S 56. *The Emanation Method.*

By OTTO HAHN.

(I) *Introduction: Peculiarity of the Emanation Method.*—In the usual tracer methods, radioactive atoms which are easily traceable in minimum concentrations are used as indicators for the behaviour of chemical elements which are isotopic with active atoms. These methods can be applied to elements which normally are solid substances as well as to gases. It is thus possible to study, not only the chemical properties, *e.g.*, of silver, phosphorus, or sodium, or of their compounds by the respective active isotopes, but also the physical behaviour of gaseous elements, such as krypton, xenon, or the emanations of the natural radio-elements.

The radioactive gaseous elements, however, can be used for other purposes too. If we have a chemical compound which contains a radio-element that forms a radioactive gas, we may investigate the molecular state of the compound, its inner surface, or its deformations due to ageing, to molecular and chemical conversions; we may also follow the processes of reaction in the solid state, from the amount of the active gas escaping from the compound.

The emanations of natural radio-elements, mainly thoron and radon, have been found to be particularly suited for such investigations. For this reason the author has called this method of investigation the " emanation method," and many reports on this subject have been published, partly by the author and his co-workers, and more recently by other investigators.

As this work does not appear to be generally known, a brief outline of this method is now given.

Nearly all work has been carried out with the natural radioactive emanations radon and thoron—in a few cases with actinon. The method may also be applied to the active rare gases krypton and xenon, now accessible, if these arise, *e.g.*, in a nuclear process, and if the behaviour of the substance in which they arise is to be studied.

By the emanating power of a substance we mean the amount of the emanation issuing from the substance related to the total amount of the emanation developed in the substance. All those substances can be examined by the emanation method into which radium, Ra-Th, Th-*X*, or Ac-*X* can be introduced and in which they can be distributed homogeneously. This introduction can be made by various methods, by common crystallisation, when the components form mixed crystals; with metal oxide gels by co-precipitation by means of ammonia or alkali; with glasses by stirring when molten; with zeolites by exchange of bases; and with metals by melting, electrolysis, or simple mixing of the ingredients by melting.

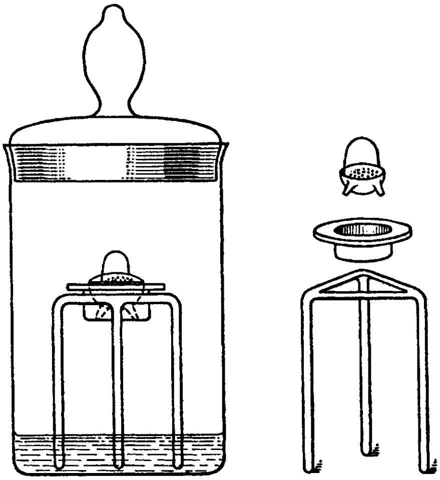
After the radioactive element has been added by one of the above methods to the inactive substance to be tested, the emanation is formed within the mass of the substance. Depending on the structure of the substance a greater or smaller portion of it can escape. Practically nothing is liberated, *e.g.*, from the interior of a polar inorganic salt: the emanating capacity is very small. A great quantity escapes from a metal hydroxide with great inner surfaces: the emanating capacity is great.

When the structure of the substance is altered, *i.e.*, when there are surface modifications, molecular transpositions, or other processes, the escape of emanation is altered which can be determined by simple electroscopic methods during the processes and also afterwards.

(II) *Methods of Measurement.*—The earlier researches dealt mainly with the behaviour of precipitates with large surfaces and their ageing under various conditions of atmospheric moisture. Instead of the emanation itself, the active deposit of the respective emanation was advantageously measured. The conditions are particularly simple if it is possible to use the γ-rays of the active deposit. For this purpose, however, we need preparations of about 0·1 millicurie of radium equivalent. The procedure is as follows :

The substance under investigation is placed in a small glass dish provided with a lid. The dish fits into a small cup, which rests on a glass tripod fused into a weighing bottle of such dimensions that the preparation is held at the centre of the weighing bottle. The weighing glass can be used as a desiccator for obtaining any desired humidity, if one chooses to test the influence of different degrees of dryness upon the emanating power (see Fig. 1).

FIG. 1.



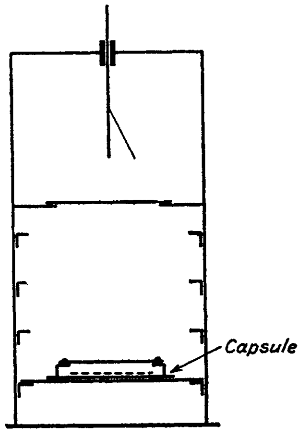
Arrangement of the weighing bottle with the substance to be investigated

When dealing with preparations that develop the short-lived thoron, they must be powdered and should not weigh more than 10—20 mg., otherwise, on its way out of the preparation, a portion of the emanation escaping will disintegrate inside the layer of material. This precaution is not needed in the case of radium emanation, because its relatively long half-life gives the radon sufficient time to diffuse out of even rather thick layers of compact material.

The preparation is allowed to stand so long, either outside the weighing bottle or in a larger vessel at a definite humidity, that radioactive equilibrium has been attained within the preparation itself between emanation and active deposit. The preparation is then placed in the weighing bottle, and the cover is sealed air-tight with sealing wax; immediately thereafter a γ-measurement is carried out in an electroscope surrounded by lead. This measurement gives the activity corresponding to the amount of emanation or of active deposit retained by the preparation. The radiations of the mother substances radium, or radio-thorium and the like, are not sufficiently penetrating to enter the γ-electroscope, and thus are not measured. That portion of the emanation in the weighing bottle corresponding to the emanating power now escapes and forms the active deposit, which collects on the walls of the vessel. In the case of thoron, radioactive equilibrium is established in 3 days; where radon is concerned, however, equilibrium is reached only after a month, but it can be computed after a couple of days. A measurement is again made, and this measurement includes the activity of the active deposit on the walls, as well as the activity of the active deposit in the preparation itself. If the activity of the preparation immediately after sealing the vessel is called A, and the activity of the preparation proper plus that outside the weighing bottle is called B, then the emanating power is $100(B - A)/B$ %.

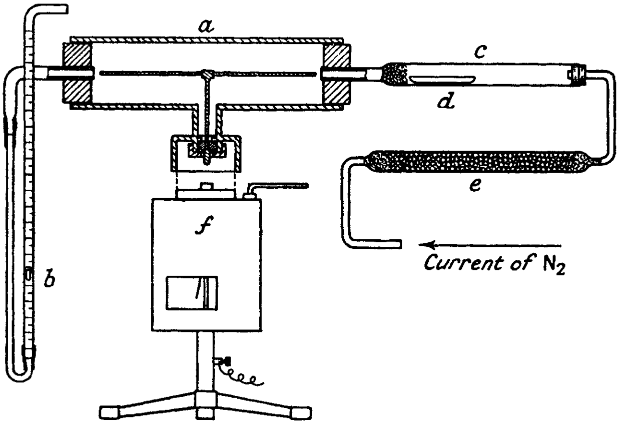
If we do not have such strong preparations at our disposal, we may also use the β-rays of the active deposit for measurements. Some thousandths of millicurie suffice for that purpose. A thin layer of the substance to be investigated is uniformly spread on a flat metal plate, and this is placed in a shallow brass capsule and sealed air-tight by means of aluminium foil 150 μ. thick; all the α- and the soft β-rays are completely absorbed by this sheet. The first measurement, carried out immediately after sealing, gives the activity in the preparation itself; the second measurement gives the activity of the preparation and of the active deposit in the interior of the capsule. The arrangement of the apparatus for making such measurements is shown by Fig. 2.

FIG. 2.



Arrangement for measuring β-radiation.

FIG. 3.



The use of the active deposit for the investigation of the emanating power is very simple and also sufficiently accurate if highly emanating preparations of not too small an activity are concerned, the emanating capacity of which is not subject to fast alterations. The difference measurements become inexact in the case of weakly emanating substances; we then preferably measure the emanation itself instead of its active precipitate. We do not give details of the measuring methods which were applied to radon as well as to thoron.

Fig. 3 represents a simple flow apparatus for thoron.

The measuring condenser is denoted by *a*; *b* indicates the flowmeter (" Rotameter ") for regulating the velocity of the current of gas; *c* is a tube of hard glass within which is placed the boat *d* containing the emanating substance to be studied. A cylinder of air or nitrogen furnishes a current of gas that passes through a tube of calcium chloride *e* before it carries the thoron into the condenser *a*, which rests on the electroscope *f*. If experiments are to be made at higher temperatures, then *c* is surrounded by an electric oven with a resistance thermometer. Every *change* in emanating power can be detected instantly and easily determined even during the experiment. In order to obtain *absolute* values for the emanating power the material must be investigated twice, *viz.*, once under the studied conditions and then again in a form which furnishes a 100% emanating discharge.*

(III) *Investigation of Surface Areas and Their Changes under Various Conditions.*—It was readily shown that the hydroxides of iron, thorium, etc., had a very great emanating power, particularly when they were precipitated at low temperature. According to their method of storage, dry or at different humidities, they show a different behaviour in the course of time, *i.e.*, they age more slowly or faster; and this ageing also is a function of the capacity for crystallisation of the hydrate.

In favourable cases ferric hydroxide and thorium hydroxide showed an emanating power for thoron of 80% and even 90%. They were especially suited for the production of the active deposits on a negatively charged plate. Above all, Th-*B* (10·6 hours) could thus be obtained most easily in an exceedingly thin layer.

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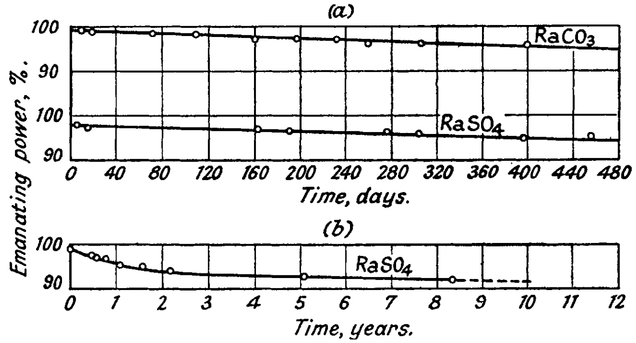
* For particulars of the earlier work on measurements of the emanation power see Otto Hahn, " Applied Radiochemistry," Cornell Univ. Press, 1936 (London : Humphrey Milford). Improvements in the more recent work may be found in some of the papers cited in this paper.

By means of the ferric hydroxide which is very rich in inner surface, even radium preparations were made which let practically 100% of their radon escape at room temperature. The radium preparations were made in such a way that a dissolved radium salt with about 50—75 times its weight of iron salt was precipitated with ammonia and ammonium carbonate or ammonium sulphate. The great capacity of crystallisation of the radium salt cannot be of effect owing to the great excess of ferric hydrate (the radium in the hydrate is like the raisins in the cake!).

Fig. 4 shows the behaviour of such dry radium preparations. We see the extremely slow ageing. Even after more than 8 years the radium sulphate, incorporated in the ferric hydroxide gave off more than 92% of all the radon produced in it (Hahn and Heidenhain, *Ber.*, 1926, **59**, 284).

FIG. 4.



Change, with time, in the emanating power of highly active radium preparations.
(*a*) *Change in the course of days;* (*b*) *change in the course of years.*

The German AUER-Incandescent Light Company formerly constructed a little apparatus, called a " Radonator " (for details, see Hahn, " Applied Radiochemistry," Cornell Univ. Press, Fig. 61, p. 219), which was used for collecting the radon from such highly emanating preparations in a strongly adsorbent charcoal, contained in a thin gold capillary. After the accumulation of the radon in the capillary, the latter could be cut into smaller pieces and applied for medical purposes.

Later, Strassmann (*Z. physikal. Chem.*, 1934, *B*, **26**, 362) obtained such high-emanating radium preparations in another way. He investigated the emanating capacity of barium salts of a large number of monobasic fatty acids and other organic barium salts. The following table shows how the emanating capacity rises with increasing chain length up to 100%; this holds not only for the long-lived radon but even for the considerably less stable thoron.

Emanation from barium salts of monobasic fatty acids.

Salt.	No. of C atoms.	d^{25}.	Relative surface per g.	Emanation, %.
Acetate	2 × 2	2·482	1·00	3— 4
Propionate	2 × 3	1·993	1·25	17—18
Butyrate	2 × 4	1·885	1·32	60—65
*iso*Butyrate	2 × 4	1·728	1·44	70
Hexoate	2 × 6	1·594	1·56	96
Palmitate	2 × 16	1·226	— *	100

* The preparation of the palmitate had a much smaller crystal diameter, so was not comparable with the other salts.

Bjerge (*Nature*, 1936, **139**, 757) used this behaviour of such long-chain organic salts for separating the short-lived ^{23}Ne from sodium stearate when the latter was irradiated with neutrons, according to the reaction: $^{23}_{11}Na(C_{18}H_{35}O_2) + n \longrightarrow {}^{23}_{10}Ne$ (40 sec.) $+ p$.

The behaviour of colloidal solutions of hydroxides may be quite instructive. Fig. 5 shows how very slowly a thorium sol crystallises. A colloidal thorium oxide solution was flocculated after various long periods. The emanating power was equally high immediately after the flocculation. The sol, however, had obviously started a gradual formation of microcrystalline particles. After the flocculation, these germs of crystal could grow. The emanating capacity quickly decreases in the preparations obtained from the old sols (Hahn and Graue, *Z. physikal. Chem.*, Bodensteinfestband, 1931, p. 608).

Fig. 6 shows the behaviour of two sorts of glass of different sensitivity to humidity, *viz.*, Jena glass, the emanating power of which is extremely low and which is very insensitive to any sort of ageing, and a pure barium glass. No alteration is found in the case of the Jena glass, but quick alteration by absorption of humidity with the barium glass (Hahn and Müller, *Glastech. Ber.*, 1929, **7**, 380).

Fig. 5.

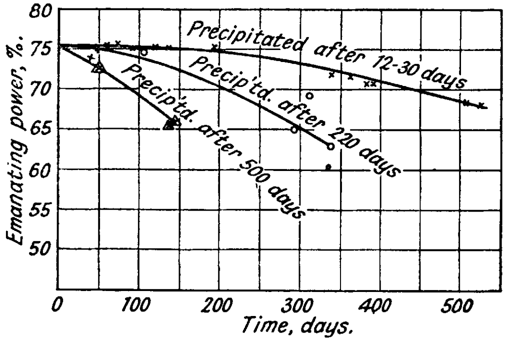
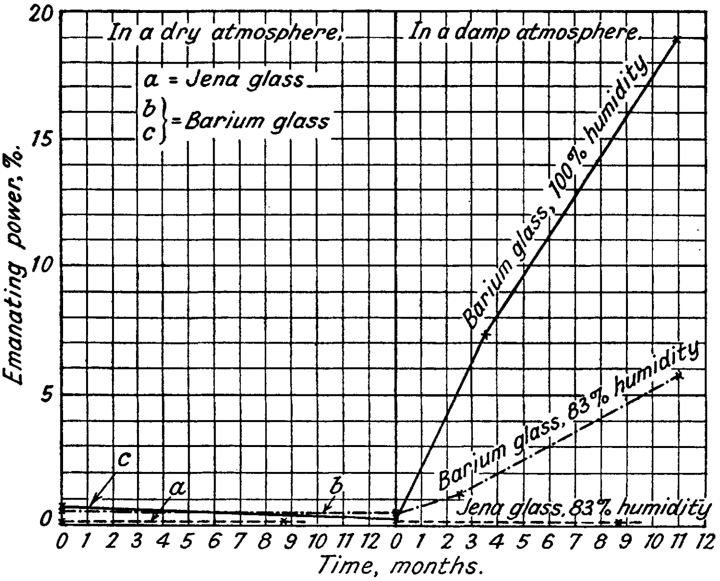


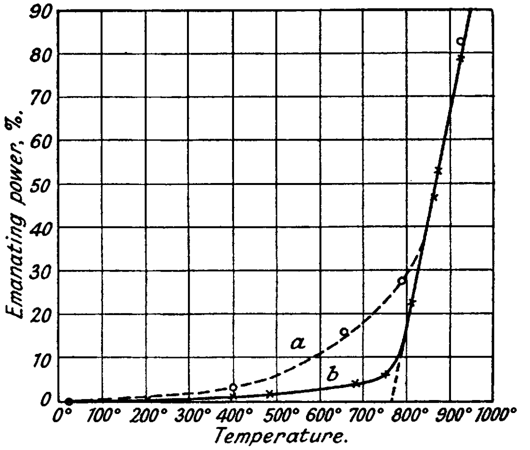
Fig. 6.



The behaviour of salts and oxides can be clearly followed by the emanation method when such preparations are gradually heated to a higher temperature. Fig. 7 shows the behaviour of barium sulphate during heating (Strassmann, *Naturwiss.*, 1931, **19**, 502). Noting first the lower, full curve, we see that the very low initial emanating capacity hardly alters during the first few hundred degrees. Even at 700° the values are still below 5%. Between 700° and 800°, however, we see a steep increase of the emanating power which causes an almost quantitative discharge of the emanation after a short time. After cooling, the emanating capacity is as low as before. When we heat once more, the steep increase again occurs at the same temperature.

Besides this very characteristic full curve, the figure shows a broken curve representing a much slower increase of the emanating capacity with rising temperature beginning at a much lower temperature. This curve was obtained for a barium sulphate dried at 110°. The steadier increase of the emanating capacity occurring at lower temperatures is undoubtedly due to a gradual distillation of adsorbed water. We see that the last particles of water are discharged only at rather high temperatures. The water being removed, we shall always obtain the lower curve on further heating. The temperature of the steep increase is undoubtedly related to the so-called loosening temperature of the respective salt. According to Tammann, this loosening temperature is equal to approximately half the absolute melting temperature of the substance concerned. According to the curve for barium sulphate, this loosening temperature occurs at 770° (in °K.), *i.e.*, at 0·56 of the melting point (in °K.) of the barium sulphate. There certainly is no doubt that this temperature of the steep increase of the emanating discharge also indicates the temperature at which these substances in the solid state can react with others, and it seems worth while to follow such reactions by means of the very sensitive emanation method.

FIG. 7.



Loosening of crystal lattice of barium sulphate at high temperatures (°C.). *a, Barium sulphate containing included water; b, ignited barium sulphate.*

These experiments have recently been taken up by Schröder (*Z. Elektrochem.*, 1948, **52**, 166) as additional work of a whole series of papers on reactions in the solid state investigated according to the emanation method. Some of his results will be dealt with later; here we only mention two investigations on the behaviour of SnO_2 and TiO_2 when gradually heated above " Tammann's loosening temperature." He reports as follows upon the curves he obtained :

" As shown in Fig. 8, the curve of stannic acid starts with a short steep increase, runs through an EV maximum of about 84% at approximately 140°, and decreases almost rectilinearly over a temperature range of almost 700° to the EV minimum of about 10%, rising again at 920°. The stannic acid thus loses its water at a low temperature, and the resulting oxide recrystallises almost continuously with increasing temperature."

The curves of the preheated oxides are also shown on a rather larger scale concerning the emanating power in the two higher curves (see right-hand ordinates). The temperature of the Tammann loosening temperature proves to be about 880° C. = 0·52 of the absolute melting point of the stannic oxide.

The EV change of titanic acid (Fig. 9) shows quite a different thermal behaviour. Its curve rises as far as 500°, and then drops very steeply and runs through a minimum of about 2% at 800°. On continuous heating titanic acid decomposes more slowly than stannic acid; titanic oxide, however, recrystallises more quickly and more thoroughly than stannic oxide. It must still be determined by experiment whether the monotropic change of the initially formed anatase into the stable rutile takes a causal part in the great EV increase of the titanic acid as far as 500°.

Here, too, the emanation method for the pre-heated preparations is represented on an enlarged scale on the right-hand side of the ordinate. We see that 20 hours' heating to 1050° compared with the 10 hours' heating results in a small further decrease of the emanating power. The loosening temperature is at about 800° = 0·52 of the absolute melting point.

(IV) *Physical Transformations.*—The preceding paragraph showed a few examples from which the so-called " loosening temperature " of the substance in question can readily be recognised by means of the emanation discharged by a preparation. At this temperature a great acceleration of the molecular motion of the crystalline or crystallised substance begins, and at this temperature reactions in the solid state become possible.*

FIG. 8. *Stannic Acid.*

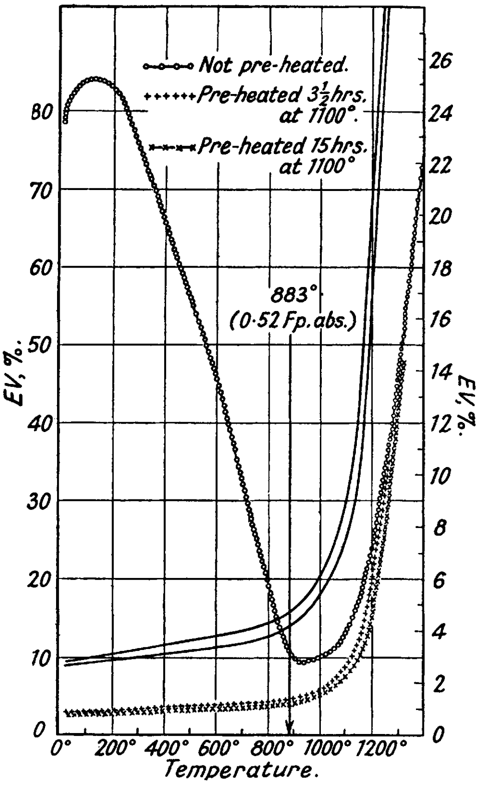


FIG. 9. *Titanic Acid.*

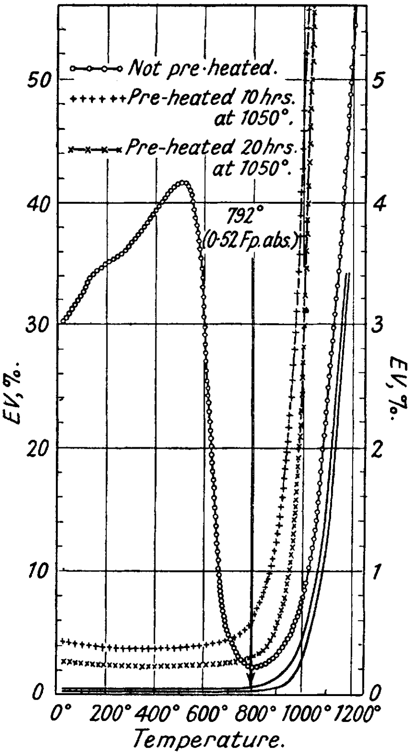
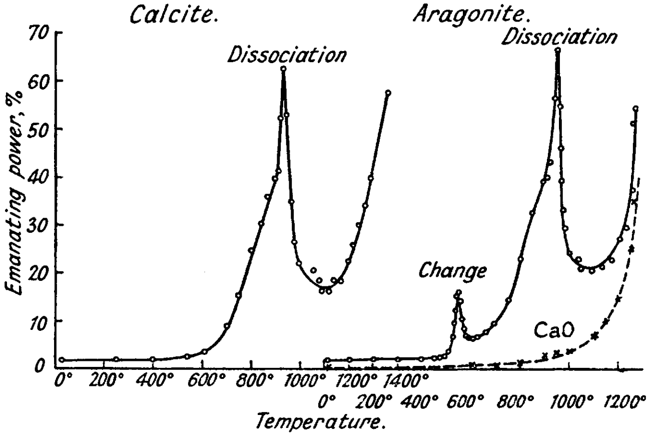


FIG. 10.



The emanation method proved to be rather instructive also for cases where *alterations of the lattice* of crystallised salts arise in heating. Zimens† (*Naturwiss.*, 1937, **25**, 429; *Z. physikal. Chem.*, 1937, *B*, **37**, 231) studied the thermal behaviour of some carbonates of the alkaline earths in the author's Institute. He represents his results as follows. Fig. 10 shows the thermal

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* See Hedvall, " Reaction in the Solid State." Hedvall was the first to study such reactions by a large variety of experimental methods.

† Alias Zinsen.

behaviour of preparations of calcite and aragonite which were precipitated together with the radium isotope Th-*X*. The preparations were heated in an atmosphere of carbon dioxide. The temperature (abscissa) was uniformly increased, and the variation of the emanation discharge was repeatedly measured.

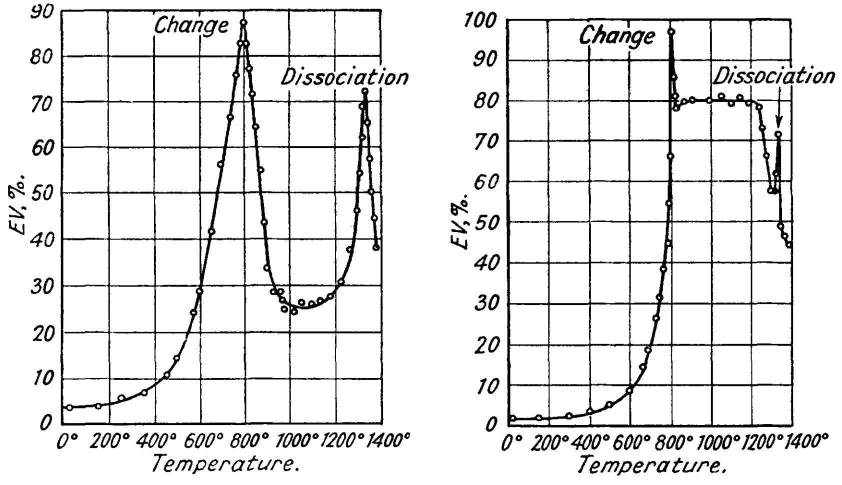
The EV of the *calcite*, lying between 1 and 2% at room temperature, increases only slightly at first, but above 600° it increases rapidly. If a preparation of *aragonite* is heated in the same way, no difference in the curves can be seen up to 450°. Just above 500° the EV suddenly increases to a maximum, then again decreases and joins the calcite curve above 600°. As is proved by *X*-ray photography, the internal molecular transformation of the rhombic aragonite into the hexagonal calcite is expressed in the EV. A preparation of aragonite whose heating is stopped after the peak at 600° shows the pure calcite lines in the Debye–Scherrer diagram.

By variation of the experimental conditions, further statements concerning the transformation can be made: in cooling of an aragonite heated to above 600° no re-transformation takes place and no peak arises in another heating. The transformation is monotropic and irreversible.

The further progress of the emanation curves for higher temperatures shows the dissociation of the carbonate at 910° and the loosening of the generated calcium oxide from 910° upwards.

In contrast to the monotropic transformation of the aragonite into calcite, barium carbonate undergoes a reversible enantiotropic transformation of the rhombic into the hexagonal carbonate at a certain temperature. This process can be very distinctly shown by means of the emanating capacity (Zimens, *Z. physikal. Chem.*, 1937, *B*, **37**, 241). At about 500° the loosening begins, and at 810° the rhombic carbonate is transformed into the hexagonal species (see Fig. 11). With this preparation, where the particles were small, the transformation starts a strong recrystallisation, as is seen by the reduction of the emanating power.

Fig. 11.



Small crystals. *Larger crystals.*

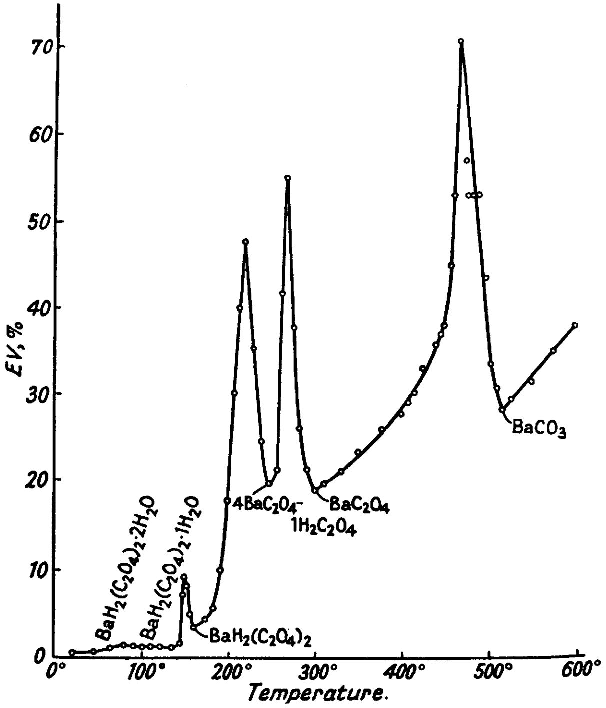
Thermal behaviour of barium carbonate.

The second curve illustrates the effect of the size of the particles. This preparation consisted of bigger particles, and this fact suffices to change the graph very distinctly: the rise begins somewhat later and, although the transformation is again shown as a pronounced peak, it does not lead immediately to recrystallisation, which does not begin before 1200°. The dissociation temperature of the carbonate is shown by the curves to be 1350°.

Another series of experiments on the applicability of the emanation method to physical transformations in heating was carried out by Werner with certain metals or metallic alloys (*Z. Elektrochem.*, 1933, **39**, 611). The experiments became somewhat more difficult, because it is not quite simple to index alloys by a substance giving off an emanation. The experiments were successful with some metallic barium alloys. The transition from metastable systems, for instance, to the normal state could definitely be recognised by means of the method. Werner investigated a deformed zinc–barium alloy and described its transition to the normal state as follows: " The deformed alloy represents a metastable system existing under a certain degree of strain. At a certain temperature the crystallites experience a spontaneous recovery from the results of the deformation. The structural elements of the lattice change to the normal condition of the lattice, with an equalisation of the internal tension and, while this change is taking place, an increased amount of emanation is able to escape through the metal structure."

(V) *Chemical Transformations.*—Many chemical compounds, especially salts with several molecules of water of crystallisation, suffer from a step-by-step dehydration on heating whose progress is very different for the various compounds and also for the individual hydrate stages of one and the same salt. Lieber (*Z. physikal. Chem.*, 1938, *A*, **182**, 153) investigated the stepwise dehydration of barium chloride, bromide, and iodide by means of the emanation method and was able to show how extremely distinctly the loss of water occurring at certain temperatures is denoted by steep peaks in the emanation discharge (for details the original paper should be consulted).

FIG. 12.



Step-wise thermal decomposition of $BaH_2(C_2O_4)_2$, $2H_2O$.

A characteristic example for another salt is now mentioned, because five different transformation processes could be proved with one single systematic heating curve; this is the decomposition of the acid barium oxalate $BaH_2(C_2O_4)_2,2H_2O$ (Sagortschew, *ibid.*, 1936, *A*, **177**, 235). Fig. 12 shows that the decomposition curve passes through five maxima and five minima. The first two maxima, particularly the first, are not very pronounced. When the heating is interrupted at the first minimum and the preparation is weighed, it is found to be the monohydrate. If the heating is repeated, the first weak maximum does not appear again. The first rise and fall of the EV is thus connected with the loss of the first molecule of water of hydration. If the preparation which has been heated to 100° is kept in humid air for some hours, it absorbs water, and the first maximum appears again when heating is repeated. If the heating is interrupted at the second minimum, and the preparation is weighed, we find that the second molecule of water has been lost, too, so the second minimum corresponds to the anhydrous salt.

The further processes are followed by normal analysis after the peaks in the emanating capacity have shown the temperature at which conversion takes place, and the corresponding results are given in the figure. It is not yet quite clear why the effect of the discharge of the two molecules of water, and of the first in particular, is so much less pronounced : probably this is due to the measuring method used, where very rapid processes are perhaps not registered, or only to a small amount.

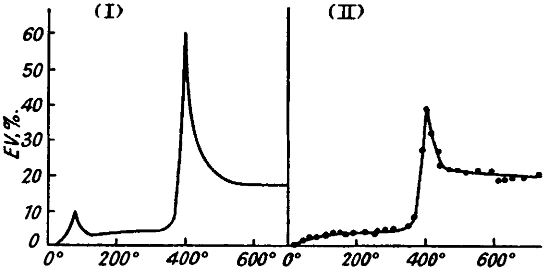
Born (*ibid.*, 1937, *A*, **179**, 256) unambiguously proved in the author's Institute that such rapid decompositions may be checked by using an electrometer arrangement instead of the earlier method of registration. The earlier method of working was the following: A constant stream of indifferent gas is continuously led over the substance to be investigated, carrying off the discharged emanation and leading it through a small ionisation chamber connected with an electroscope after a short distance. The intensity of the ionisation current, and thus the quantity of emanation, is measured with the time of charge and discharge of the electroscope. In most cases the fixation of a measuring point requires several minutes. The electroscope has to be charged, and the discharge over a certain potential range must not last less than about 20 seconds in order to secure an adequate measuring accuracy. That means, however, that it will usually require several minutes. All the alterations which take place during the measurement are therefore perhaps not expressed in detail or may be obscured.

In the new arrangement an electrometer makes a deflection which is continuously proportional to the straightly flowing ionisation current. This enables us to perceive and to follow very quick variations of the ionisation current, *i.e.*, of the emanation discharge. The utility of the arrangement is exemplified by the decomposition of thorium oxalate.

Fig. 13, curve I, first shows a small peak at 80—100°, then runs parallel to the abscissa up to about 350°, where the rapid increase to the pronounced maximum at 400° starts. After the decrease, the emanating capacity remains for a further 800° at a considerable height without great fluctuations. In order to interpret this general curve more accurately the heating was repeated stepwise as usual, and weighings were taken. The result was that a dihydrated oxalate was produced from the hexahydrate after the first peak. Anhydrous oxalate was present at 300°, and thorium oxide with at most 1% of over-weight at 450°.

Curve II of Fig. 13 shows the corresponding curve of the formerly used electroscope arrangement. We see that the effect of water discharge was completely masked in the simple electroscope observation, and that the influence of the oxalate decomposition on the emanation discharge is insufficiently expressed.

FIG. 13.



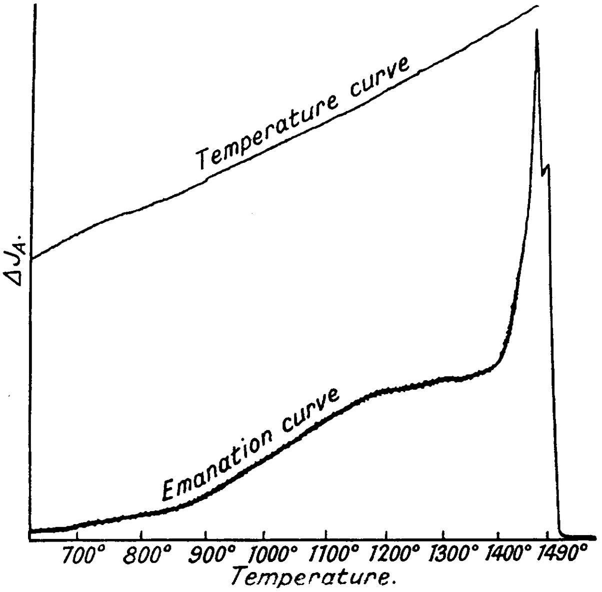
Decomposition of thorium oxalate.

Zimens (*ibid.*, 1940, *A*, **186**, 94) more recently made another essential step forward; he built a fully automatic apparatus for measurement of the emanations and their progress in the continuous heating of preparations. He used a type of electrometer valve instead of an electroscope or an electrometer, thus making possible the recording of curves on a film by means of a mirror galvanometer. The exact curve of temperature is simultaneously recorded by means of a thermocouple. According to Zimens, such an apparatus, though rather complicated, has the following advantages: In his apparatus the temperature curves of the emanating power are recorded completely automatically (by means of an electrometer valve). (i) The measurements are made continuously; hence every detail is recorded even with rapid variations of EV. (ii) The influences of irregular increases of temperature upon the EV curve, which have sometimes been considerable, can be observed owing to the simultaneous record of the temperature–time curve. The temperature record is very useful even for isothermal measurements. (iii) There will not be any sources of personal error, which might be considerable in measurements which often last several hours.

An example of the automatic recording on photographic paper is given in Fig. 14. It shows the variations of the escaping fraction of emanation (Tn) from a sample of Fe_2O_3 when heated in an atmosphere of oxygen (Zimens, *ibid.*, 1943, *A*, **192**, 48). The temperature of transformation from Fe_2O_3 into Fe_3O_4 at 760 mm. oxygen pressure derived from this curve is 1405°. With the temperature curve (above) the uniformity of the heating can be controlled.

(VI) *Reactions in the Solid State.*—After the preceding examples on the use of the emanation method for the investigation of physical as well as chemical transformations of solids, it is natural to apply the method to the study of chemical reactions in the solid state as well, *i.e.*, for reactions in which mixtures of two chemical compounds show a reaction with one another at high temperatures. We have repeatedly referred to the so-called " loosening temperature " at which the molecular motion of the lattice components becomes so rapid that we can expect chemical reactions. Such reactions have already been studied by Hedvall and his co-workers, by Hüttig, by Fricke and others by various methods, and lately the emanation method has also been used.

FIG. 14.



Transformation of Fe_2O_3 *into* Fe_2O_4.

Only one series of very detailed investigations made by Schröder in Fricke's laboratory in the Technische Hochschule of Stuttgart during the last few years can be mentioned (for full references, see Schröder, *Z. Elektrochem.*, 1940, **46**, 680). Schröder checked his results obtained by the emanation method by a variety of ordinary methods and was able to prove that the emanation method affords results which cannot be attained as simply, if at all, by other methods. He chiefly studied the processes taking place between the oxides of bivalent or tervalent metals and leading to compounds of the spinel type.

The processes were controlled by means of *X*-ray photography and analytical characterisation of the intermediate products. Schröder investigated, *e.g.*, the formation of zinc–iron spinel, $ZnFe_2O_4$, and of cadmium–iron spinel, $CdFe_2O_4$, of chrysoberyl, $BeAl_2O_4$, and of other compounds. At first the single components were checked as to their behaviour during heating and after successive sudden cooling to room temperature; afterwards the molecular mixtures were checked in the same way. Besides the loss of water and of carbon dioxide of the carbonate-containing hydrates, grain size, changes in colour of the oxides, and other phenomena were correlated with the emanation discharge.

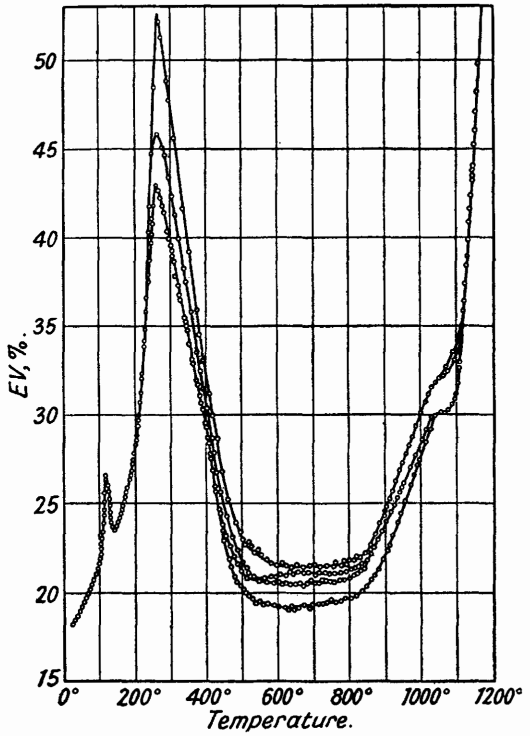
Zinc–iron spinel. Schröder (*Z. Elektrochem.*, 1922, **48**, 241) studied the reaction $ZnO + Fe_2O_3 = ZnFe_2O_4$. First, the emanation discharge of the oxide indicated by radiothorium (as the source for the emanation) is followed during the continuous rise of temperature in the streaming apparatus. We obtain a curve where the points of increased emanation discharge are indicated by the characteristic, more or less pronounced " peaks." The remaining alterations indicated by the discontinuities of the heating curve are controlled by the room-temperature curve : to each heating curve a sufficient number of preparations were pre-heated to the different temperatures and then, under equal conditions, measured at room temperature.

The curves recorded during heating are called " running curves " (" laufende Kurven ") = L.T. curves, and the curves recorded at room temperature are correspondingly called R.T. curves.

In the reaction in question the zinc oxide was activated by radio-thorium, the ferric oxide being inactive. Since the radio-thorium could be precipitated simultaneously in the pure crystalline zinc hydroxide only to a small extent in the absence of carbon dioxide, some basic zinc carbonate was precipitated intentionally together with the hydroxide. This precipitates in a highly disperse form, including the radio-thorium, and does not give it off during washing.

Fig. 15 shows the behaviour of the basic carbonate containing zinc hydroxide on continuous heating (L.T. curve). In order to be able to determine the reproducibility of the processes, the curve was recorded with several preparations produced at different times. We observe a pronounced peak at 120°; on continued heating, the emanation discharge decreases and then rapidly increases again to a high maximum at about 255°. A rapid decrease follows again, and above approximately 850° another increase begins which becomes extremely rapid above 1100°.

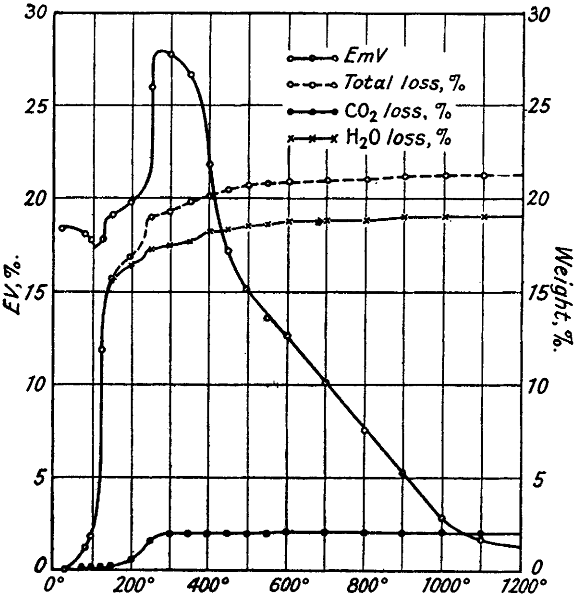
FIG. 15.



L.T. curve of CO_2*-containing* $Zn(OH)_2$.

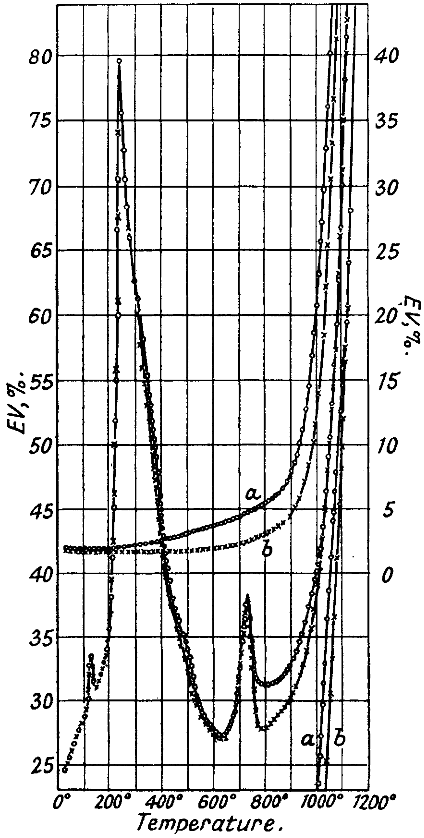
Which processes are reflected in these discontinuities was determined, on the one hand, by the record of the room temperature curve (R.T. curve) and, on the other hand, by analytical methods and X-ray photography. The R.T. curve (Fig. 16) indicated the remaining alterations at the different stages of the tempered preparations. The loss of water and of carbon dioxide and the loss in total weight are recorded on the right-hand ordinate. From Figs. 16 and 17 we draw the following conclusions. The temperature of dissociation of the crystallised $Zn(OH)_2$ lies at 120°. The pronounced peak at about 255° shows the dissociation temperature of the zinc carbonate. That the water discharge is not so strongly pronounced in the L.T. curve, despite the much greater water loss compared with the CO_2 loss, as the high peak in the CO_2 discharge shows, depends upon the fact that the $Zn(OH)_2$ contained much less radio-thorium yielding an emanation than did the $ZnCO_3$. The intensified emanation discharge again starting at about 800° in the L.T. curve causes the beginning of the accelerated molecular motion which, of course, is not visible in the R.T. curve. It shows only the surface diminution of the oxide taking place with increasing temperature after the first strong loosening during the dissociation (for fuller details, the original paper must be consulted). Here we are primarily interested in recording the heating curve of the mixture zinc oxide–ferric oxide after the behaviour of the basic zinc oxide alone had been followed (Schröder, *Z. Elektrochem.*, 1942, **48**, 241). Fig. 17 represents the result (*idem, ibid.*, p. 301). The general progress over the first 600° is quite analogous to the L.T. curve of the zinc component without iron. Above 600° another well-pronounced peak is visible for the mixture and thus indicates a fresh process. This process is the beginning of the reaction leading to the formation of the zinc–iron spinel. Again, two different mixtures of preparations were used for recording the curve. The peak which corresponds to the spinel formation lies at exactly the same point, which is therefore reproducible.

Fig. 16.



R.T. curve of CO_2*-containing* β-$Zn(OH)_2$.

FIG. 17.

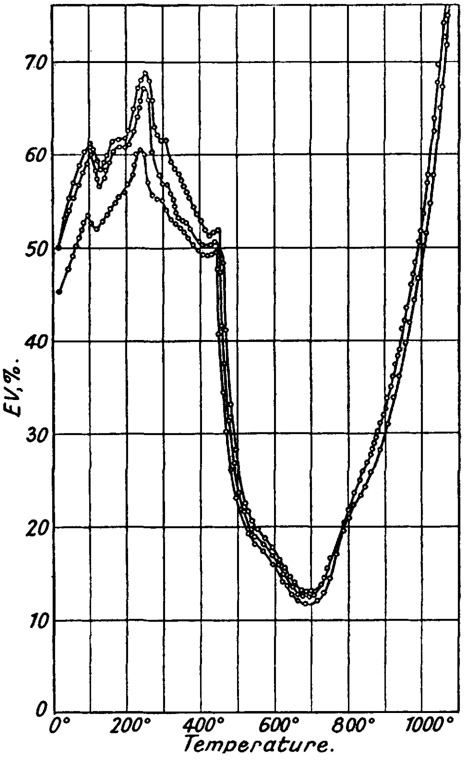


Active ZnO *and inactive* Fe_2O_3*: L.T. curve of mixture.*

The two curves *a* and *b* represent the behaviour of two mixtures pre-tempered to high temperatures. The upper curves are plotted on an enlarged scale (right-hand ordinate) in respect of the emanation capacity. For *a*, the mixture was pre-tempered continuously up to 1100°; for *b* it was heated to 1100° for a further 2½ hours. The somewhat lower curve *b* allows the conclusion that the spinel is somewhat spoilt in baking caused by the long duration of heating. The *formation* of the spinel itself, however, can no longer be seen from these pre-heated samples; *X*-ray photographs proved that the peak freshly produced in the L.T. curve corresponds with the spinel formation. The reaction proper starts at about 700° and is finished at about 800°.

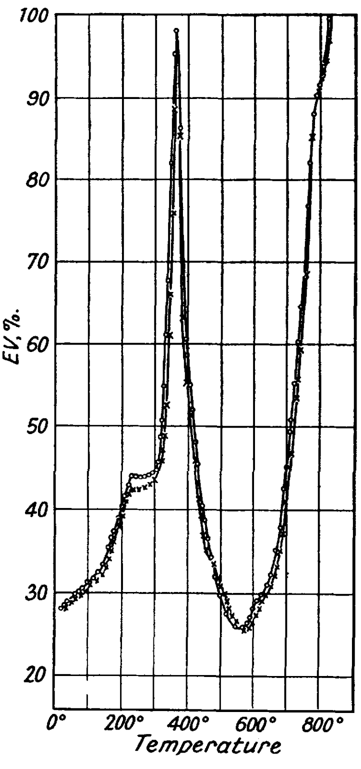
Cadmium–iron spinel. In the foregoing example the zinc hydroxide (containing carbonate) was indicated by radio-thorium, the iron component not being activated; we could, of course, alternatively " indicate " iron and add zinc in an inactive state. The spinel formation should be denoted at the same point. Schröder carried out such a complete investigation, for instance, with the formation of the cadmium–iron spinel. He first studied the emanation discharge of the individual activated components, the cadmium hydroxide (containing carbonate) and the ferric hydroxide. Then he prepared the mixtures, on the one hand the iron component and inactive cadmium carbonate, and, on the other hand, the active cadmium component and inactive ferric hydroxide. In Figs. 18 and 19 we see the L.T. curves for the components. Schröder (*ibid.*, 1940, **46**, 680) summarises his results as follows : FeO•OH discharges its adsorption water up to 150° ; the decomposition of the hydroxide subsequently begins and passes its maximum at 250°. Above 350° the resulting γ-Fe_2O_3 is transformed into α-Fe_2O_3 which causes a weak " glowing " at 450° and continues to recrystallise up to about 700°, whereat the " loosening " begins with the strong rise in the emanating power. In the L.T. curve for cadmium carbonate (to which a basic carbonate had been added to give sufficient absorption of radio-thorium), the first discontinuity corresponds with the water discharge, and the very steep peak shows the temperature of dissociation of the carbonate into the oxide. It lies at 357°, in good agreement with the temperature given in the literature. The " loosening " of the lattice starts below 600° in this case.

FIG. 18.



L.T. curve of γ-FeO·OH.

FIG. 19.



L.T. curve of $CdCO_3$.

The R.T. curves were recorded as well as the L.T. curves depicted, and the processes were controlled analytically, chemically, and by *X*-ray photography (Schröder, *loc. cit.*; *ibid.*, 1941, **47**, 196).

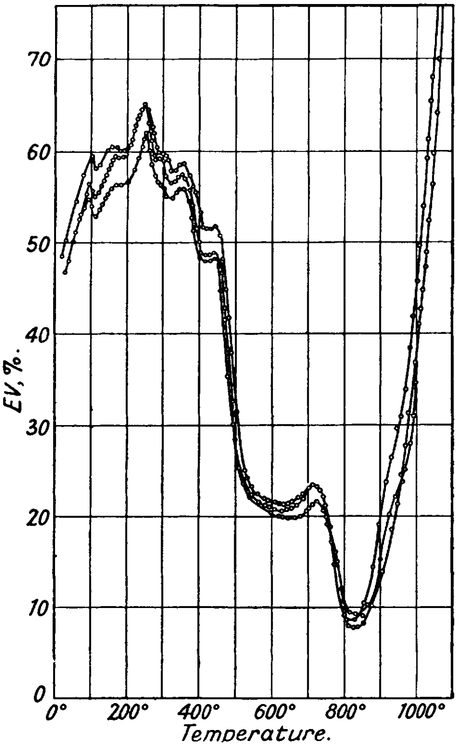
The behaviour of the individual components having been studied, that of the mixtures is shown in Figs. 20—23, the L.T. curves as well as the R.T. curves being given.

Fig. 20 shows the L.T. curve for active ferric hydroxide and inactive cadmium carbonate. The initial curve is quite analogous to that of the ferric hydroxide only. Another peak arises above 700°. The corresponding R.T. curve is represented in Fig. 21. It shows the processes associated with the various heating stages : *X*-ray results, and loss of CO_2 and H_2O.

Finally, we represent the curves for the mixture of active carbonate and inactive ferric hydroxide. Here the peak corresponding to the spinel formation is even more pronounced; it lies at the same point as in the reverse case.

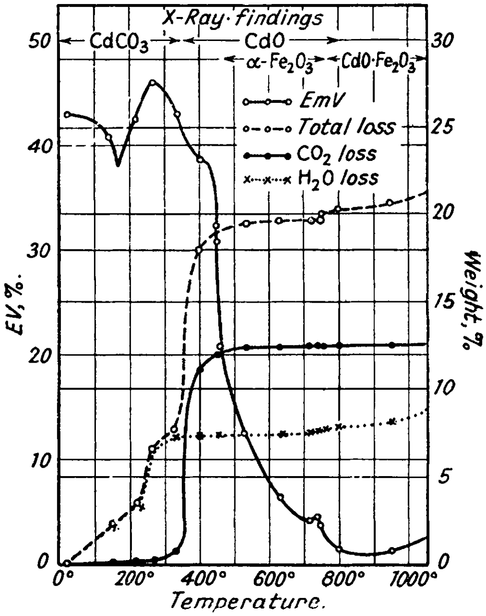
The R.T. curve associated with the last-mentioned L.T. curve is represented in Fig. 23, with an indication of the processes associated with the individual stages.

FIG. 20.



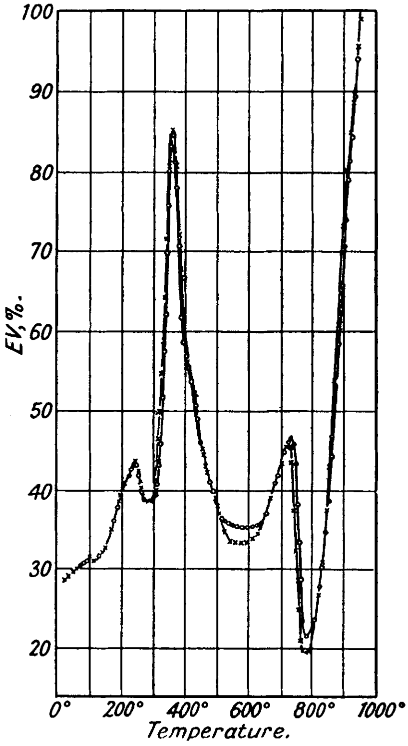
L.T. curve of mixed active FeO·OH *and inactive* $CdCO_3$.

FIG. 21.



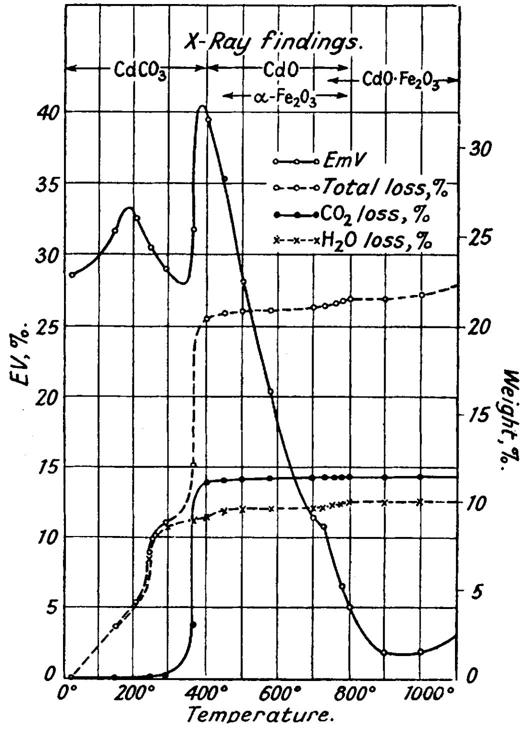
R.T. curve of mixed active FeO·OH *and inactive* $CdCO_3$.

FIG. 22.



L.T. curve of mixed active $CdCO_3$ *and inactive* FeO·OH.

FIG. 23.



R.T. curve of mixed active $CdCO_3$ *and inactive* FeO·OH.

Fricke and Kubach (*Z. Elektrochem.*, 1949, **53**, 76) recently applied the emanation method to the investigation of the processes of conversion $Cu(OH)_2 \longrightarrow CuO \longrightarrow Cu \longrightarrow CuO$ both for the pure substance and on silica gel. The reactions were followed essentially as described for Schröder's work above. The process of reduction as well as the subsequent oxidation can be clearly interpreted for these processes by the amount of emanation discharged in the respective case. The same authors also gave improved working directions for the application of the " copper pile " (" Kupferturm ") which serves for removing the last traces of oxygen from nitrogen and inert gases. In order to maintain the capability of reaction one should operate the copper pile at 160°, instead of 200° as was stated previously.

(VII) *Absolute Surfaces and Diffusion Constants.*—Flügge and Zimens (*Z. physikal. Chem.*, 1939, *B*, **42**, 179) have tried a quantitative approach to the problem of the escape of rare-gas atoms from solids, and Zimens (*ibid.*, 1942, *A*, **191**, 95; 1943, **192**, 1; see also his " Handbuch der Katalyse," Vol. IV, pp. 221 *et seq.*, Verlag Springer, Wien, 1943) has continued his work experimentally as well as theoretically. In short, the results of these investigations are as follows. The measured emanation power is, in general, a very complex quantity. Essentially, one must distinguish between the fraction of emanation atoms escaping by the recoil when the radioactive disintegration of the mother atoms takes place, and the fraction escaping by diffusion of the emanation atoms through the solid substance. The measured emanation power (ϵ) consequently is composed of the " recoil fraction " (ϵ_R) and the " diffusion fraction " (ϵ_D); *i.e.*, $\epsilon = \epsilon_R + \epsilon_D$. For all quantitative evaluations it is necessary to determine ϵ_R and ϵ_D separately. This can be done, *e.g.*, by measuring the emanation power ϵ with two emanations of different half-life, or by measuring the temperature coefficient of ϵ, or by observation of the emanation power with the long-lived radium emanation as a function of time.

If the recoil-fraction ϵ_R and the diffusion-fraction ϵ_D are known separately, it is possible to ascertain from ϵ_R a characteristic surface-quantity for the sample, and from ϵ_D the diffusion coefficient of the rare-gas atoms in the solid. These quantities then can be easily studied as functions of temperature, of time, etc.

The experimental technique of preparation of samples, of measuring the emanation power, and of studying ϵ as a function of temperature, etc., has been described and summarised by Zimens (*Z. physikal. Chem.*, 1942, *A*, **191**, 1). In this paper also the applications of artificial radioactive rare gases are discussed, and some experiments with the 9·2-hour xenon (^{135}Xe) are described. The paper includes a list of all publications on the " emanation method " during the years 1923 to 1942.

(VIII) *Application to Nuclear Physics.*—In Section (III) reference was made to work by Bjerge (*loc. cit.*), who used Strassmann's report on the 100% emanation power of salts from organic long-chain monobasic acids to separate a neon of a half-life period of 40 seconds from a " highly emanating " sodium stearate. Dr. Strassmann and the author made use of our experiences on highly emanating hydroxides for the precipitation of short-lived fission products from uranium (*Naturwiss.*, 1940, **28**, 54) and thorium (*ibid.*, p. 61). We prepared ammonium uranate and thorium hydroxide of a very large surface area. When irradiated with the neutrons from our radium-beryllium preparations the gaseous fission products, xenon and krypton, even the very short-lived ones, diffused from the preparations into the air, and their decay products, cæsium and rubidium, could easily be deposited at a negatively charged plate of cadmium from which the fission products could easily be dissolved and the chemical separations undertaken. The experiments were performed in such a way that other fission products due to the recoil were not present.

By taking all due precautions we succeeded in measuring the cæsium isotopes separated as cæsium silicotungstate from all the other fission products 1·2—1·4 minutes after interruption of the radiation! In the case of rubidium precipitated as rubidium stannous chloride the measurements could be started after 1·6—1·8 minutes. In addition to the cæsium and rubidium isotopes which we had detected previously, we thus succeeded in establishing the existence of a cæsium of a half-life period of about 40 seconds and of a rubidium of a half-life period of about 80 seconds.

Grateful acknowledgement is made of the permission to reproduce diagrams as follows: to the Oxford University Press and Cornell University Press for Figs. 1, 2, 3, 4, 6 and 7 from O. Hahn's "Applied Radiochemistry"; to Akademische Verlagsgesellschaft Geest und Portig, Leipzig, for Figs. 10, 11, 12, 13, and 14 from *Z. physikal. Chem.*; and to Dr. Dietrich Steinkopf, Frankfurt a. M.-Griesheim, for Fig. 7 from *Kolloidchem. Beih.*

GÖTTINGEN. [*Read, March 28th,* 1949.]