, followed by the measurement of the proportion of radioactive noble gas capable of being liberated from the specimen under certain conditions[4,10]. This liberated fraction of the emanation or the emanating power of the given substance is in general a function of the temperature, surface area, and state of the crystal lattice of the solid. The term emanation coefficient is generally used to denote the ratio of the fraction of the emanation liberated to the total quantity of emanation formed in the test specimen when a steady state is established. Since the radioactive gas liberated is inert and does not react with the solid, the results obtained are not complicated by any side chemical reactions.

The classical emanation method was developed chiefly by the work of Kolovrat-Chervinskii, Hahn, Zimens, Flügge, Starik, and others. The most complete theory of emanation was first given in papers by Flügge and Zimens[3,14,15], who emphasised the existence of two fundamentally different mechanisms for liberation of atoms of the emanation. The first involves that fraction of the atoms which is liberated directly as a result of the recoil energy on radioactive disintegration of the radioactive mother element, and the second involves the atoms of emanation formed within the solid and liberated by diffusion through the vacant sites, capillaries, and cracks in the solid. The values of the emanating power due to the processes of radioactive recoil and diffusion are denoted by the symbols E_0 and Ed respectively. Thus the total emanating power of a specimen determined experimentally, which is usually denoted by the symbol EV, consists of two parts: $EV = E_0 + Ed$. Zimens examined the liberation of emanation both from a single particle[15] and from an aggregate of particles[14]. A recoil atom from a particle will be liberated only when the mother element is situated at a distance x which does not exceed the recoil free path R. The average fraction of atoms formed in the range R from the surface will then be given by the ratio of the volume in which the atom of emanation is formed to the total volume.

The average fraction of atoms formed at a distance $x < R$ from the surface and ejected from the particle is

$$\frac{\int_0^R \frac{2\pi R(R-x)}{4\pi R^2}\,dx}{R} = \frac{\int_0^R \frac{R-x}{2R}\,dx}{R} = {}^1/_4 . \quad (1)$$

Thus

$$E_0 = {}^1/_4 \cdot \frac{R \cdot S}{v},$$

where S is the surface area, and v the volume of the particle, or

$$E_0 = \frac{R}{4} \cdot \rho \cdot \frac{S}{m}, \quad (2)$$

where ρ is the density and m the mass of the particle.

This is applicable to particles with dimensions $\geq 10^{-4}$ cm. The diffusion component of the emanation will in general depend on the diffusion coefficient D for the inert gas through the solid and the radioactive decay constant λ for the emanation.

Zimens[15] put forward the equation

$$E_d = \sqrt{\frac{D}{\lambda}}\,\rho\frac{S}{m} . \quad (3)$$

Thus

$$EV = E_0 + E_d = \left(\frac{R}{4} + \sqrt{\frac{D}{\lambda}}\right)\rho\frac{S}{m} . \quad (4)$$

When the process of emanation for an aggregate of particles is considered, it is also necessary to make allowance for the indirect effect of the recoil produced when the recoil atom collides with a neighbouring particle in the solid. For particles smaller than 1 μm, the distances between the particles generally do not exceed the recoil free path, and the atoms of emanation are liberated chiefly as a result of the indirect effect of the recoil. The proportion of these atoms is a sensitive function of the composition of the solid and of the presence of various impurities. A paper by Götte[16], for example, reports an increase in the emanation of thoron from zinc hydroxide from 22% to 60% when inactive iron hydroxide is added. The development of a theory of the process of emanation for an aggregate of particles is complicated by the need to make allowance for the length and diameter of the pores, the ratio of the volume of the pores and the volume of an individual particle, and the possible adsorption of emanation on the surface of the particles.

The practical utilisation of Eqns. (1)–(4) requires a knowledge of the magnitude of the recoil free path R, for which Flügge and Zimens[3] put forward the equation

$$R = g\frac{1}{\rho}\left(\frac{\overline{AB}}{s}\right) \quad (5)$$

where g is a proportionality factor, ρ the density, and $\overline{AB}/s$ the mean ratio of the atomic weight to the stopping power of the solid, which Flügge and Zimens[3] assumed, without sufficient justification, to be equal to the stopping power of the solid with respect to α-particles[17]. Flügge and Zimens also assumed that the recoil free path R was proportional to the square of the recoil energy ϵ_0:

$$R \propto C\epsilon_0^2. \quad (6)$$

To calculate the proportionality factor g in Eqn. (5), it is necessary to determine the emanating power due entirely to recoil. This can be done, for example, by measuring the coefficient of emanation for the liberation of two forms of emanation with different half-lives, or by measuring the temperature coefficient of emanation[10]. For radon and thoron the constant g can be found directly by measuring the emanating power of glass rods with known dimensions[18]. The values of the factor g are 57×10^{-8} for radon and 74×10^{-8} for thoron.

If it is assumed that all the recoil atoms are liberated immediately after formation and that their rate of liberation is independent of the quantity of inert gas in the specimen, the measured emanating power for a freshly prepared specimen will be due almost entirely to recoil. The diffusion component, however, will be a function of the total concentration of gas and the age and temperature of the specimen. Since the recoil energy for α-radiation is of the order of 100 000 eV, whereas the thermal energy amounts to ~ 0.1 eV, the recoil emanation is almost independent of temperature, and the temperature coefficient of the evolution of emanation is determined by the diffusion component[10]:

$$E_d = Ae^{-\epsilon_{EV}/RT} \quad (7)$$

where ϵ_{EV} is the activation energy of the emanation process. It should be noted that the applicability of Eqns. (2)–(6) is limited, since they make no allowance for side processes such as adsorption, the indirect effect of the recoil, and possible changes in the specimen itself.

Baulch and Duncan[19] compare calculated and experimental values of the recoil free path for atoms of emanation, obtained from the equation of Flügge and Zimens[15] and from their own formulae[19]. They consider that both of Zimens' equations—formulae (5) and (6)—which give the relationship between the length of the free path and the energy of the recoil atoms, are unsatisfactory. From Bohr's classical equation[20] for the adiabatic collision of a recoil atom with an atom of the retarding gas

$$R_0 = \frac{m_e \epsilon}{\pi N \hbar^2 Z_1^{2/3} Z_2} \quad (8)$$

(where m_e is the mass of the electron, N is the number of atoms of the stopping material in 1 cm^3, Z_1 and Z_2 are the nuclear charges of the recoil atom and the colliding atom respectively, R_0 is the mean free path of the recoil atom, and ϵ is the energy of the recoil atom), Baulch and Duncan put forward an equation for calculating the number of recoil atoms with free path length R.

These workers[19] determined the free path and the energy of the recoil atoms for ThC″ and RaA. The recoil atoms moved a known distance from the source to a metal collector plate through a gaseous stopping medium, whose pressure was measured with high accuracy. The activity of the collector plate was then measured with a Geiger counter. In the treatment of the results, allowance was made both for the geometric factor (i.e. the dependence of the number of recoil atoms reaching the plate on the geometry of the apparatus used) and for the degree of straggling (i.e. the deviation of the free path from its mean value). Allowance for these factors in the comparison of theoretical and experimental results leads, in their opinion[19], to satisfactory agreement with experiment. Thus for thoron with a recoil energy of 103 keV, the calculated mean free path in air at atmospheric pressure is 0.059 cm, while the value found experimentally[3] is 0.083 cm; in barium stearate the calculated free path is 960 Å, while that determined experimentally is 940 Å.[21]

The recoil energy ϵ_R was calculated from the equation

$$\epsilon_R = 4\epsilon_\alpha/M \quad (9)$$

where ϵ_α is the energy of α-decay, and M the mass of the recoil atom.

In conclusion, Baulch and Duncan[19] point out that formula (8) gives better agreement with experiment than do Eqns. (4)–(6), proposed by Flügge and Zimens, since the mean free path of the recoil atoms is proportional to the recoil energy to the first power—rather than to the square—of the recoil energy. Moreover, Eqn. (5) was derived without allowance for the degree of straggling, which depends on the stopping medium, and on the unjustified assumption that the stopping power of a substance is the same with respect to α-particles and to recoil atoms. It should be noted that there are a large number of systems for which the theoretical calculation of R_0 does not give satisfactory agreement with experiment, and further fairly complicated experiments are required, so that most authors dealing with the emanation method restrict themselves to a qualitative treatment of the results obtained.

The choice of method for the introduction of the emanating radioactive mother element and the nature of its distribution in the solid being studied are very important in the emanation method. This problem was examined in some detail by Zimens[4], who demonstrated the possibility of a uniform distribution of the radioactive element for most precipitates with an extensively developed surface, even when there is no isomorphism. He also described various types of emanation–temperature curves, which have generally figured in all subsequent studies using the emanation method. These curves are of the following types—(1) temperature curves (LT) obtained by measuring the emanating power EV with continuous rise in the temperature of the specimen; (2) temperature curves (RT) obtained by measuring EV after the heating has been interrupted at a given point and the specimen cooled; (3) isotherms, representing the dependence of EV on time or specimen weight at constant temperature; (4) cooling curves characterising EV directly during the cooling of a specimen previously heated to a high temperature; and (5) duplicate curves obtained by measuring the emanation of a specimen during repeated continuous increase in temperature at a given rate.

Later work using the classical emanation method demonstrated that the temperature variation of EV was almost completely unaffected by two methods of introducing the original mother isotope into the test solid (coprecipitation and impregnation). The introduction of radiothorium by the impregnation of a previously prepared precipitate of the test solid generally leads to higher absolute values of the emanating power compared with specimens labelled with radiothorium during precipitation, but does not alter the nature of the variation in EV with temperature. This has been shown by Zhabrova and Shibanova[22,23], who impregnated magnesium and zirconium hydroxides with aqueous solutions of radiothorium, and also by Zaborenko and Tetner[24], who impregnated inorganic salts with alcoholic radiothorium solutions.

In addition to the classical version of the emanation method, various modifications of the method are now used, distinguished chiefly by a fundamentally different method for introducing the radioactive inert gas into the solid being studied. Characteristic features common to all these methods are that the radioactive inert gas is liberated only by diffusion and is not replenished on liberation, so that allowance must be made for its decay with time.

One of these modifications of the classical emanation method is the method of surface radioactive gas labelling, developed by Jech in Czechoslovakia[6,25,26]. In this method, the radioactive inert gas—radon, xenon (^{131}Xe), or krypton (^{85}Kr)—is introduced into thin surface layers by ion bombardment of the surface of the solid in a high-frequency discharge[6]. The depth of penetration into the solid amounts to 10–30 Å. Both the quantity of radioactive gas introduced into the surface of the specimen, and the rate of its liberation, depend on the structure and the state of the surface. This was first used to study the thermal decomposition of nickel oxalate and to examine the surface of glasses subjected to different treatments[25]. Unlike the emanation method, which is based on the continuous formation of radioactive inert gas inside the solid, the method of surface gas labelling is based on the introduction of a definite limited quantity of radioactive gas; as already noted, the radioactive atoms penetrate to a very shallow depth, and can be liberated only by diffusion. This labelled-surface method can be used to determine the topography of various surface structures, and also to observe the course of surface chemical reactions, which alter the rate of evolution of the surface gas label.

Another method for introducing the emanation was proposed by Lindner[8]. It is based on the introduction of atoms of radium emanation (radon) into the surface of the solid being studied, by recoil when the specimen is placed in $^{226}RaCl_2$ solution. The radon penetrates to a depth of 100–150 Å, and the remaining radium chloride is removed by washing. With a sufficiently small particle size ($\sim$ 0.5 μm) the atoms of the emanation are distributed uniformly throughout the substance. The need to bring the test specimens into contact with solution and water undoubtedly restricts the possible applications of this method for introducing a radioactive noble gas into a solid surface.

The principle for utilisation of the emanation method proposed by Yajima and others[7,27] is closely related to those described above. Radioactive isotopes (xenon, krypton, etc.) were used, but they were introduced into the solid by mixing it with uranium dioxide and then irradiating the mixture with thermal neutrons. Thus, as a result of the recoil energy, the radioactive inert gases, which are fission products, are trapped by the surrounding powder[28], and their rate of liberation is determined by the state of the crystal lattice of the solid. A correlation was established[27] between the evolution of gaseous fission products and changes in the crystal structure of various specimens of haematite. Yajima et al.[27] prefer this method of introducing the radioactive gas, since it eliminates chemical treatment and can be applied to many solids, including metals. It should be noted that the specimens may exhibit induced activity, and this may introduce difficulties into subsequent work.

In all these varieties of the emanation method, the radioactive gas is present in the solid as a result of radiation effects. In the classical version, when the radioactive isotope of thorium ^{228}Th is introduced into the test solids, the ThX and then the thoron, formed by successive radioactive disintegration, penetrate into the lattice of the solid as a result of the recoil energy.

The radioactive gas label (Rn, ^{85}Kr) is introduced into the lattice of the solid by ion bombardment in an electrical discharge, etc. Thus the principle of the introduction of the radioactive gases is essentially radiative. Until recently, however, no work had been done making use

of different versions of the emanation method to study the same materials. Thus comparison of results obtained on the thermal decomposition of hydroxides[23] and oxalates[29], obtained by the classical emanation method and by surface gas labelling, are of undoubted interest; this comparison has shown that, for the simple topochemical processes of the conversion of hydroxide into oxide, the extremal points for the liberation of the emanation and the radioactive gas label generally coincide. There obviously should not be a sharp difference between these methods, since, as noted above, the radioactive gas is in all instances present in the lattice of the solid as a result of radiation effects. In the former case, however, the radioactive gas produced is present—according to calculations based on the formula of Flügge and Zimens[3]—at a depth of 300–400 Å and is generated continuously. In the latter case the radioactive gas is present at a depth of several dozen Ångström units, and is not replenished on liberation. Thus in some instances the fixation of high-temperature processes by the method of surface gas labelling is difficult, so that the thermally activated liberation of the radioactive gas, due to diffusion, and the state of the surface of the specimen before the deliberate introduction of the radioactive gas label, acquire considerable importance. Moreover, the surface layer may be broken down on the introduction of radioactive atoms of radon or krypton, and some of the radioactive gas is liberated during the annealing of the defects at 50–100°C, Thus the fairly broad low-temperature peaks for the liberation of ^{85}Kr, observed e.g. in the decomposition of oxalates[29], can be assumed to be due to thermal diffusion with simultaneous partial dehydration. These characteristic features of the methods possibly explain the differences observed[29] in the study of more complicated multistage processes, e.g. the decomposition of oxalates. Further deeper and more detailed comparison of different versions of the emanation method with different treatments of the solids being studied is of interest: it may give new information on fine changes in their structures and surfaces.

The use of the emanation method in most instances requires continuous recording of the α-activity of the inert gases (radon, thoron, and actinon) with time.

The flow method for measuring the quantity of emanation liberated has been described in detail[9,30,31]. The basic scheme used in the measurements is shown in Fig. 1: the inert carrier gas is passed at a definite rate from the purification and drying system into a reaction vessel, which is placed in a furnace and contains a known weight of the test substance, after which it passes together with the liberated fraction of the emanation through a system of traps and driers into the measuring chamber of the recording instrument. The procedure used in the measurements has remained basically unchanged. The changes introduced have been concerned with improving the design of the measuring chambers and of the counting and recording apparatus.

Many authors[30,32-34] have used ionisation chambers of volume 200–600 cm^3 as detectors for measuring α-activity. The conditions for measuring thoron and actinon by means of an ionisation chamber have been examined in most detail by Voltz and Adloff[35], who give equations relating the rate of flow of carrier gas with the distance from the chamber to the emanation source and with the geometry of the apparatus used, and also discuss in detail the influence of traces of moisture and organic substances on the conditions of ionisation in the chamber. Traces of

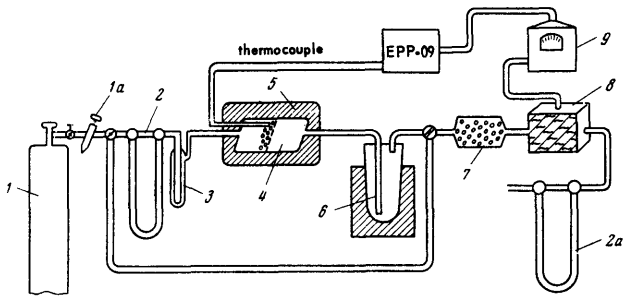


Fig. 1. Basic scheme for measuring the emanation of solids in a current of inert carrier gas:
1) cylinder containing inert carrier gas; 1a) fine control valve; 2, 2a) flowmeters to measure rate of flow of carrier gas; 3, 6, 7) system of traps for purifying and drying the gas being passed through; 4) reaction vessel containing test substance; 5) electric furnace; 8, 9) measuring chamber and recording instrument for determining and automatically recording the quantity of radioactive inert gas liberated.

organic substances generally influence the rate of collection of the ions formed, as a result of changes in their mobilities. This has been demonstrated by Roginskii and his coworkers[36]. Only hydrogen had almost no influence on the degree of ionisation, acetone vapour increased it, and isopropyl alcohol and propene decreased it by 20–40%. The use of ionisation chambers ensures high efficiency and high sensitivity (10^{-11}–10^{-13} c) in the measuring instruments used. A complicating feature in this instance is the need for fairly complicated electronic apparatus to measure the small ionisation current. Because of the high sensitivity of the electronic recording assemblies, thorough elimination of mechanical, electrical, and magnetic interference is necessary. Thus in recent years most workers[12,13,25] have begun to use scintillation counters with measuring chambers of different designs for measuring the α-activity of the emanation. This apparatus is more simple and stable in operation, and is almost unaffected by impurities in the carrier gas, but it requires slightly greater activities, since the efficiency of the assemblies used generally does not exceed 20%. At the same time, certain difficulties are encountered in the elimination of the "radioactive memory" of the scintillation measuring chambers.

Ordinary paired end-face counters are used to measure the β- and γ-activities of krypton, xenon, and other radioactive inert gases[26,37].

3. EMANATING POWER AS A FUNCTION OF THE SPECIFIC SURFACE OF SOLIDS

Although Kolovrat-Chervinskii[1] was the first to examine in detail only the conditions of liberation of emanation, Hahn[2,9,38] pointed out various possible promising applications of the emanation method to the study of physicochemical changes taking place in solids. Hahn first used the emanation method to study the surface of metal hydroxide gels and the changes in it during aging and dehydration[39]. Hahn[40] subsequently studied the change on heating occurring in the surface of $Fe_2O_3 \cdot xH_2O$ labelled with RdTh,

and noted the high emanating power of the original hydroxide due to the presence of an extensively developed internal surface in $Fe(OH)_3$ (Fig. 2). The initial decrease in the emanation, measured at the temperature of the experiment or at room temperature, was attributed to "aging", which masks the increase in emanating power due to the removal of water vapour, which entrains thoron. With careful heating or preliminary drying, the relationship between these processes can apparently be reversed. Above 400°C rapid crystallisation of the highly disperse gel takes place, with the evolution of a large quantity of heat, and this naturally leads to a decrease in surface area and to a more rapid decrease in the emanation. The subsequent increase in emanating power at 800°C was attributed[40] to the liberation of traces of water trapped inside the crystal lattice during precipitation of the gel from the colloidal solution. At 1000°C secondary ordering of the lattice is observed, leading to smoothing of the surface and an increase in the size of the particles of iron oxide formed. The temperature of the start of these processes, which can be determined accurately by the emanation method, was called the break temperature (*Knietemperatur*) by Hedvall[41]. The marked increase in the emanation above 1080°C is due to the increase in the mobility of the atoms or ions forming the crystal lattice. As pointed out by Tammann[42], for many powdered crystalline substances the temperature of the start of appreciable displacement of the atoms or ions in the lattice and increase in the rate of diffusion of the atoms between the crystalline solids in the case of a mixture of powders is close to 50–60% of the absolute melting point of the given substance, provided that no phase changes occur above this temperature (termed the Tammann temperature). Thus by studying the variation in the emanation with temperature it is possible to determine the Tammann temperature, above which reactions in the solid state become possible. The emanation method was used also[40] to study the behaviour of iron(III) oxide subjected to different treatments, and the temperature variation in the emanation of thorium oxalate and hydroxide was given for comparison. The emanation was not measured continuously, however, and the specific surface of the materials studied was not determined; these are unsatisfactory features of the work cited.

Hahn[2] also made an extensive study of the dependence of the emanation of various glasses on the state of their surfaces. Strassmann[43,44] observed an increase in the emanation coefficient for the barium salts of monobasic aliphatic acids with increase in the length of the carbon chain; for barium palmitate the emanation coefficient amounted to 100%. These substances, like various metal hydroxides with an extensively developed internal surface and hence a high emanation coefficient, found application in nuclear physics for the separation of short-lived decay products[45]. More detailed studies of the dependence of the emanation of inorganic salts and minerals on the state and "preservation" of their salts were made by Khlopin[46] and by Starik and Melikova[47]. These studies showed that the dependence of the emanation coefficient on the specific surface for various radon isotopes could give information on the form in which the radioactive mother substances were present in the solid; this in itself is very important for radiochemistry. An attempt to measure the surface area of cubic crystals by measuring the free path of emanation recoil atoms was made by Kurbatov[48] and later by Flügge and Zimens[49] on the basis of Eqns. (2)–(5) given above.

If radium isotopes yielding radon and thoron on radioactive decay are introduced into the specimen being studied, we have, from Eqn. (3),

$$\left.\begin{aligned} EV_{Rn} &= \left(\frac{R_{Rn}}{4} + \sqrt{\frac{D}{\lambda_{Rn}}}\right)\rho\frac{S}{m} \\ EV_{Tn} &= \left(\frac{R_{Tn}}{4} + \sqrt{\frac{D}{\lambda_{Tn}}}\right)\rho\frac{S}{m} \end{aligned}\right\} . \qquad (10)$$

The experimental values of EV and the recoil free paths R calculated from Eqn. (5) can be used to find the diffusion coefficient D and the specific surface S from the set of equations (10). Thus Strassmann[44], from the observed emanating power due to recoil E_0 and the length of the free path R, determined the specific surfaces for various specimens of barium salts, and Heckter[18] made the same determinations on powdered glass specimens. The use of the emanation method to determine the absolute value of the surface area and the diffusion coefficient for the atoms of the inert gas in the solid is restricted, however, by the inaccuracy of the equations used, as noted above.

Zhabrova, Shibanova (Sinitsyna), Roginskii, and Gordeeva compared the dependence of the specific surface and emanation coefficient on the temperature conditions and degree of dehydration of magnesium, thorium, and zirconium hydroxides[11,50]. The change in the same sense in these two characteristics of a solid (Fig. 3) leads to a linear relationship between them; this may also be true for a number of other metal oxides.

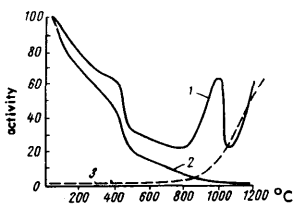


Fig. 2. Typical curves showing the change in emanation as iron hydroxide gel is heated: 1) activity during heating; 2) activity after heating; 3) activity on repeated heating.

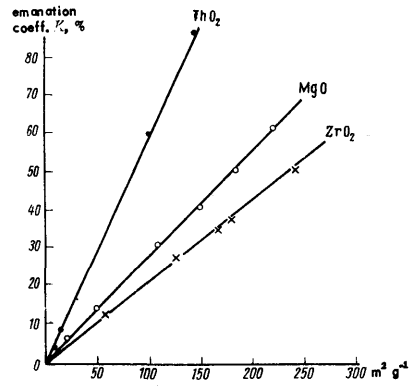


Fig. 3. Dependence of the emanation coefficient with respect to thoron on the specific surface for the oxides of thorium, magnesium, and zirconium.

4. THE USE OF RADIOACTIVE INERT GASES TO STUDY PHASE TRANSITIONS, CHANGES IN CRYSTAL STRUCTURE, AND THE MOBILITY AND DIMENSIONS OF PARTICLES

It can be seen from the work already cited that the emanation method makes it possible to follow changes in crystal structure and phase transitions occurring in salts and oxides when heated to high temperatures. Strassmann[44] observed a sharp increase in the emanation of barium sulphate between 700° and 800°C, when almost quantitative liberation of the emanation takes place in a short time interval. This temperature range corresponds to the Tammann temperature, at which breakdown and sintering of the salt begin. A more detailed study of barium sulphate and carbonate was made by Zaborenko and Babeshkin[32], who recorded the α-activity continuously. They confirmed the breakdown of the barium sulphate lattice in the range 650–800°C, but they also observed an increase in the emanation accompanying the polymorphic transformation of the salt above 1100°C. The emanation method was also used to determine the temperature of the two phase changes for barium carbonate. The enantiotropic transitions in barium carbonate were reported even earlier by Zimens[51,52], who used the emanation method to study the thermal behaviour of the alkaline-earth metals. The heating curves obtained in a current of carbon dioxide for calcium carbonate labelled with ThX showed changes in EV corresponding to the phase change from aragonite to calcite, the subsequent dissociation of the carbonate, and the breakdown of the structure of the calcium oxide formed.

Zaborenko and coworkers[12] showed, for the example of $KCl-CaCl_2$ and $CaO-Fe_2O_3$ (Fig. 4), that it is possible in principle to study equilibrium diagrams by the emanation method. The melting points of the eutectics on the emanation curves were determined from the temperatures of the maximal rates of decrease in emanating power. The observed temperature ranges corresponding to the phase transitions showed good agreement with published data.

In a study of phase changes in quartz, Sizmann and Rupp[53] made use of the absorption of radioactive krypton when the specimen was heated in a current of ^{85}Kr. It was observed that there was a marked increase in absorption of the gas at the point corresponding to the irreversible conversion of β-quartz into β-cristobalite (930° ± 15°C), whereas no such increase was observed for the reversible conversion of α-quartz into β-cristobalite (270°C) or of α-quartz into β-quartz (575°C). This difference was attributed to the difference in the phase transitions: in the first instance, a new crystal lattice was formed; whereas in the second, only rearrangement took place.

As noted above, the emanation method makes it possible to determine the temperature at which breakdown of the crystal lattice of a solid takes place. Schröder and Fricke[54] studied this problem, and also established the influence of preliminary aging of aluminium, iron, titanium, and tin oxides on the Tammann temperature and the shape of the emanation curves. They noted[54] that a sharp increase in the emanating power of the specimen always occurred at the temperature corresponding to the increase in mobility of the crystal lattice. For oxides previously heated at high temperatures, the start of the rising section on the heating curves is indistinct, and generally corresponds to a temperature which is higher than half the absolute melting point of the given oxide. For oxides which have not been subjected beforehand to treatment at high temperatures, the Tammann temperature corresponding to breakdown of the solid can be determined accurately from the inflection or minimum on the emanation curve, above which there is a prolonged increase in the liberation of emanation with rise in temperature (Fig. 5). An exception is aluminium oxide, for which the breakdown of the lattice does not give a sufficiently marked change in emanation; this was attributed to the low degree of ordering of its primary and secondary structures. When the emanation method is used to study processes taking place at high temperatures (1100–1200°C), allowance must be made, in accordance with Anderson's data[55], for the possibility of diffusion of ThX to the surface of the solid; this may lead to an increase in emanation which is not associated with a change in the specimen itself.

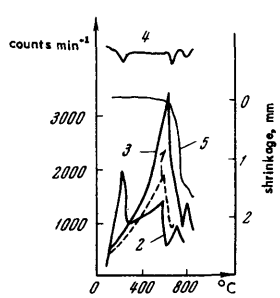


Fig. 4. Heating curves for mixtures of potassium chloride and calcium chloride activated with radiothorium. Emanation polythermals (mole % of $CaCl_2$): 1) 25; 2) 40; 3) 60; 4) differential thermal analysis curve (60); 5) shrinkage curve (60).

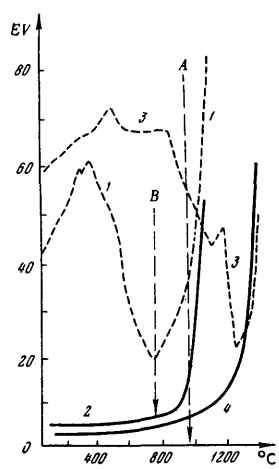


Fig. 5. Emanating power of: 1) γ-FeOOH; 2) α-Fe_2O_3 previously heated at 1000°C; 3) γ-AlOOH; 4) α-Al_2O_3 previously heated at 1000°C. A = 939°C (0.5 × m.p. of Al_2O_3); B = 685°C (0.52 × m.p. of α-Fe_2O_3).

A very interesting series of papers by Gregory and Moorbath[56,57] describe a study of the diffusion of thoron in barium stearate, and also during the dehydration and phase transitions of aluminium oxide. Unlike many other workers, these authors carried out a theoretical treatment of their results, and observed good agreement between experimental and calculated values. On the basis of the theory of emanation put forward by Flügge and Zimens[14,15], Gregory and Moorbath calculated the diffusion coefficient, activation energy, and mean particle size for aluminium oxide heated at various temperatures. From a study of the dependence of the emanating power of α-Al_2O_3 on the partial pressure of oxygen, they concluded[56,57] that a relationship exists between the degree of non-stoichiometry (defectiveness) of the aluminium oxide lattice and the rate of diffusion of thoron. The dependence of the emanating power on the defect nature of and quantity of non-stoichiometric oxygen in nickel oxide and zinc oxide containing added lithium and gallium oxides was studied by Shibanova and Zhabrova[58]. Thus, for example, a marked increase in the emanation (Fig. 6), evidently due to breakdown of the crystal lattice, begins with the original ZnO specimen (curve *1*) close to Tammann temperature (850–900°C). When lithium oxide is added, the increase in the quantity of emanation liberated from zinc oxide with rise in temperature is more clearly defined, and the temperature at which the ions of the crystal lattice begin to become mobile (the Tammann temperature) is lowered (curve *2*). The addition of the oxide of a metal with higher valency, in particular gallium oxide, leads to a marked decrease in the rate at which the emanating power of zinc oxide increases with rise in temperature (curve *3*). The effects observed are reversible, since repeated heating of the zinc oxide specimens containing the added oxides gives analogous results, with a slight decrease in the absolute magnitude of the emanation.

Thus the data obtained by the emanation method agree with the ideas regarding the defect nature of ZnO as due to the presence of interstitial Zn^+ ions, formed on the introduction of Li_2O into zinc oxide[59]. When Ga_2O_3 is added, the defect nature of the ZnO crystal lattice should diminish, leading to a decrease in emanating power. The same investigation showed that increase in the lithium concentration above 1 at.% does not lead to further increase in the emanation. This is probably due to the limited solubility of the added oxide in the zinc oxide being studied.

Yajima and coworkers[60], in a study of the diffusion of ^{133}Xe in natural and synthetic graphite specimens, mixed with uranium oxide and irradiated with neutrons, also observed a relationship between the rate of liberation of the radioactive inert gas and the density of dislocations in the specimens. The use of radiochemical emanation methods for the comparative study of defects produced during the irradiation of solids by various forms of ionising radiation evidently deserves attention. The few papers devoted to this problem, by Jech, Zhabrova, and Shibanova[29,61] and by Mundt and Richter[62], however, are purely qualitative.

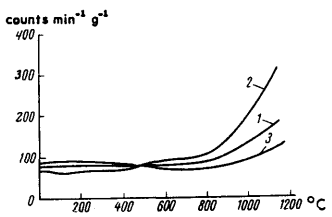


Fig. 6. Temperature dependence of emanating power for:
1) original zinc oxide; and zinc oxide modified with:
2) lithium oxide; 3) gallium oxide.

One of the narrower fields of application of this method is the use of emanation to study the physicochemical properties of metals and alloys[63]. In particular, Werner[64] followed the change in the internal deformation stress of zinc–barium alloys from the liberation of emanation.

5. STUDY OF THE THERMAL DECOMPOSITION AND REACTIONS OF SOLIDS BY EMANATION METHODS

The possibility of using the emanation method to observe phase transitions, the start of breakdown, and increase in the mobility of the atoms of the crystal lattice of solids led, as expected, to the extensive application of this method to study reactions in the solid state; interest in these reactions has increased considerably in the last ten years. This problem has formed the subject of several papers by Schröder and his coworkers[65–69], who studied the changes in the surface and the state of the crystal lattice of individual components of the reaction, and also the formation of chemical compounds, chiefly of the spinel type. They investigated the reactions involved in the preparation of iron–zinc and iron–cadmium spinels[66]. The indicator element was radiothorium, which was introduced into the specimens during the precipitation of highly disperse gels of basic zinc carbonate or zinc hydroxide and iron hydroxide. It was shown that basic zinc carbonate retains radiothorium much more strongly than does zinc hydroxide. The temperature curves for the emanation were used to find the decomposition temperature of basic zinc carbonate (~ 120°C) and the temperature corresponding to the start of appreciable displacement of the ions or atoms of the crystal lattice, ~ 800°C for zinc oxide. Study of the liberation of emanation as a mixture of zinc and iron oxides was heated established that spinel formation takes place in the range 700–800°C, the result being independent of the reactant containing the indicator element. Similarly, the increase in the liberation of emanation was used to determine the temperatures of dissociation, breakdown of the crystal lattice of the components, and spinel formation for mixtures of iron and cadmium oxides.

Later, Schröder[67,68] used the emanation method to study the thermal decomposition of aluminium and beryllium hydroxides. It was again confirmed that the emanation temperature curves obtained directly by heating (the *LT* curve) or by measuring the emanating power of rapidly cooled specimens (the *RT* curve) could be used to detect both chemical changes and allotropic transformations, and also changes in the active states, particularly in the specific surface. The opposite directions followed by the *LT* and *RT* curves at the start of heating (up to 150–160°C) were attributed to a combination of two processes: the liberation of adsorbed water led to an increase in the emanation, and recrystallisation of the hydroxide led to a decrease in the emanation. An interesting result was the detection[68] of an unstable state of beryllium oxide above 600°C, also observed with zinc oxide[65] at a temperature of ~ 25% of the absolute melting point. Hüttig[70]

considered that this temperature corresponded to the start of movement of the ions or atoms on the surface of the solid. The increase in emanation observed with γ-AlOOH, at 1150°C was attributed to the effect described by Hedvall [71], who predicted an increase in the mobility of the ions and the relative maximum of both physical and chemical activities in the transition state, in particular in the transition from γ-Al_2O_3 to α-Al_2O_3.

Schröder and Fricke [69] gave data on the thermal behaviour of a stoichiometric mixture of γ-AlOOH and $Be(OH)_2$, with coprecipitation of both aluminium hydroxide and beryllium hydroxide with radiothorium nitrate. With mechanical mixing of the hydroxides, the emanation curves obtained on heating the mixture differed little from the curves obtained for the starting materials. With jointly precipitated aluminium and beryllium hydroxides, however, the behaviour of the mixture on heating was quite different. When γ-AlOOH and $Be(OH)_2$ were heated separately, a decrease in emanation—due to recrystallisation—was observed at 900° and 800°C respectively whereas with the coprecipitated specimens the liberation of emanation increased sharply above 850°C, corresponding to the formation of beryllium aluminate, and the decrease in EV due to recrystallisation began only at 1150°C. All these results obtained by Schröder and his coworkers were confirmed by X-ray diffraction and analytical data, but unfortunately automatic continuous recording of the α-activity of the emanation liberated was not used, so that rapid processes might have been missed. The method used in the work cited was also used to study the processes involved in the transformation of copper hydroxide [72] $Cu(OH)_2 \rightarrow CuO \rightarrow Cu \rightarrow CuO$; an unambiguous interpretation of both reduction and oxidation processes was made possible by measurement of the quantity of emanation liberated.

The formation of zinc aluminate [73] and magnesium aluminate [74] was studied by the emanation method at a higher methodological level. It was suggested that it is possible to obtain a chemical compound by reaction in the powdered state, even when the lattice parameters of the components are dissimilar, if the mixture is heated sufficiently slowly [73]. In this instance, several intermediate states are observed, when the more mobile component envelops the granules of the passive component and subsequently diffuses into its lattice, with formation of the chemical compound [75]. The theories developed were verified for the example of zinc aluminate formation; the variation in emanation with temperature was recorded both for the individual oxides and for a mixture of zinc oxide and aluminium oxide (Fig. 7). The increase dEV/dt, where EV is the emanating power and t the temperature, is much more marked with zinc oxide than with alumina, owing to the greater mobility of the ions in the zinc oxide lattice. From a comparison of the emanation curves obtained by heating a mixture of inactive zinc oxide and aluminium oxide labelled with radiothorium (curve *6* in Fig. 7) and a mixture of inactive aluminium oxide and zinc oxide containing radiothorium (curve *5*), it was concluded that spinel formation took place above 850°C. [73] An unsatisfactory feature of this work [73] is the lack of data on the specific surfaces of the oxides and their mixtures, although, as shown by Schwab [76], the change in surface area during reactions of powdered components in the solid state may give additional information on the existence of various intermediate stages.

Curves giving the change in emanation when a mixture of barium and calcium carbonates labelled with ThX is heated, and also when Fe_3O_4 labelled with radiothorium is

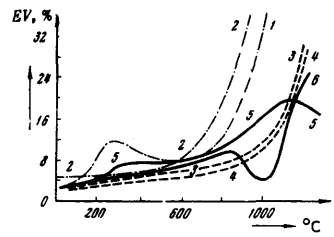


Fig. 7. Temperature dependence of the emanating power of oxides activated with radiothorium:
1) ground ZnO; 2) unground ZnO; 3) ground Al_2O_3; 4) unground Al_2O_3; 5) mixture of activated ZnO with inactive Al_2O_3; 6) mixture of activated Al_2O_3 with inactive ZnO.

heated in an atmosphere of oxygen, were given by Zimens [30], who also described one of the first assemblies for the automatic recording of rapid changes in the quantity of emanation being liberated. The change in the structure of iron oxides was studied in more detail by the emanation method in subsequent work by the same author [14]. The influence of the addition of SiO_2 on the thermal decomposition of iron hydroxide was studied by Götte [77], using the emanation method. Unfortunately, Götte did not give a sufficiently unambiguous interpretation of the results obtained.

Cook [78] used the emanation method to study the processes involved in the dehydration of iron and chromium hydroxides at various temperatures. A most interesting feature is the proposed separation of the emanating power into its components by determining its temperature dependence for specimens subjected to preliminary heating and treatment at a given temperature until a constant value of the emanation was established. This makes possible an indirect determination of the influence of temperature and pretreatment of the specimen on the recoil component of the emanation. Cook [78] correctly pointed out that reliable interpretation of the results is impossible without a detailed study of the changes in the individual components of the emanating power at various temperatures, and allowance for possible errors in the determination of the apparent emanating power; this was also pointed out by Zimens [14].

The decomposition of the hydroxides of zinc, nickel, magnesium, aluminium, zirconium, and thorium over a wide temperature range has been studied simultaneously by the emanation, thermographic, and surface gas labelling methods [11,23]. With all the systems studied, the maximum emanating power coincided almost exactly with the onset temperature of the endothermic effect due to dehydration, determined thermographically. In the zirconium hydroxide–oxide system (Fig. 8), as in the system formed by heating thorium hydroxide, a second emanating power maximum is observed at 400°C. The thermogram for zirconium hydroxide shows a marked exothermic effect at the same temperature. This maximum is due to the crystallisation of previously formed amorphous zirconium dioxide, as has been confirmed by X-ray diffraction studies. The characteristic analogy between thermographic analysis and the emanation method has also been demonstrated in a study of the phase changes in manganese dioxide [79]. The unamibiguous nature of the results obtained

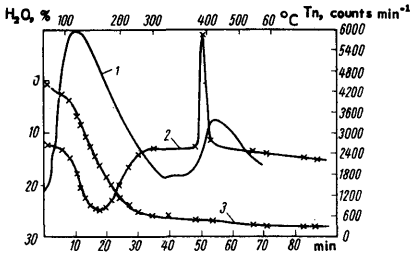


Fig. 8. Curves for zirconium hydroxide: 1) emanation curve; 2) thermogram; 3) change in weight of specimen.

on studying the dehydration of a wide range of metal hydroxides by several methods indicated[79] that the emanation method is applicable also to systems whose oxides do not form true substitutional solid solutions with the added radioactive isotope. The regular distribution of the indicating element was undoubtedly due to the penetration of recoil atoms formed by the disintegration of the radioactive mother element added, and to the high degree of dispersion of the materials studied (5×10^{-6}–5×10^{-5} cm).

Combined investigations of the thermal decomposition of thorium nitrate, thorium oxalate, and barium chloride by emanation, thermogravimetric, and dilatometric methods have been made also by Bussière[13] and by Zaborenko[12]. Particular attention was paid to the methodological aspects of the problem and to the design of assemblies which made possible simultaneous measurement of all the characteristics being studied (the emanation, change in weight of the specimen, and temperature); this eliminated the possibility of errors associated with differences in experimental conditions.

In the study of processes taking place in solids, a knowledge of their kinetics is extremely important. The emanation method is one of the few methods which make it possible to follow changes in structure and surface directly during a topochemical process at a given temperature. The first attempt to use the emanation method to study the kinetics of the formation of calcium silicate from silicon dioxide and calcium oxide was made as early as 1937. Jagitsch[80] published curves giving the time dependence of the liberation of emanation at a given temperature, and put forward a kinetic equation for the change in emanation with time. An unsatisfactory feature of the work was that direct measurement of the emanation was not carried out continuously during the reaction, and only one of the reactants—the silicon dioxide—contained the indicator element. Characteristic "kinetic" curves, giving the change in emanating power with time during dehydration of the hydroxides of magnesium, zinc, thorium, zirconium, and aluminium over the range 100–1000°C, were studied by Roginskii, Zhabrova, and Shibanova (Sinitsyna)[11,81]. The specimens were heated at a definite temperature for a time sufficient to ensure almost complete conversion of the hydroxide into the oxide. The percentage decomposition of the original hydroxide was determined in parallel by weighing at measured time intervals. It was established that the kinetic curves pass through a maximum corresponding in almost all instances to a fairly high percentage decomposition (~ 75–80%). With increase in the temperature of decomposition, the maximum was displaced towards the ordinate axis and at the same time a sharper decrease in activity with increase in the duration of heating was observed. This characteristic form of the kinetic curves giving the time dependence of the emanating power at the temperature of the experiment can be attributed to the combined effects of dehydration, leading to an increase in the specific surface and hence in the emanation of the specimen, and thermal sintering, leading to a decrease in emanation.

6. THE LIBERATION OF RADIOACTIVE INERT GASES DURING CHEMISORPTION AND CATALYTIC PROCESSES ON SOLID SURFACES

Chemisorption and catalytic processes are accompanied by changes in the surface of the catalysts, the formation of surface compounds, blocking of the surface by the reaction products, etc. The use of the emanation method, which is extremely sensitive to all forms of surface and structural changes in solids, to the study of the state of the surface of a catalyst during chemisorption and catalysis is of interest in this connection. Unfortunately, this problem has as yet formed the subject of only a few studies, and these are purely qualitative in character.

Thus Fricke and his coworkers[82,83], in a study of the dependence of the emanating power of magnesium, aluminium, and zinc oxides and γ-Fe_3O_4 on the conditions (temperature, duration of heating, and gaseous medium) of preparation, density, and particle size, observed an increase in the emanation of active magnesium and aluminium oxides as a result of the adsorption of water vapour and carbon dioxide; this was attributed to breakdown of the secondary structure of the oxide. However, these workers did not compare the changes in emanating power with the sorption properties of the magnesium oxide.

Using the method of surface gas labelling described above, Jech[84] established that about half of the radon introduced is liberated from the surface of a platinum catalyst when a hydrogen–oxygen mixture is passed over the catalyst. It was also found that removal of the gas marker takes place chiefly as a result of the reaction of hydrogen with chemisorbed oxygen. An analogous phenomenon is observed in the adsorption of water vapour on platinum at room temperature[84]. It is suggested that this method might be used to detect the location and distribution of active sites on a catalyst surface.

Zhabrova et al.[36] have studied the emanating power of various oxide catalysts (ThO_2, ZrO_2, MgO, and ZnO containing added Na_2O and $ZnSO_4$), labelled with radiothorium, during the chemisorption of the gases and vapours formed in the decomposition of isopropyl alochol. The results obtained show that the physical sorption of gases and vapours of various types has almost no influence on the emanating power of thorium and zirconium oxides. The chemisorption of acetone, water, isopropyl alcohol, and carbon monoxide on the oxides of thorium, zirconium, nickel, and magnesium leads to marked changes in the emanation of these oxides. The original values of the emanating power are generally restored only by regenerating the catalyst in a current of air at 400–500°C. It was suggested that the change in the emanating power of oxide catalysts during chemisorption and catalytic processes may provide a unique criterion indicating the formation of surface chemical compounds and, as can be seen from data on the change in the emanation of modified zinc oxide

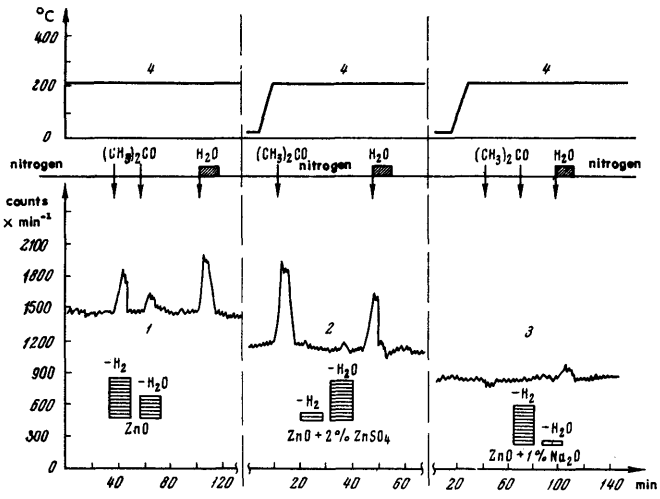


Fig. 9. Emanating power during the chemisorption of acetone and water for:
1) zinc oxide; 2) ZnO + $ZnSO_4$; 3) ZnO + Na^+; 4) temperature of the experiment. The lower diagrams represent schematically the relative proportions of dehydration and dehydrogenation for the various zinc oxide specimens.

specimens during the chemisorption of acetone (Fig. 9), characterising to some extent the strength of the bond formed by the chemisorbed substances with the surface. The results obtained by the emanation method must naturally be subsequently combined with kinetic data on the chemisorption and the characteristics of the catalytic activity of the catalysts studied.

The above results obtained by a large number of workers show the promising possibilities offered by the use of emanation methods in the study of solid-phase topochemical reactions, changes in specific surface, breakdown and thermal sintering, and crystallisation and phase transitions in solids.

It is fairly difficult to obtain radioactive materials with a high specific activity and a minimum concentration of impurities, and also to develop methods of introducing the original radioactive materials, for example in the study of almost insoluble polymers. It is also necessary to make allowance for the characteristic features of each version of the emanation method, described above.

The high sensitivity of the emanation method makes it possible to detect fine differences in the crystal structures of solids, for which X-ray diffraction does not always give sufficient information. At the same time the emanation method is a sensitive analogue of differential thermal analysis, and makes it possible to detect crystallisation and phase changes accompanied by extremely small thermal effects, which are almost undetectable by the latter method.

The method of ion bombardment has recently begun to be used in the study of the mechanism of the diffusion of inert gases in oxides and metals[85-87]. This new approach, making it possible to determine the activation energy of diffusion[86,88] and to study the low-temperature diffusion of radioactive inert gases, which depends on the previous treatment of the surface[87], undoubtedly deserves further development.

It is also of interest to use both the emanation method and the introduction of radioactive inert gases by ion bombardment for the solution of a number of problems related to the state of the active surface of catalysts at various stages in their preparation and application. In most instances, emanation methods must be combined with other methods—sorption, kinetic, X-ray diffraction, thermographic, etc. —and may then give new data in the study of surfaces, structures, and chemical reactions taking place in the solid phase.

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PRIMARY PRODUCTS OF THE RADIOLYSIS OF WATER AND THEIR REACTIVITY

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INTRODUCTION

It is well known that radiolytic transformations in dilute aqueous solutions result from reactions of the solutes with products of the radiolysis of water†. Until recently, research workers considered that these products were the H atom, the OH and HO_2 radicals, molecular hydrogen, and hydrogen peroxide. The latest stage in the development of the radiation chemistry of water and aqueous solutions has been marked by the discovery of yet another primary product of the radiolysis of water—the hydrated electron e^-_{aq}.

In recent years, considerable progress has also been made in the study of the kinetics of radiation reactions in aqueous solutions. The absolute values of the rate constants of many reactions involving intermediate products

† The radiolysis of water and aqueous solutions has been examined in detail by a number of authors [1-4].