JOURNAL OF MATERIALS SCIENCE 4 (1969) 919–927

Application of Inert Radioactive Gases in the Study of Solids*

Part 1 *Classical Emanation Method and Surface Labelling Method. Apparatus and Comparison of Methods in the Study of Ferric Oxide and Thorium Oxalate*

V. BALEK
Department of Radiochemistry, Charles University, Prague, Czechoslovakia

Received 24 March 1969

Two methods based on the release of inert radioactive gases were used to study processes taking place on heating of solids: the classical emanation method and the surface labelling method. The results obtained with the use of these methods are compared for the study of (a) substances which do not change chemically when being heated in the temperature range studied (e.g. α-Fe_2O_3), (b) substances in which dehydration and thermal decomposition takes place (e.g. $Th(C_2O_4)_2.6H_2O$).

For substances which exhibit chemical and structural changes when being heated, results of investigation by means of the two above mentioned radiochemical methods are compared with DTA and dilatometric data, obtained under identical experimental conditions. Apparatus permitting simultaneous measurement of the release of two radioactive gases, DTA and dilatometric measurement is described.

From the substances which do not change when being heated, values of the activation energy of diffusion of inert gases incorporated by different ways are discussed. The advantages of the emanation and surface labelling methods over other physico-chemical methods are given and the possibilities of their application for the study of processes taking place in solids on heating, are described.

1. Introduction

Methods utilising inert radioactive gases for the study of solids are based on the measurement of the release of radioactive inert gas atoms which have been previously incorporated in the solids. The classical emanation method, which employs natural radioactive inert gases (radon isotopes), was developed by Hahn [1], Zimens [2], Starik [3] etc. In this method, incorporation of the inert gas is usually carried out by co-precipitation of trace amounts of the mother isotope of the gas (Th^{228} or Ra^{224}) from a solution in the course of preparation of the substance studied. The inert radioactive gas formed in the substance as a consequence of radioactive disintegration does not react with the substance, being released from the crystal lattice only as a consequence of physical-chemical processes taking place in this substance. Reviews of applications of the emanation method are given by Hahn [4], Wahl and Bonner [5] and recently by Zhabrova [6] and Balek [7].

It is true that in post-war years, interest in this method waned, although recently it has again been growing in connection with new problems in solid state physics and chemistry. New applications are being found for the emanation method and improved apparatus is available for measuring the radioactivity of gases. Recently, different variants of this method were suggested [7], also using inert gases produced by nuclear reactions in nuclear reactors. This paper [7]

---

*The experimental part of this study was carried out during the author's stay at the Radiochemistry Dept, Moscow State University.

described the use of inert gas radioisotopes (Xe^{133} and Kr^{85}) formed by uranium fission [8], and nuclear reactions of the (n, p), (n, α) or (n, γ) types [9-11]. The energy of Rn^{222} recoil as a product of Ra^{226} disintegration has been employed to incorporate radon into powdered substances [12]. Diffusion of Kr^{85} at high temperatures and pressures was used in the production of radioactive "kryptonates" of various substances [13]. Many authors [14–16] have also used accelerated inert gas ions for introducing these gases into solids. The result is a volume or surface-labelling of the solids concerned, which is dependent on the energy of ionic bombardment of the inert radioactive gas used.

Radioactive inert gases, incorporated in differing ways, were recently used to study the properties of refractory and nuclear ceramic materials [17], glass-like materials [18], inorganic polymers [19] and organic polymeric materials [20, 21].

The purpose of this paper is to describe apparatus used for the simultaneous measurement of both alpha-radioactive emanation and beta-radioactive inert gas isotopes (e.g. Xe^{133}, Kr^{85}), and at the same time for differential thermal analysis (DTA) and dilatometry of the same sample under identical conditions. The results of these methods will be mutually compared for materials exemplifying a substance which does not change chemically on being heated (e.g. α-Fe_2O_3) and a substance in which thermal decomposition does take place (thorium-oxalate hydrate). In conclusion some recommendations are given for the use of these methods in the study of solids.

2. Experimental

2.1. Incorporation of Inert Gases into Solid Substances

2.1.1. The Classical Emanation Method [*1*, *2*]

The substances studied were activated in the process of their preparation by a solution of Th^{228} in HCl, in such a way as to achieve an activity of the sample of 0.01 μCi per gram of the substance. The average crystallite size of the substances studied were 2 μm (for ferric oxide) and 10 μm (for thorium oxalate).

2.1.2. The Surface Labelling Method

A scheme of the glass apparatus proposed by Jech [16] is shown in fig. 1.

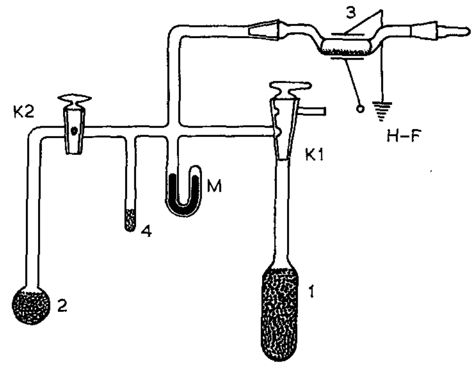


Figure 1 Scheme of apparatus for surface labelling of solid samples by inert gas. 1-adsorption pump, 2-inert radioactive gas reservoir, 3-sample cell, 4-metallic calcium for gas purification, HF-high-frequency field generator, M-vacuometer, K1, K2-valves in glass apparatus.

The sample to be activated is placed in the glass cell [3] connected to the vacuum apparatus. When a vacuum of 10^{-2} torr has been achieved by means of an adsorption pump [1] (the pressure being measured by the vacuum gauge, M), a small amount of the radioactive gas is introduced into the cell above the sample: the gas is obtained by desorption from the reservoir [2]. The final pressure after desorption is usually 0.05 to 0.5 torr. Moreover, electrodes are applied to the cell and with a high-frequency transformer (Tesla, Czechoslovakia) an electromagnetic field of a maximum voltage of 15 kV is formed for a period of 0.1 to 3.0 sec. The gas ions formed are accelerated and, on incidence at the sample surface, penetrate to a depth of 10 to 30 Å [16]. The penetration depth of the ions depends on their energy, as well as on the crystal structure and mass of the substance bombarded. When labelling has been completed in this way, the remaining radioactive gas is adsorbed again at liquid nitrogen temperature on charcoal in the reservoir [2], and after having been purified, if necessary, it is ready to be re-used.

2.1.3. Measurement of the Radioactivity of the Gas Released from the Sample

A sample of roughly 100 mg, labelled with the inert gas, is placed in a quartz crucible in a metal ("thermographic") block fitted with three openings (see fig. 2). Apart from the activated sample, a thermographic standard (Al_2O_3) and a sample for dilatometric measurement are placed in the remaining two openings. This arrangement [22] makes possible emanation, DTA and dilatometric measurements simultaneously and under

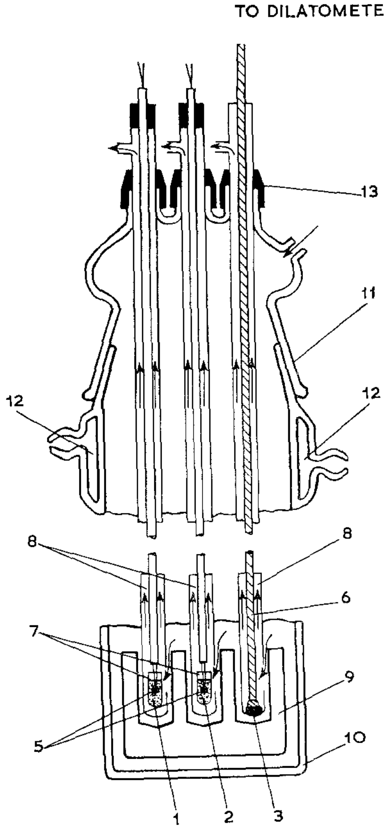


Figure 2 Reaction vessel for the emanation apparatus. 1 – activated sample, 2 – thermographic standard, 3 – sample for dilatometric measurements, 5 – thermocouples, 6 – quartz rod of dilatometer, 7 – quartz crucibles for samples, 8 – holder tube, 9 – metal block, 10 – quartz reaction vessel proper, 11 – ground glass joint, 12 – cooler, 13 – rubber seal.

absolutely identical conditions. The thermographic block is heated in an electric furnace: with a linear rate of temperature rise, a rate of 8 to 10° C per min is usually used, corresponding to the optimum for emanation as well as DTA measurement. The temperature was measured by means of a chromel–alumel thermocouple immersed directly in the sample.

The radioactive gas released from the solid substance is carried by a carrier gas stream (air or nitrogen) at a flow-rate of 300 ml/min into cells for gas radioactivity measurement. A device has been designed (fig. 3) to permit simultaneous recording of the alpha-activity of radon and beta-activity of xenon used in the surface-labelling method. To measure the alpha-activity of the emanation, a scintillation counter is used; this utilises ZnS as scintillator and has a photomultiplier connected to a counting-rate meter.

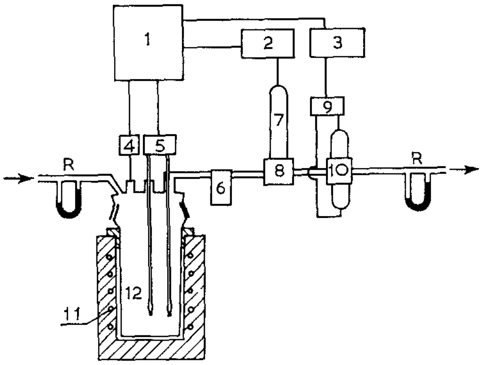


Figure 3 General scheme of emanation apparatus. 1 – recorder, 2 – counting-rate meter for alpha-radiation, 3 – counting-rate meter for beta-radiation, 4 – dilatometer detector, 5 – thermocouples, 6 – gas drier, 7 – photomultiplier, 8 – alpha-scintillation chamber, 9 – cathode follower, 10 – chamber for measuring beta-activity of gases, 11 – electrical furnace, 12 – reaction vessel, R – flowmeter.

The beta-activity of xenon is measured by coupled Geiger-Müller-tubes with a counting-rate meter.

This method, in which radioactivity of the emanation is measured with the use of a scintillation chamber, has a number of advantages compared to equipment with an ionisation chamber [6, 23]. This is mainly due to the fact that ionisation is influenced by the chamber filling, gas humidity etc, while in the scintillation apparatus any gas whatever may be used as the emanation carrier. This is especially valuable when reactions in solids are to be studied in different media. The efficiency of the scintillation counter employed was 16%.

Curves of the relationship between radioactive gas release and the time, were recorded together with temperature rise curves, DTA and dilatometric curves.

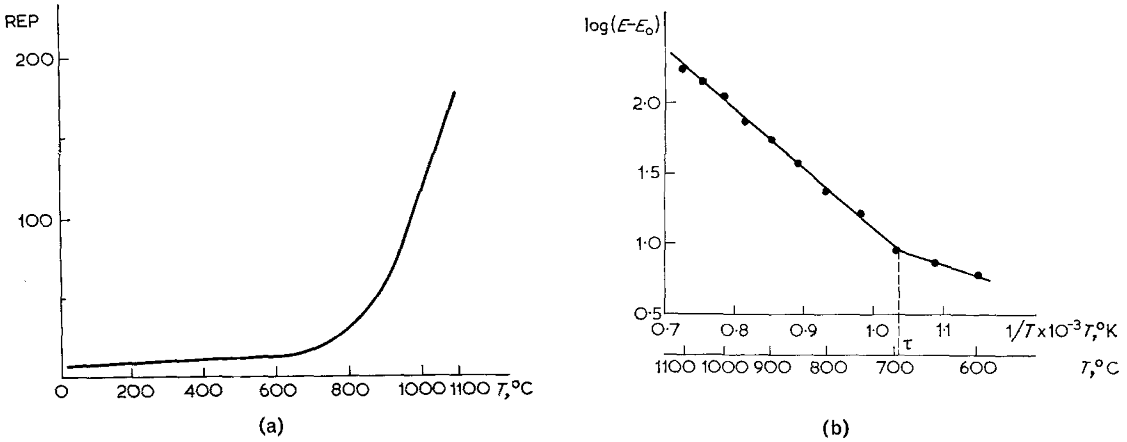
The maximum statistical error of activity determinations was not more than ± 5%. To measure dilatometric changes, a quartz dilatometer with detector based on the differential transformer principle was employed. The sensitivity of the measurement was 4 μm per 1 cm scale length, the error being ± 1%. The sensitivity of the thermocouples in differential arrangement was 2° C per 1 cm scale length, with temperature readings precise to ± 0.5%.

A good reproducibility of results was achieved with the apparatus described above. Nonetheless the curves shown in this communication are each the result of at least three replications.

3. Results and Discussion

3.1. Ferric Oxide

The temperature-dependence of the rate of emanation release from ferric oxide* is shown in fig. 4.



(a) (b)

Figure 4 Emanation curve of ferric oxide obtained by decomposition of basic iron carbonate by means of heating to 900° C (a) in $E = f(T)$ co-ordinates, (b) in $\log(E - E_r) = f(1/T)$ co-ordinates E_r being the value of E at room temperature.

Flügge and Zimens [24] have shown by theoretical consideration, that if no chemical or physical conversions take place in a solid substance, the dependence of the emanation power E on temperature for a small crystallite of the substance concerned will be defined by the exponential function:

$$E = E_r + E_d = \frac{r_0}{4}\frac{S}{m}\rho + \sqrt{\frac{D_0}{\lambda}}\frac{S}{m}\rho\exp\left(-\frac{Q}{2RT}\right) \qquad (1)$$

where E_r = part of emanation released due to the recoiled emanation atoms, E_d = diffusion part of the released emanation atoms. r_0 = range of recoiling atoms, S = specific surface, m = crystallite mass, D_0 = pre-exponential term in the expression

$$D = D_0 \exp(-Q/RT)$$

where D is the diffusion constant, Q = activation energy of diffusion of the emanation in the solid, R = gas constant, ρ = density, λ = decay constant of emanation, T = absolute temperature.

The emanation curve may alternatively be constructed on a semilogarithmic scale, i.e. in the form of $\log E_d = f(1/T)$ (curve 4b), E_d being evaluated from E (emanation power at the relevant temperature) and E_r (value of E measured at room temperature):

$$E_d = E - E_r\dagger$$

In the curve 4b two sections may be distinguished, a low-temperature section with a low value of $\partial \log E_d/\partial T$ and a high-temperature section with a larger value of $\partial \log E_d/\partial T$. The discontinuity on the curve lies at 693° C, i.e. 0.53 of the absolute melting temperature of ferric oxide. With other crystalline, powdered inorganic substances the discontinuity on the curve also occurs at a value corresponding to 0.5 to 0.6 of their absolute melting temperature [24]. Tammann [25] demonstrated that this temperature (the "Tammann temperature") corresponds to the beginning of sufficiently intensive motion of atoms or ions in the crystal lattice, to cause effective diffusion rate in the solid. Based on the classical emanation method it is therefore possible to determine this temperature range, which is of great practical importance, since above this approximate temperature it is possible that solid state

---

*Fe_2O_3 was prepared by thermal heating of basic carbonate of iron at 900° C as described in [27]. Specific surface area being 2 m^2/g.

†Specific surface of ferric oxide studied changed from 2 m^2/g to 1 m^2/g during heating in the temperature range 20 to 1100° C. E is taken as approximately constant in this temperature region because it is much smaller than E at higher temperatures.

reactions can occur by diffusion mechanisms.

The slope of the individual sections of the curve 4b (Arrhenius plot) can be used to determine the activation energy of the emanation process in a solid for a specified temperature range. The activation energy of radon-diffusion in ferric oxide was evaluated as $Q = 15 \pm 3$ kcal/mol in the range of 600 to 700° C and $Q = 40 \pm 5$ kcal/mol in the range of 850 to 1100° C.

These values agree very well with the emanation data reported by Cook [26] (8.4 and 42.2 kcal/mol respectively) and also with values of Q obtained by Lindner and Matzke [12] from the measurements utilising recoil incorporation of radon. They obtained the knee on the Arrhenius plot at about 660° C and activation energy should be equal to 12 kcal/mol below and 45 kcal/mol at the knee temperature.

As the author will show in another communication [27] the activation energy of the diffusion process of emanation in ferric oxide depends on the manner of preparing this oxide.

The dependence of the release rate of radioactive xenon incorporated into Fe_2O_3 (haematite) by means of ionic bombardment is given in fig. 5. The shape of the graphical representation of this relationship was derived independently by Redhead [28], Kelly and Matzke [29] and Carter [30]. They have shown that for single-jump diffusion with a discrete activation energy Q, the experimental data generally involve peaks, the maxima (T_m) of which are governed mainly by Q's; one exception is single-jump diffusion with a uniform spectrum of Q, where there is no maximum. It was shown [28] that the shapes of curves depend markedly on the type of diffusion though they are quite sensitive to variations in the heating rate β_{min} or the penetration range R_m.

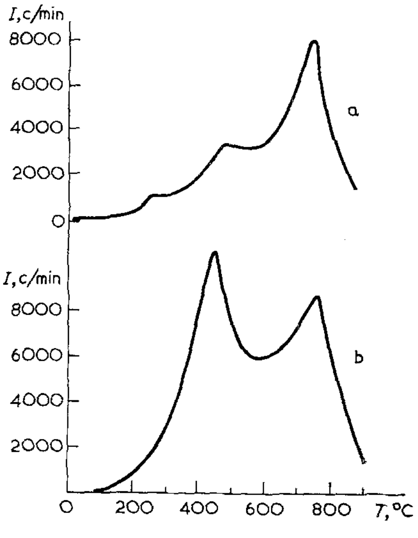


Figure 5 Temperature dependence of release rate of xenon, incorporated in ferric oxide by the surface labelling method. Duration of ion bombardment in high-frequency field (TESLA) (a) 1 sec, (b) 5 sec.

To obtain the parameter of T_m for the different geometries and types of diffusion Kelly and Matzke [29] have used the theory for constant temperatures. The derivation of the (Q/T_m) formulae for various depth distributions and types of motion is discussed fully in [29], the results used in the present work being contained in tables 2 and 3 of [29]. Under a condition of linearly increasing temperature basic expressions for the Q/T_m was derived:

$$Q/T_m \approx A + 4.6 \log_{10} T_m/R_m^2 . \beta_{min} + 4.6 \log_{10} D_0/(3 \times 10^{-1}) \quad (2)$$

where Q is in cal/mol, β_{min} is in ° C/min, D_0 is the pre-exponential factor of the diffusion rate constant in cm²/sec and R_m is the median range of the ions involved in units λ, which is the mean atomic spacing. A is the numerical factor depending on the geometry and type of diffusion.

For the single-jump diffusion with discrete Q this relation can be written as

$$Q/T_m \approx 69.5 + 4.6 \log_{10} T_m/R_m^2 \beta \pm 4.6 \quad (3)$$

assuming $D_0 = 3.10^{-1+1}$ cm²/sec and taking R_m equal to 1.

For the ferric oxide studied here, three peaks appear on the curve of xenon-rate release as a function of temperature (fig. 5) owing to the existence of several processes which influence the release of xenon from the ferric oxide on heating.

The peak at 230 to 250° C probably relates to the release of xenon captured close to the surface or on point defects (so called "damage diffusion" [32]). The activation energy of this process, evaluated by means of relation 3 is equal to $Q = 36 \pm 4$ kcal/mol.

The second peak, at 460 to 480° C, may be ascribed to conversion of the quasi-amorphous (metamict) state of the oxide caused by ion bombardment in a thin surface layer to the crystalline state. Proofs are given by Jech and Kelly [32] and Matzke [33]. This explanation is verified in our experiments by the fact that the magnitude of this peak increased substantially when accelerated ions were allowed to interact with the surface of the substance for a prolonged period of time (fig. 5b), i.e. by increasing the radiation dose. The activation energy of gas release due to this conversion, as calculated from the Jech and Kelly theory [31], is equal to 56 ± 4 kcal/mol.

Normal volume diffusion is expected to start at about 0.5 absolute melting temperature ~ 650° C for Fe_2O_3) or at the temperatures of onset of self-diffusion (about 785° C for Fe in Fe_2O_3 [34] and 685° C for O in Fe_2O_3 [35] - calculation of the onset temperatures are given in [32].) Therefore the third peak with the maximum at 780° C (curves on fig. 5) could well represent normal volume diffusion of the gas. For this process, an activation energy of $Q = 78 \pm 5$ kcal/mol was evaluated.

Our results obtained for diffusion of Xe in ferric oxide (Xe having been incorporated by ion bombardment) are in good agreement with the results of Matzke [36] and with data published by Ichiba [37], who used the recoil energy of xenon as uranium fission products to incorporate it into the sample.

Similar effects were also observed on α-Al_2O_3 and α-Cr_2O_3 (also oxides of the corundum type) by Kelly and Jech [32] and Matzke [33, 36].

We should also mention that with the classical emanation method as well as with the method which uses ionic bombardment to incorporate an inert gas, the gas atoms can cause radiation damage. In the first case the recoiled atoms have an energy of roughly 85 keV, in the second case the ions are accelerated to an energy of up to 1 keV (in the case of labelling by the method proposed by Jech [16]) or up to 80 to 100 keV (using various ion sources [33]). In both cases, the crystal lattice is damaged by radiation. This damage during ionic bombardment (mean doses are 10^{12} to 10^{16} ions/cm^2) is far greater especially in surface layers; this leads to the formation of an amorphous layer. On experimental curves, therefore, peaks appear corresponding to the annealing of point defects or the transition of the crystal lattice from the damaged to the normal state.

Doses of radiation caused by recoiled radon atoms vary from 10^4 to 10^8 ions/cm^2 when the classical emanation method is used [33]. These are doses which do not usually cause radiation damage with inorganic substances, especially those of the cubic type. Any damage is local and no layer of new damaged phase is formed.

Comparing Q-values obtained with the emanation method and with the surface labelling method, we find that the activation energy of the corresponding processes differs. The cause of this difference probably consists in the character of the methods. The emanation method, in contrast to ion bombardments at low energies, is sensitive to grain-boundaries. Moreover, in the case of the emanation method the radioactive gas is constantly produced in the substance, and therefore the activation energy of diffusion of the emanation, calculated from the Arrhenius relationship, corresponds to a state in which the individual diffusion stages are not resolved. On the other hand, according to the theory of Kelly and Matzke [29] for diffusion of gas atoms incorporated into solids by means of ionic bombardment, Q-values obtained for individual diffusion stages (e.g. damage diffusion, volume diffusion etc.) are resolved. For example, at the temperature at which volume diffusion takes place, the gas which was originally located in sites from which it could diffuse by the mechanism of surface or damage diffusion, has already been released.

3.2. Thorium Oxalate, $Th(C_2O_4)_2.6H_2O$

Bussière [38] studied this substance by means of the emanation method, DTA and thermogravimetry (TGA) using apparatus which allowed all three measurements to be made simultaneously and independently. We therefore thought it interesting to carry out emanation experiments together with a release of radioactive xenon incorporated by means of ionic bombardment. The apparatus employed permitted recording of DTA curves at the same time.

Fig. 6 shows the results of thorium oxalate decomposition studies in air. The phenomena shown on the emanation curve correspond to three processes: the first, at a temperature of 40 to 220° C, is caused by step-wise dehydration of the hydrate [39, 40]. In this temperature range, the DTA curve shows two endothermic effects which correspond to serial elimination of four and then one water molecule. On the emanation curve these processes are imperfectly resolved, this fact may be related to the small degree of difference between the structures of thorium oxalate dihydrate and monohydrate. The authors [41] showed that the substance studied has a finely crystalline structure at 150° C, which differs substantially from the initial structure,

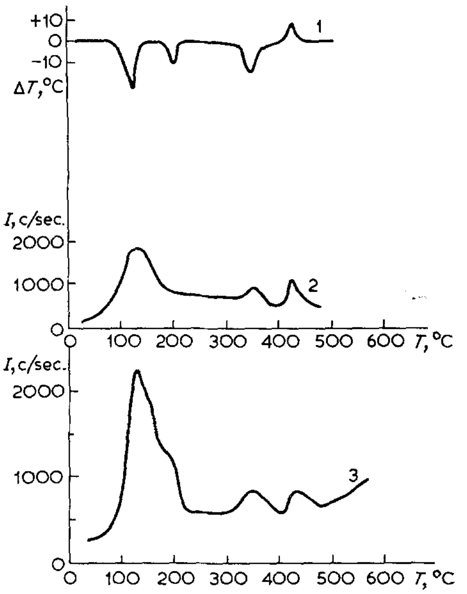


Figure 6 Results of a thermal study of thorium oxalate. $6H_2O$. 1 – DTA curve, 2 – temperature dependence of xenon release, 3 – emanation curve.

while on heating from 150 to 250° C only slight structural changes take place. The flat peak on the emanation curve in the temperature range of 300 to 400° C and the corresponding effects on the DTA curve are due to stepwise decomposition of thorium oxalate monohydrate. According to thermogravimetric measurements [39] dehydration is accompanied by decomposition of the oxalate to ThO_2. Some authors supposed [42, 43] that thorium carbonate is an intermediate in this process of decomposition.

Our results agree well with Bussière's data [38], however in contrast to Bussière's interpretation of the cause of the last peak on the emanation curve at 400 to 450° C, accompanied by an exothermic effect on the DTA curve, we suppose that this peak is related to conversion of the amorphous thorium oxide formed in the course of thermal decomposition, to the crystalline oxide. This explanation is confirmed by the results of X-ray analysis, according to which a sample, when heated to 370° C, contains amorphous material of the composition ThO_2, while in samples heated to 430° C a crystalline phase of thorium oxide appears. Since this effect also occurs on DTA curves recorded in an atmosphere of gaseous nitrogen, the cause of this effect cannot be the oxidation of carbon monoxide formed in the decomposition.

The curve of the rate of the release of xenon which had been incorporated into the sample by ionic bombardment (fig. 6, curve 2) and recorded together with the emanation curve, fully confirms the above reaction scheme. Our results agree well with the work of Jech, Zhabrova, Roginskij, and Shibanova [40]. The results show, that on decomposition of thorium oxalate, as in the case of thorium hydroxide [44], the amorphous oxide is formed first, converting on further heating to crystalline ThO_2.

4. Conclusions

The classical emanation method as well as the surface labelling method are based on studying the rate of release of a radioactive inert gas from solids. Variations in the rate of the inert gas release from solids demonstrate, in an indirect manner, all the processes which are related to changes in the magnitude of the surface concerned or of conditions for diffusion of the inert gas in the solid. These include solid chemical reactions (dehydration, thermal decomposition, synthetic reactions), polymorphic transformation, conversions of metastable amorphous structures into crystalline ones, changes in the concentrations of defects in the crystal lattice etc. In a number of cases, these changes may be followed directly from the shapes of the emanation curves. For fuller interpretation, however, other physico-chemical methods are frequently employed, e.g. DTA, TGA, dilatometric measurements, X-ray analysis etc.

The emanation method has a number of advantages over the others: under dynamic experimental conditions it makes possible structural changes of substances to be studied even when these changes are not related to a thermal effect (e.g. phase transformations of the II order [45]). In other cases, when finely crystalline or amorphous phases are formed, the emanation method is substantially more sensitive than X-ray analysis [46].

From emanation curves, the activation energy of the process of inert gas diffusion in the substance may be calculated; this activation energy depends on the state of the crystal lattice.

In the case of the classical emanation method the sample contains the mother isotope Th^{228}, which is a constant source of short-lived emanation (Rn^{220}). In the case of the surface labelling method, the amount of gas incorporated into the substance is limited, decreasing constantly on heating. When the entire amount of incorporated gas is liberated before the studied effects have taken place at an elevated temperature, the sample is generally cooled and incorporation of the gas is repeated [46]. Since in this case the gas is incorporated into the surface layers of the sample, its maximum rate of release is achieved precisely at the moment of change of the state of the surface.

The surface labelling method is especially valuable when it is impossible to activate the substance in the course of its preparation.

On incorporation of the inert gas by means of ionic bombardment, large amounts of radiation defects of various kinds are formed, mainly in the surface layers of the substance. These effects may manifest themselves on the curves of inert gas release. On the other hand, it thus becomes possible to study the annealing of the radiation defects on the basis of inert gas release. By means of suitable choice of the conditions for ionic bombardment (ion energy and radiation dose) it is possible to create various types of defects in a solid.

Simultaneous measurement of the radioctive inert gas release incorporated into the sample by the classical emanation method as well as by the ionic bombardment method may offer valuable information on the individual stages of reactions which take place on heating of solids.

Acknowledgement

In the course of this work, the author received help from a number of institutes and individual scientists. I wish to use this occasion to express my thanks to Professor An. N. Nesmeyanov, Head of the Radiochemistry Department, Moscow State University, where the greater part of the experiments were carried out, and to Professor K. B. Zaborenko, under whose guidance the author worked. I am greatly indebted to Professor Č. Jech of the Physical Chemistry Institute, Czechoslovak Academy of Sciences, Prague, for the incentive to carry out this work and for valuable critical discussion. I thank Professor Roger Kelly, McMaster University, Hamilton, Canada, Dr P. Bussière, Institute of Catalysis, Lyon, France and Dr Hj. Matzke, Euratom, Ispra, Italy, for valuable advice and discussion.

References

1. O. HAHN, "Applied Radiochemistry" (Cornell University Press, New York, 1936) p. 191.
2. K. E. ZIMENS, *Z. physik. Chem.* **A191** (1942) 1; **A191** (1942) 95; **A192** (1943) 10.
3. I. E. STARIK, "Osnovy radiokhimii" (Izd Akad Nauk, USSR, Moscow, 1960).
4. O. HAHN, *J. Chem. Soc.* **S56** Suppl. 1949 259.
5. A. C. WAHL and N. A. BONNER, "Radioactivity Applied to Chemistry" (Wiley, New York, and Chapman & Hall, London, 1951).
6. G. M. ZHABROVA and M. D. SHIBANOVA, *Uspekhi Khimiji* **36** (1967) 1407.
7. V. BALEK, *Chem. Listy* **58** (1964) 1261.
8. S. YAJIMA, S. ICHIBA, Y. KAMEMOTO, and K. SHIBA, *Bull. Chem. Soc. Jap.* **33** (1960) 426; **34** (1961) 133.
9. S. KALBITZER, *Z. Naturforsch.* **17a** (1962) 1071.
10. F. W. FELIX and H. SEELIG, *Nukleonik* **8** (1967) 389.
11. R. KELLY, *Can. J. Chem.* **39** (1961) 2411.
12. R. LINDNER and HJ. MATZKE, *Z. Naturforsch.* **15a** (1960) 1082.
13. D. CHLECK, R. MAEHL, O. CUCCHIARA, and E. CARNEVALE, *Int. J. Appl. Rad. and Isotopes* **14** (1963) 581.
14. G. CARTER, *Vacuum* **9** (1959) 190.
15. R. KELLY and F. BROWN, *Acta Met.* **13** (1965) 169.
16. Č. JECH, *Int. J. Appl. Rad. and Isotopes* **8** (1960) 179.
17. M. D. FRESHLEY, F. E. PANISKO, and R. E. SKAVDAHL, *Trans. Am. Nucl. Soc.* **9** (1966) 397.
18. M. E. LEVINA, B. S. SHERSHEV, and K. B. ZABORENKO, *Radiokhimija* **4** (1963) 480.
19. A. I. CZEKHOVSKHIKH, D. NITZOLD, K. B. ZABORENKO, and S. I. VOLFKOVICH, *Zh. neorg. Khim.* **11** (1966) 1948.
20. K. B. ZABORENKO, D. NITZOLD, and V. I. KOROBKOV, *Radiokhimija* **5** (1963) 642.
21. K. B. ZABORENKO and I. N. BEKMAN, *ibid* **10** (1968) 268.
22. K. B. ZABORENKO, L. L. MELICHOV, and V. A. PORTYANOJ, *ibid* 7 (1965) 319.
23. K. E. ZIMENS, *Z. physik. Chem.* **A186** (1940) 94.
24. S. FLÜGGE and K. E. ZIMENS, *ibid* **B42** (1939) 179.
25. G. TAMMANN and A. SWORYKIN, *Z. anorg. allgem. Chem.* **176** (1928) 46.
26. L. G. COOK, *Z. physik. Chem.* **B42** (1939) 221.
27. V. BALEK, *J. Materials Sci*, submitted for publication.
28. P. A. REDHEAD, *Vacuum* **12** (1962) 203.
29. R. KELLY and HJ. MATZKE, *J. Nucl. Matls.* **20** (1966) 171.
30. G. CARTER, *Vacuum* **12** (1962) 245.
31. Č. JECH and R. KELLY, *J. Phys. and Chem. Sol.* in press.
32. *Idem, Proc. Brit. Ceram. Soc.* **9** (1967) 259.
33. HJ. MATZKE, *Can. J. Phys.* **46** (1968) 621.
34. R. LINDNER, *Arkiv. Kemi* **4** (1952) 381.
35. W. G. HAGEL, *Trans. Met. Soc. AIME* **236** (1966) 179.
36. HJ. MATZKE, *J. Materials Sci.* **2** (1967) 444.
37. S. ICHIBA, *J. Jap. Soc. Powder Metall.* **9** (1962) 169.
38. P. BUSSIÈRE, B. CLAUDEL, J. P. RENOUF, Y. TRAMBOUZE, and M. PRETTRE, *J. Chim. Phys.* **58** (1961) 668.

39. D. K. SRIVASTAVA and A. P. VASUDEVA MURPHY, *J. Sci. and Ind. Res.* **21B** (1962) 525.
40. Č. JECH, G. M. ZHABROVA, S. Z. ROGINKSIJ, and M. D. SHIBANOVA, *Dokl. Akad. Nauk USSR* **164** (1965) 1343.
41. A. V. SKHARIN, G. M. ZHABROVA, N. P. TOPOR, and M. YA. KUSHNAREV, *Izv. Toms. Politech. Instituta*, in press.
42. R. BECKETT and M. E. WINIFIELD, *Austral. J. Sci. Res.* A4 (1951) 664.
43. R. W. M. DÉYE and P. G. SEELMANN, *J. Inorg. and Nucl. Chem.* **1** (1955) 143.
44. K. B. ZABORENKO and R. THÄTNER, *Zhur. neorg. Khim.* **11** (1966) 2198.
45. V. BALEK, *J. Radioanal. Chem.* **2** (1969) 315.
46. K. B. ZABORENKO and V. BALEK, *Zhur. neorg. Khim.* **14** (1969) 1469.

Letters

Precipitation Hardening in Magnesium-Tin Alloys

In aged magnesium-tin alloys the Mg_2Sn precipitates lie mainly parallel to the (0001) plane of the matrix [1, 2] and the precipitation is preceded by formation of short-range order [2]. In the first part of this work the influence of tin on the critical resolved shear stress (crss) of magnesium was determined [3]. In the second part, undertaken in order to investigate the behaviour of precipitation-hardened magnesium-tin alloys, microhardness measurements were made on magnesium-1.65% tin (7.75 wt %) alloys and the precipitation was checked in the electron microscope on carbon replicas. This work is described here.

Small pieces of the alloys, cut from the same ingot, were homogenised, quenched and aged at 200, 250 and 300° C. The same procedure for homogenisation as employed by Hardie and Parkins [4], has been used here. For the ageing treatment the samples were enclosed in evacuated pyrex tubes. From hardness measurements on pure magnesium and on the alloy, both heat-treated in the same way, it was deduced that the polishing method did not alter the hardness appreciably. After three hours homogenisation at 550°C, the hardness did not change any more, whereas the crss remained constant after 6 h. In both cases the measurements were made on samples in the as-quenched condition. A homogenisation time of 5 h was applied to all samples, though there was still a proportion of relatively big Mg_2Sn particles.

The microhardness of magnesium-tin alloys increases with increasing tin content (fig. 1). The agreement with other published results [4] is perfect if the difference in method is taken into account. This increase in hardness is linear, but the straight line does not pass through the result for pure magnesium. The initial steep increase up to a "transitional" concentration, followed by a line of lower slope has been reported recently in other magnesium alloys tested in tension [5]. After the homogenisation, the samples were aged at the three mentioned temperatures. The precipitation was checked in the electron microscope, and the microhardness measured with a Vickers pyramid. The hardness of this alloy, plotted against the log of ageing time, passes through a maximum (fig. 2). Owing to uncertainties inherent in microhardness measurements [6], especially for cph structures [7], the Rockwell-B hardness was determined for one ageing temperature. The maximum occurred after the same ageing time, but the hardness itself was lower. The latter fact was probably due to the higher load used, since an increase in load for the microhardness determinations similarly produced a decrease of hardness. The microhardness of the compound Mg_2Sn was found to be as high as

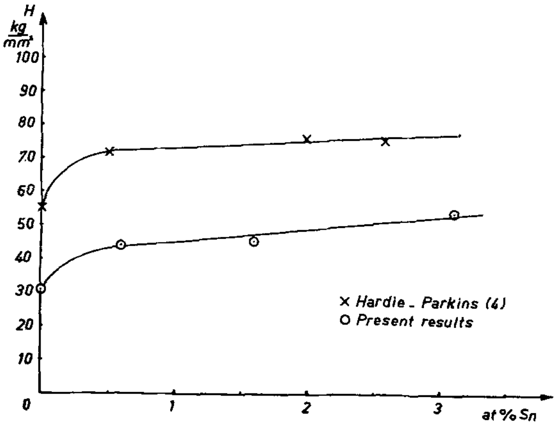


Figure 1 Microhardness of homogenised magnesium-tin alloys plotted as a function of tin content.