Production of Sodium Chlorite

SURVEY OF PREVALENT MANUFACTURING METHODS

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A detailed electrochemical and thermodynamical analysis has been made of the various reactions involved in the reduction of chlorine dioxide to produce sodium chlorite. This has led to a choice of lead oxide as the most suitable reducing agent available. An experimental study has been made of the lead oxide process which has proved to give excellent yields of sodium chlorite, together with a valuable coproduct, lead dioxide. The favorable economics of the process should be of decisive importance in further technical developments.

SODIUM chlorite, the sodium salt of chlorous acid, had not been commercially available until about 10 years ago, and was introduced by the Mathieson Alkali Works under the trade name Textone. This salt has been used as an excellent bleaching agent in the pulp and textile industries, particularly in the final whitening of kraft pulp without loss of strength.

The properties and reactions of sodium chlorite have been thoroughly investigated and reviewed by Taylor, White, Vincent, and Cunningham (*31*), and further references to the literature in this field may be found in Gmelin's "Handbuch" (*13*), and also in the recently published survey by White (*34*).

Solid sodium chlorite has good stability when stored under proper conditions. It is readily soluble in water, and a saturated solution contains about 40% sodium chlorite at room temperature. The neutral and slightly alkaline solutions are likewise stable, and only a very slow decomposition takes place on boiling. The chlorites are decomposed by strong acids with the generation of chlorine dioxide; chlorine dioxide is liberated also from chlorites by chlorine according to the reaction

$$2ClO_2^- + Cl_2 \longrightarrow 2Cl^- + 2ClO_2$$

The reaction between chlorine dioxide and sodium hydroxide is as follows:

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

In a pure state sodium chlorite was first prepared by Reychler (*27*) from chlorine dioxide and sodium peroxide, and later by Levi (*23*) from chlorine dioxide, hydrogen peroxide, and sodium hydroxide according to the reaction

$$2ClO_2 + H_2O_2 + 2NaOH \longrightarrow 2NaClO_2 + 2H_2O + O_2$$

in which hydrogen peroxide acts as a gentle reducing agent.

From an electrochemical point of view, the reduction of chlorine dioxide to chlorite ion may be written

$$ClO_2 + e \longleftrightarrow ClO_2^-$$

and generally the production of an alkaline metal chlorite will be executed by a proper reduction of chlorine dioxide in alkaline solutions—e.g., sodium chlorite by absorption of chlorine dioxide in a solution of sodium hydroxide in the presence of a suitable reducing agent.

Commercial production of sodium chlorite was started by the present Mathieson Chemical Corporation at Niagara Falls, N. Y., in 1940. Published accounts (*34*) state that chlorine dioxide is reduced by carbon powder dispersed in an alkaline medium containing caustic soda and lime, according to the reaction

$$4ClO_2 + 4NaOH + Ca(OH)_2 + C \longrightarrow 4NaClO_2 + CaCO_3 + 3H_2O$$

After filtering to remove the calcium carbonate, the solution of sodium chlorite is evaporated and drum-dried. The commercial product, known as Textone, contains upward of 80% sodium chlorite (actually 85 to 88% dry basis).

The I. G. Farbenindustrie A.-G. at Griesheim, Germany, piloted a different process during World War II (*10, 21*). Chlorine dioxide gas was reduced with zinc dust dispersed in water, to produce zinc chlorite.

$$2ClO_2 + Zn \longrightarrow Zn(ClO_2)_2$$

The zinc chlorite was converted to sodium chlorite by double decomposition with caustic soda, producing zinc hydroxide as a coproduct. After filtering, the solution of sodium chlorite was evaporated and dried. However, absorption yield and chemical efficiency were far from satisfactory. Hydrogen peroxide in an alkaline solution is an effective reducing agent for chlorine dioxide in the production of sodium chlorite. This fact was well known to Levi (*23*) many years ago. The Germans also piloted this process coincidentally with the zinc process. While technically attractive, the comparatively high cost of peroxide makes such a process commercially uneconomical.

Other attempts to realize a technical production of sodium chlorite in European countries during the last years may be illustrated by a few patented processes.

One of these (*30*) is founded on a direct hydrolytic conversion of chlorine dioxide by the alkaline medium—i.e., without any substantial reducing agent—and the products obtained are separated by crystallization and evaporation. According to Sevón and Sundman (*29*) an aqueous solution of chlorine dioxide is treated with circulating sodium amalgam, which is used as cathode of an electrolytic sodium chloride cell, and the chlorite solution formed is repeatedly saturated with chlorine dioxide. The conversion of chlorine dioxide to sodium chlorite with ammonia as reducing agent resulting in a yield of nearly 80% was proposed in a Dutch patent (*25*). Finally, the use of various metallic catalysts, accelerating the reaction between chlorine dioxide and alkali—e.g., silver, nickel, manganese, copper, cobalt, iron, and gold or their compounds—has been described in (*26*), but these scattered experiments and observations have only little bearing on the industrial production of sodium chlorite. On the whole, many reducing agents have been suggested in the patent literature, and apparently there are several possibilities. Before describing the author's experiments, the technical basis for evaluation of various reducing agents will be critically examined from the thermodynamical and electrochemical viewpoint.

EXAMINATION OF VARIOUS REDUCING AGENTS

In conjunction with the author's work on the technical production of chlorine dioxide (*17, 18, 20*) of which a general survey was published in 1947 (*20*), several methods of preparing sodium chlorite have also been investigated. This experimental work

was executed in 1943 in the research laboratory of Mo och Domsjö Aktiebolag, Örnsköldsvik, Sweden. The essential problem was to find a gentle reducing agent, suitable for practical use, which was able to suppress almost completely the unfavorable formation of chlorate and chloride in the conversion of chlorine dioxide in alkaline solution. The first reduction step, $ClO_2 \longleftrightarrow ClO_2^-$, generally proceeds with a much higher speed and on a higher potential level than the second reduction, $ClO_2^- \longleftrightarrow Cl^-$. In practice, the principal object is to avoid the presence of unnecessary amounts of a too strongly reducing agent in the solution, as the concentration of chlorite gradually increases and the alkalinity simultaneously decreases. However, a certain measurable and not too low solubility of the reducing agent seems to be fundamental to a rapid and effective conversion of chlorine dioxide to chlorite. With respect to the separation and purification of the sodium chlorite, it is also important that the generated oxidation product have as low a solubility as possible in the alkaline reaction solution.

The science to master all those difficulties, associated with a technical and economical production of a tolerably pure sodium chlorite, is essentially equivalent to the solution of two chemical problems—viz., on the one hand in finding a simple method to produce a continuous stream of chlorine dioxide, substantially free from chlorine [with an average molecular ratio $(ClO_2)/(Cl_2)>20$] with a fairly good yield (at least 85 to 90% with respect to the chlorate consumed), and on the other hand to select a reducing agent which in the presence of sodium hydroxide in water solution transfers the chlorine dioxide to sodium chlorite with the highest possible yield (98 to 100%). Moreover, from an economical point of view, it is fundamentally important that the insoluble oxidation product, generated from the selected reducing agent in the transformation of chlorine dioxide to sodium chlorite, be favorably utilized, either as a valuable by-product for sale on the market of chemicals, or be brought back to the original reducing state in a cheap and simple technical process. According to the writer's investigations a profitable production of sodium chlorite should be possible on the basis of his process for generating chlorine dioxide (*20*) together with a properly selected reducing agent, mentioned in (*6*).

Two earlier patents (*32, 33*) describe the production of water-soluble chlorites by introducing gaseous chlorine dioxide into an alkaline solution containing a solution or suspension of reducing inorganic sulfur compounds—e.g., sulfites, or finely divided sulfur, respectively—and powdered carbon or reducing carbon compounds—e.g., sugars. However, these methods are impaired by certain disadvantages. Thus the alkaline solutions, described in the patents just mentioned, were generally rather diluted—e.g., 5 to 20 grams of sodium hydroxide per liter—and the recommended quantities of reducing agents in suspension, such as carbon, were very large—e.g., 50 to 200 parts by weight in 1000 parts of water in transforming 25 parts by weight of chlorine dioxide to sodium chlorite. The use of such easily soluble reducing agents as sodium sulfite and sugars may permit a rather complete and rapid absorption of chlorine dioxide, but with a yield not generally higher than about 80% in the conversion to chlorite. These compounds in alkaline solutions have strong reducing properties and, therefore, a marked tendency toward the formation of chloride. According to Vincent (*33*) the highest yields (90 to 95%) are said to be reached in the use of powdered petroleum coke or carbon powder of animal origin, but in this case the alkali concentration was as low as about 4 parts of sodium hydroxide in 1000 parts of water. Carbon black can also be used.

With respect to the practical development of this process, information from reliable sources indicates that fairly concentrated solutions may be produced.

In order to build up a solution of about 15% sodium chlorite, the entire amount of carbon and lime required, plus a small excess, is added to the water. Only a small part of the caustic soda required is added initially. As chlorine dioxide is absorbed, caustic soda is added little by little, so as to maintain an alkalinity in the later stages of around 0.1 *M* sodium hydroxide. In this way a concentrated solution of sodium chlorite is formed, although the alkalinity is maintained low throughout. The rate of absorption of chlorine dioxide is much greater at low alkalinity than at high alkalinity and, furthermore, the chemical efficiency is higher. At high alkalinity the sodium chlorite solution becomes dark due to colloidal dispersion of carbon which cannot be removed by filtration. At low alkalinity the solution remains very pale.

Carbon, particularly carbon black, absorbs sodium hydroxide from solution. The carbon is of micron size and the surface exposed is enormous. It appears as if the carbon has attached to it hydrophilic hydroxyl groups, and that such a complex is very effective for both absorbing and reducing chlorine dioxide. Efficiency of reduction in the plant based on the chlorine dioxide used averages about 92%. Chemical losses to sodium chlorate and sodium chloride are about equal. Reduction is carried out in a semicontinuous manner by the use of two absorption towers in series.

An interesting investigation on the various methods of generating chlorine dioxide, and, in a more limited extension, also on the reduction of chlorine dioxide to sodium chlorite by several reducing agents was recently published by Campiche (*4*). From this work it is evident that neither zinc and aluminum, recommended by Erbe (*9*), nor carbon in the form of petroleum coke, gives any satisfactory yields of chlorite, although the figures of Campiche in some cases seem to be remarkably low with respect to the formation of chlorite. Concerning the German zinc dust process it is interesting to note that Bigorgne (*2*) in his experiments on the reaction between various metallic dusts and chlorine dioxide in water reports a yield of 82 to 85% for zinc with respect to metal in solution. However, with respect to total metal the yields were only 66, 57, 64, and 34% for cadmium, zinc, magnesium, and aluminum, respectively.

The only reducing agent, investigated by Campiche, which was found to give good yields (98 to 100%) of sodium chlorite without any appreciable formation of chlorate and chloride, was hydrogen peroxide. However, this gentle reducing agent will be too expensive to consume on a large technical scale, inasmuch as no credit can be given for any valuable coproduct. In fact, the costs of hydrogen peroxide in the manufacture of sodium chlorite may be calculated to be about 40% higher than the costs of sodium chlorate required for the generation of chlorine dioxide.

A summary of the essential characteristics of the prevalent methods of producing sodium chlorite is presented in Table I.

TABLE I. TECHNICAL METHODS OF CONVERTING CHLORINE DIOXIDE TO SODIUM CHLORITE

Reducing Agent	Type of Reducing Process	Oxidation Product of the Reducing Agent	Producer
Hydrogen peroxide in solution	Homogeneous	Oxygen gas	I. G. Farbenindustrie, A.-G.
Carbon powder of micron particle size in slightly alkaline suspension	Microheterogeneous	Carbonate, precipitated as $CaCO_3$	Mathieson Chemical Corp.
Zinc powder in water suspension	Heterogeneous	Zinc chlorite in water suspension, converted to sodium chlorite and zinc hydroxide by caustic soda	I. G. Farbenindustrie, A.-G.

In the author's opinion the most interesting and promising methods for the technical production of sodium chlorite, at the present time, are indicated by Cunningham (*6*). These methods involve the use of certain reducing metallic compounds, preferably oxides or hydroxides of multivalent metals in a lower valence state. In point of principle, the oxidized forms of these compounds may be brought back to the original reducing state after the completed reaction, and unlike carbon they are all

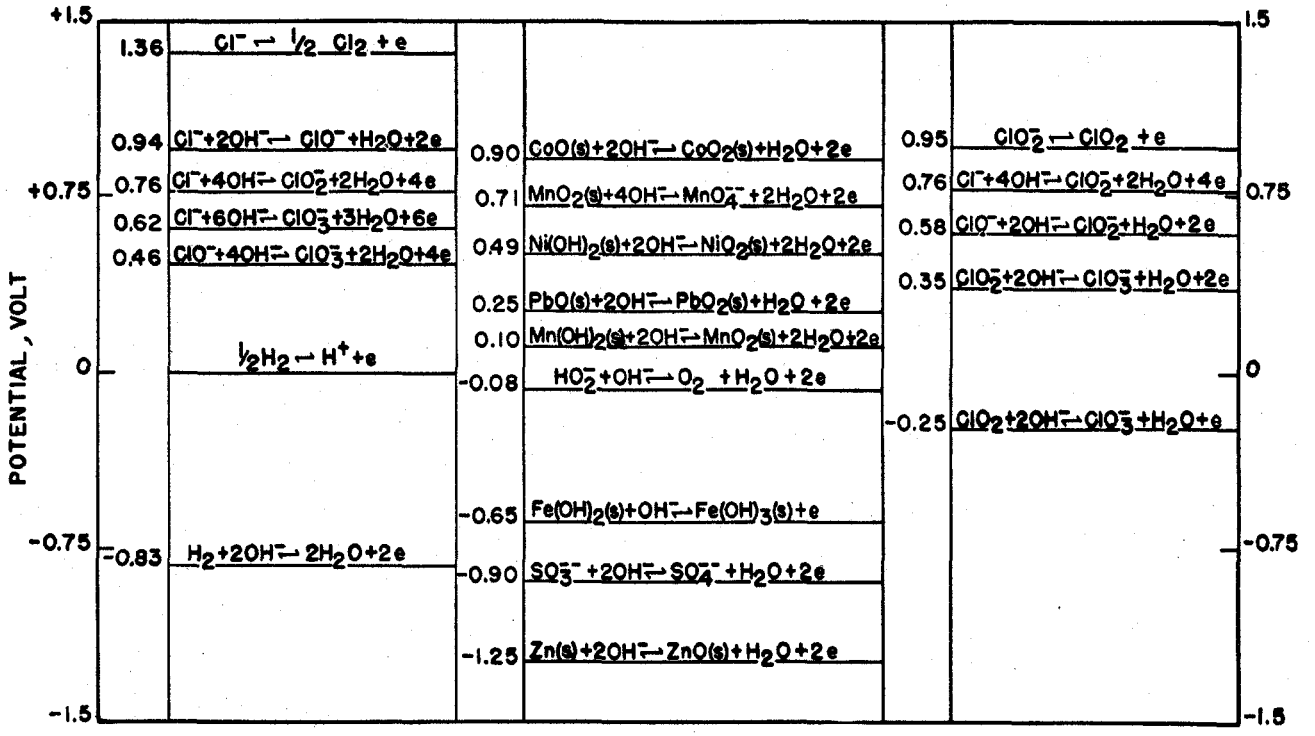

Figure 1. Oxidation-Reduction Potentials in Normal Alkaline Solution

Referred to standard hydrogen potential

characterized by well defined electrochemical potentials. The use of manganous oxide and hydroxide seems to have been the principal object. The following oxides and hydroxides are said to be most suitable as reducing agents: manganous oxide, manganous hydroxide, cuprous oxide, lead oxide (PbO), lead hydroxide, ferrous oxide, and ferrous hydroxide. Also the following cations are stated as capable of being used for the purpose of reducing chlorine dioxide to chlorite in an alkaline solution: Ni^{++}, Co^{++}, Sn^{++}, and Hg^{+}, although they are characterized as inferior to the compounds just mentioned.

A distinct advantage in the use of these reducing agents over the before-mentioned carbonaceous matter consists in the much higher alkali concentrations of the absorption solution—e.g., 50 to 100 parts of sodium hydroxide per 1000 parts of water. This circumstance most probably may be due to the generally larger contact surface and perceptibly higher solubility of the metallic compounds, inasmuch as petroleum coke and other kinds of powdered carbon must be supposed to be almost insoluble in the reaction solution. Consequently, the very low alkali concentrations and (stoichiometrically) large amounts of carbon recommended in (*33*) should be necessary in order to suppress the hydrolytic conversion

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

as much as possible.

These metallic compounds were examined closely to see to what extent they may be really applicable to practice. According to the writer's investigations there is only one or two of all these compounds—viz., lead oxide and lead hydroxide—which will perform all the requirements of a reducing agent intended for the purpose of manufacturing sodium chlorite on a practical scale.

Lead oxide has the very good property of being rather stable to oxygen in the air at ordinary temperature, whereas many of the other oxides and hydroxides—e.g., manganous hydroxide and ferrous hydroxide—are rather sensitive to, and readily oxidized by, oxygen in air. Consequently, they are difficult to control and to handle without losses of reduction capacity on a large scale. Moreover, the solubility of lead oxide in 0.1 to 1 *N* solutions of sodium hydroxide, unlike the other oxides, is of such a magnitude—viz., 0.01 to 0.1 gram mole per liter (*1*, *11*)—that an almost complete conversion of chlorine dioxide to chlorite may be realized with a technically reasonable rate.

It is well known that lead oxide and lead carbonate can be easily oxidized to lead dioxide from alkaline solutions at 40° to 50° C.—e.g., by introducing chlorine gas into a hot solution of sodium carbonate or acetate (*28*). Working with chlorine dioxide as the oxidizing agent it is generally necessary to perform the oxidation of lead oxide to lead dioxide at somewhat higher alkalinity than when using chlorine, because the oxidation intensity of chlorine dioxide against lead oxide at too low alkalinity is insufficient to permit a complete and rapid conversion to lead dioxide.

The author has tested some of the other compounds of the patent assigned to Cunningham (*6*), especially manganous hydroxide which gave a moderate yield of chlorite together with varying amounts of chlorate and chloride. It was further established that thallous hydroxide, not mentioned in the patent, may be used as a fairly good reducing agent in transforming chlorine dioxide to chlorite. Thallous hydroxide seems to be the only heavy metal hydroxide which is easily soluble in water with a strong alkaline reaction (solubility 260 grams per liter at 0° C., and 520 grams per liter at 40° C.). It is oxidized by chlorine dioxide to the insoluble thallic hydroxide under excellent conditions for a complete and rapid conversion of chlorine dioxide to chlorite.

Among the other hydroxides, ferrous hydroxide gives still lower yields of chlorite than manganous hydroxide and more chloride. A peculiar behavior was shown by the green nickelous hydroxide, inasmuch as the use of this compound resulted in a very small yield of chlorite and a large proportion of chlorate, far more than in the case of reacting chlorine dioxide with sodium hydroxide alone. This was apparently due to the autocatalytic action of the higher black oxide, formed during the conversion process. A similar action may be valid for the cobalt oxide.

In his works on the formation of chlorites by the reaction between chlorine dioxide and various metals Bigorgne (*3*) has studied the action of chlorine-free aqueous chlorine dioxide on nickel filings and found that at lower temperatures (below 25° C.) the chlorite of this metal was formed. However, this unstable compound is readily converted to the chloride and chlorate at 45° C., and if free chlorine is present in the chlorine dioxide solution the chlorite is rapidly destroyed.

THEORETICAL DISCUSSION OF THE CHEMICAL REACTIONS

In order to illustrate and support a logical, thermodynamical interpretation of the reactions just mentioned, the characteristic electrochemical potential levels have been graphically represented in Figure 1 for several oxidation-reduction processes taking place in alkaline solutions. Figure 1 should help in solving the problem of converting chlorine dioxide to sodium chlorite.

Much of the data in Figure 1 and further data were compiled from the "Reference Book of Inorganic Chemistry" (*22*), and also from the "Handbook of Chemistry and Physics" (*15*). The sign of all potentials is given according to the European convention.

As the reversible electromotive force, E (in volts), is a direct measure of the maximum available work or free energy change, ΔF (in calories) of a chemical process, the following simple relationship is valid at 25° C.:

$$\Delta F = n23.070E$$

where n is the number of Faradays of electricity which flow through the imaginable circuits.

Referring to the graph, it is a remarkable fact that from a thermodynamical viewpoint the potential level (about 0.25 volt) of the system PbO (s)/PbO_2 (s) in normal alkaline solution has a very favorable situation to effect a conversion of chlorine dioxide to chlorite with a high yield—i.e., without any appreciable formation of either chlorate or chloride. Strictly speaking, chlorite as well as hypochlorite are unstable ions, tending to decompose into chloride and chlorate ions. However, from experience the very moderate reduction intensity of lead oxide in alkaline solutions gives full security that no formation of chloride from chlorite will occur, and no catalytic interaction, resulting in a formation of chlorate, such like that of nickel dioxide and cobalt dioxide on the higher levels, can take place with lead dioxide. This may be fully appreciated from a glance at the next level above—viz.,

$$ClO_2^- + 2OH^- \longleftrightarrow ClO_3^- + H_2O + 2e \ (0.35)$$

Moreover, the stability of lead oxide to oxygen in air is sufficiently well established, thanks to a very low reaction velocity against oxygen acting on the neighboring level (0.40) according to the half reaction:

$$4OH^- \longleftrightarrow O_2 + 2H_2O + 4e$$

According to the measurements of Grube (*14*) a solution containing 0.007 mole per liter of plumbite, 0.007 mole per liter of plumbate, 1 N potassium hydroxide, at room temperature has a potential equal to +0.347 volt—i.e., almost exactly the same value as that of the $ClO_2^- \longrightarrow ClO_3^-$ transformation, and only about 0.05 volt below the OH^-/O_2 potential.

The primary reduction of chlorine dioxide to chlorite takes place at such a high potential, about +0.95 volt for the reversible process $ClO_2^- \longleftrightarrow ClO_2 + e$ (*19*), that even such gently reducing agents as cobaltous hydroxide and nickelous hydroxide may well be used. However, the conversions of chlorine dioxide and chlorite to chlorate take place at much lower levels (−0.25 and +0.35 volt, respectively), and therefore these processes are strongly catalyzed by such oxidizing components as nickel dioxide and cobalt dioxide, acting on very high potential levels. The first reaction step

$$Co(OH)_2 + OH^- \longleftrightarrow Co(OH)_3 + e$$

seems to be connected with a passably low potential (say about +0.2 volt), and hence the process

$$Co(OH)_2 + ClO_2 + OH^- \longrightarrow Co(OH)_3 + ClO_2^-$$

may be easily accomplished. However, the second half-reaction

$$Co(OH)_3 + OH^- \longleftrightarrow CoO_2 + 2H_2O + e$$

is associated with a very high level (above 1 volt), which may be reached by the presence of chlorine in the chlorine dioxide gas, according to the half-reaction

$$2Cl^- \longleftrightarrow Cl_2 + 2e \ (1.36 \text{ volts})$$

This fact may be responsible for a steadily increasing formation of chlorate.

Another interesting feature of the graph is the rather high value of the potential (0.76 volt) corresponding to the transformation of chlorite to chloride. This level is situated below that of the potential (+0.8 volt) for the direct reduction of chlorine dioxide to chloride (not drawn in the figure). Consequently, the reducing components of all systems situated below this level have an inherent tendency to form the chloride ion from chlorine dioxide and chlorite. However, as will be seen from the following half-reaction equations:

$$ClO_2 + 2H_2O + 5e \longleftrightarrow Cl^- + 4OH^- \ (+0.8)$$

$$ClO_2^- + 2H_2O + 4e \longleftrightarrow Cl^- + 4OH^- \ (+0.76)$$

the hydroxyl ions in alkaline solution have a restraining influence upon these reduction processes, whereas the oxidation of chlorine dioxide and chlorite to chlorate are proceeding in reaction with the hydroxyl ion on rather low potential levels.

From the potentials of the following half reactions:

$$ClO_2^- + 2OH^- \longleftrightarrow ClO_3^- + H_2O + 2e \ (E_1 = 0.35)$$

$$Cl^- + 4OH^- \longleftrightarrow ClO_2^- + 2H_2O + 4e \ (E_2 = 0.76)$$

$$Cl^- + 6OH^- \longleftrightarrow ClO_3^- + 3H_2O + 6e \ (E_3 = 0.62)$$

the so-called Luther's rule gives: $2E_1 + 4E_2 = 6E_3$. As E_3 is situated between E_1 and E_2, it is evident that an inherent tendency for decomposition exists in a solution of chlorite, according to the reaction

$$3ClO_2^- \longrightarrow 2ClO_3^- + Cl^-$$

In comparatively diluted solutions of sodium chlorite, and at a rather high concentration of hydroxyl ions this tendency may be almost negligible. On the other hand, in highly concentrated solutions and at low alkalinity the risks of such a decomposition will be appreciable, particularly at higher temperatures.

Also another possibility of decomposition should not be omitted—viz.,

$$ClO_2^- \longrightarrow Cl^- + O_2$$

which may be determined by the following partial reactions:

$$Cl^- + 4OH^- \longleftrightarrow ClO_2^- + 2H_2O + 4e \quad (0.76)$$

$$4OH^- \longleftrightarrow O_2 + 2H_2O + 4e \quad (0.40)$$

However, this process usually seems to be of little importance in this connection, as was also found by Taylor, White, Vincent, and Cunningham (*31*).

The reduction of chlorite to chloride ion most probably goes stepwise from chlorite to hypochlorite and further to chloride.

Examining the following three steps:

$$Cl^- + 2OH^- \longleftrightarrow ClO^- + H_2O + 2e \quad (E_1 = 0.94)$$

$$ClO^- + 2OH^- \longleftrightarrow ClO_2^- + H_2O + 2e \quad (E_2 = 0.58)$$

$$Cl^- + 4OH^- \longleftrightarrow ClO_2^- + 2H_2O + 4e \quad (E_3 = 0.76)$$

the relationship

$$2E_1 + 2E_2 = 4E_3$$

will be obtained. Consequently, under comparable conditions, the first reduction step, $ClO_2^- \longrightarrow ClO^-$, will require a far higher energy—i.e., a more intense reducing agent—whereas the final step, $ClO^- \longrightarrow Cl^-$, will proceed with a very high speed on about the same high potential level as that of the reaction $ClO_2 \longrightarrow ClO_2^-$. These facts may be the reason why hypochlorite almost never may be found in the final reaction solution.

Moreover, from the potentials of the half-reactions

$$Cl^- + 2OH^- \longleftrightarrow ClO^- + H_2O + 2e \quad (0.94)$$

$$ClO_2^- + 2OH^- \longleftrightarrow ClO_3^- + H_2O + 2e \quad (0.35)$$

the conversion $ClO^- + ClO_2^- \longrightarrow ClO_3^- + Cl^-$ will be expected to proceed with a measurable velocity in moderately alkaline solutions, as was stated by Dolch (*8*) many years ago.

Generally the interaction between a reducing agent, *R*, and chlorite ions may be symbolized by the following steps:

$$ClO_2^- + R \longrightarrow ClO^- + RO$$

$$ClO^- + R \longrightarrow Cl^- + RO$$

in which the second step usually will be very rapid in comparison with the competing reaction

$$ClO^- + ClO_2^- \longrightarrow ClO_3^- + Cl^-$$

The formation of chloride ion is found to be almost negligible for special gentle reducing agents, such as hydrogen peroxide, thallous hydroxide, and lead oxide, whereas those agents—e.g., ferrous hydroxide, sulfite ion, and nascent hydrogen—evolved by zinc, aluminum, or sodium amalgam, acting on very low potential levels, have a marked tendency for chloride formation. This unfavorable reduction will, of course, increase with decreasing potential of the reducing agent. Consequently, the original German zinc dust process according to Erbe (*9*) is far from ideal in the production of sodium chlorite, as the fundamental reaction in this process should be:

$$Zn + 2OH^- \longleftrightarrow Zn(OH)_2 + 2e$$

on the very low potential level of -1.25 volts.

The action of manganous hydroxide, like that of cobaltous hydroxide and nickelous hydroxide, may be divided into two steps—viz.,

$$Mn(OH)_2 + OH^- \longleftrightarrow Mn(OH)_3 + e$$

at a very low potential (about -0.4 volt), and

$$Mn(OH)_3 + OH^- \longleftrightarrow MnO_2 + 2H_2O + e$$

proceeding at a much higher level, say about $+0.6$ volt. Consequently, the gross reaction

$$Mn(OH)_2 + 2OH^- \longleftrightarrow MnO_2 + 2H_2O + 2e$$

should be connected with a potential level of about $+0.1$ volt, a value which may be calculated from the standard potential of the reaction

$$Mn^{++} + 2H_2O \longleftrightarrow MnO_2 + 4H^+ + 2e \ (1.33)$$

and from the solubility product of manganous hydroxide, which is given as 4×10^{-14} in (*15*, page 1423).

The considerable distance between the presumable potential levels of the reactions $Mn(OH)_2 \longleftrightarrow Mn(OH)_3$ and $Mn(OH)_3 \longleftrightarrow MnO_2$, coming up to about 1 volt, may be quite similar to that of the cobalt compounds. However, the driving (reducing) force in the interaction with chlorine dioxide is much stronger by manganous hydroxide than by cobaltous hydroxide. This will be evident in an increasing yield of chlorite with smaller amounts of chlorate, but indicating a certain formation of chloride.

Like the other compounds already mentioned, the oxidation of lead oxide or lead hydroxide to lead dioxide in alkaline solution may be broken up into two separate steps on different potential levels, according to the half-reactions

$$Pb(OH)_2 + OH^- \longleftrightarrow Pb(OH)_3 + e$$

$$Pb(OH)_3 + OH^- \longleftrightarrow PbO_2 + 2H_2O + e$$

Although the first step may be connected with a small negative value of the potential, say between -0.1 and -0.2 volt, this negativity is still very moderate and only slightly below the level of the favorable peroxide half-reaction

$$HO_2^- + OH^- \longleftrightarrow O_2 + H_2O + 2e \quad (-0.08)$$

Consequently, no appreciable formation of chloride from the chlorine dioxide will arise. From experience it may be said further that the upper level of the second step is not sufficiently high to cause any noticeable formation of chlorate, and hence this level must be situated at a rather short distance above that corresponding to the previously postulated half-reaction

$$Mn(OH)_3 + OH^- \longleftrightarrow MnO_2 + 2H_2O + e$$

The potential of the saturated system PbO/PbO_2 or $Pb(OH)_2/PbO_2$ in normal alkaline solution is connected with the standard potential of the half-reaction

$$Pb^{++} + 2H_2O \longleftrightarrow PbO_2 + 4H^+ + 2e \quad (1.45)$$

and the solubility product of lead hydroxide, $L_{Pb(OH)_2} = 1.2 \times 10^{-15}$ according to Glasstone (*11*), by the expression

$$E^h = E_0^h + \frac{RT}{2F} \ln \frac{K_w^2 (H^+)^2}{L_{Pb(OH)_2}}$$

giving a numerical value of $E^h = 1.45 - 1.20 = 0.25$ volt. Glasstone (*12*) has found a 0.27-volt potential for the lead oxide–lead dioxide electrode in normal sodium hydroxide solution.

It should also be of special interest to check the electrochemical potential of the lead oxide process:

$$PbO\ (s, yellow) + 2OH^- \longleftrightarrow PbO_2(s) + H_2O + 2e$$

from free energy data of the individual reaction components given in the literature (*16*). The following values of the free energy of formation (in kilogram calories per mole at 25° C.) are stated:

PbO (s, yellow)	=	−44.896
$2OH^- = 2(-37.455)$	=	−74.910
PbO_2 (s)	=	−52.070
H_2O (l)	=	−56.560

The free energy change will be 119.806 − 108.630 = 11.176 kg.-cal., corresponding to a potential

$$E = \frac{11.176}{2(23.070)} = 0.24 \text{ volt}$$

This is in good agreement with the value just calculated.

It may also be mentioned that the free energy change of the reaction

$$Pb + PbO_2 \rightleftharpoons 2PbO$$

has been determined to be about −38 kg.-cal. from electrochemical measurements (*24*), thus predicting a spontaneous interaction between lead and lead dioxide in the direction of the upper arrow.

From the electrochemical potential

$$E^h = E_0^h + \frac{RT}{2F} \ln \frac{(SO_4^{--})(H^+)^4}{(H_2SO_3)}$$

corresponding to the half-reaction

$$H_2SO_3 + H_2O \longleftrightarrow SO_4^{--} + 4H^+ + 2e \ (0.14)$$

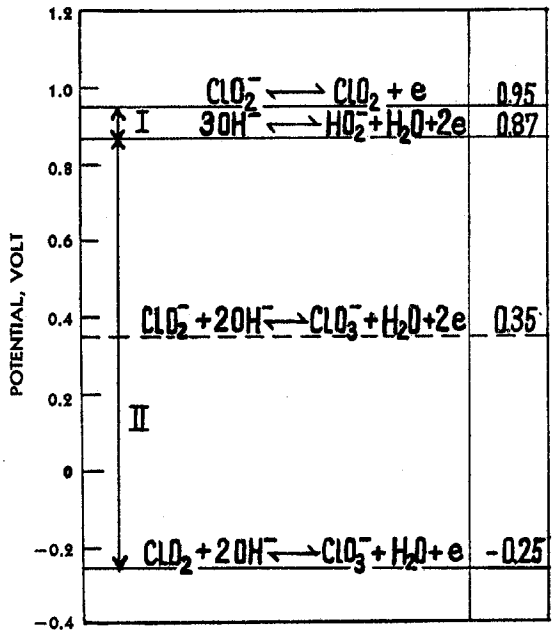

Figure 2. Electrochemical Half-Reactions Probably Determining the Hydrolytic Conversion of Chlorine Dioxide

and the dissociation constants of sulfurous acid, $K_1 = 1.7 \times 10^{-2}$ and $K_2 = 5 \times 10^{-8}$ (*15*, page 1426), the following expression for the level of the half process

$$SO_3^{--} + 2OH^- \longleftrightarrow SO_4^{--} + H_2O + 2e\ (-0.90)$$

may be evaluated

$$E^h = E_0^h + \frac{RT}{2F} \ln K_1K_2(H^+)^2$$

giving a numerical value of 0.14 − 1.04 = −0.90.

Owing to the high solubility of sodium sulfite it is possible to obtain a very rapid and complete absorption, and also an unexpectedly good conversion of chlorine dioxide to sodium chlorite, although the tendency toward formation of chloride is considerable. However, at higher concentrations of chlorite this destruction to chloride will cause serious losses, and the presence of sodium sulfate in the chlorite solution is another disturbing factor in this process. The use of a slightly soluble sulfite, such as calcium sulfite, suspended in the alkaline medium does not give as good an effect as sodium sulfite, as was stated in some experiments.

According to the author's experience and general conception, the lack of solubility of many reducing agents causes great difficulties in order to reach the highest yields of chlorite, inasmuch as the direct conversion of the chlorine dioxide by the alkaline medium will come to the front. In point of principle, the total conversion of the chlorine dioxide may be expressed as a sum of two (independent) reactions:

1. The direct hydrolysis of chlorine dioxide to chlorite and chlorate by the alkaline medium.
2. The heterogenous interfacial reduction of chlorine dioxide to chlorite or chloride by the suspended reducing agent.

For instance, such agents as zinc and aluminum must be considered insoluble in the metallic (reducing) state, although they may transiently go into solution by an oxidation reaction, giving nascent hydrogen under certain conditions. According to a German patent (*9*) the use of these metallic agents is said to give a formation of sodium chlorite equal to 70 to 80% of the chlorine dioxide absorbed. The experiments of Campiche (*4*) do not agree with this assertion.

When chlorine dioxide is introduced into a pure alkaline solution—e.g., sodium hydroxide—the following elementary processes may simply be supposed to govern the chemical conversion

$$ClO_2 + e \longleftrightarrow ClO_2^-\quad (+0.95) \qquad (1)$$

$$ClO_2 + 2OH^- \longleftrightarrow ClO_3^- + H_2O + e\quad (-0.25) \qquad (2)$$

giving together the gross reaction

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

Possibly the driving force in this conversion process is given by the elementary reaction

$$3OH^- \longleftrightarrow HO_2^- + H_2O + 2e\ (+0.87) \qquad (3)$$

The mutual situation of the potential levels in Figure 2 indicates the possibility of the slow combined reaction, Equations 1 + 3, according to the formula

$$2ClO_2 + 3OH^- \longrightarrow 2ClO_2^- + HO_2^- + H_2O\ (I)$$

Therefore, it seems reasonable to suppose that the generated, unstable peroxide ion, developing its oxidizing properties on a high potential level, will be responsible for the formation of chlorate according to the very rapid combined reaction

$$2ClO_2 + HO_2^- + OH^- \longrightarrow 2ClO_3^- + H_2O\quad (II)$$

The two reactions, I and II, should give the hydrolytic gross reaction written above and illustrated in the Figure 2.

In the ample presence of hydrogen peroxide, acting on a much lower potential level, according to the half-reaction

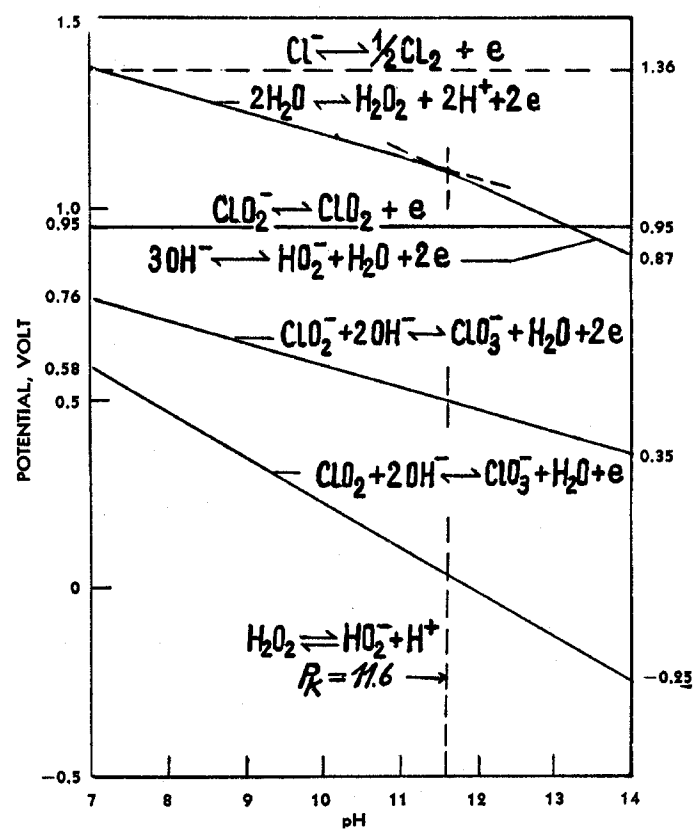

Figure 3. Influence of Alkalinity on Electrochemical Half-Reactions Governing the Hydrolytic Conversion of Chlorine Dioxide

$$HO_2^- + OH^- \longleftrightarrow O_2 + H_2O + 2e \ (-0.08)$$

the reducing ability of this compound is developed, and hence the following reaction will be predominant:

$$2ClO_2 + HO_2^- + OH^- \longrightarrow 2ClO_2^- + H_2O + O_2$$

Therefore, the conversion of chlorine dioxide to chlorite may proceed with a high yield under very favorable conditions, as was stated by previous investigators.

The situation of the potential level for the process

$$ClO_2 + 2OH^- \longleftrightarrow ClO_3^- + H_2O + e$$

at −0.25 volt in normal alkaline solution is surprisingly low. The accuracy of this value may easily be checked by examining the potentials of the three half-reactions

$$ClO_2^- \longleftrightarrow ClO_2 + e \qquad (E_1 = +0.95)$$

$$ClO_2 + 2OH^- \longleftrightarrow ClO_3^- + H_2O + e \qquad (E_2 = -0.25)$$

$$ClO_2^- + 2OH^- \longleftrightarrow ClO_3^- + H_2O + 2e \qquad (E_3 = +0.35)$$

from which the following relation is obtained:

$$E_1 + E_2 = 2E_3$$

Therefore, from a thermodynamic viewpoint the formation of chlorate from chlorine dioxide should be possible by the influence of any sufficiently active oxidizing agent above this level. Fortunately, however, the very low solubility and rather moderate oxidizing intensity of such reaction products as lead dioxide and oxygen, generated from the corresponding soluble and quickly reducing agents (PbO as plumbite and hydrogen peroxide) in the rapid conversion of chlorine dioxide to chlorite, from a kinetic point of view precludes any appreciable formation of chlorate in competition with the chlorite formation.

Only the most intense oxidizing agents, such as hypochlorite, and particularly the higher nickel and cobalt oxides, acting on very high potential levels (well above +0.6 volt) have appeared sufficiently active at ordinary temperature to produce any considerable formation of chlorate in competition with the reducing conversion to chlorite by the corresponding lower oxides or hydroxides. Consequently, the chlorate formation in most of the other cases—e.g., with manganous hydroxide or ferrous hydroxide as reducing agents—should result from the simultaneous, purely hydrolytic conversion

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

in which the presumably slow primary step

$$2ClO_2 + 3OH^- \longrightarrow 2ClO_2^- + HO_2^- + H_2O$$

should be followed by the very rapid reaction

$$2ClO_2 + HO_2^- + OH^- \longrightarrow 2ClO_3^- + H_2O$$

In addition, at higher concentrations of chlorite the following second step may be possible:

$$ClO_2^- + HO_2^- \longrightarrow ClO_3^- + OH^-$$

although the previous reaction generally should be given the preference as the most probable. The difference between the standard potentials of the reacting systems OH^-/HO_2^- and ClO_2/ClO_3^- in normal alkaline solution is about 1.1 volts, whereas the corresponding value for the last-mentioned reaction only goes up to about 0.5 volt.

These statements may contribute to an explanation of the complete and rapid oxidation of chlorine dioxide by hypochlorite in alkaline solution according to the following reaction:

$$2ClO_2 + ClO^- + 2OH^- \longrightarrow 2ClO_3^- + Cl^- + H_2O$$

in which the standard potential difference between the systems Cl^-/ClO^- and ClO_2/ClO_3^- at normal alkalinity corresponds to the very high value of 1.2 volts.

The considerable influence of the alkalinity on the difference between the potentials of the systems ClO_2^-/ClO_2, ClO_2^-/ClO_3^-, and ClO_2/ClO_3^- will be evident from Figure 3, giving also an essential explanation of the variation in the rate of hydrolysis, according to the reaction

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

As will be seen from Figure 3, the potential level of the probable rate-determining elementary process

$$3OH^- \longleftrightarrow HO_2^- + H_2O + 2e$$

by decreasing alkalinity rises above the level of the ClO_2^-/ClO_2 system at a pH of 13—i.e., at 0.1 N alkalinity. The difference between the standard potentials of the following half-reactions:

$$2H_2O \longleftrightarrow H_2O_2 + 2H^+ + 2e \quad (+1.78) \qquad (4)$$

$$3OH^- \longleftrightarrow HO_2^- + H_2O + 2e \quad (+0.87) \qquad (5)$$

may be checked from the expressions of the corresponding potentials.

$$E^4 = E_0^4 + \frac{RT}{2F} \ln (H_2O_2)(H^+)^2$$

$$E^5 = E_0^5 + \frac{RT}{2F} \ln \frac{(HO_2^-)}{(OH^-)^3}$$

Putting $E^4 = E^5$, the ionization product of water $K_w = 1.0 \times 10^{-14}$, and the first ionization constant of hydrogen peroxide $K_{H_2O_2} = 2.4 \times 10^{-12}$ (*22*, appendix XI, page 507), one should get

$$E_0^4 - E_0^5 = -\frac{RT}{2F} \ln \frac{K_w^3}{K_{H_2O_2}}$$

The potentials of the two processes have the same common value, 1.08 volts at an alkalinity of pH = 11.6. In neutral solution (pH = 7) the potential E_0^4 has the same value as that of the reaction: $Cl^- \longleftrightarrow {}^1/_2Cl_2 + e$ (1.36). These facts seem to give an essential explanation of the great difference in the rate of hydrolysis of chlorine and chlorine dioxide.

Obviously, the energy of activation for the simple reversible process

$$ClO_2 + e \longleftrightarrow ClO_2^-$$

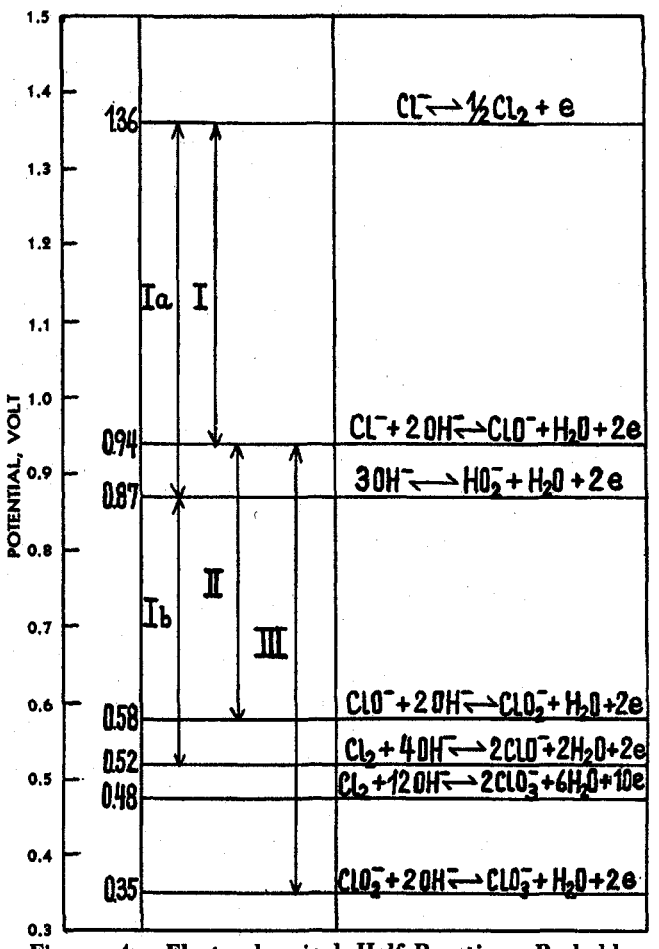

Figure 4. Electrochemical Half-Reactions Probably Determining the Hydrolytic Conversion of Chlorine in Alkaline Solution

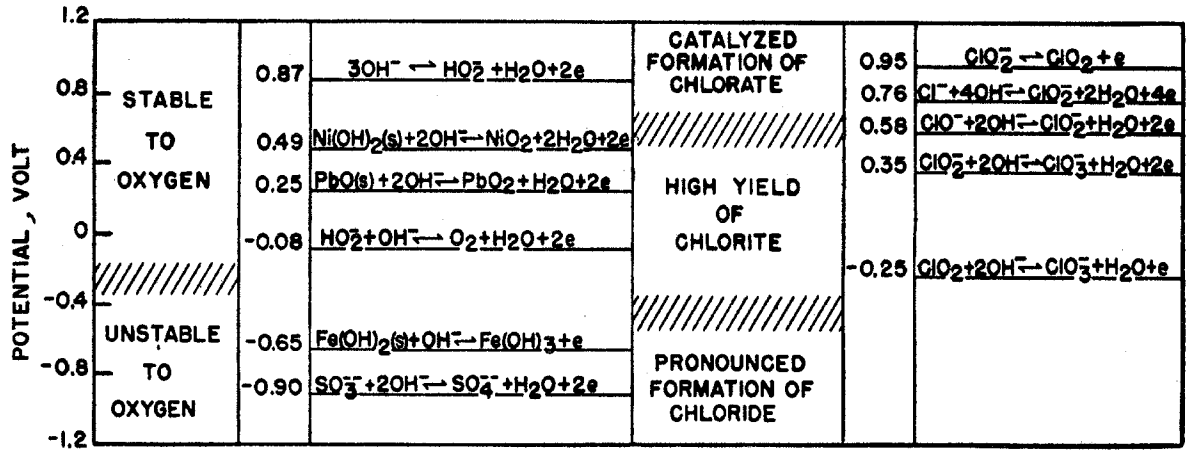

Figure 5. Approximately Estimated Potential Spaces in Normal Alkaline Solution Indicating Disturbing Influences on Conversion of Chlorine Dioxide to Sodium Chlorite

coupled with a suitable reducing component, must be very low, as this process is characterized by a single electron transfer. Contrariwise, the corresponding energies of the far more complicated conversions: ClO_2 (or ClO_2^-) $\longrightarrow$ ClO_3^- (or Cl^-) must be considerable. This supposition is also in good agreement with the fact that a stable and well defined potential, corresponding to a rapid and reversible interaction, is developed only between the components chlorine dioxide and chlorite, whereas no measurable exchange with chlorate or chloride will be found (*7*).

In the conversions of gaseous chlorine to hypochlorite and chlorate the following potentials are approximately valid:

$$Cl_2(g) + 4OH^- \longleftrightarrow 2ClO^- + 2H_2O + 2e\ (+0.52)$$

$$Cl_2(g) + 12OH^- \longleftrightarrow 2ClO_3^- + 6H_2O + 10e\ (+0.48)$$

In comparison, the potential for a similar conversion to chlorite, according to the hypothetical reaction formula:

$$Cl_2(g) + 8OH^- \longleftrightarrow 2ClO_2^- + 4H_2O + 6e\ (+0.56)$$

may be calculated from the following reactions:

$$Cl_2 + 4OH^- \longleftrightarrow 2ClO^- + 2H_2O + 2e\ (E_1 = 0.52)$$

$$ClO^- + 2OH^- \longleftrightarrow ClO_2^- + H_2O + 2e\ (E_2 = 0.58)$$

$$Cl_2 + 8OH^- \longleftrightarrow 2ClO_2^- + 4H_2O + 6e\ (E_3 = 0.56)$$

in which $2E_1 + 4E_2 = 6E_3$.

From the mutual situations of the potential levels, drawn in the graph of the Figure 4, it will be seen that the reduction of chlorine to chloride is accomplished at an extraordinarily high potential (+1.36), and the oxidation of chlorine to chlorate on the very low level of +0.48 volt. Hence, the hydrolytic conversion to chlorate and chloride should be the most probable from a purely thermodynamical point of view. However, as is well known from experience, at lower temperatures and sufficient alkalinity the primarily generated hypochlorite is found to be substantially stable.

In the hydrolytic conversion of chlorine according to the reaction:

$$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O\ (I)$$

it may also be permitted to suppose the following transient reactions:

$$Cl_2 + 3OH^- \longrightarrow HO_2^- + H_2O + 2Cl^-\ (Ia)$$

$$Cl_2 + OH^- + HO_2^- \longrightarrow 2ClO^- + H_2O\ (Ib)$$

However, as the potential of the elementary reaction

$$ClO^- + 4OH^- \longleftrightarrow ClO_3^- + 2H_2O + 4e \qquad (6)$$

is situated at the same low value (0.48) as that of the conversion $Cl_2 \longrightarrow ClO_3^-$, the high oxidation potential (0.94) of the process

$$ClO^- + H_2O + 2e \longleftrightarrow Cl^- + 2OH^- \qquad (7)$$

will be developed under suitable conditions—i.e., at higher temperatures and concentrations of hypochlorite, especially at very low alkalinity—in a mutual reaction between the hypochlorite ions by Equations 6 and 7, giving the following well known decomposition:

$$3ClO^- \longrightarrow ClO_3^- + 2Cl^-$$

From a kinetical viewpoint the primary reaction may be

$$2ClO^- \longrightarrow ClO_2^- + Cl^-\ (II)$$

obtained by combining the elementary processes

$$ClO^- + 2OH^- \longleftrightarrow ClO_2^- + H_2O + 2e\ (0.58)$$

$$Cl^- + 2OH^- \longleftrightarrow ClO^- + H_2O + 2e\ (0.94)$$

with a standard potential difference as small as 0.36 volt. However, a similar analysis of the second step

$$ClO^- + ClO_2^- \longrightarrow ClO_3^- + Cl^-\ (III)$$

proves that the corresponding difference between the potentials of the systems Cl^-/ClO^- and ClO_2^-/ClO_3^- has a value of 0.59 volt. Finally, the mutual situations of the potential levels for the systems Cl_2/ClO^-, Cl_2/ClO_2^-, and Cl_2/ClO_3^- give evidence to the fact that no direct formation of chlorite from chlorine and hydroxyl ion will be probable.

When a mixture of chlorine dioxide and chlorine is introduced into an alkaline solution, the following hydrolytic reactions may be supposed to go on:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

The interaction between hypochlorite and chlorite will proceed with a moderate velocity to chlorate and chloride, according to the aforementioned formula.

The driving force of the possible combined conversion of chlorine and chlorine dioxide to chloride and chlorate, according to the reaction

$$^1/_2Cl_2 + ClO_2 + 2OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$$

should be very strong, owing to the great difference (1.6 volts)

between the standard potentials of the systems Cl^-/Cl_2 (1.36) and ClO_2/ClO_3^- (−0.25).

Referring to Figure 3, the possibility of a destroying oxidation of chlorite ions by chlorine may be noted.

$$Cl_2 + ClO_2^- + 2OH^- \longrightarrow 2Cl^- + ClO_3^- + H_2O$$

In this reaction the driving force corresponds to a standard potential difference of 1.0 volt between the systems Cl^-/Cl_2 (1.36) and ClO_2^-/ClO_3^- (0.35) in normal alkaline solution.

Now, assuming a gaseous mixture of chlorine dioxide and chlorine with a molecular ratio: $(ClO_2)/(Cl_2) = 2n$, and substantially complete absorption in the alkaline solution, one should get the following complete gross reaction:

$$2nClO_2 + Cl_2 + 2(n + 1)OH^- \longrightarrow (n - 1)ClO_2^- + (n + 1)ClO_3^- + 2Cl^- + (n + 1)H_2O$$

In the presence of a suitable reducing agent, R, one may be able to convert the chlorine dioxide almost completely to chlorite—i.e., without appreciable formation of chlorate. However, the chlorine may in every case be reduced to chloride, and hence the following ideal formula will express the final result:

$$2nClO_2 + Cl_2 + (n + 1)R + 2(n + 1)OH^- \longrightarrow 2nClO_2^- + 2Cl^- + (n + 1)RO + (n + 1)H_2O$$

Thus, working with sodium hydroxide as the absorption medium, a value of $n = 10$ would give only a few (6 to 7) per cent of sodium chloride in the sodium chlorite produced. In order to reach such favorable conditions, the physical and chemical properties of the selected reducing agent have proved to be of very great importance, inasmuch as this agent must be sufficiently soluble, active, and situated on a moderately low potential level. It has been stated that lead oxide has these valuable properties.

Figure 5 gives a rough picture of the chemical disturbance in the formation of chlorite from chlorine dioxide, associated with the thermodynamics and kinetics of the various possible reactions. A rather limited potential space of the reducing agent may be most suitable for a quantitative conversion of chlorine dioxide to sodium chlorite. However, the practical utilization of this fact presumes a rapid reducing agent of sufficient solubility in order to avoid a direct hydrolysis by the alkaline medium.

USE OF LEAD OXIDE AS REDUCING AGENT

The ordinary yellow lead oxide (litharge) of commercial quality has been used by the author in several experiments, and proved to give excellent yields of sodium chlorite, according to the gross reaction

$$2ClO_2 + PbO + 2NaOH \longrightarrow 2NaClO_2 + PbO_2 + H_2O$$

As already mentioned, lead oxide is to be considered as a very weakly reducing agent, perfectly stable in air, and at ordinary temperature oxidized to lead dioxide only by very strong and quickly reacting agents of a high oxidation potential, such as chlorine and chlorine dioxide in alkaline solutions.

The cooperation of hydroxyl ions in the reduction of chlorine dioxide to chlorite as also in the equilibrium between the systems ClO_2^-/ClO_2 and PbO (s)/PbO_2 (s) gives evidence to the fact that the actual process will be most rapid and complete at high alkalinity.

A fundamental property of the lead oxide is the moderate solubility of this compound in alkaline solutions. The solubility of lead oxide in solutions of sodium hydroxide of varying strength at 18° and 74° C. was determined more than 40 years ago by Berl and Austerweil (*1*), whose data are plotted in Figure 6. A formation of monosodium plumbite, corresponding to the equilibrium

$$PbO + OH^- \rightleftharpoons PbO_2H^-$$

may exist in solutions up to concentrations between 1 and 2 *N* sodium hydroxide, inasmuch as the ratio $(PbO_2H^-)/(OH^-)$ is rather constant, corresponding to an approximately linear variation in the solubility with the hydroxyl ion concentration.

The color of lead oxide may vary from lemon-yellow to reddish-yellow, owing to the existence of two forms, the yellow orthorhombic, and the red tetragonal, which have been identified by x-ray examinations. The solubilities of the two forms in normal caustic soda at 20° C. were determined by Glasstone (*11*), who found the value 0.047 gram mole per liter for the yellow form, and 0.029 gram mole per liter for the red form.

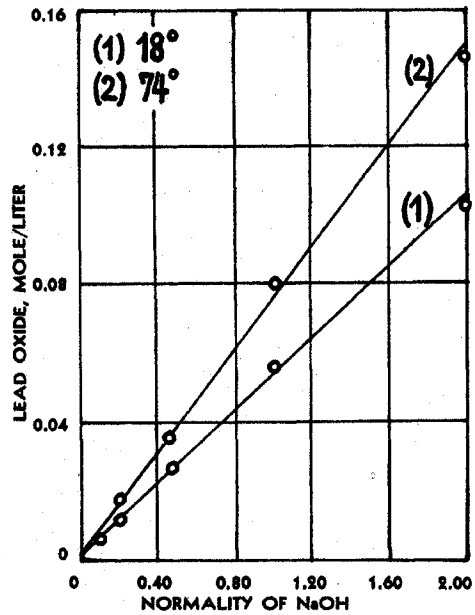

Figure 6. Solubility of Lead Oxide (Yellow) in Sodium Hydroxide Solutions

The conversion of chlorine dioxide to sodium chlorite by reaction with an alkaline solution of sodium plumbite in contact with suspended, finely divided yellow lead oxide may be expressed in the following way:

$$PbO + OH^- \longrightarrow PbO_2H^-$$

$$2ClO_2 + PbO_2H^- + OH^- \longrightarrow 2ClO_2^- + PbO_2 + H_2O$$

giving together the gross reaction:

$$2ClO_2 + PbO + 2NaOH \longrightarrow 2NaClO_2 + PbO_2 + H_2O$$

Working with an initial suspension of yellow lead oxide in sodium hydroxide solution, containing for instance about 50 grams of sodium hydroxide and 145 grams of lead oxide per liter, one may get an average concentration of sodium plumbite of about 0.04 to 0.03 mole per liter during the reaction with chlorine dioxide. Of course these figures do not quite correspond to the real equilibrium concentration owing to lack of time, but the distance from this equilibrium of saturation may be rather small. To give an idea about the rapidity of dissolution, 10 grams of commercial yellow lead oxide were shaken by hand with 100 ml. of 1 *N* and 0.1 *N* sodium hydroxide, respectively, and the amount of lead oxide dissolved during varying time intervals from 10 to 120 seconds was measured. The results obtained are plotted in Figure 7.

Lead oxide dissolves very rapidly in 1 *N* sodium hydroxide, but considerably slower in the 0.1 *N* solution; hence the supply of chlorine dioxide should be properly adjusted to the decreasing alkalinity during the reaction. In practice, the lower limit of concentration may not be too far below 0.1 *N* sodium hydroxide, corresponding to an actual concentration of plumbite of about 0.002 to 0.003 mole per liter in the presence of a sufficient amount of suspended lead oxide. In spite of such rather low concentrations of the reducing agent, it has proved possible to obtain a rather rapid and substantially complete conversion of the

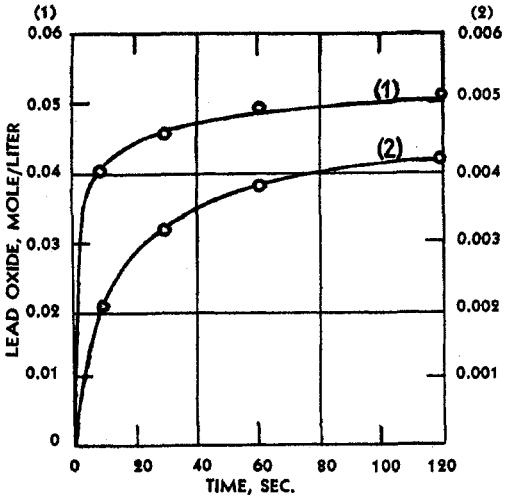

Figure 7. Comparable Experiments on Rate of Dissolving Lead Oxide (Yellow) in 1 *N* (1) and 0.1 *N* (2) Sodium Hydroxide Solutions

chlorine dioxide to sodium chlorite (98 to 100%), obviously due to the comparatively low velocity of the hydrolytic reaction

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

Of course, the suspension must be vigorously stirred in order to maintain a continuous formation of plumbite solution from the suspended solid lead oxide. A too ample supply of chlorine dioxide gas sometimes will cause a very rapid and dense precipitation of insoluble lead dioxide, clogging the openings of the gas distribution pipes.

An important factor is the steadily decreasing absorption of chlorine dioxide with decreasing alkalinity and increasing concentration of sodium chlorite in the solution. In order to get a complete absorption during the whole process it is suitable to conduct the gases through a number of reaction vessels connected in series. In this way the reaction may be carried on to very low (slightly above 0.01 *M*) concentration of free sodium hydroxide with correspondingly small amounts of lead oxide (below 0.001 mole per liter) in the solution. Even the last traces of plumbite can be almost entirely converted to insoluble lead dioxide by a carefully controlled treatment of the filtered solution with chlorine dioxide and adjusting the final alkalinity; or eventually it may be precipitated as basic lead carbonate by proper addition of sodium carbonate to the slightly alkaline solution, and only the most rigorous demands upon purity may call for a special refining of the sodium chlorite by crystallization.

It should be of historical interest to mention that an electrochemical method of producing lead dioxide by a direct conversion of lead oxide, suspended in a solution of an alkali metal chloride—e.g., sodium chloride—was patented about 50 years ago by the Chemische Fabrik Griesheim Elektron (*5*). In this process the oxidation of lead oxide to lead dioxide should take place by a rapid reaction between freshly liberated chlorine and sodium plumbite in the continuously generated alkaline solution.

In most of the author's experiments the reaction between chlorine dioxide and lead oxide–sodium hydroxide solution has been executed by introducing a stream of air or nitrogen, containing about 12% by volume of chlorine dioxide [with an average molecular ratio $(ClO_2)/(Cl_2) = 24$] at a rate of about 60 liters of gas mixture—i.e., about 7.2 liters of chlorine dioxide—per hour into a mixture, initially containing 50 grams of sodium hydroxide and 145 grams of lead oxide in a reaction volume of 1 to 2 liters. This suspension was held in continuous, intensive motion by a rotating stirrer. These conditions mean a supply of chlorine dioxide and a consumption of sodium hydroxide approximately between 0.15 and 0.30 mole per liter per hour—i.e., 0.0025 to 0.0050 mole per liter per minute—and thus a consumption of 0.00125 to 0.0025 mole of lead oxide per liter per minute. However, as no considerable difference in the yield of sodium chlorite was found in these experiments, the conversion may be realized with a still higher speed. From the curves in Figure 7 it is evident that the yellow lead oxide, suspended in 1 *N* sodium hydroxide, goes into solution with a speed permitting a conversion of at least 0.02 to 0.03 mole of chlorine dioxide per liter per minute, or about 1 to 2 moles per liter per hour. On the whole, it appears possible to convert from 0.25 to 0.50 mole of chlorine dioxide to sodium chlorite per hour per liter of solution between the limits of alkalinity, corresponding to 1 *N* and 0.1 *N* sodium hydroxide during the production process.

The chlorine dioxide was generally prepared by introducing a finely divided gaseous mixture of 6 liters of sulfur dioxide and 54 liters of air or nitrogen per hour under vigorous stirring into a solution obtained by mixing 210 ml. of a solution containing 6 gram-moles of sodium chlorate per liter with 290 ml. of a solution containing 14 gram equivalents of sulfuric acid per liter. The average yield of chlorine dioxide, calculated on the amount of sodium chlorate consumed, was determined to be 89%, according to the following reactions:

$$2NaClO_3 + 2H_2SO_4 \longrightarrow 2HClO_3 + 2NaHSO_4 \quad (8)$$

$$2HClO_3 + SO_2 \longrightarrow 2ClO_2 + H_2SO_4 \quad (9)$$

$$2HClO_3 + 6SO_2 + 6H_2O \longrightarrow 2HCl + 6H_2SO_4 \quad (10)$$

$$HClO_3 + 5HCl \longrightarrow 3Cl_2 + 3H_2O \quad (11)$$

Supposing $2x$ and z to be fractional numbers of chlorate or chloric acid molecules, reacting according to by-reactions (*10*) and (*11*), respectively, one should get the following expressions, determining the yield, Y_1, of chlorine dioxide:

Consumption, Moles	Production, Moles
$NaClO_3$, 2	ClO_2, $(2 - 2x - z)$ HCl, $(2x - 5z)$ Cl_2, $3z$

$$Y_1 = \frac{2 - 2x - z}{2}$$

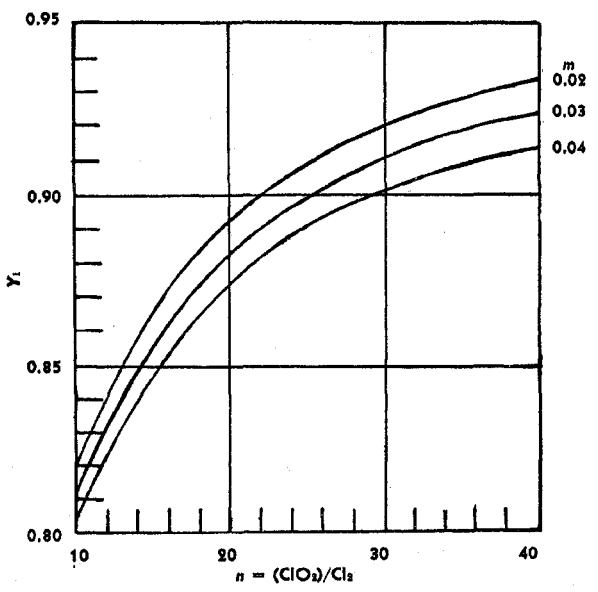

Figure 8. Yields of Chlorine Dioxide from Sodium Chlorate Calculated According to Formula

$$Y_1 = \frac{n}{n+2}(1 - m)$$

TABLE II. CONVERSION OF CHLORINE DIOXIDE TO SODIUM CHLORITE BY MEANS OF SODIUM PLUMBITE

(Yield of $NaClO_2$ calculated on $NaClO_3$ consumed in the generation of ClO_2)

Expt. No.	$NaClO_3$ Consumed, G.	$NaClO_2$ Produced, G.	$NaClO_3$ Produced, G.	NaCl Produced, G.	NaOH Remaining, G.	$\frac{(NaClO_2)}{(NaCl)}$, Mole Ratio	ClO_2 Absorbed, %	Yields of $NaClO_2$, %
1	27.3	19.4	0.11	0.92	1.68	13.6	93.6	83.6
2	23.7	17.4	0	0.73	3.01	15.4	96.9	86.5
3	118.6	83.0	0.01	4.53	7.78	11.8	92.4	82.2
4	118.6	84.2	0.04	4.82	9.80	11.4	93.5	83.5
5	136.5	90.8	0.64	4.50	5.32	13.0	87.8	78.3
6	136.5	90.6	0.32	5.25	3.28	11.2	87.6	78.1

TABLE III. CONCENTRATION OF SODIUM CHLORITE SOLUTION BY REPEATED ABSORPTION AND CONVERSION OF CHLORINE DIOXIDE IN LEAD OXIDE–SODIUM HYDROXIDE SUSPENSIONS

Absorption No.	Grams per Liter				$\frac{(NaClO_2)}{(NaCl)}$, Mole Ratio	Specific Gravity of Solution, d_4^{20}
	$NaClO_2$	$NaClO_3$	NaCl	NaOH		
1	90.0	0.32	5.25	4.41	11.1	1.068
2	164.3	...	9.60	2.46	11.1	1.119
3	221.3	2.58	13.6	1.27	10.5	1.162
4	272.8	...	16.7	3.36	10.6	1.197
5	319.6	4.47	19.6	1.99	10.6	1.230

From chemical analysis the fractional amount, m, of chlorine, remaining as hydrogen chloride in the final solution, and the ratio, n, of $(ClO_2)/(Cl_2)$ in the effluent gas mixture are calculated. The numerical values of these quantities were in average: $m = 0.030$ and $n = 24$.

From the relations

$$m = \frac{2x - 5z}{2} \text{ and } n = \frac{2Y_1}{3z}$$

the following simple expression of the yield of chlorine dioxide is obtained

$$Y_1 = \frac{n}{n+2}(1 - m)$$

and the following numerical values of x, z, and Y_1 are calculated:

$$x = 0.093,\ z = 0.025, \text{ and } Y_1 = 0.89.$$

In comparison, from the data given in (*21*), the following values may be calculated for the I. G. Farbenindustrie process of producing chlorine dioxide—$m = 0.029$, $n = 20$, and $Y_1 = 0.88$. The function, $Y_1(m, n)$, is graphically represented in Figure 8 for $m = 0.020 - 0.040$ in the interval of $n = 10 - 40$.

Table II contains a summary of six experiments on the conversion of chlorine dioxide to sodium chlorite, in which the over-all yields of sodium chlorite were calculated on the basis of the amount of sodium chlorate consumed in the generation of chlorine dioxide.

The most remarkable fact shown by this table is the negligible formation of chlorate, indicating an almost complete suppression of the direct hydrolysis.

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

Moreover, the rather small amounts of chloride will entirely originate from the chlorine accompanying the chlorine dioxide in the gas stream. Thus, in all six experiments together 20.75 grams of sodium chloride and 385.4 grams of sodium chlorite were produced, corresponding to a molecular ratio $(NaClO_2)/(NaCl)$ of about 12.

These facts indicate a theoretical yield of almost 99 to 100% in the chemical conversion of chlorine dioxide to sodium chlorite.

According to the data given in (*21*), the corresponding ratio in the sodium chlorite liquor for the hydrogen peroxide process may be calculated to 9.7, and for the zinc dust process as low as about 5.

The average over-all yield of sodium chlorite in the six experiments of Table II was 81%, calculated on the total weight of sodium chlorate consumed in the generation of chlorine dioxide. This over-all yield, Y, may be given by the following expression:

$$Y = Y_1 \times Y_2 \times Y_3$$

where

Y_1 = yield of chlorine dioxide from sodium chlorate, 89%

Y_2 = yield of absorbed chlorine dioxide, 91%

Y_3 = yield of the chemical conversion of chlorine dioxide to sodium chlorite, nearly 100%.

The average yield of sodium chlorite, produced in the second step of the reactions

$$NaClO_3 \xrightarrow[H_2SO_4]{SO_2} ClO_2 \xrightarrow[NaOH]{PbO} NaClO_2$$

corresponding to $Y_2 \times Y_3$, was found to be 91%.

However, from analysis of the reaction solutions the conversion, Y_3, was found to be almost 100%, and hence the average absorption yield, Y_2, may be calculated to be 91%. The incompleteness of absorption was also directly confirmed by experimental control. Consequently, one should get the following account of the utilization of sodium chlorate in these experiments:

$NaClO_2$, produced	81%
ClO_2, unabsorbed	9%
NaCl, produced	7%
HCl, losses	3%

The heavy slurry of lead dioxide formed in the reaction may be separated easily from the slightly alkaline solution of sodium chlorite, and the filtered liquor once more charged with calculated amounts of sodium hydroxide and lead oxide. This procedure is repeated several times, until a sufficiently concentrated solution of sodium chlorite suitable for evaporation and drying is obtained.

Table III contains a summary of five experiments in this direction. It was found that the absorption of chlorine dioxide

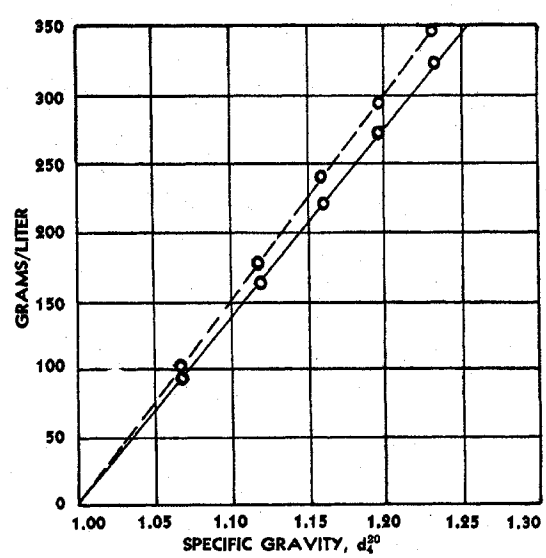

Figure 9. Relation between Specific Gravity and Concentration of Sodium Chlorite

Dotted line indicates the total concentration of salts in reaction solution

steadily decreases with increasing amounts of sodium chlorite in the reaction mixture. Therefore, in order to reach a complete absorption, the gas stream must be conducted through two absorption vessels However, it must be emphasized that no decrease in the yield of the chemical conversion has been observed in these operations. As will be seen from the table, a gradually increasing concentration of sodium chlorite to about 320 grams per liter was obtained without any appreciable losses of chlorine dioxide caused by chemical reactions.

The linear relation of the concentration to the specific gravity of the solutions is shown in Figure 9.

The final solution may be concentrated further and dehydrated to complete dryness by hot air or in a vacuum at lower temperatures—e.g., 50° to 100° C.—giving a product of nearly white or slightly yellow color. The composition of a sample from such an experiment was as follows: sodium chlorite, 89.3%; sodium chlorate, 2.6%; sodium chloride, 7.7%; sodium hydroxide, 0.4%.

These figures indicate a very small decomposition of the sodium chlorite during drying, according to the reaction:

$$3NaClO_2 \longrightarrow 2NaClO_3 + NaCl$$

ECONOMY OF THE LEAD OXIDE PROCESS

An economical viewpoint of considerable interest is the proper utilization of the lead dioxide. According to the United States chemical sales market price in June 1949 the prices quoted for yellow lead oxide (litharge) and lead dioxide (powdered) were, respectively, 13.75 and 41 cents per pound—i.e., the price of lead dioxide was about threefold that of litharge. The importance of such a favorable margin is obvious to everybody. On the assumption that one could sell the total output of lead dioxide, the selling prices of this profitable coproduct would support almost all the charges included in the production of sodium chlorite. In July 1949 the price of yellow lead oxide was 14.75 cents, whereas the price of lead dioxide suddenly dropped to 33 cents, but even this change does not seriously disarrange the favorable economy of the lead oxide process.

This state of affairs will be clear from the fact that the prices for sodium chlorate and caustic soda at the same time were only 7.5 cents per pound for sodium chlorate and 2.5 cents for sodium hydroxide.

According to the writer's suggestion, the technical production of sodium chlorite, therefore, may be favorably realized on the basis of the following reactions:

A. Generation of chlorine dioxide.

$$2NaClO_3 + 2H_2SO_4 \longrightarrow 2HClO_3 + 2NaHSO_4$$

$$2HClO_3 + SO_2 \longrightarrow 2ClO_2 + H_2SO_4$$

B. Conversion of chlorine dioxide to sodium chlorite.

$$PbO + NaOH \longrightarrow NaOPbOH$$

$$2ClO_2 + NaOPbOH + NaOH \longrightarrow 2NaClO_2 + PbO_2 + H_2O$$

With an over-all yield of 100%, the production of 2 moles (181 grams) of sodium chlorite together with 1 mole (239 grams) of lead dioxide would require a consumption of 2 moles (213 grams) of sodium chlorate, 2 moles (80 grams) of sodium hydroxide, and 1 mole (223 grams) of lead oxide, as well as certain quantities of the cheap chemicals, sulfuric acid and sulfur dioxide, which for the sake of simplicity will be omitted.

Thus, the hypothetical consumption of precious chemicals for 1 pound of sodium chlorite (100%) and 1.32 pounds of lead dioxide produced, would be as follows: 1.18 pounds of sodium chlorate, 0.44 pound of sodium hydroxide, and 1.23 pounds of lead oxide.

Calculating for the generation of chlorine dioxide with a yield of at least 87% on sodium chlorate consumed, and 98% in the conversion of chlorine dioxide to sodium chlorite at substantially complete absorption, one should get an over-all yield of about 85% in the transformation of sodium chlorate to sodium chlorite via chlorine dioxide.

Supposing further a molecular ratio $(ClO_2)/(Cl_2)$ of about 20 in the gas stream, the chlorine should be responsible for 10% of the consumption of sodium hydroxide and lead oxide. Hence, the following consumptions and costs of chemicals for producing 1 pound of sodium chlorite (100%) and 1.47 pounds of lead dioxide will be obtained:

	Consumptions	Costs
$NaClO_3$	$\frac{1.18}{0.85} = 1.39$ lb.	$1.39 \times \$0.075 = \$0.104$
NaOH	$\frac{0.44}{0.90} = 0.49$ lb.	$0.49 \times \$0.025 = \$0.012$
PbO	$\frac{1.23}{0.90} = 1.37$ lb.	$1.37 \times \$0.137 = \$0.188$
		\$0.304

As the costs of sulfuric acid and liquid sulfur dioxide, which is a very convenient source of sulfur dioxide in regulating the evolution of chlorine dioxide, may not exceed 4.5 cents, the total costs of chemicals in the proposed lead oxide process for producing sodium chlorite would be estimated to be 35 cents per pound of sodium chlorite.

As a coproduct, 1.47 pounds of lead dioxide will be obtained with a possible credit value of 1.47 × 41 cents per pound = 60 cents according to the United States market price in June 1949 (or 1.47 × 33 cents = 48.5 cents in July 1949).

As the writer is not familiar with the consumption of lead dioxide in the United States no further speculations should be done about the quantities which might be possible to sell on this market. However, regardless of this commercial point of view, the lead oxide process should be able to be worked favorably. The lead dioxide may be easily reconverted to lead monoxide by a simple decomposition or reduction process—e.g., by heating alone or with a cheap gaseous reducing agent, such as hydrogen or carbon monoxide. Hence, the real costs of chemicals would drop to about 20 cents per pound of sodium chlorite. In fact, experiment 2 in Table II was carried out with regenerated lead oxide, giving an excellent yield of sodium chlorite.

Finally, it will be of special interest to compare these costs of producing sodium chlorite with those which should be obtained in the use of hydrogen peroxide as reducing agent. The price of hydrogen peroxide (100% by volume strength) on the United States market was 19.5 cents per pound in June 1949. About 0.75 pound of this chemical (30% by volume, or 27% by weight hydrogen peroxide) may at least be consumed in the production of 1 pound (100%) of sodium chlorite, corresponding to a cost of 15 cents. Calculating with the same costs of chemicals as before in the generation of chlorine dioxide (about 15 cents per pound of sodium chlorite produced), the total costs of chemicals in the hydrogen peroxide method should be estimated to 30 cents per pound (100%) of sodium chlorite.

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Compressibility of Ethane-Propylene Vapor Mixtures

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The compressibilities of four ethane-propylene vapor mixtures (0.1861, 0.4033, 0.6016, and 0.7998 mole fractions of ethane) over a range of pressures from 10 to 220 atmospheres and temperatures from 100° to 250° C. are presented. Measurements were correlated by means of the Benedict-Webb-Rubin equation of state to a density of 9.0 moles per liter, with an over-all average deviation of 0.61%

A BASIC approach to the analysis and correlation of compressibility data for gases has been by the use of an equation of state; for pure components this involves fitting the equation of state to the experimental data by evaluating a number of constants. These constants are peculiar to the given substance and can be used to interpret a proposed molecular picture. A logical approach to the pressure-volume-temperature (P-V-T) relations of mixtures is the method by which the pure component constants (in the equation of state) combine to describe the properties of the mixture. Much success in this direction has been obtained by Beattie and co-workers (*2*, *3*) and Benedict and co-workers (*5*, *6*) for hydrocarbon mixtures. Hope for the solution of the general problem of the P-V-T relations of mixtures lies in the use of these methods, as compared to the extremely long-range methods of obtaining the experimental data for all possible hydrocarbon gas mixtures.

The purpose of this work was to increase the P-V-T data of hydrocarbon mixtures by experimental measurements, and to correlate the data by one of the methods of combining constants of the pure components of the mixture. The P-V-T data of four ethane-propylene mixtures (0.1861, 0.4033, 0.6016, and 0.7998 mole fractions of ethane) were determined at pressures from 10 to 220 atmospheres and temperatures from 100° to 250° C. (isotherms at every 25° C.).

The system, ethane-propylene, has been investigated by Lu, Newitt, and Ruhemann (*8*). These investigators determined the phase equilibria at temperatures from −30° to 70° C. and pressures from 1 to 52 atmospheres which included the critical envelope. Their measurements involved the compressibility of the two pure components and nine mixtures. Although the work of Lu *et al.* contributes to the important subject of phase equilibria, none of the data can be used for comparison with the data of this investigation because of the temperature and pressure ranges.

APPARATUS AND EXPERIMENTAL TECHNIQUE

The apparatus and experimental technique used in this work have been described in detail (*7*). The gas samples were Phillips Petroleum Company research grade hydrocarbons certified by the National Bureau of Standards as 99.9 mole % ethane and 99.70 mole % propylene. The data are believed to be accurate within ±0.25% (*7*).

EXPERIMENTAL P-V-T DATA

Prior to the determination of the P-V-T data of the ethane-propylene mixtures it was necessary to select suitable data for the two pure components, in order that subsequent correlation of the mixture data could be accomplished. The compressibility of ethane vapor in the superheated region has been studied by Beattie, Hadlock, and Poffenberger (*1*), Beattie, Su, and Simard (*4*), and Reamer, Olds, Sage, and Lacey (*10*). Beattie's data cover temperatures from 25° to 275° C. and pressures from 10 to 350 atmospheres, whereas Reamer and co-workers determined

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