

investigated and give promise of extensive commercial utilization.

(3) Semon, W. L., U. S. Patent 1,929,453 (Oct. 10, 1933).

(4) Whitby, G. S., and Katz, J. R., *IND. ENG. CHEM.*, **25**, 1204 (1933).

### Literature Cited

(1) Carothers, W. H., *IND. ENG. CHEM.*, **26**, 30 (1934).

(2) Ostromislensky, I., Canadian Patent 270,225 (Apr. 26, 1927).

RECEIVED March 18, 1935. Presented before the Division of Industrial and Engineering Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.



# Vapor Pressure and Dehydration of Unstable Salt Hydrates

## Sodium Perborate



**I**N RECENT years sodium perborate has been used in many new and important ways. This results from the more economical and improved methods of manufacture which allow it to be placed on the market at a much reduced price. Earlier uses were limited to some special preparations such as washing powders, cosmetics, dentifrices, and other pharmaceutical preparations, but at present it finds many other important industrial uses as an oxidizer in such processes as bleaching, dyeing, laundering, and electroplating.

Sodium perborate is prepared commercially today on a large scale and comes on the market supposedly as a tetrahydrate,  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ , but more correctly  $\text{NaBO}_3 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ , containing about 10 per cent available oxygen. It crystallizes in transparent monoclinic crystals which are comparatively stable in air. A water solution of sodium perborate slowly decomposes to yield active and then gaseous oxygen. This decomposition is accelerated by catalysts and by slightly elevated temperatures, 40° to 60° C. Its oxidizing qualities depend upon these properties. The behavior and properties of sodium perborate in water solutions have already been carefully studied by a number of investigators (3, 5, 8, 16, 17, 21, 27).

There is little information readily available on the behavior of sodium perborate and other unstable salt hydrates upon dehydration. The conditions under which dehydration takes place are known to affect the properties of the product markedly. Thus Foerster (10) has found that sodium perborate dehydrated at 120° C. *in vacuo* possesses properties different from those of the hydrated crystalline salt. With properly controlled dehydration these new and sometimes enhanced properties may be used to advantage in certain operations and preparations. The conditions under which dehydration

A study is made of the factors influencing the rate of dehydration of salt hydrates. A partial explanation of the mechanism of dehydration is given, and equations are developed which give the rate of dehydration for hydrates having different rates of nucleus formation. The influence of temperature, air pressure, air velocity, depth of material and area exposed, and size of particles on the rate of dehydration is evaluated. Interest is centered in sodium perborate, and a study is made of the effects of dehydration upon its properties and constitution. Since no values for the vapor pressure of this hydrate at different temperatures could be found, this phase of the problem was first investigated.

T. IVAN TAYLOR AND GERWIN G. TAYLOR

University of Idaho, Moscow, Idaho



may be carried out without decomposition and the effect of various conditions on the final product are not too well known.

As far as the authors are aware, there has been surprisingly little work done in developing the theory of dehydration and applying it to practical operations. It was therefore thought worthwhile to make a study of dehydration in general. More work is needed along this line and some similar work is being continued in this laboratory. A knowledge of the vapor pressure of a hydrate at different temperatures is essential in determining the conditions under which the hydrate itself is stable; it also yields values which may be of use in determining dehydration rates under certain conditions.

Since no values for the hydrate of sodium perborate could be found, this phase of the problem was first investigated.

### Vapor Pressure

A number of methods have been successfully used for the measurement of vapor pressure of salt hydrate pairs (2, 6, 18, 19, 31). Since sodium perborate gradually decomposes, the static tensimeter method was considered unreliable. The method most applicable to sodium perborate for varying temperatures seemed to be the gas current saturation method which also has its limitations. The experimental set-up was modeled after that described by Schumb (23) which is a modified form of the method of Baxter and Lansing (2).

The details of the set-up can best be obtained from the above references. In brief, the method consists in slowly forcing or drawing a measured amount of dry gas, free from carbon dioxide, through an intimate mixture of the pair of hydrates (or the hydrate and the anhydrous salt) and collecting the water vapor thus taken up by the gas in weighed adsorption tubes containing phosphorus pentoxide or magnesium perchlorate. From a knowledge of the volume of gas

(reduced to dry basis) going through the apparatus, of the average pressure in the tube containing the hydrate mixture, and of the weight of the water obtained, the partial pressure of the water vapor in the tube may be calculated by use of Dalton's law.

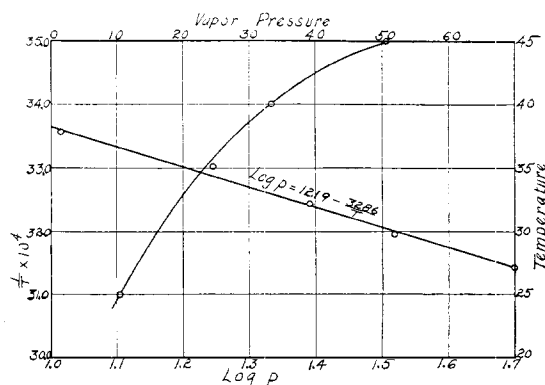


FIGURE 1. EFFECT OF TEMPERATURE ON VAPOR PRESSURE

Instead of drawing air, nitrogen was forced through the apparatus. This procedure required some modification of the method of collecting and measuring the gas. The air-dried, unsized sodium perborate hydrate of the empirical formula  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O} (\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O})$  was mixed with one-tenth its weight of finely ground dehydrated salt of the empirical formula  $\text{NaBO}_3 \cdot \text{H}_2\text{O} (\text{NaBO}_2 \cdot \text{H}_2\text{O}_2)$  and charged into a "saturator" tube 6 cm. in diameter and 40 cm. in length. This was placed in a thermostat constant to  $\pm 0.01^\circ \text{C}$ . and connected to two water-adsorption tubes, the last one being used as a guard against moisture from the aspirators. Nitrogen was generally run through the saturator tube for 12 to 24 hours before starting measurements. The adsorption tubes were connected, and nitrogen was run through at an average rate of not more than one-half liter an hour for a total of 12 to 18 hours. All the necessary precautions were taken, as suggested by the writers cited for measurement of the pressures and volumes and for final calculations. The whole method was checked against hydrate pairs of known vapor pressure.

The vapor pressures of sodium perborate samples obtained from several different companies including one of German make were determined as above at  $25^\circ \text{C}$ . The results are given in Table I and are the average of several independent runs, each checking to less than 2 to 3 per cent of the average value. The agreement is good except for the sample from company E even though there are rather wide variations in the percentage of available oxygen.

TABLE I. VAPOR PRESSURE OF SODIUM PERBORATE AT  $25^\circ \text{C}$ .

Company	Grade	Vapor Pressure Mm. Hg	Available Oxygen Per cent
A	U. S. P.	$10.4 \pm 0.20$	10.5
B	Unspecified	$10.5 \pm 0.25$	8.8
C	Analytical reagent	$10.3 \pm 0.20$	10.3
D	C. P.	$10.0 \pm 0.25$	9.7
E	U. S. P.	$9.1 \pm 0.25$	10.5

To determine the relation between vapor pressure and temperature, the thermostat was filled with a thin transformer oil. This proved much more satisfactory than water because there was no evaporation. For the higher temperatures, some water tended to condense in the delivery tube. Instead of immersing the delivery tube and the adsorption tubes in the thermostat, a heating device for the delivery tube was made from a 3.5-cm. glass tube which was wound with

resistance wire and covered with alundum cement and asbestos. The temperature inside the tube was regulated by means of a lamp bank to the same temperature as, or slightly higher temperature than, that of the thermostat. This arrangement was more satisfactory both in this and certain dehydrating experiments because it was difficult to remove all oil from the tubes. Sodium perborate from Roessler and Hasslacher was used in these experiments. The results averaged from several independent runs are as follows:

Temp. $^\circ \text{C}$ .	Vapor Pressure Mm. Hg	Temp. $^\circ \text{C}$ .	Vapor Pressure Mm. Hg
25	10.37	40	33.07
35	24.60	45	50.78

Values at or above  $50^\circ \text{C}$ . were not considered reliable because at this temperature the vapor pressure was of such height that sodium perborate began to react with the water vapor, and a gummy mass resulted. An increase in air velocity helped somewhat, but there was danger that equilibrium would not be established.

The curves in Figure 1 represent vapor pressure plotted against temperature, and the logarithm of the vapor pressure against the reciprocal of the absolute temperature. The latter is nearly a straight line. A three-constant equation of the form,

$$\log p = \frac{A - B}{T + C}$$

where  $p$  = vapor pressure  
 $T$  = absolute temperature  
 $A, B, C$  = constants

was used for similar vapor pressure curves by Antoine (1) and later extended by Siggel (24). Menzies and Hitchcock (18) have found that a two-constant equation of the form

$$\log p = A + \frac{B}{T}$$

describes the results even better. Such an equation represents closely the average results obtained. Evaluating the constants, we obtain the equation

$$\log p = 12.19 - \frac{3286}{T}$$

for the relation between vapor pressure and temperature.

### Heat of Hydration

The heats of hydration can be calculated (19) from the vapor pressures by the Clapeyron-Clausius equation in the form:

$$Q = 4.575 \frac{T_2 T_1}{T_2 - T_1} \log \frac{(P_2/\pi_2)}{(P_1/\pi_1)}$$

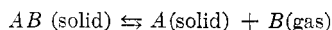
where  $Q$  = heat of hydration, gram cal./mole of water  
 $P_1, P_2$  = vapor pressures at  $T_1$  and  $T_2$ , respectively  
 $\pi_1, \pi_2$  = vapor pressures of water at  $T_1$  and  $T_2$ , respectively

The value calculated from the foregoing for the reaction  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O} \rightarrow \text{NaBO}_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$  between  $25^\circ$  and  $45^\circ \text{C}$ . is 4510 calories per mole of water or 13,530 calories for the total reaction. Since the average value of the heat of vaporization of water between  $25^\circ$  and  $45^\circ \text{C}$ . is 576 calories per gram, and since the heat of efflorescence equals heat of hydration plus heat of evaporation, the heat of efflorescence per gram of water is 826 calories.

### Dehydration

The factors governing the rate of dehydration of salt hydrates from which the free or mechanical moisture has been

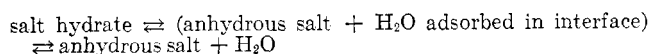
removed are, in a measure, different from those encountered in ordinary drying operations. Since the water is chemically combined, the mechanism of dehydration is, moreover, fundamentally different. In ordinary drying we are generally concerned with the removal of moisture which is not strictly chemically combined, and which will diffuse as water or vapor when a concentration gradient is set up. In dehydration we are concerned with a reversible chemical decomposition of the type



and vapor diffusion. If conditions are such that vapor diffusion is the controlling factor, then the equations describing the rate of dehydration will be similar to those describing the rate of drying where vapor diffusion is the controlling factor. If there is immediate removal of water vapor, the limiting factor will be the rate of the forward reaction. A knowledge of the nature and mechanism of this type of reaction is therefore important.

Langmuir (13) suggested a partial explanation of the mechanism for the reaction  $AB(\text{solid}) \rightleftharpoons A(\text{solid}) + B(\text{gas})$ , and Crowther and Coutts (9) applied it to salt hydrates. Since then, a number of researches by Topley and his associates (25, 26, 28, 29, 30), Bradley, Hume, and Colvin (4, 12), and Garner and Tanner (11) have added much to our knowledge of this type of heterogeneous equilibrium, especially in connection with hydrates. A brief statement of the nature and mechanism of such an interface reaction as developed by this and the previous investigations follows.

From a consideration of the phase rule and the two opposing reactions at equilibrium where two distinct solid phases are concerned, Langmuir showed that the reactions can proceed only at the interface. One of the fundamental conceptions of an interface reaction then is that the only molecules, ions, or ionic groups which react are those in a layer immediately adjacent to molecules, ions, or ionic groups in the lattice of the resultant solid phase. It follows that the rate of such a reaction will be proportional to the area of the interface and not to the quantities of solid phases present. The resultant anhydrous salt is found to be so porous in comparatively thin layers that it offers very little resistance to the escape of gaseous molecules formed in the interface. The presence of other gas molecules within the interstices of the particles of the anhydrous phase offer the greatest resistance. The gas, if not removed by use of high vacuum, quickly establishes an adsorption equilibrium in the interface zone and exerts a retarding effect on the net rate of the forward chemical reaction. The two stages in such an interface reaction for a hydrate may be represented as follows:



These reactions, as will be seen later, possess a large temperature coefficient so that the rate-governing process in the interface is subject to considerable activation with increase in temperature. This activation, as some writers suggest (30), may be in the vibrational degrees of freedom. However, the senior author in collaboration with H. P. Klug is working on an explanation of the mechanism within the interface on the basis of molecular rotation in light of Pauling's work (20) and recent developments in this direction.

If we have a perfect crystal of  $AB$ —for example, a salt hydrate—there is no second solid phase and consequently no interface at which the reaction can take place. It is for this reason that the well-known induction period is observed in many hydrates. As soon as a nucleus of anhydrous phase is formed on the surface, the reaction will proceed from it in all directions. The ease of formation of such nuclei is dependent upon the particular hydrate, upon the surrounding

conditions such as temperature and pressure of water vapor, and upon the preparation and history of the hydrate. It has been found by direct microscopic observation that nuclei generally begin on the edges of the crystals and often where deformation has occurred. Once the reaction has started, and when the gaseous phase is removed as fast as it is formed, it has been shown that the rate of advance of the interface is nearly constant and practically the same in all directions. Hume and Colvin (12), however, made direct observations on certain crystals and found small variations in the rate of advance of the interface parallel to the different crystal faces. The presence of small amounts of water vapor seems to have little effect on the linear rate of propagation of the interface, but its presence does show up in a decreased rate of nucleus formation.

From the above considerations it follows that the rate of dehydration of a particular hydrate at any one temperature is governed by four factors:

1. Rate of nucleus formation.
2. Rate of linear propagation of interface.
3. Size and shape of reactant particles.
4. Rate of removal of water vapor and vapor pressure of the hydrate.

When water is removed from the interface by use of a vacuum, rapid diffusion of water molecules takes place and the fourth factor is eliminated. Since vacuum apparatus is not always available in practice, and in certain cases its use may not be advisable, some type of air drier is used. The removal of water vapor, as is shown later, may then become the controlling factor. In order to get at the absolute rate of the forward reaction under various conditions, equations are first developed assuming immediate removal of water vapor from the interface. After further experimental work a modification of these equations by use of empirical relations evaluating the effect of air pressures, water vapor, and air velocities will be attempted for various hydrates under different conditions.

If one is working *in vacuo* with a hydrate that has a high rate of nucleus formation compared to the linear rate of propagation, the induction period is negligible and the particle may be considered to be almost immediately covered with a thin layer of anhydrous salt. Assuming the particles to be spherical, an equation for the fraction of a particle decomposed at a time  $t$  after the beginning of the reaction may be developed (compare citation 29) as follows: Since  $u$ , the linear rate of propagation of the interface in centimeters per second, is constant, the radius of the undecomposed hydrate after a time  $t$  is  $(r - ut)$ , where  $r$  is the radius of the original particle. The volume of the resultant is then given by

$$v = \frac{4}{3} \pi r^3 - \frac{4}{3} \pi (r - ut)^3 \quad (1)$$

The fraction decomposed at the time  $t$  is obtained by expanding the last term in Equation 1 and dividing by the original volume. This gives the expression,

$$\alpha = 3\left(\frac{ut}{r}\right) - 3\left(\frac{ut}{r}\right)^2 + \left(\frac{ut}{r}\right)^3 \quad (2)$$

Differentiating with respect to time, we can obtain the rate:

$$\frac{d\alpha}{dt} = \frac{3u}{r} - \frac{6u^2t}{r^2} + \frac{3u^3t^2}{r^3} \quad (3)$$

This equation holds good for values up to  $t = r/u$  when decomposition should be complete. The rate of decomposition varies inversely as the radius of the particle. In practice, however, as  $r$  becomes smaller, the rate of nucleation takes on more importance and the theoretical conditions cannot be realized. It can be seen that under the above conditions

where nucleus formation is very rapid, the maximum velocity of decomposition will be greatest at the beginning of the reaction when the area of the interface is greatest.

In the above case only spherical particles are considered. The same reasoning can be followed in the case of a contracting rectangular parallelepiped, provided nucleus formation is rapid enough and spreads immediately over the entire surface. Let  $a$  = length,  $b$  = breadth, and  $c$  = height of each crystal;  $V$  = volume of each crystal =  $abc$ ;  $t$  = time after beginning of decomposition;  $u$  = linear rate of propagation;  $\alpha$  = fraction decomposed at time  $t$ ; then

$$\alpha = \frac{V - (a - 2ut)(b - 2ut)(c - 2ut)}{V}$$

Multiplying and collecting terms,

$$\alpha = \frac{2ut(ab + bc + ac) - 4u^2t^2(a + b + c) + 8u^3t^3}{abc} \quad (4)$$

If two of the dimensions, say  $a$  and  $b$ , are the same, or are near enough the same that we can let  $l = \sqrt{ab}$  without great error, then

$$\alpha = \frac{2ut(l^2 + 2lc) - 4u^2t^2(2l + c) + 8u^3t^3}{l^2c} \quad (5)$$

For the simpler case of a cube, or when the three dimensions are near enough the same that we can let  $d = \sqrt[3]{abc}$ , we obtain the equation,

$$\alpha = 6\left(\frac{ut}{d}\right) - 12\left(\frac{ut}{d}\right)^2 + 8\left(\frac{ut}{d}\right)^3 \quad (6)$$

The rate of dehydration is obtained for any of these cases by differentiating with respect to time. Thus, for the case of a cube,

$$\frac{d\alpha}{dt} = \frac{6u}{d} - \frac{24u^2t}{d^2} + \frac{24u^3t^2}{d^3} \quad (7)$$

In many cases nucleus formation is not so rapid as assumed above, and the particle may develop only a small number of nuclei before its decomposition is complete—that is, before

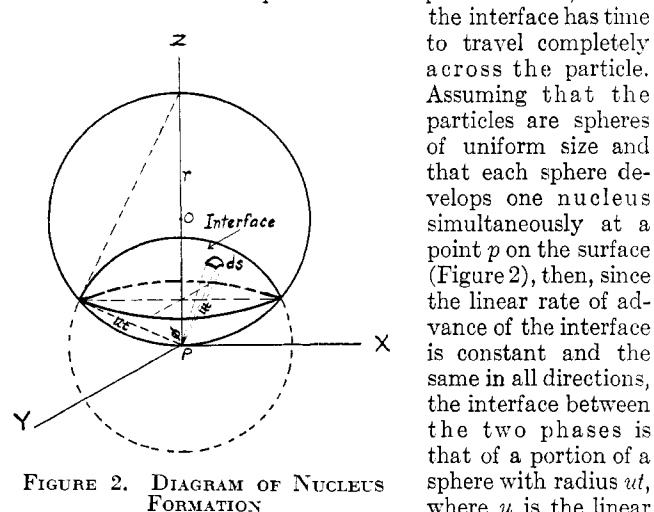


FIGURE 2. DIAGRAM OF NUCLEUS FORMATION

$t$  is the time after the beginning of the decomposition. The area of this interface is given by the equation:

$$S = \int_0^{2\pi} \int_0^{\cos^{-1} \frac{ut}{r}} (ut)^2 \sin \phi \, d\phi \, d\theta = 2\pi(ut)^2 - \frac{\pi(ut)^3}{r} \quad (8)$$

Since this surface is traveling forward with a velocity  $u$ ,

$$\frac{dV}{dt} = Su = 2\pi u^3 t^2 - \frac{\pi u^4 t^3}{r}$$

from which,

$$V = \frac{2\pi u^3 t^3}{3} - \frac{\pi u^4 t^4}{4r} \quad (9)$$

The fraction  $\alpha$  decomposed at time  $t$  is obtained by dividing by  $\frac{4}{3}\pi r^3$ :

$$\alpha = \frac{1}{2} \left(\frac{ut}{r}\right)^3 - \frac{3}{16} \left(\frac{ut}{r}\right)^4 \quad (10)$$

Differentiating with respect to  $t$ , one obtains the rate as follows:

$$\frac{d\alpha}{dt} = \frac{3}{2} \frac{u^3 t^2}{r^3} - \frac{3}{4} \frac{u^4 t^3}{r^4}$$

This equation gives a close approximation in cases where rate of nucleus formation is slow compared to the linear rate of propagation. By increasing the size of the particles sufficiently, this equation will also approximate the first case, provided the velocity of nucleus formation is not too great. This gives an autocatalytic type of sigmoid curve. The rate is slow at first because of the small interfacial area, but increases to a maximum as the interfacial area becomes larger. This maximum occurs when  $t = 4r/3u$  or when  $\alpha = 16/27 = 59.26$  per cent.

Hume and Colvin (12) draw attention to the possibility in which the rate of linear propagation is so great compared to nucleus formation that the particle may be regarded as completely decomposed as soon as it develops a nucleus. If there is immediate diffusion of water vapor from the particle as assumed in all the above cases, and the decomposed particles do not nucleate the undecomposed, then the rate of decomposition is simply proportional to the rate of nucleus formation, or,

$$\text{Rate of decomposition} = K_0 N_t \quad (11)$$

where  $K_0$  = number of nuclei forming per second  
 $N_t$  = number of undecomposed particles present at time  $t$

This is of the nature of a unimolecular reaction. All the above examples should approach this type of behavior if the particles were sufficiently reduced in size. In practice, however, it may be that the relative rate of nucleus formation and linear rate of propagation are such that this cannot be realized. As in unimolecular reactions, equations for rate can be developed on the probability of nucleus formation (4).

Before the equations developed in the foregoing paragraphs are of any practical use, one must obtain the value of  $u$  either by direct observation or calculation from an experimental curve in which time is plotted against fractions decomposed from results obtained by dehydration *in vacuo*. The value of  $u$  may be calculated from the curve by choosing a time and reading the fraction decomposed on the other axis. The size and shape of the crystal is obtained by direct observation with a microscope. Since  $u$  is the only other quantity in the above equations, it may easily be calculated. The value of  $u$  is constant and should apply over the entire range of the curve. The value of  $u$  is generally too large if calculated from the lower part of the curve but is quite satisfactory when calculated from the curves at about 60 to 80 per cent decomposition. In the latter stages it may be assumed that all the particles are completely covered with anhydrous phase, and the interface is changing in area as required by the theory. It has been found that experimental curves agree fairly closely

with the curves plotted by calculating the value of  $u$  as above and substituting arbitrary values of  $\alpha$  and  $t$ . However, the very first and last parts quite often do not and cannot be expected to agree too closely because of the abnormal initial induction period observed with some crystals in the first place, and the early extinction of the smaller particles in the

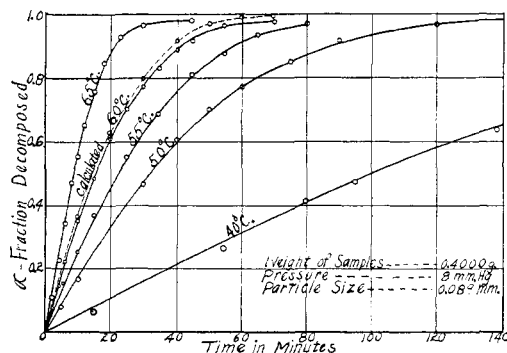


FIGURE 3. EFFECT OF TEMPERATURE ON RATE OF DEHYDRATION IN VACUO

second place. It is also not probable that nucleation falls strictly into these two classes assumed above. Intermediate cases may occur as well. Another apparent difficulty is that the last traces of water cannot readily be driven off.

The constants for a number of the more common hydrates are to be determined so that they may be used in the foregoing equations. These equations apply strictly to systems in which there is immediate escape of water molecules. This escape is realized only *in vacuo* because there are few air molecules to interfere with free escape of water molecules. Where there is free and fast circulation of dry air around each particle, diffusion of water vapor will be comparatively rapid and the foregoing equations will apply approximately. The retarding effect of the air may be evaluated empirically.

At atmospheric pressures the rate of diffusion of water vapor will more often be the controlling factor, and the net rate of loss of water will depend upon the vapor pressure of the hydrate pair at the temperature of dehydration and upon the rate of removal of liberated water vapor. Several factors may interfere with free escape of resultant gaseous water molecules. When the larger particles develop comparatively thick layers of anhydrous salt, some interference results. However, the greatest resistance to rapid diffusion is caused by the presence of air molecules within the porous structure of the anhydrous phase and by the stagnant film of air around the outer surface of the particle. The gaseous phase is further retarded when it has to travel through the interstices between a loose or compressed mass of crystals and finally through a stagnant film of air over the surface. For hydrates which have a high absolute rate of decomposition and fairly high vapor pressure, the rate of dehydration, as will be shown later, is largely controlled by the latter factor.

The results reported in this paper are principally those on vacuum and tray drying. For the particular hydrate in question, information with regard to maximum safe temperature of dehydration and the effect of dehydration on the properties of the salt was needed.

### Results in Vacuo

For work *in vacuo*, a quartz spiral spring balance was made and calibrated as described by McBain (15). Its sensitivity was 9.19 cm. per gram. Fresh phosphorus pentoxide was placed in the bottom of the balance case to take up the water liberated from the hydrate. The balance case was immersed in a bath that could be kept constant at any desired temperature, and connections were made to a manometer and vacuum

pumps. By use of a cathetometer the change in length of the spiral with time of dehydration could be measured and curves showing loss of weight against time constructed. Such curves were made from measurements under varying conditions of temperature, pressure, and size of particles.

The curves obtained for a number of the runs *in vacuo* are given in Figures 3 and 4. Figure 3 shows the dehydration curves with change in temperature, 100 per cent representing the theoretical loss of 3 molecules of water. These curves show that under the conditions indicated there is a very short induction period and a high rate of nucleation. These conditions give the maximum slope near the beginning of the curve, since it is then that the interfacial area is greatest. This finding was borne out by the direct microscopic observation that, in less than 2 minutes at 50° C. and atmospheric conditions, the particles were completely covered with an opaque layer of anhydrous salt.

Sodium perborate forms long monoclinic crystals when crystallization takes place slowly, but fragments of these crystals approximating cubes are formed when crystallization takes place more rapidly. The equation derived in the previous section for a contracting cube with a high rate of nucleus formation should apply to these curves. Calculating  $u$  from the equation

$$\alpha = 6 \left( \frac{ut}{d} \right) - 12 \left( \frac{ut}{d} \right)^2 + 8 \left( \frac{ut}{d} \right)^3$$

by reading a value of  $\alpha$  corresponding to a time on the curve for 60° C., we obtain 0.00062 mm. per minute when the average value for  $d$  is 0.089 mm. as checked by direct microscopic observation. Since  $u$  is essentially constant, a calculated curve can be made by assuming values of  $t$  and calculating the

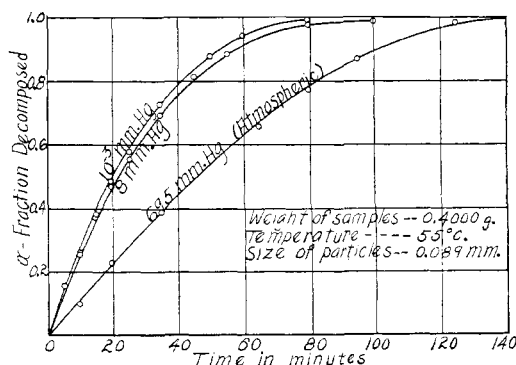


FIGURE 4. EFFECT OF GAS PRESSURE ON RATE OF DEHYDRATION

corresponding values of  $\alpha$ . The dotted curve at 60° C. shows fair agreement with the experimental curve. Values of  $u$  calculated for each of the curves are given in Table II. In Figure 5,  $1/T \times 10^4$  plotted against the  $\log(u \times 10^4)$  gives a nearly straight line represented by the equation  $\log u = 13.86 - 4409/T$ .

TABLE II. EFFECT OF TEMPERATURE ON LINEAR RATE OF ADVANCE OF INTERFACE

$t$ ° C.	$u$ Mm./min.	$\frac{1}{T} \times 10^4$	$\log(u \times 10^4)$
50	0.000261	30.96	0.4150
55	0.000419	30.49	0.6222
60	0.000620	30.03	0.7924
65	0.00129	29.58	1.1106

The abnormal difference between the curve at 40° and 50° C. might be due to the slow rate of nucleus formation, or it may be that 40° is below the transition temperature of the hydrate. Several attempts were made to determine the tran-

sition temperature of sodium perborate hydrate, but, because of its unstable nature in the presence of water and higher concentrations of water vapor, accurate measurements could not be made. In order to establish the relation of rate of dehydration and nucleus formation to the transition temperature further work is needed on more stable hydrates.

The energy of activation can be calculated from the slope of the curve in Figure 5 or from the Arrhenius equation  $\frac{d \ln u}{dT} = \frac{Q}{RT^2}$  in the form:

$$Q = \frac{4.575 (\log u_2 - \log u_1) T_2 T_1}{T_2 - T_1}$$

The value of  $Q$  obtained from the values of  $u$  at 50° and 55° C. is 20,170 calories per mole of water. The temperature coefficient calculated from values at these temperatures is 3.20 per 10° C.

The curves of Figure 4 show the effect of atmospheric and small gas pressures on the rate of dehydration. There is but little difference between the curves obtained under fairly high vacuum (10<sup>-3</sup> mm. of mercury) and that obtained from the oil pump (8 mm. of mercury). There is, however, an appreciable retardation at atmospheric pressure. The self-cooling of the hydrate under the higher vacuum may account for the fact that its rate is not greater. The presence of a small amount of gas serves to conduct heat to the salt from the walls of the balance case by convection, a process which is much faster and more efficient than radiation at low temperatures. The rate actually measured under the higher vacuum probably corresponds to that of a lower temperature than the temperature of the bath.

Some runs were made for particles of different sizes, but the range of size of crystals obtainable was not great enough to draw any definite conclusions. As mentioned before, however, the rate should vary inversely as the size of the particle, within certain limits. Experiments up to the present show qualitatively that this is true. The rate curves were also plotted for results on samples from different companies and on samples prepared by different methods, both before and after recrystallizing. There was some variation, but all

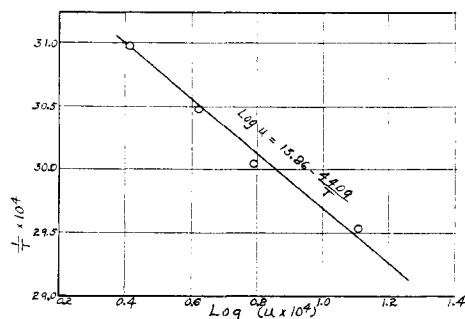


FIGURE 5. RELATION OF LINEAR RATE OF PROPAGATION TO TEMPERATURE

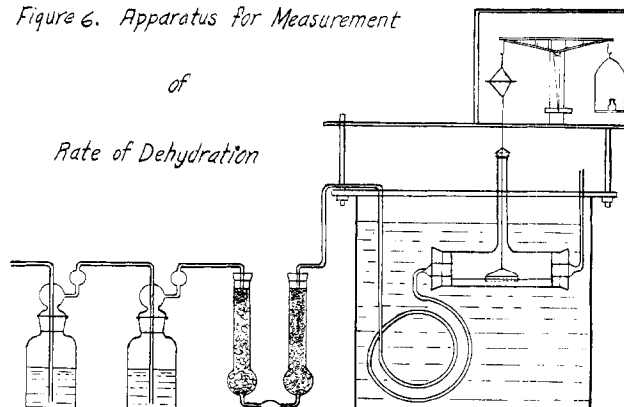
had essentially the same slope and total loss of moisture. One sample in which the small crystals had apparently united to form much larger monoclinic crystals while standing in the bottle was very difficult to dehydrate, even after nucleation by grinding with some dehydrated salt. After recrystallization it behaved normally. This behavior is not easily interpreted.

### Results at Atmospheric Pressure

A number of different set-ups were used to study the rate of dehydration at atmospheric pressure, but the one used for most of the work reported in this paper was made by arranging

a balance over an oil thermostat which could be kept constant to  $\pm 0.02^\circ$  C. The pan was removed from one arm of the balance so that small trays 2.5  $\times$  6 cm., ranging from 0.1 to 1.0 cm. deep, could be attached and lowered into the thermostat as shown in Figure 6. A long tin coil immersed in the oil was used to bring the air to temperature. Air velocities

Figure 6. Apparatus for Measurement



were regulated by means of needle valves and measured with a gas flowmeter made by the American Meter Company. This gave the volume rate which was converted to linear rate by dividing by 12.67 sq. cm., the area of the part of the tube through which the air flowed. The air was dried by passing it through two sulfuric acid wash bottles and phosphorus pentoxide tubes.

By weighing at intervals until very little or no loss of weight occurred, dehydration curves were constructed from measurements made under varying conditions: (1) temperature, (2) air velocity, (3) depths of materials and area exposed, (4) size of particles.

Some representative curves plotted as percentage decomposition against time for runs at 50° and 60° C. with varying air velocities are given in Figures 7 and 8. The weight of the samples for trays 0.2 cm. deep was 2.575 grams and that for trays 0.1 cm. deep was 1.000 gram. Both trays had an area of 15 sq. cm. The particles of hydrate used for these experiments had an average size of 0.089 mm. One hundred per cent decomposition represents the theoretical loss of 3 molecules of water or 35.5 per cent.

These curves show that the rate of dehydration increases markedly with temperature and air velocity. It was originally thought that, by increasing the air velocity sufficiently, a point would be reached at which a further increase in velocity would not increase the rate of dehydration. This would undoubtedly be true if the velocity were increased enough, but the apparatus was limited in range of air velocities obtainable. The general effects of high air velocities are to be studied on more suitable hydrates. The relation between the air velocities and the rate of dehydration is shown in Figure 9 to be approximately linear when the rates calculated from the straight portions of each curve are plotted against air velocities on logarithmic paper. The slope of the lines is about 0.35, which gives the exponent of velocity. The curves of Figure 7 for trays 0.1 cm. deep give a similar straight line with a little greater slope, and for the high air velocities, the rate starts to fall off abnormally as was expected.

The curves in Figure 7 show that the fraction of the particles dehydrated after a given time is much smaller in trays 0.2 cm. deep than in trays 0.1 cm. deep. However, if grams of water lost are plotted against time as in Figure 10, the maximum slopes in all cases are approximately the same. Since the area in each case is the same, this means that the rate of

dehydration is more nearly proportional to the area of the upper surface of the tray of the hydrate than to the total amount of hydrate present or to its depth. This conclusion was tested by covering half the surface with aluminum plates. There was very little difference in the curves for particles of different sizes. The range in size obtainable was not sufficient to say what the effect of particle size in general will be, especially in cases where internal diffusion is controlling.

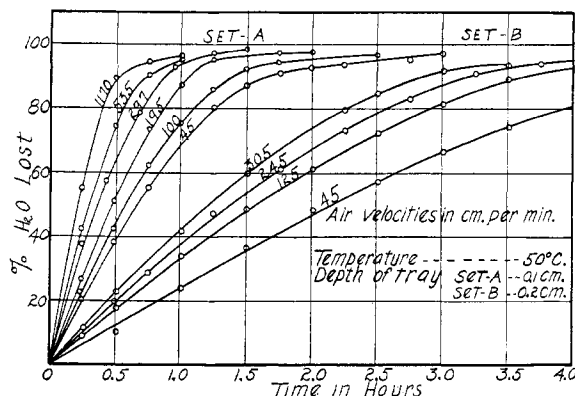
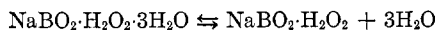


FIGURE 7. EFFECT OF AIR VELOCITY ON RATE OF DEHYDRATION AT 50° C.

The mass of crystals seems to decompose and allow water vapor to come to the surface as fast as it can be removed by the air stream over the range of velocities studied. Thus the process during the early stages of dehydration using low air velocities suggests something similar to the constant-rate period observed in ordinary drying operations (7). An increase in air velocity sweeps away the water vapor faster by decreasing the thickness of air film over the surface of the hydrate, thereby allowing faster diffusion of water vapor into the air stream. This allows a greater forward velocity to take place in the reaction:



For the air velocities used, the absolute speed of the reaction is apparently greater than the rate of diffusion. With higher air velocities or with other hydrates, especially those of the

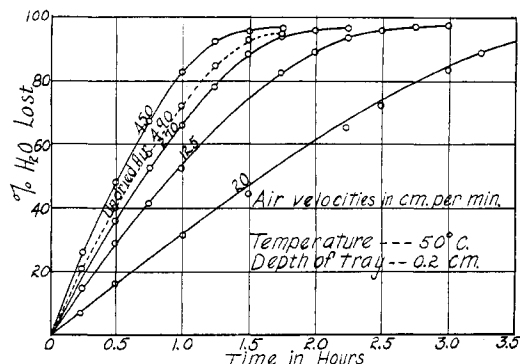


FIGURE 8. EFFECT OF AIR VELOCITY ON RATE OF DEHYDRATION AT 60° C.

zeolite type whose vapor pressure varies continuously with decomposition, internal diffusion may be the controlling factor. Since there is comparatively easy conduction of heat to all sides of the tray at atmospheric pressures, and since the rate at which heat is needed to keep conditions isothermal is small, it is doubtful that the increase in rate with increasing air velocities could be due to an increase in rate of heat supply.

The rate of dehydration starts falling off after about 70 per cent decomposition is reached. Internal diffusion of vapor through the drier surface layer and the increasing thickness of dehydrated phase probably becomes the controlling factor. It is possible too that the rate of decomposition near the surface is retarded because of the smaller particles being completely dehydrated and that the interfacial area of others is becoming small. A combination of these two factors probably represents the actual conditions.

An increase in temperature increases both the vapor pressure of the hydrate and the absolute rate of the forward reaction as well as decreases the viscosity of the air film. At any one set of conditions during the early stages of the dehydration, the rate of transfer of water vapor by means of diffusion through the gas film toward the body of moving air is given approximately by Newton's equation as follows:

$$\frac{dw}{dt} = kA(P_h - P_a)$$

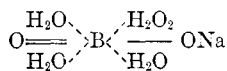
where  $w$  = weight of water vapor  
 $t$  = time  
 $A$  = area of surface  
 $P_h$  = vapor pressure of the hydrate  
 $P_a$  = partial pressure of water vapor in the air  
 $k$  = film constant of diffusion

The value of  $k$  is affected by the thickness of the air film, the viscosity and the direction of air flow. If dry air is used,  $P_a$  is generally small since the amount of water vapor taken up is small compared to the large volume of air; the rate is then proportional to the vapor pressure of the hydrate at the temperature of dehydration, to the area, and to the film coefficient of diffusion.

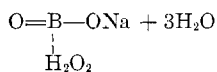
It may be concluded that, in the design of a drier for dehydration purposes at atmospheric pressures, the one which furnishes a high effective air velocity across the greatest area of hydrate will be the most efficient. A tray drier is therefore not very efficient for this type of hydrate. One which furnishes a maximum air velocity around each individual particle, such as certain designs of rotary driers, will be most efficient. It should, in general, be operated at the highest safe temperature with as high flow of dry air as practicable without loss of the small particles. When a tray drier is used for unstable salt hydrates such as sodium perborate which reacts with liberated water vapor if it is not removed rapidly, the maximum safe drying temperature will be a function of the depth of the layer. This is due to the slow removal of liberated water vapor at the bottom of the layers. Tests in which varying depths of hydrate were placed in an oven at different temperatures showed that at 70° C. the maximum depth before melting and decomposition occurred was 1.5 cm.; at 75° C., 0.5 cm.; at 80°, 0.2 cm.; and at 85°, 0.15 cm. By increasing air velocity over the surface, the maximum depth before decomposition occurs can be increased.

### Effect of Dehydration on Properties of Sodium Perborate

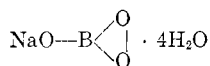
There has always been some controversy concerning the structure and behavior of sodium perborate. Tanatar (27) was the first to describe sodium perborate as an addition product of hydrogen peroxide and to give it the formula  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  instead of  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , a substitution product of hydrogen peroxide. On the basis of the Riesenfeld reaction (22) in which potassium iodide added to a dilute solution of sodium perborate causes a liberation of gaseous oxygen instead of free iodine, and on the basis of the behavior of sodium perborate on dehydration, Foerster (10) also described sodium perborate as an addition product of hydrogen peroxide. He represented sodium perborate as:



which on dehydration gives



Bosshard and Zwicky (3) disagreed with Foerster because they failed to obtain hydrogen peroxide from a solution of sodium perborate by boiling under reduced pressure. They concluded that sodium perborate was a substitution product of hydrogen peroxide containing the group  $\text{—O—O—}$  and gave it the formula



LeBlanc and Zellman (14), on the basis of a delayed Riesenfeld reaction with only slight liberation of free iodine at  $0^\circ\text{C}$ ., distinguished between a "true" perborate and a "pseudo" perborate. According to their conclusions the true perborate has the formula  $\text{MeBO}_3 \cdot x\text{H}_2\text{O}$ , while the pseudo perborate has the formula  $\text{MeBO}_2 \cdot \text{H}_2\text{O}_2 \cdot x\text{H}_2\text{O}$ . The normal or ordinary sodium perborate, according to their views, is a pseudo perborate and gives immediate oxygen evolution with potassium iodide. Menzel (17), however, did not agree with this differentiation, and on the basis of some cryoscopic and osmotic measurements, showed that solutions of perborates behaved as ternary electrolytes, in which case the perborates of the type corresponding to sodium perborate should be repre-

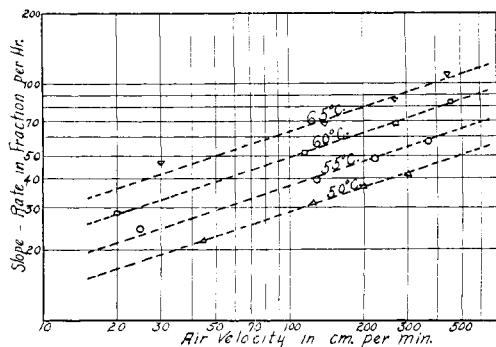
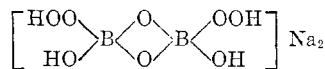


FIGURE 9. RELATION OF RATE OF DEHYDRATION TO AIR VELOCITY

sented by the formula  $\text{Me}_2(\text{B}_2\text{O}_6 \cdot 2\text{H}_2\text{O}_2) \cdot x\text{H}_2\text{O}$ . Reasoning from the Werner structure of borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$ , he gives the following structural formula for sodium perborate,  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ :



This group  $\text{>B} \begin{array}{c} \diagup \text{OOH} \diagdown \\ \diagdown \text{OH} \diagup \end{array}$  is hydrolyzed to hydrogen peroxide with relative ease and therefore shows the Riesenfeld reaction. The comparative stability of the group, on the other hand, accounts for the fact that hydrogen peroxide is not obtained on distillation.

A sample of sodium perborate kept in a vacuum desiccator over phosphorus pentoxide at about  $35^\circ\text{C}$ . for nearly 6 months showed a loss of only 37 per cent. Since 3 molecules of water represent a loss of 35.5 per cent and 4 molecules a loss of 46.8 per cent, the residue after removal of 3 molecules

of water does not appear to be an ordinary lower hydrate. Hydrated sodium perborate is therefore not likely to be a compound represented by  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ . Moreover, since gaseous oxygen is given off in solution with potassium iodide just as it is with hydrogen peroxide, it appears that the compound is more likely to be represented by  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ . Menzel has given sufficient evidence to show that in solution 2 molecules are united to give a ternary electrolyte as repre-

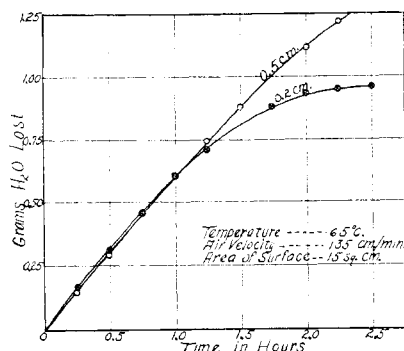
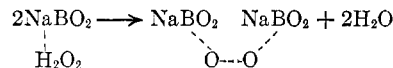


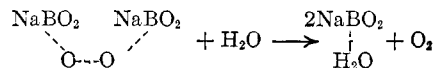
FIGURE 10. EFFECT OF DEPTH AND SURFACE EXPOSED ON RATE OF DEHYDRATION

sented above, the anion being a complex of two  $(\text{BO}_2 \cdot \text{H}_2\text{O}_2)$  groups. Whether we are fully justified in carrying these structures over to the solid state cannot be decided with surety until sufficient x-ray data are obtainable.

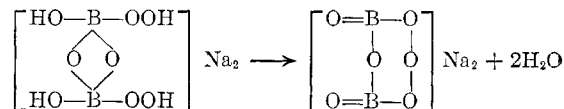
When the hydrate is dehydrated at  $50^\circ$  to  $60^\circ\text{C}$ . until there is a loss in weight equivalent to 3 molecules of water or 35.5 per cent, there is a gain in percentage available oxygen up to 15.7 per cent, which corresponds closely to the expected 16.2 per cent. By prolonging the dehydration at  $60^\circ$  to  $65^\circ\text{C}$ ., or on heating to a higher temperature for a shorter time, the color of the residue changes to a weak yellow at lower temperatures and a definite yellowish color at the higher temperatures. There is some loss in active oxygen and water, and, when the product is put into water, gaseous oxygen is evolved. The violence of the action and the amount of oxygen evolution depends upon the time and temperature of heating. Foerster (10) has represented this change as



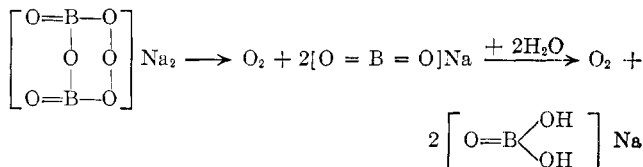
This, on reaction with water, gives oxygen as follows:



Menzel (17) chose to represent this change on the basis of his dimeric formula given above as follows:



Then, on further heating or addition to water,





After dehydration of sodium perborate at 50° to 55° C., samples were heated to various temperatures for 3 to 4 hours, and determinations were made on the change in available oxygen, gaseous oxygen evolution, heat of solution, and solubility. The results are given in Table III.

TABLE III. EFFECT OF HEATING ON PROPERTIES OF SODIUM PERBORATE

Temp. of Heating ° C.	Available Oxygen Per cent	Gaseous Oxygen Evolution Per cent	Solubility at 25° C. G./100 cc. H <sub>2</sub> O
Hydrate	10.53	...	2.81
60	15.2	Small	5.64
90	15.7	0.3	9.25
110	13.4	1.8	16.0
140	5.57	4.9	26.5
160	2.92	4.3	...
250	0.24	0.1	35.4

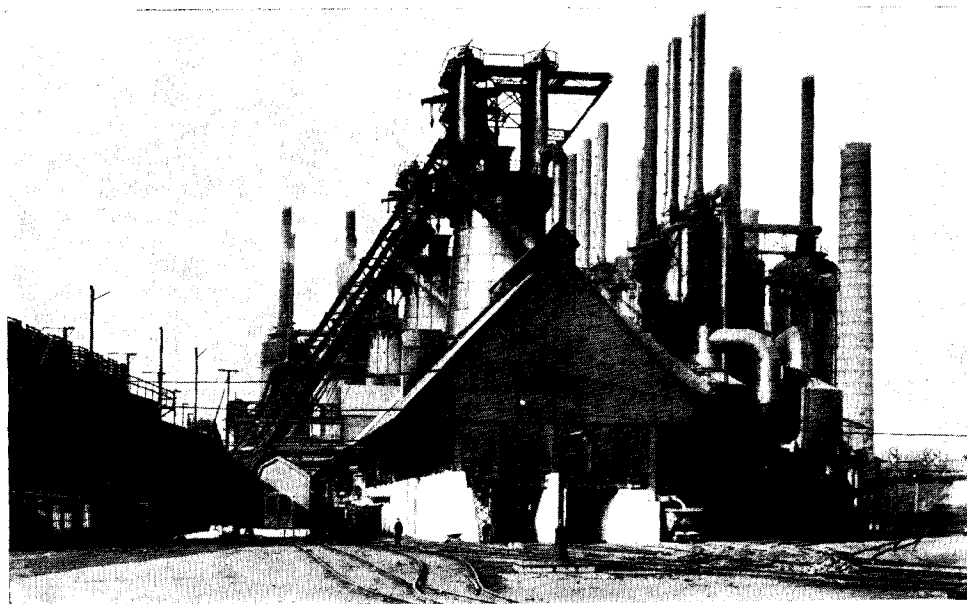
The solubility of dehydrated sodium perborate seems to behave somewhat differently from that of lithium perborate as reported by Menzel (17). The solubility was increased by dehydration; and, when heating at 60° C. was prolonged, the solubility was almost three times as great. It was found however, that after standing a while, this solution began to turn cloudy, and soon a precipitate of the less soluble crystalline sodium perborate hydrate separated. The heat of solution at 25° C. and a dilution of 500 moles of water per mole of solute changes progressively on dehydration from -11,920 to +8170 calories when heated for 3 hours at 140° C. The last value is not accurate because the molecular composition of the product is not known accurately. This applies as well to some of the values in Table III since considerable variations were found in samples heated longer or in a different way. By using properly dehydrated and heated sodium perborate, much stronger oxidizing solutions can be obtained. There is only a small loss of total available oxygen after proper dehydration and heating, but the percentage of available oxygen is increased from 9-10 per cent to 15-16 per cent. Since the average solubility is about twice that of the original hydrate, a solution of about three to four times the oxidizing capacity can be obtained. With the higher temperatures sometimes used with the hydrated salt, there is considerable

loss of oxygen due to decomposition. The dehydrated salt affords greater oxidation at lower temperatures with the loss of only a small percentage of gaseous oxygen.

### Literature Cited

- (1) Antoine, *Compt. rend.*, **110**, 632 (1890).
- (2) Baxter and Lansing, *J. Am. Chem. Soc.*, **42**, 419 (1920).
- (3) Bosshard and Zwicky, *Z. angew. Chem.*, **23**, 1153 (1910); **25**, 942 (1912).
- (4) Bradley, Colvin, and Hume, *Proc. Roy. Soc. (London)*, **137A**, 531 (1932).
- (5) Bruhat and Dubois, *Compt. rend.*, **140**, 506 (1905).
- (6) Carpenter and Jette, *J. Am. Chem. Soc.*, **45**, 578 (1923).
- (7) Carrier, *J. IND. ENG. CHEM.*, **13**, 433 (1921).
- (8) Constam and Bennett, *Z. anorg. Chem.*, **25**, 265 (1900); **26**, 451 (1901).
- (9) Crowther and Coutts, *Proc. Roy. Soc. (London)*, **106A**, 215 (1924).
- (10) Foerster, *Z. angew. Chem.*, **34**, 354 (1921).
- (11) Garner and Tanner, *J. Chem. Soc.*, **1930**, 47.
- (12) Hume and Colvin, *Proc. Roy. Soc. (London)*, **125A**, 635 (1929); **132A**, 548 (1931); *Phil. Mag.*, [7] **8**, 589 (1929).
- (13) Langmuir, *J. Am. Chem. Soc.*, **38**, 2263 (1916).
- (14) LeBlanc and Zellman, *Z. Elektrochem.*, **29**, 173, 192 (1923); *Z. anorg. allgem. Chem.*, **180**, 129 (1929).
- (15) McBain, *J. Am. Chem. Soc.*, **48**, 69 (1926).
- (16) McKeown and Stewart, *Chem. Markets*, Jan., 1932.
- (17) Menzel, *Z. anorg. allgem. Chem.*, **164**, 22 (1927); **167**, 193 (1927); **219**, 35 (1934); *Z. physik. Chem.*, **105**, 422, 431 (1923).
- (18) Menzies and Hitchcock, *J. Phys. Chem.*, **35**, 1660 (1931).
- (19) Partington and Winterton, *J. Chem. Soc.*, **1930**, 635.
- (20) Pauling, *Phys. Rev.*, **36**, 431 (1930).
- (21) Pessarjewsky, *Z. anorg. Chem.*, **32**, 341 (1902); *Z. physik. Chem.*, **43**, 170 (1903).
- (22) Riesenfeld, *Ber.*, **42**, 4377 (1909).
- (23) Schumb, *J. Am. Chem. Soc.*, **45**, 342 (1923).
- (24) Siggel, *Z. Elektrochem.*, **19**, 340 (1913).
- (25) Smith and Topley, *Proc. Roy. Soc. (London)*, **134A**, 224 (1931).
- (26) Spencer and Topley, *J. Chem. Soc.*, **124**, 2633 (1929); *Trans. Faraday Soc.*, **27**, 94 (1931).
- (27) Tanatar, *Z. physik. Chem.*, **26**, 132 (1898); **29**, 162 (1899); *Z. angew. Chem.*, **22**, 1713 (1909).
- (28) Topley, *Proc. Roy. Soc. (London)*, **136A**, 413 (1932).
- (29) Topley and Hume, *Ibid.*, **120A**, 211 (1928).
- (30) Topley and Smith, *Nature*, **128**, 290 (1931).
- (31) Wilson, *J. Am. Chem. Soc.*, **43**, 704 (1921).

RECEIVED January 8, 1935.



TYPICAL BLAST FURNACE,  
BETHLEHEM PLANT,  
BETHLEHEM STEEL CO.,  
BETHLEHEM, PA.