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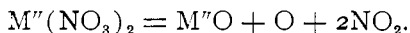
 THE DISSOCIATION OF LEAD NITRATE.¹

BY LEO BAEKELAND.

Received January 21, 1904.

It is generally accepted that all nitrates of heavy metals, under the action of heat, decompose, producing NO₂, oxygen and a metallic oxide. Whenever the oxides of the metal are not stable at high temperatures, further decomposition may set in, thus producing oxygen and metal.

The final reaction can be summarized as follows:



In the case of lead nitrate, the decomposition begins at a temperature between 205° and 223°. Even at these temperatures the decomposition proceeds very slowly and it is only when temperatures as high as 357° are reached that the reaction becomes more energetic.

However, if the experiment be carried on *in vacuo* nitrous gases develop more abundantly, even at temperatures as low as 205° to 223°.

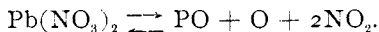
It is interesting to note that ordinary lead nitrate, as sold in the trade under the name of chemically pure, gives off acid vapors at much lower temperatures; in some cases simple heating at 100° may produce this result. This is due to the presence of very small amounts of moisture. In the experiments I am about to describe I used a specially prepared lead nitrate, very

¹ Read at the December meeting of the New York Section.

pure and entirely free from any traces of moisture. I soon found out that unless these precautions are observed, the most variable results will be obtained.

In order to purify lead nitrate, I make a cold saturated solution in distilled water, to which I add afterwards concentrated nitric acid, which causes the lead nitrate to precipitate in small white crystals. After the liquid is drained off the crystals are redissolved in water, reprecipitated with nitric acid and this cycle of operations is repeated six times in succession, when finally the crystalline powder is dried in an air-bath at a temperature not exceeding 100° , so as to drive off all free nitric acid while hot. The crystalline mass is afterwards pulverized in a warm mortar, and is heated during twenty-four hours at about 120° , then finally the temperature is raised to 160° for about one hour, after which time the white crystalline powder is introduced hot in a previously heated glass-stoppered bottle. It is kept for use in a sulphuric acid desiccator. These painstaking precautions prevent absorption of moisture from the air, and make it possible to obtain constant results.

If such pure lead nitrate be enclosed in a sealed glass tube, in which a vacuum has been made, and if this tube be suspended in a bath of boiling mercury vapor, which is a convenient way of keeping it steadily at 357° C., red nitrous vapors appear very soon, showing that decomposition has begun, and after awhile the red coloration of the gases becomes very intense. If at this moment the heat be withdrawn and the tube be allowed to cool slowly, it will be found that after a few hours all red vapors have disappeared and on opening the tube vacuum will be reestablished, showing conclusively that under the above conditions all gaseous products have been reabsorbed. We have here to deal with an example of a reversible reaction:



This case is more interesting from the fact that in this instance a solid body dissociates, forming one new solid and two different gaseous products.

This is the reason why I have tried to investigate this reaction from a physical standpoint so as to determine, by experiment, the pressure of the dissociation at different temperatures and

how this pressure is influenced by an excess of either one of the gaseous products of dissociation.

I soon found out that the study of this reaction involved the use of very delicate and painstaking methods, and unless great precautions are used no reliable data can be obtained.

In order to reduce the errors of observation I had to repeat some of these experiments several times, and if it is taken into consideration that some of the experiments extend over a number of weeks, the fact that the observations are not more numerous may be excused.

Description of the Apparatus.—Fig. 1 shows the apparatus

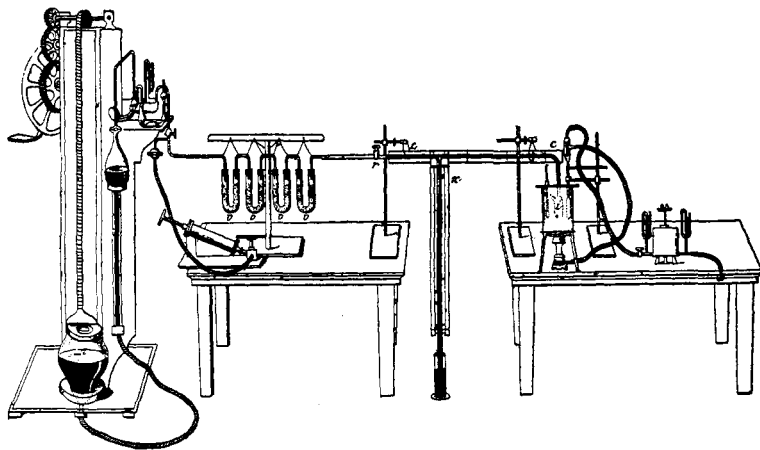


Fig. 1.

used for the first method. A glass reservoir *i*, of about 50 cc. capacity, heated at constant temperature, contains pure lead nitrate and is connected by means of a capillary tube *c c* with a mercury vacuum pump. A manometric tube, *x*, plunges into a reservoir of mercury; this tube narrows down to a capillary space on its upper part.

The four U-tubes contain phosphoric anhydride and caustic potash so as to absorb any traces of moisture or acid vapors.

The reservoir *i* is provided with a lateral glass tube through which the lead nitrate can be introduced without incurring the possibility of introducing moisture at the same time.

After the air of the apparatus has been carefully evacuated, the cock *r* is closed so as to discontinue all connection with the

vacuum pump, and the reservoir *i* is now heated to the proper temperature. For all temperatures below 357° a bath of Woods' alloy was used. The temperature was kept steady by the use of a specially constructed thermoregulator. For higher temperatures a bath of mercury vapors was employed.

At temperatures below 300° the gaseous products are evolved rather slowly, and it takes ten, sometimes twenty-four, hours before the mercury column shows the maximum depression. At 357° indications become totally erroneous, on account of the fact that the surface of the mercury in the manometer column is rapidly attacked by the nitrous gases, evolving thus new gaseous products. At low pressures, and under absolutely dry conditions, mercury is not acted upon by the nitrous gases; at higher pressures, the surface of the metal covers itself with a gray substance and nitric oxide is formed.

This was conclusively shown by direct experiments which were carried out with the object of studying this question.

The continuous production of nitric oxide under the above condition increases indefinitely the pressure of the gases and renders it impossible to observe the pressure of dissociation; furthermore, the mercury meniscus becomes so covered with products of corrosion that readings become impossible.

In order to obviate the above-mentioned irregularities I had to modify my apparatus for all experiments carried on at high temperatures. This was accomplished, as shown in Fig. 2, by fusing with a capillary on the upper part of the manometric tube, a glass bulb of about 500 cc. capacity, which was provided on its lower capillary extension with a glass cock *r* communicating with a wider glass tube which acts as a mercury manometer; for this purpose it was connected through a thick flexible rubber tube with an upright glass tube *t'*. The cathetometer readings of the difference in height of the mercury column in *t* and *t'* gave me the pressure of dissociation, due corrections being made, of course, for error of meniscus and variations in barometric pressure.

The glass bulb *b* was encased in a copper reservoir, of which the temperature was kept invariably at 100° by means of circulating water vapor.

In order to make my determinations I first opened the cocks *r* and *r'*, then poured mercury into *t'* until its level in tube *t* was

situated at about 2 or 3 millimeters below the point where this tube narrows to a capillary opening. Shutting off this cock, *r*,

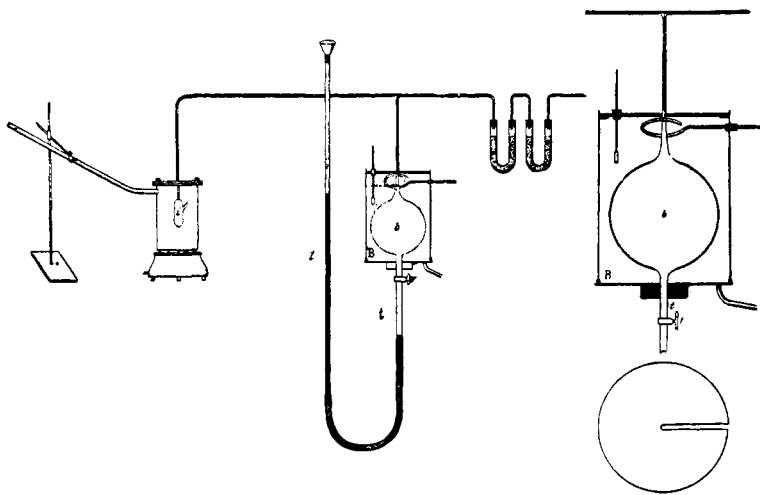


Fig. 2.

I made a vacuum in the apparatus then, after cock *r*' was shut off, also, I started heating either at 357° in a bath of boiling mercury vapors, or at 448° in vapors of boiling sulphur.

After twenty-four hours' steady heating, I opened *r*, and by lifting or lowering *t*' or, if necessary, by adding some more mercury I was able to bring the mercury column to its original height in the tube *t*. By making a quick reading, I prevented any appreciable action of the nitrous gases upon the mercury.

In all my experiments and at temperatures ranging from 223° to 448° , the pressure of the evolved gases increased until a maximum was reached. Arrived at this limit, this pressure remained practically the same and increased no further. In some cases it was necessary to heat for several days before this limit of pressure was obtained. This pressure, which represents the pressure of dissociation of lead nitrate, varies with the temperature and is practically constant for each temperature. The following table indicates the average pressure for several different temperatures:

Temperatures. °C.	Pressure of dissociation. Millimeters.
223	6.2
230	6.9
250	11.8
274	32.6
296	78.4
357	514.0
448	1180.0

The above figures are the average results of a considerable number of observations; they are graphically illustrated by the accompanying curve (Fig. 3).

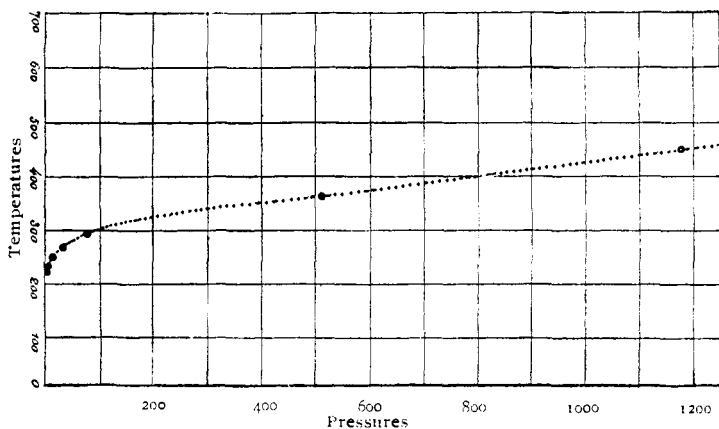


Fig. 3.

Some direct experiments have shown me that the pressure of dissociation acted the same whether I used 10 or 70 grams of material, provided the experiment was carried out at the same temperatures and provided also that the amount of lead salt used was sufficient to evolve enough gaseous products so as to reach the limit of pressure.

Whenever this limit was reached the pressure remained stationary. If, at that time, communication with the vacuum pump was reëstablished so as to evacuate the gaseous products, a new amount of gas was liberated until the corresponding maximum pressure was again obtained. For instance, in four successive evacuations at 357° the limit of pressure was always from 508 to 519 mm. which approximates sufficiently the average pressure of 514 mm.

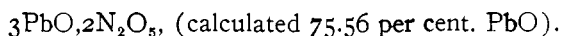
In other experiments I carried the number of evacuations far

enough to decompose a considerable amount of the lead nitrate used. The results of this work are condensed in the following table:

Temperature. °C.	Maximum of dissociation after each evacuation of mercury. mm.	Duration of each experiment.	Composition of lead salt.
357	514	24 hours, 1st evacuation	{ PbO = 67.37 { N ₂ O ₅ = 32.63
			100.00
	517	48 hours, 2d evacuation	?
	508	3 days, 3d evacuation	?
	515	4 days, 4th evacuation	?
	514	5 days, 5th evacuation	?
	510	9 days, 6th evacuation	?
	296	11 days, 7th evacuation	?
	257	12 days, 8th evacuation	?
	260	13 days, 9th evacuation	?
	259	14 days	{ PbO = 73.98 { N ₂ O ₅ = 26.02
			100.00

As will be noticed from above results, the pressure of dissociation remains constant until the composition of the lead nitrate has undergone a considerable alteration by progressive elimination of gaseous products. At a certain point the partially decomposed salt shows a considerable decrease in its pressure of dissociation, which at 357° drops suddenly from 514 mm. to 260 mm. When this occurs, the residue in the reservoir acquires a slightly yellowish color.

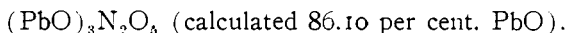
In the same way when lead nitrate was kept heated for about ten days in an open vessel at 357°, the partially decomposed salt gave, on investigation, a pressure of dissociation of 260 mm. In the above table it is shown that the composition of the partially decomposed lead nitrate indicates 73.98 per cent. of lead oxide, which would correspond to a basic lead nitrate,



We have to deal here, very probably, with a basic nitrate of which the pressure of dissociation is considerably lower than that of ordinary lead nitrate. It became interesting to determine whether the basic nitrate is the only intermediate product of decomposition of the lead nitrate, or whether more basic nitrates are

produced subsequently, of which the pressure of dissociation is still smaller.

For this purpose I left the apparatus in continuous communication with the vacuum pump while heating the lead nitrate at 357° C. By constant evacuation I was able to hasten decomposition. From time to time I shut the glass stop-cock so as to ascertain whether red gases were still accumulating. After ten days I was thus able to find out that no further nitrous gases were evolved, that the residue so obtained underwent no further decomposition at this temperature and showed no pressure of dissociation. On analysis, I found this product to contain 86.03 per cent. of lead oxide which might correspond to a basic nitrate,



Although this salt is stable at 357° C., it decomposes at a red heat, leaving a residue of pure lead oxide, while nitrous gases escape.

According to these observations it is very probable that under the action of heat, lead nitrate decomposes first in oxygen, nitrogen peroxide, and a new salt, $(\text{PbO})_3(\text{N}_2\text{O}_5)_2$, more stable than lead nitrate, and of which the pressure of dissociation is smaller. Later on, this salt decomposes further in a more basic nitrate, $(\text{PbO})_3\text{N}_2\text{O}_6$, stable at 357° , which is destroyed at a red heat and leaves then a residue of lead oxide.

In how far is the pressure of dissociation of lead nitrate influenced by the relative proportions of nitrogen peroxide and oxygen in the gaseous products?

In order to determine this question, I introduced into my apparatus variable amounts of oxygen or nitrogen peroxide, of which the pressure was carefully measured before I began to heat the reservoir containing the lead nitrate. Then the operation was conducted as usual and after a pressure limit was reached it was measured by the ordinary means. By subtracting the partial pressure of the oxygen or nitrogen peroxide from the final observed pressure, I obtained the partial pressure of dissociation of lead nitrate under these special conditions. The necessary correction involved by the dilatation of the gas first introduced was made by calculating the dilatation of the amount of this gas contained in the reservoir.

The following tables, which condense these results, show that in each case there was a considerable decrease in the pressure of dissociation. From the standpoint of chemical dynamics, it might be very interesting to extend these observations. Unfortunately, these researches involve many delicate precautions which might be easily avoided by selecting compounds more suitable than lead nitrate for this class of work.

Temperatures. °C.	Partial pressure of excess of oxygen. mm.	Total pressure of all gaseous products. mm.	Real pressure of dissociation in presence of excess of oxygen. mm.	Pressure of dissociation for lead nitrate without excess of oxygen. mm.	Ratio between partial and total pressure.	Ratio between pressure without and with excess of oxygen.
357	425	583	158	514	7 : 10	10 : 3
357	425	592	167	514	7 : 10	10 : 3
357	467	586	119	514	8 : 10	10 : 2
Temperatures. °C.	Partial pressure of nitrogen peroxide in excess. mm.	Total pressure of all gaseous products. mm.	Real pressure of dissociation in presence of excess of nitrogen peroxide. mm.	Pressure of dissociation for lead nitrate without excess of nitrogen peroxide. mm.	Ratio between partial and total pressure.	Ratio between pressure without and with excess of nitrogen peroxide.
357	630	780	130	514	8 : 10	10 : 3
357	640	790	150	514	8 : 10	10 : 3

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

NEW METHOD OF DETERMINING COMPRESSIBILITY, WITH APPLICATION TO BROMINE, IODINE, CHLOROFORM, BROMOFORM, CARBON TETRACHLORIDE, PHOSPHORUS, WATER AND GLASS.¹

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IT HAS been suggested recently that since the volume of a solid or liquid must be determined in part by the internal pressures to

¹ Indicated by the difference between total pressure of gaseous products and partial pressure of excess of nitrogen peroxide.

² This paper is an abbreviated statement of the chief points in an investigation printed as a monograph by the Carnegie Institution (Publication No. 7), entitled "New Method for Determining Compressibility."