THE DISSOCIATION OF LEAD NITRATE

BY J. LIVINGSTON R. MORGAN.

In a recent paper with the above title,¹ Baekeland has given the vapor pressure of solid lead nitrate at different temperatures; but for some reason has made no application of the possible theoretical relations to his results. As the application of some of these shows much concerning the equilibrium, which is lost by his purely qualitative treatment, and as Mr. Baekeland has evidently no intention of considering the question further, the results of such application are presented in this paper.

When heated, lead nitrate dissociates according to the following scheme :

Baekeland's results are as follows :

TABLE I.
Dissociation pressure of $\text{Pb}(\text{NO}_3)_2$

Temperatures. °C.	Pressures in millimeters
223	6.2
230	6.9
250	11.8
274	32.6
296	78.4
357	514.0
400	800.0 ²
448	1180.0

In addition to these vapor pressures of the pure lead nitrate, he also gives the vapor pressure in the presence of an excess of oxygen and an excess of nitrogen peroxide. The

¹ Jour. Am. Chem. Soc. 26, 391-399 (1904).

² Interpolated from Mr. Baekeland's curve, l. c. 396.

average values only of these are given in Tables II and III in order to reduce the experimental error to as low a value as possible.

TABLE II.

Vapor pressure of $\text{Pb}(\text{NO}_3)_2$ in presence of an excess of oxygen
(in mm.) $t = 357^\circ \text{C}$.

Excess of free oxygen	Total pressure of gases	Dissociation pressure of $\text{Pb}(\text{NO}_3)_2$
425	587	162
467	586	119

TABLE III.

Vapor pressure of $\text{Pb}(\text{NO}_3)_2$ in presence of an excess of nitrogen peroxide (in mm.) $t = 357^\circ \text{C}$.

Excess of free nitrogen peroxide	Total pressure of gases	Dissociation pressure of $\text{Pb}(\text{NO}_3)_2$
635	785	150

Application of the Law of Mass Action

Applying first the law of mass action to the reaction

it is apparent that

$$\pi_1 K = \sqrt{p_1} p_2^2 \pi_2,$$

where K is the dissociation constant for the temperature in question, π_1 and π_2 the active masses of the solids, $\text{Pb}(\text{NO}_3)_2$ and PbO , p_1 the partial pressure of the oxygen, and p_2 that of the nitrogen peroxide. Omitting the active masses of the solids as constant, we should have then at any one temperature,

$$\sqrt{p_1} p_2^2 = \text{constant.} \quad \text{I.}$$

At 357°C , from Table I, we find the total pressure of the gases from pure $\text{Pb}(\text{NO}_3)_2$ equal to 0.514 meter of mercury. Of this one-fifth must be oxygen and four-fifths nitrogen peroxide; hence $p_1 = 0.103$, $p_2 = 0.412$, and

$$\sqrt{P_1 P_2} = \sqrt{0.103(0.412)^2} = \text{constant} = 0.062.$$

This constant value should also be given when one of the products of dissociation is previously present. From Table III we find that in presence of 0.635 (meter of mercury) of nitrogen peroxide we have 0.150 of gases from the $\text{Pb}(\text{NO}_3)_2$. Of this the oxygen is one-fifth $(0.150) = 0.030$, and the nitrogen peroxide is four-fifths $(0.150) = 0.120$, which when applied in the equation gives,

$$\sqrt{0.03(0.120 + 0.635)^2} = 0.098.$$

That this high value is due to a slight experimental error is shown by the fact that a change of pressure of 10 mm in the nitrogen peroxide does not change the pressure of the gases from the $\text{Pb}(\text{NO}_3)_2$. We may assume then that an excess of the nitrogen peroxide keeps the reaction in its normal form. When an excess of oxygen is present, on the other hand, the reaction apparently becomes abnormal. From Table II, by aid of the law of mass action, we have

$$\sqrt{0.032} + 425(0.128)^2 = 0.011$$

and

$$\sqrt{0.024} + 467(0.096)^2 = 0.0091.$$

It has already been observed that under certain conditions a basic nitrate of lead $3\text{PbO} \cdot 2\text{N}_2\text{O}_5$, or $(\text{PbO})_3\text{N}_2\text{O}_5$, can be formed which has a very much smaller vapor pressure than the normal salt. From these results it would seem that an excess of oxygen favors the formation of this from the normal salt, and causes a different reaction to take place, and consequently gives a different constant.

Application of van't Hoff Equation

The values in Table I can be used in van't Hoff's equation to find the heat of dissociation of lead nitrate. We have

$$q = \frac{i \times R \times 2.302 \times T_1 \times T_2 \left(\log \frac{P_2}{T_2} - \log \frac{P_1}{T_1} \right)}{T_2 - T_1} \quad \text{II}$$

where i is the number of gram-molecules of gas formed from one

of the original substance (2.5 in this case); R the molecular gas constant, i. e., Ostwald 0.02 cal ; 2.302, the reciprocal of the modulus of the system of logarithms; T , the lower absolute temperature, for which the dissociation pressure is P_1 ; T_2 the higher, corresponding to P_2 and q the heat of dissociation for the mean temperature, viz. $\frac{T_1 + T_2}{2}$. Before using this equation, however, we must consider just what value should be found. The heat of formation of $\text{Pb}(\text{NO}_3)_2$ has been determined by experiment only from the elements. To get the value from PbO , O and 2NO_2 , it is necessary to know the heat value of PbO and 2NO_2 . We find

From these equations we get as the experimental value of the heat of formation of $\text{Pb}(\text{NO}_3)_2$

This value, it is to be remembered, is under atmospheric pressure. The q , found by aid of equation II, however, is for the case that no external work is done by the gases as they form, or done on them when they disappear. To get the above result of 604 Ostwald calories in terms of no external work, it is necessary then to subtract from it the heat value of the work done by the atmosphere during the decrease in volume. If this is done, the negative value will correspond to the q in equation II. For the loss of every gram-molecule of gas the work, in terms of heat, is RT Ostwald calories, where $R = 0.02$. In the case of lead nitrate we have a loss in volume equal to that of 2.5 gram-molecules of gas; i. e., $\frac{1}{2}\text{O}_2 + 2\text{NO}_2$, so that the amount to be subtracted from the 604 in order to compare it with q (equation II) is $2.5 \times 0.02 T$, where T is the average temperature, the $\frac{T_1 + T_2}{2}$ of equation II.

¹ Ostwald's Lehrbuch, II, 341.

² Ostwald. 1. c. 348.

³ Berthelot. Comptes rendus, 90, 779 (1880).

Applying the values given in Table I to equation II and comparing them with the experimental values, we get the following results :

TABLE IV.
Heats of dissociation of $\text{Pb}(\text{NO}_3)_2$

Temperatures (absolute)			Heat of dissociation in Ostwald calories	
T_1	T_2	Average	Equation II.	Observed
523	547	535	579	578
547	569	558	593	576
569	630	599	523	574
630	673	646	147 ¹	572
630	721	675	172	571

The equation (II) holds perfectly for the first result where the difference in temperature and pressure is small. The other results, with the exception of the second, are all low, which may be due to experimental errors.

Résumé

The application of the law of mass action to Baekeland's vapor pressures of lead nitrate, shows the constant product $\sqrt{p_{\text{O}}}(p_{\text{NO}_2})^2$ to have the value 0.062 at 357° C.

The addition of NO_2 in excess shows the presence still of the normal scheme of dissociation.

The addition of oxygen evidently favors the formation of other salts, richer in oxygen, and the scheme of dissociation is changed.

The application of van 't Hoff's law gives for the case of low temperature the value of the heat of dissociation equal to the negative value of the heat of formation under like conditions, i. e., 578 Ostwald calories.

Laboratory of Physical Chemistry.

¹ This value in Table I was interpolated from the curve given in the paper, so great stress may not be laid upon it.