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AQUEOUS OXIDATION OF GALENA

by

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in the Department

of

Mining and Metallurgy

We accept this thesis as conforming to the  
standard required from candidates for the  
degree of MASTER OF APPLIED SCIENCE

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Members of the Department of  
Mining and Metallurgy

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## Abstract

To complement the data on the aqueous oxidation of sulphide minerals, that is, treatment of sulphides in aqueous solution at elevated temperatures under oxygen pressure, a study was undertaken of the aqueous oxidation of galena in sodium hydroxide solution. It was hoped by the study of the kinetics of the reaction to learn something of the mechanism involved.

The reaction was followed by means of a cathode-ray polarograph. A crystal of galena was mounted in a small autoclave equipped with suitable electrodes, and during the course of the reaction photographs were taken at intervals of the current-voltage curves. From the height of the lead wave relative concentrations could be recorded, and after a suitable time the run was stopped and the solution assayed to give absolute values to the wave heights.

The variables of oxygen partial pressure agitation, sodium hydroxide concentration, temperature, silicate-ion, and electrical potential were investigated. It was found that the polarograph under these conditions gave reproducible results.

On the basis of the experimental results three alternative mechanisms for the reaction were proposed. One of these was too indefinite to treat quantitatively, but the other two were examined by calculations using the theory

of absolute reaction rates. One was found to give agreement in rate with experiment, a model in which desorption accompanied by hydration and ionization was the rate-controlling step.

The experimental results were reviewed in the light of this mechanism and appeared to show no serious contradictions, so this model is put forward as a postulate of the reaction of galena with oxygen in sodium hydroxide solution.

### Acknowledgement

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## AQUEOUS OXIDATION OF GALENA

### Introduction

The first mention of pressure oxidation of sulphides in aqueous solution in technical literature is German Patent D.R.P. Nr. 524,353, April 16, 1931, awarded to I. G. Farbenindustrie Akt.-Ges. in Frankfurt. This was for a process for the production of metal sulphates from metal sulphides by oxidation in aqueous solution by the use of oxygen or an oxygen-containing gas. The reaction was known previously, however, and was used in a cyclic process for the separation of  $H_2S$  from illuminating gas. In 1939 Dr. A Bognar was awarded Hungarian Patent 122479 for the treatment of ores and flue dusts at high temperatures and pressures in the



presence of some liquid water, with or without the addition of sulphur or sulphur-bearing material, to form water-soluble sulphates of metals. In the same year Tronev, Bondin, and Zviagincev<sup>1,2</sup> published two papers in which they describe the oxidation of zinc and copper sulphides in alkaline solutions and in water using high pressure air at temperatures up to 250°C.

At the University of British Columbia work on pressure oxidation has been done by R. Carter<sup>3</sup>, W. K. A. Congreve<sup>4</sup>, R. B. McIntosh<sup>5</sup>, and J. F. Stenhouse<sup>6</sup>. Of these, the paper by J. F. Stenhouse is the only one which deals exclusively with the mechanism and fundamental reactions of the process. Mr. Stenhouse oxidized pyrite in sodium hydroxide solution and measured the rate of the reaction by the rate

1 Tronev, V., and Bondin, S., Oxidation of Zinc Sulphide and Transference of Zinc into Aqueous or Alkaline Solution under Air Pressure, *Comptes Rendus Acad. of Science U.R.S.S.* 23, pp. 541-3, Moscow, 1939.

2 Zviagincev and Tronev, V., Oxidation of Copper Sulphide and Transference of Copper into Aqueous Solution under Air Pressure, *Comptes Rendus Acad. of Science U.R.S.S.* 23, pp. 543-4, Moscow, 1939.

3 Carter, R., Influence of Roasting Temperature on Gold Recovery from a Refractory Gold Ore, M. A. Sc. Thesis, University of British Columbia, 1949.

4 Congreve, W. K. A., Use of High Pressure Oxygen in Extraction Metallurgy, Report to the Research Committee, The University of British Columbia, 1949.

5 McIntosh, R. B., Recovery of Cobalt from Taylor Gem Ore by Aqueous Oxidation, M. A. Sc. Thesis, University of British Columbia, 1950.

6 Stenhouse, J. F., Humid Oxidation of Pyrite, M. A. Sc. Thesis, University of British Columbia, 1950.

of consumption of oxygen. This reaction involved the formation of a coating of the oxides of iron on the fine particles of pyrite.

After studying the previous work in this field, it was decided that the mechanism of oxidation where all products were soluble in the medium had not been adequately investigated. The pressure oxidation of galena in sodium hydroxide solution appeared to offer a suitable reaction for study. A method of following the reaction without removing material from the autoclave was felt to be desirable. For this purpose the polarograph seemed to offer good hope of success. After considering the different modifications of this device, the model built by J. E. B. Randles<sup>7</sup> was thought to be most suitable. A copy of his instrument was built and after some initial difficulties was made to give reproducible results.

## Equipment

### The Cathode-Ray Polarograph

The circuit of the cathode-ray polarograph used in this research is given in Figures 1 and 2, page 4. It consists of six units: a low voltage electronically smoothed power supply, a source of increasing potential, which also includes the current-measuring circuit; a synchronizing unit

<sup>7</sup> Randles, J. E. B., A Cathode-Ray Polarograph, Transactions of the Faraday Society, #44, 1948, pp. 322-327.

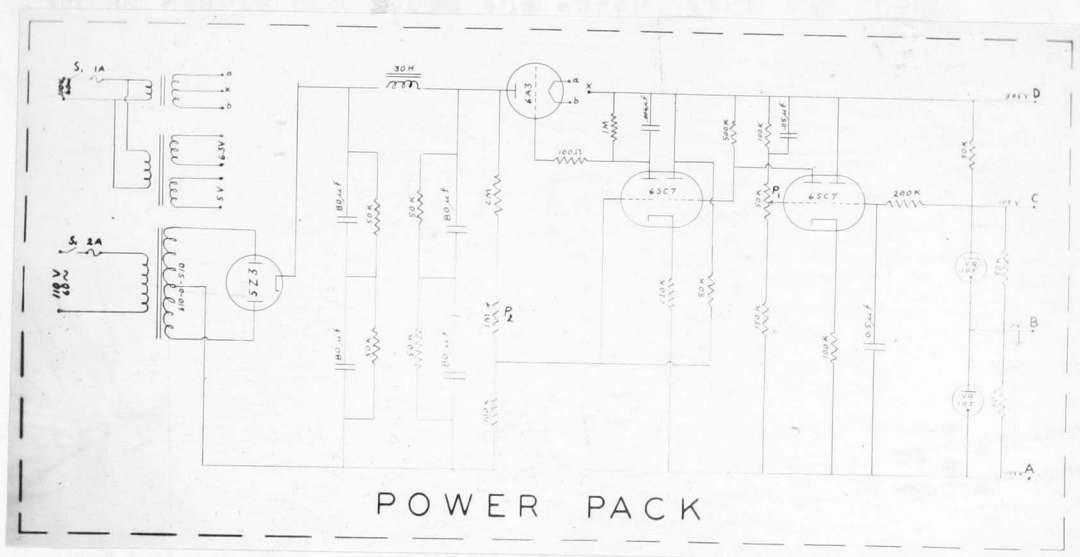


Figure 1  
Power Supply

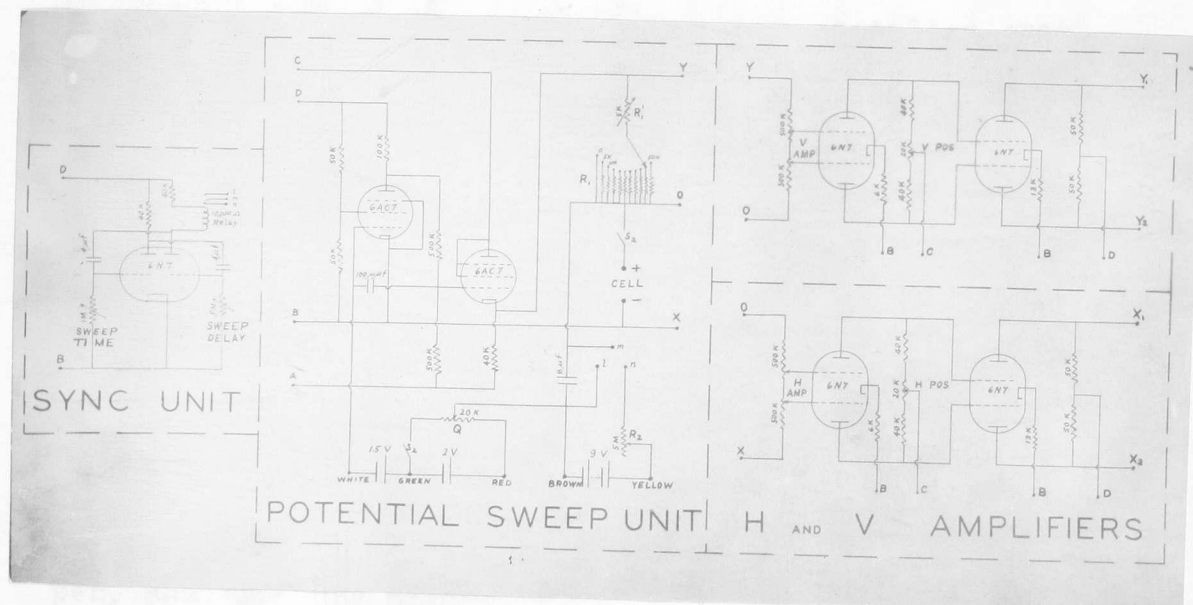


Figure 2  
Other Circuits

which starts and stops the sweep after the appropriate time intervals; a direct current amplifier to amplify the horizontal voltages to give the horizontal sweep; a direct current amplifier to amplify the vertical (current) signals; and a cathode-ray tube with its high-voltage power supply for the visual presentation. The cathode-ray tube used was incorporated in an oscilloscope, Triplet Model 3440 (five-inch), whose chassis was grounded to the chassis housing the rest of the electronic equipment. The output of the D. C. amplifiers was connected directly to the deflection plates of the cathode-ray tube. The whole is shown in Fig. 3, page 6.

#### The Autoclave

The autoclave is illustrated in Fig. 4, page 6. All surfaces exposed to the solution are stainless steel, with the exception of the stirring mechanism and the thermometer well. Magnetic material was necessary for the stirrer, so mild steel was used in the absence of conveniently available magnetic stainless. The thermometer well was an emergency repair after a previous arrangement failed, and as it served the purpose it was not replaced. It consisted of a piece of ordinary iron pipe welded over at the end. Various materials were tried for use as a liner--glass, Inconel, copper, and type 304 stainless steel. On a short-term basis the stainless steel was the only satisfactory material. The glass dissolved at an excessive rate, the Inconel apparently displaced lead from the solution, and the copper dissolved and reprecipitated as a cupric hydroxide suspension.

The heating and stirring devices are shown in

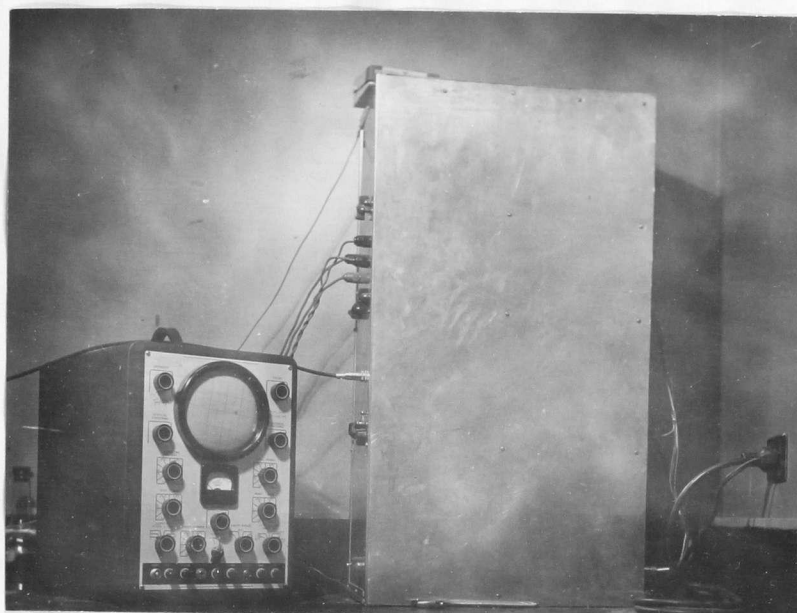


Figure 3

## Electronic Equipment

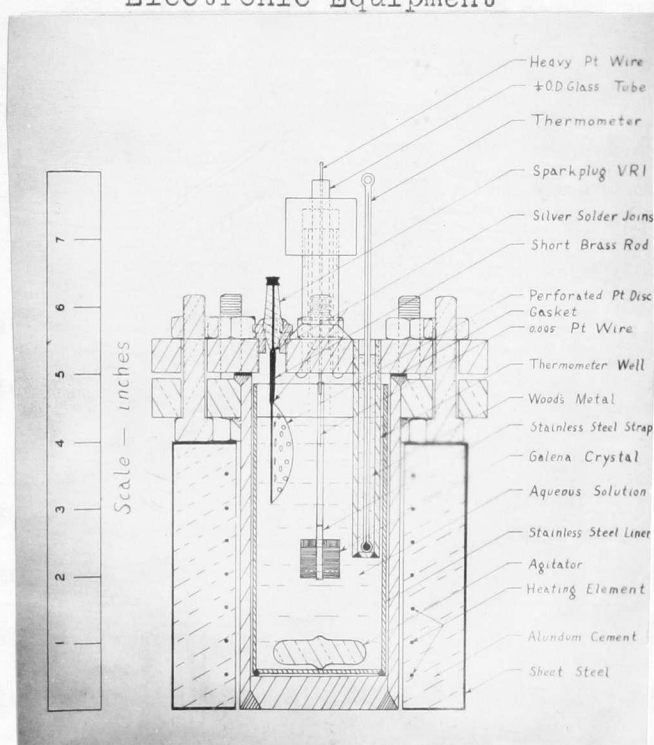


Figure 4

## Autoclave and Accessories

Fig. 5, page 8. Heat is supplied from an element made by shaping coiled nichrome wire about a form of the same diameter as the body of the autoclave, plastering with alundum cement, baking, and setting the resulting cylinder, after removal of the form, in a metal can. The space between can and cylinder was then chinked with more alundum. The element was designed to give 500 watts at 110 volts. The actual heat supplied was controlled by a variac and approximated 100 watts. The temperature of the contents of the autoclave was read off the thermometer which was inserted in its well and connected thermally with molten Wood's metal.

The contents of the autoclave were stirred by rotating a 2.5-inch Alnico magnet just below the bomb, which moved the cylindrical rotor on the inside. A rim was turned onto the rotor to reduce its bearing surface. The speed of rotation of the magnet could be varied from 80 to 250 RPM by changing pulleys on the belt drive, and by varying the series resistance controlling the variable speed motor.

Oxygen and other gases were supplied from commercial bottles, regulated by the usual diaphragm valves, and the pressures read off the Bourdon gauges incorporated into the regulator assemblies. A piece of high-pressure rubber hose gave flexibility to the gas connections, and a shut-off valve allowed the autoclave to be disconnected while at elevated temperatures.

The autoclave had been tested to 200 p.s.i. This restricted the temperature and pressure ranges investigated.

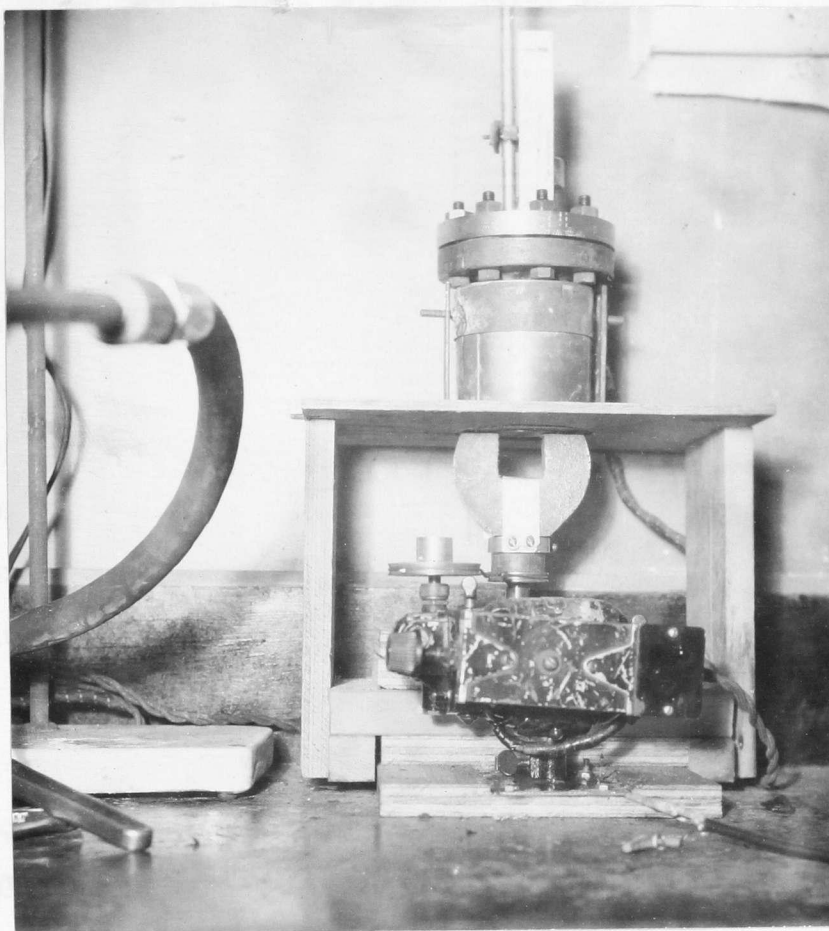


Figure 5

Autoclave Assembly, Heating and Stirring Mechanisms

### The Electrodes

The electrodes were made as follows: The platinum micro-electrode was made by fusing the end of a piece of fine wire and welding the other end to a coarser platinum wire. The heavy wire was fused into a piece of pyrex capillary tubing, which was held in a rubber packing under a stainless steel pipe plug. This is all shown in Fig. 4. The unpolarized electrode was a piece of perforated platinum foil, which was brazed to a short rod connected to the centre electrode of a Champion VR-1 model aircraft spark-plug.

### Theory of Operation of the Polarograph

The voltage of the potential sweep of the cathode-ray polarograph increases at a rate of approximately one volt per second. This is about one hundred times as fast as in the normal polarograph. The result of this high rate is to change the law of operation from dependency on the laws of spherical diffusion<sup>8</sup> to dependency on the rate of depletion from very thin layers about the electrode. The theory of operation is explained by Randles<sup>9</sup>, who worked out the solution of the differential equation for plane diffusion, which this process approximates, by numerical methods. Mathematical difficulties here are caused by the complicated equation for the boundary conditions. The

8 Kolthoff and Lingane, Polarography, Interscience Publishers Inc., New York, 1941.

9 Randles, J. E. B., The Current Voltage Curves, Transactions of the Faraday Society, #44, 1948, pp. 327-338.



results of the use of this rapid sweep are:

1. The usual sharp rises associated with diffusion current regions are replaced by current maxima.
2. If the point for the beginning of the sweep is taken at a voltage where the preceding reaction is controlled by steady state diffusion, the current rise for the succeeding reaction is independent of the preceding current value.
3. Peak height, in addition to being a function of all the quantities listed for diffusion current in conventional polarography, is also directly proportional to the rate of change of voltage.
4. The half-wave potential, basis of identification by polarography, corresponds to the current maximum.
5. The peak height is proportional to the rate of an electrode process. For a very slow process there will be a slow rise and no maximum in the mathematical sense.

There are no particular disadvantages for analytical work in such a device, and for following rapid reactions the advantages are obvious. They were realized by Snowdon and Page<sup>10</sup>, who built a more refined machine than Randles' and used it to follow very rapid reactions in synthesis and decomposition of organic compounds.

Because of the nature of the process being

<sup>10</sup> Snowdon, F. C., and Page, H. T., A Cathode-Ray Polarograph, Analytical Chemistry, Vol. 22, No. 8, August, 1950, pp. 969-80.

investigated, which only takes place at high temperatures and pressures, the usual dropping mercury cathode and calomel half cell for the anode and reference, potential could not be used, or, at least, not easily. It has been stated in Randles' papers and others that reactions at solid electrodes will give consistent analytical results, although some of the simplifying assumptions used in the mathematical derivations of the polarographic current curves are no longer true. Consistent results were obtained in this application.

The requirement for the unpolarized electrode is that it have a large area compared to the micro-electrode, and that it have a steady, known half-cell potential, varying little with current. The second criterion is probably not met by a sheet of smooth platinum, but if the potential is reasonably steady, a given ion can be identified by the running of suitable standards under the same conditions. At elevated temperatures and pressures the half-wave voltages are not known anyway. There was little fluctuation of the potentials of lead and oxygen waves under like conditions.

## Experimental

### Materials

"Bakers Analyzed" chemicals and distilled water were used throughout for making up medium.

Two types of galena were used, a ground

concentrate from the Consolidated Mining and Smelting Company of Canada, and handpicked crystals from Violamac Mines (B.C.) Limited at Sandon, B. C. The analyses are given below:

C. M. & S. Concentrate OGS 740

| Ag          | Pb    | Zn   | Fe   |
|-------------|-------|------|------|
| 94.7 oz/ton | 82.7% | 1.6% | 1.0% |

Spectrographic Analysis

Low

Trace

Ca Al Si Mg Sb Mn Cu

Cd As B Sn Ge V Ti Ba Sr Bi

The analysis of three crystals of the same type as those used for the research, from Violamac Mines, gave the following analysis:

|    |            |    |             |
|----|------------|----|-------------|
| Ag | 126 oz/ton | Au | 0.02 oz/ton |
|----|------------|----|-------------|

Spectrographic Analysis

|    |      |    |   |                 |
|----|------|----|---|-----------------|
| Sn | 0.2% | Si | ) |                 |
| Sb | 0.06 | Fe | ) | less than 0.05% |
| Zn | 0.03 | Mg | ) |                 |
|    |      | As | ) |                 |

The results of the spectrographic analysis are from the Provincial Assay Office, Victoria, B. C., who kindly did this work.

Experimental Procedure

1 Rates on Crystals

A slab of galena crystal measuring approximately 0.2 by 0.3 by 0.5 inches was broken from a larger piece. The surfaces were ground flat and parallel to the 100 axes on No. 2 emery, the crystal was measured by a micrometer, washed in cold, running water, and placed in a stainless

steel wire holder as illustrated in Fig. 5. The holder was placed in its position in the liner, 155 ml. of medium added to bring the liquid up to the required level, the rotor dropped in, and, in later experiments, a few ml. of water were introduced between the liner and the body of the autoclave. After washing the lid and electrodes the lid was bolted into position, the autoclave placed in the heating jacket, and the gas line connected. The shut-off valve was then closed and gas pressure turned on against it. (This step was a precaution against steam getting into the line if the shut-off valve did not close properly.) The heat was then switched on, the agitator started, and the polarograph switched on. When the autoclave was up to temperature, the top valve was opened to allow oxygen to reach the solution. This was taken as time zero. Photographs were taken of the cathode-ray tube face at 15-minute intervals, each time shutting off the agitation and allowing the solution to come to rest. The electrodes were only connected to the polarograph while taking a reading. After about 180 minutes the top valve was closed, the heat and oxygen turned off and the autoclave quenched under a tap. This was taken as  $t_{\text{final}}$ , and five minutes were added for reaction occurring after the apparatus had been shut off.

The autoclave was opened when cool and the solution with washings put aside for assay. The assay procedure is given in Appendix A. The crystal was then examined under the microscope and sometimes photographed.

The photographic plates showing the current-voltage curves were then developed and the peak heights measured,

corrected, and plotted. The rate curve was extrapolated to  $t_{\text{final}}$  plus five minutes, and the ordinate at this point corresponded to the total lead content of the solution.

The polarograph was set while taking the first reading and the adjustments were not changed during the run.

The results were consistent within 5%, except for a few anomalously high rates. These were considered to be due to spalling of small fragments of galena, which would be ground under the rotor and give an increase in surface area.

## 2 Rates on Pulps

When a rate determination was made on ground galena, the procedure was exactly the same except that a weighed amount of pulp was placed in the liner instead of a crystal.

## 3 Qualitative Investigation of the Effect of Applied Fields

When it was desired to investigate the effect of an applied field, a small galena crystal was set in solder in a cup drilled into the end of a brass rod. The other end of the brass rod was welded to the centre electrode of a model aircraft sparkplug, and all metal and crystal except for a small window to a 100 plane was painted with a plastic-base varnish. The closed autoclave containing medium was then brought up to boiling-point, the sparkplug screwed into position so that the crystal was below the level of the

liquid, oxygen pressure applied, and EMF's measured by a vacuum-tube voltmeter. Sometimes the electrodes were connected to the periodic voltages from the polarographic apparatus and the wave forms observed.

## Results

### Products of the Pressure Oxidation of Galena in Sodium Hydroxide Solution

Analysis showed the products of the reaction could be considered to be sodium plumbite and sodium sulphate, or, more correctly, sulphate-ion and plumbite-ion. No higher valence forms of lead and no lower valence forms of sulphur, for example, polythionates, were found. Apparently the sulphur atom was oxidized completely before it had travelled far into the solution.

### The Wave Forms

The wave forms for the platinum micro-electrode were all similar to the example shown in Fig. 6, page 16. These were the results of employing the microelectrode as a cathode. If the microelectrode was made anodic no current maxima were observed except for the evolution of oxygen, which occurred at a very low potential.

Quantitative results were all based on the waves for the reduction of oxygen and of lead-ion to metallic lead. There was no shift in the half-wave voltages for these reactions as might have been expected, due to poisoning of the platinum anode, or because of the build-up of

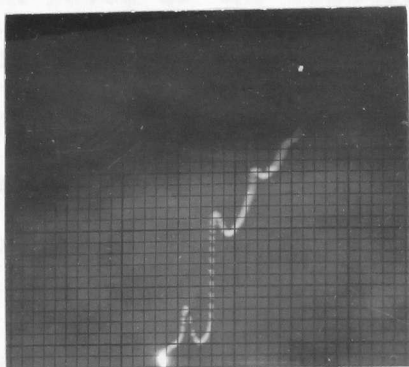


Figure 6

Polarogram

Photograph showing, from left to right, a lead oxidation wave, oxygen reduction wave, and lead reduction wave. Curves

lead on the cathode. Wave heights were measured by drawing tangents as described in Kolthoff and Lingane, for although the maximum was easy to read, the beginning of the rise was not so definite. The vertical distance from the lower tangent to the maximum was called the wave height. As the lines on the photographic plate were of appreciable thickness, the centre of this line was taken as the true value.

Because of the rapid attack of sodium hydroxide on glass, it was necessary to use a wire dipping into the solution as the micro-electrode. As current is a function of surface area, this made current readings very sensitive to changes in level of the solution. For this reason, and because no other suitable substance was found, oxygen was used as a reference standard. It was considered in the case of measuring rates of oxidation of galena crystals that the reaction was slow enough that the surface layers of solution would always be saturated with oxygen, after the first few minutes. After water was introduced between liner and autoclave, the changes in level became almost insignificant.

The wave forms of the reaction at a galena electrode were much more complicated and no attempt was made to get quantitative information from these.

#### The Rate Curves

The rate curves for crystals were all of the form shown in Figures 7 and 8, page 18. The initial toe of the curve is caused by diffusion of oxygen into the liquid gradually reaching equilibrium, at which time some



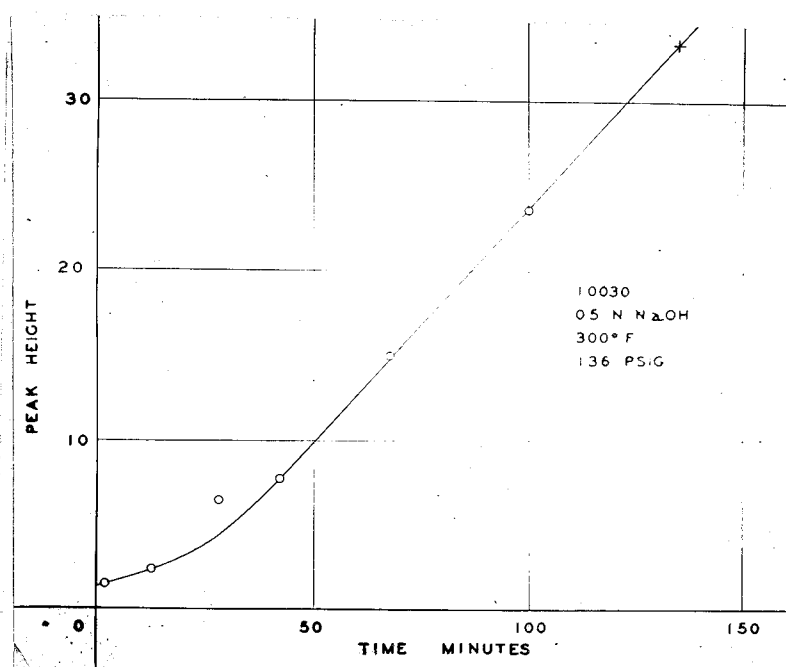


Figure 7

Rate Curve for a Crystal

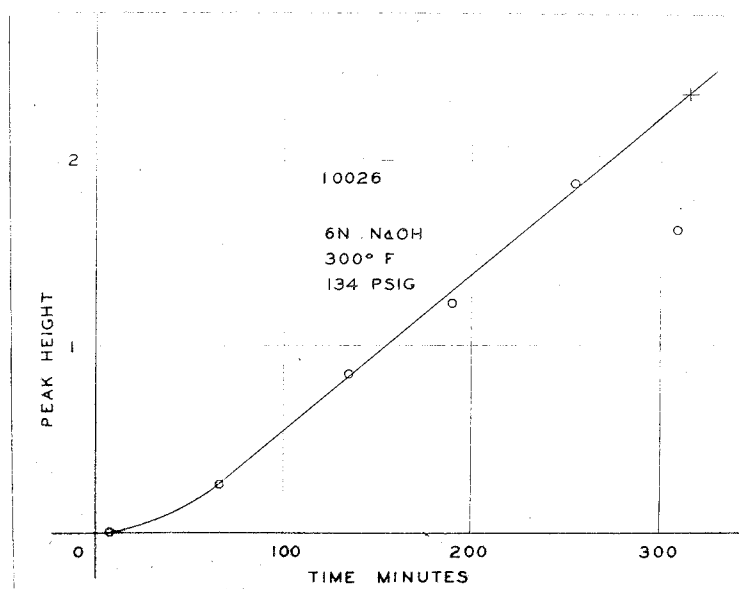


Figure 8

Rate Curve for a Crystal

other step controls the over-all rate. It is considered that the medium was approaching saturation with oxygen. It may be noted in the two examples given that saturation was much more rapid with more concentrated sodium hydroxide. This can be explained by two contributing factors: oxygen is less soluble in concentrated caustic, and the reaction rate is slower. It will be noted that the curves are essentially straight after the initial toe. This would seem to mean that the products, at least in these low concentrations, have no effect on the reaction, and that the effective surface area remains constant, or that these effects exactly cancel. The reaction was always slow enough and the time short enough that the overall size of the crystal was not much changed. There was an increase in area, however, due to pitting effects. The straightness of the line after the initial period was checked by stopping the reaction after shorter periods than usual and seeing if the concentration-time relationship was linear. This was found to be so within the experimental error.

The rate curve for ground pulps was found to have the shape shown in Fig. 9, page 20. It appears reasonable considering the reduction in area as the pulp is consumed. There appears to be no initiation period here, no doubt due to the fine particles approaching the oxygen-rich gas-liquid interface in the early stages. With incomplete reactions the residue consisted entirely of coarser particles, no doubt due to the effect mentioned above, and perhaps due in part to the higher surface energies of very fine particles.

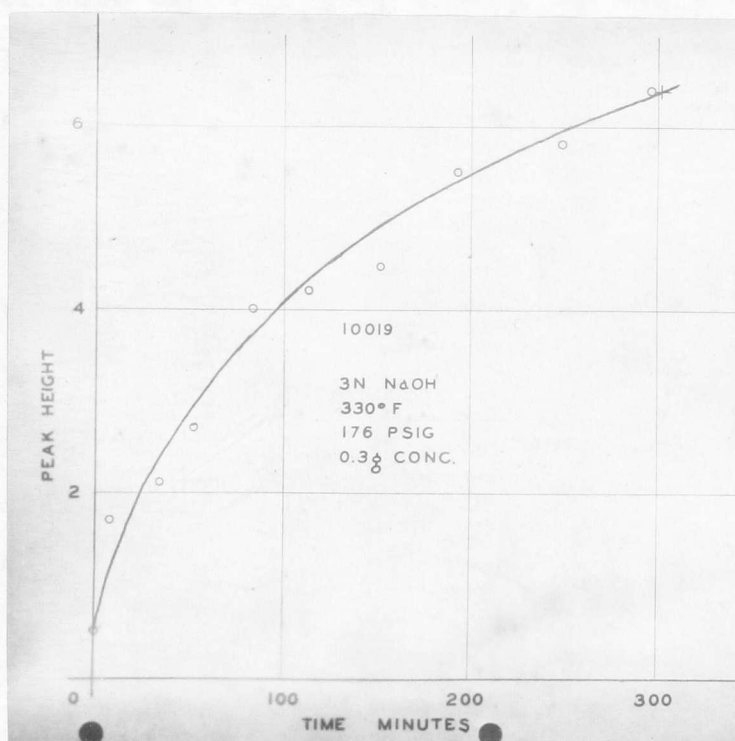


Figure 9

Rate Curve for a Pulp

All rate relationships were worked out from data on single crystals. There are two dangers in this: a difficult sampling problem is created and lack of homogeneity in a large slab might produce effects which would not be met in a ground pulp. Nevertheless, as it was desired to measure the rates of flow of medium past the surface and to avoid the effects of attrition, almost all the work was done on single crystals. No difference in rate between individual slabs of galena was found.

#### Appearance of the Crystal after Oxidation

All crystals, regardless of rate of reaction or sodium hydroxide concentration, had three attributes in common when viewed under the microscope: the surface was crossed by etched lines, apparently some sort of block boundaries, it was covered with fine pits of varying size, formed by the intersection of  $11\bar{1}$  planes, and there was no evidence of change of phase in the surface.

As agitation was particularly poor during the cooling period, while reaction was still taking place, there was some accumulation of product, particularly in high caustic concentrations. In one case, in 0.5 N NaOH at  $93^{\circ}\text{C}$ , the surface showed a web of the yellow product (hydrated  $\text{PbO}$ ) along the ridges between these pits. Unfortunately this was not photographed. The coatings were only loosely adherent.

Two photomicrographs are given on page 22. Fig. 10 shows the boundary lines or grooves and Fig. 11 shows the pits.

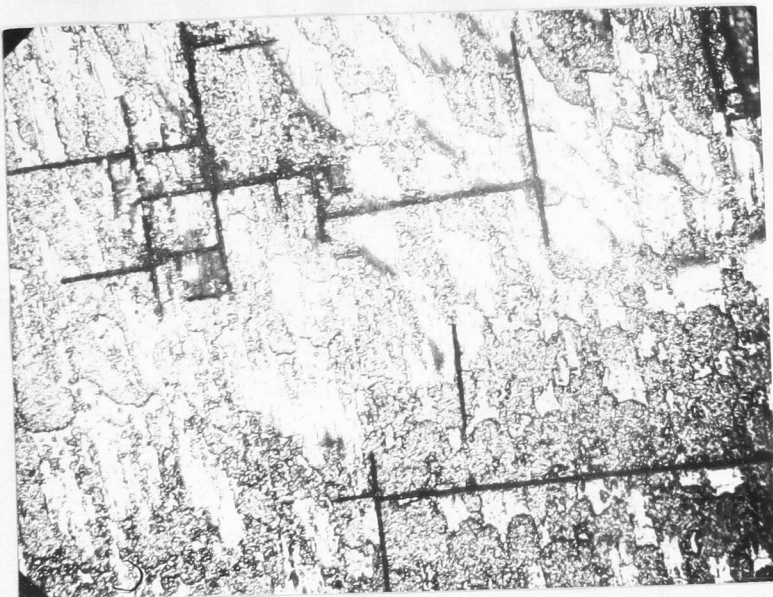


Figure 10 35x

Photomicrograph of Galena Crystal after Attack in 0.5 N  
Caustic at 150°C for 200 minutes

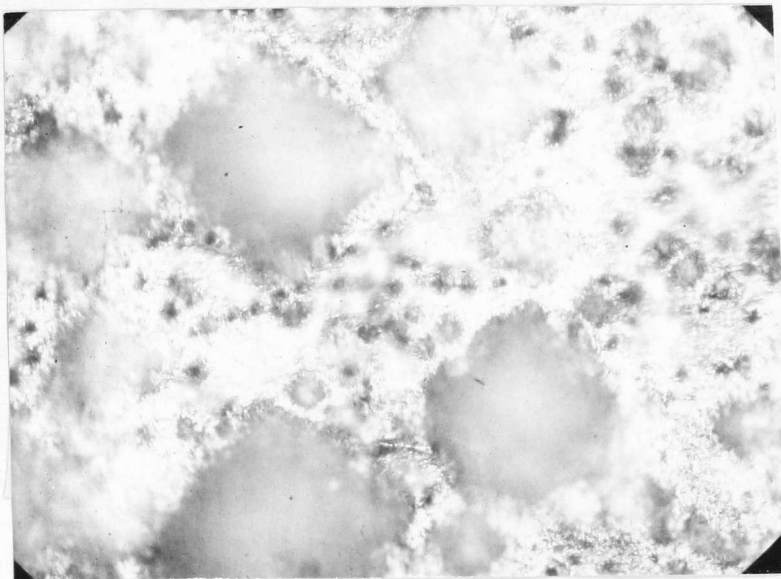


Figure 11 500x

Photomicrograph of Galena Crystal after Attack in 0.5N  
Caustic at 175°C for 132 minutes

### Investigation of Variables

The following variables were investigated with respect to reaction rates of single crystals of galena, measured as rate of production of lead-ion:

1. Oxygen partial pressure.
2. Agitation, i. e. rate of flow of medium past the particle.
3. Concentration of sodium hydroxide.
4. Temperature.
5. Effect of silicate-ion.
6. Effect of substituting sodium acetate for sodium hydroxide.
7. Effect of electrical potential (qualitatively only).

#### 1 Oxygen Partial Pressure

The effect of oxygen partial pressure was investigated in 0.5 N NaOH at 123°C in the range zero to 11 atmospheres. The results are tabulated below:

| P<br>atm. | $P^{\frac{1}{2}}$ | Rate<br>moles $\text{cm}^{-2}\text{sec}^{-1}$ | $\frac{\text{Rate}}{P^{\frac{1}{2}}}$<br>moles $\text{cm}^{-2}\text{sec}^{-1}\text{atm}^{-\frac{1}{2}}$ |
|-----------|-------------------|---|---|
| 0         | 0                 | 0   |   |
| 1.97      | 1.41              | $5.77 \times 10^{-9}$                         | $4.1 \times 10^{-9}$  |
| 5.64      | 2.38              | $10.08 \times 10^{-9}$                        | $4.2 \times 10^{-9}$  |
| 10.96     | 3.31              | $13.14 \times 10^{-9}$                        | $4.0 \times 10^{-9}$  |

-- where P is the partial pressure of oxygen in atmospheres.

It was noted that at zero partial pressure of oxygen (actually not quite zero because commercial nitrogen

was used) not only could no lead or sulphur be detected in the solution, but the surface showed no trace of any kind of attack after 3 hours at 123°C.

An attempt was also made at this time to investigate the roast reaction. The crystal was heated under nitrogen pressure with sodium plumbite solution at 123°C for 3 hours. Again no reaction appeared to take place, the surface was unchanged, and there was no increase in lead content of the solution.

## 2 Agitation (Rate of Flow of Medium Past the Particle)

Rate of flow past the particle were calculated from the speed of rotation of the magnet. No allowance was made for drag of the walls of the vessel, and the rate calculated for the middle of the "leading-edge" of the crystal was taken as the average.

No difference in specific rate was detectible in 0.5N NaOH solution at 150°C under 5.64 atmospheres partial pressure of oxygen when the "average" rate of flow of solution past the crystal was varied from 9 cm/sec to 48 cm/sec. Under the same conditions of temperature and pressure, the rates in 3N and 6N NaOH were dependent on agitation, as shown in the table below:

| Velocity of<br>Medium   | Rate (moles cm <sup>-2</sup> sec <sup>-1</sup> atm <sup>-<math>\frac{1}{2}</math></sup> ) x 10 <sup>+9</sup> |      |      |
|-------------------------|--|------|------|
|                         | 0.5N   | 3N   | 6N   |
| 9 cm sec <sup>-1</sup>  | 6.17   | 2.44 | 0.53 |
| 48 cm sec <sup>-1</sup> | 6.17   | 3.47 | 2.01 |

To relate the velocities to something more familiar, the free settling velocities of galena in cold water<sup>11</sup> are given below for a few screen sizes, with approximate Reynold's numbers:

| Screen Size<br>Openings/inch | Settling Velocity<br>cm/sec | Reynold's Number |
|------------------------------|-----------------------------|------------------|
| 100                          | 6.72                        | 9.9              |
| 150                          | 5.27                        | 5.5              |
| 200                          | 2.86                        | 2.1              |
| 325                          | .85                         | 0.37             |

The Reynold's numbers for the flow velocities associated with the reaction rates above vary from 1480 to 85. It would appear from these numbers that the influence of agitation becomes appreciable as soon as flow, by the Reynold's criterion, becomes viscous. From the Reynold's numbers for ground pulps it would appear that this situation would always obtain, and that increased agitation would give increases in rates of reaction. This would be independent of any aeration effects.

### 3 Concentration of Sodium Hydroxide

The effect of concentration of sodium hydroxide on the solubility of oxygen in aqueous solutions at 25°C is given by Geffcken<sup>12</sup>. The rate of the reaction is known

<sup>11</sup> Richards, R. H., and Locke, C. E., Textbook of Ore Dressing, Third Edition, 4th impression, McGraw-Hill Book Co. Inc., New York and London, 1940.

<sup>12</sup> Geffcken, G., Beitrage zur Kenntniss der Loslichkeit-beeinflussung, Z. f. Phys. Chemie 49, 257-302, 1904.



from experiment to vary with the square root of the partial pressure of oxygen, and therefore, assuming oxygen obeys Henry's Law, the reaction rate should vary with the square root of the oxygen concentration in solution. Therefore, at constant partial pressure of oxygen the rate should vary as the square root of  $L$ , the Ostwald solubility, which is defined as concentration of gas in the liquid divided by concentration in the gas phase.

In Fig. 12, page 27,  $L^{\frac{1}{2}}$  and  $K$ , the specific reaction rate, are plotted in arbitrary units against normality of sodium hydroxide.  $L^{\frac{1}{2}}$  and  $K$  are so adjusted that they have the same ordinate at 0.5 N NaOH. Curves are plotted for different fluid velocities. These curves would seem to indicate that the effects of sodium hydroxide are, first, to reduce the solubility of oxygen in the solution, and, second, to increase the viscosity of the liquid to cause diffusion through the films around the particle to control the rate.

It is realized there is an extrapolation here from 25°C to 150°C. The assumption implied is that the variation of oxygen solubility with sodium hydroxide concentration follows the same shaped curve at 150°C as it does at 25°C. It might be expected that the curve would be somewhat flatter at the high temperatures, thus showing an even greater film effect.

#### 4 Temperature

The effects of temperature were investigated in

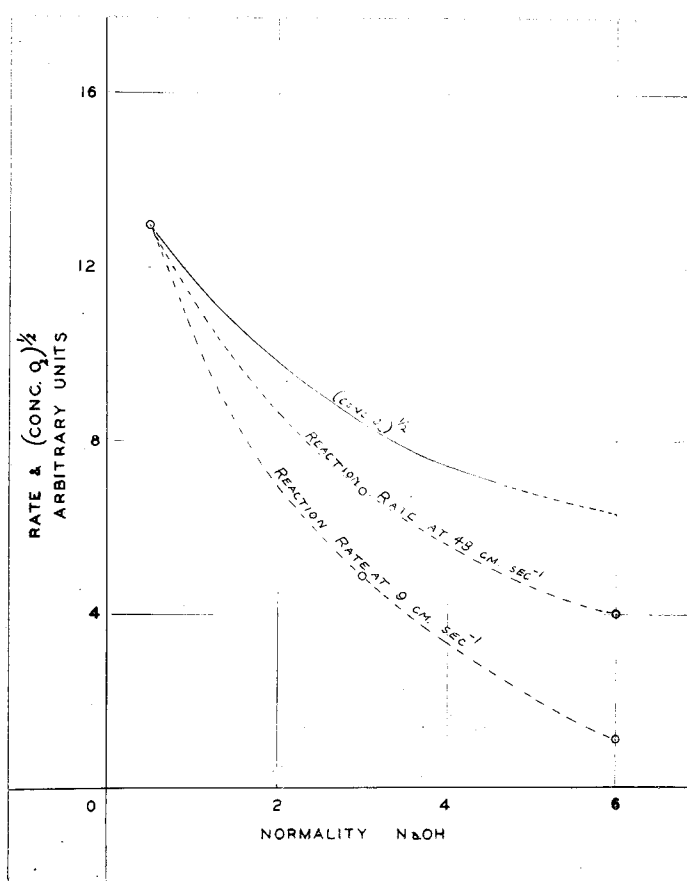


Figure 12

Rate vs. Normality NaOH

Plot of  $L^{\frac{1}{2}}$  and Reaction Rate in arbitrary units against normality of sodium hydroxide. Temperature  $150^{\circ}\text{C}$ , pressure 5.64 Atmospheres.

0.5 N NaOH solution under an oxygen partial pressure of 5.64 atmospheres, in the range 93°C to 175°C.

The Arrhenius plot is shown in Fig. 13, page 29. The slope corresponds to an apparent activation energy of 6820 calories per mole. It is known that the solubilities of gases in liquids decrease with temperature, so it was wondered if there should be a correction for this effect. However, when log L was plotted against reciprocal temperature, using values from International Critical Tables<sup>13</sup>, and from the Handbook of Chemistry and Physics<sup>14</sup> for solubility in water, it was seen that the slope of the curve was very flat in the beginning of the range investigated by the author, with decreasing slope apparently the trend. The correction at the low temperature end of the reaction rate plot only amounts to 60 calories per mole. Again, it is not known what effect sodium hydroxide has on the solubility-temperature curve.

#### 5 Effect of Silicate-ion

Stenhouse<sup>15</sup> found that silica had a pronounced effect on the oxidation of pyrite. This was attributed to some sort of poisoning of the surface with silicate-ion. In fluid velocities of 48cm/sec, 5.64 atm. partial pressure

13 International Critical Tables of Numerical Data, McGraw-Hill Book Co. Inc., New York, 1926.

14 Handbook of Chemistry and Physics 30th Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1946.

15 Stenhouse, J. F., *ibid.*

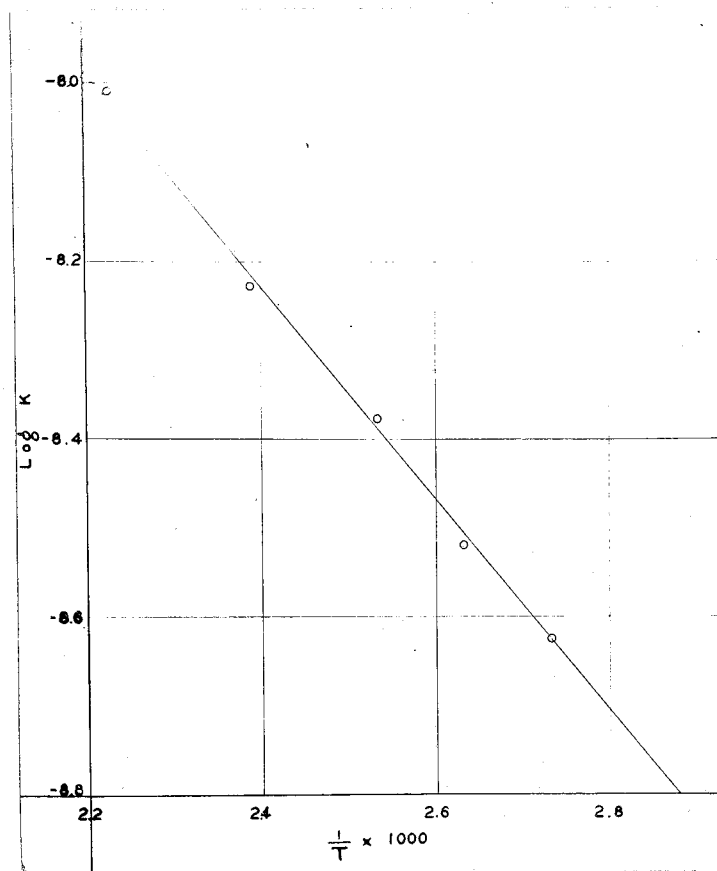


Figure 13

Arrhenius Plot

Log K (in moles  $\text{cm}^{-2} \text{sec}^{-1} \text{atm}^{-\frac{1}{2}}$ ) versus  $\frac{1}{T}$

of oxygen, at a temperature of  $122^{\circ}\text{C}$ , it was found that in 0.5 N NaOH, 0.015 Molar silicate-ion had very little effect, and 0.03 Molar silicate-ion gave a reduction in rate of approximately 10%. It was noticed, however, that at points of low turbulence where a little oxide coating might be expected to accumulate, a fine-grained black, adherent coating formed. It was therefore deduced that silicate-ion has little affinity for sulphide surfaces, but is readily chemisorbed to oxide surfaces, probably in the case of pyrite sealing them against diffusion of ions. This would be similar to surface reactions occurring in flotation.

#### 6 Effect of Substituting Sodium Acetate for Sodium Hydroxide

When sodium acetate was substituted for sodium hydroxide, the medium at  $122^{\circ}\text{C}$  attacked the mild steel in the autoclave and even removed the adherent oxide coating from the stainless steel. The result was such a reduction in oxygen concentration of the solution that there was no reaction with the galena. Shortage of time prevented treatment in glass containers.

#### 7 Effect of Electrical Potential

Various measurements of the potential of galena under pressure were made, but unfortunately no solution was found for the problem of a reference electrode. All measurements were against bright platinum in the same solution. Potential differences at  $100^{\circ}\text{C}$  in 1 N NaOH solution approximated 0.5 volts, the galena being negative. The emf

appeared to be substantially independent of oxygen pressure, as voltages of the same order were measured in solutions from which the oxygen had been removed by boiling.

Using a vacuum tube voltmeter and platinum probes, and reversing probes frequently, an apparent emf in the order of 10 millivolts was found between a 111 plane and a 100 plane of a galena crystal in a solution exposed to the air at 50°C. The 111 plane was relatively positive.

When positive potentials from the polarographic apparatus were applied to galena crystals, a coating, apparently PbO, was formed on the exposed face and the current tended to drop. When negative potentials were applied, there was increased etching of the surface and on the plastic varnish around the crystal a deposit of PbO was left in a circular pattern with the crystal the centre. If a coating existed on the crystal, it was very rapidly removed. The hydrogen overvoltage on galena appeared to be high.

In 3 N NaOH solution, at room temperature, electrolysis of a galena crystal at 1.5 volts with galena the cathode and with an inert anode produced H<sub>2</sub>S and a coating of spongy lead on the cathode.

In view of the increased rate of reaction with moderate negative potentials applied to the crystal, there was some worry that the contact between stainless steel and galena would produce a cell which would produce fields in the solution and distort the results. Two experiments were done to qualitatively investigate this possibility. In

each, fragments of the same crystal were oxidized side by side on a stainless steel rack. In the first experiment, one crystal was insulated with a thick coating of Carbocoat, a plastic varnish, and the other made fair contact with the stainless steel surface. In the second experiment, one crystal was insulated by being placed in an alundum boat, and the other in contact with clean stainless steel. In both cases oxidation was for a relatively short time, so that differences in rate should be more easily observable under the microscope. In neither case was there any apparent difference in rate. After the first few experiments the stainless steel was covered with a thick adherent coating of oxide, which should have behaved as an insulating layer. For these reasons it is not believed that the physical situation of the crystal had an appreciable effect on the rate.

## Discussion of Results

### Numerical Values

The numerical values of such quantities as activation energy are considered to be correct within a few percent under the conditions of the experiment. If control is by some other mechanism in another experiment, then of course there will be no relationship between the two values. Particle size will have effects also. Probably the greatest discrepancies in extrapolating this data to reactions with

suspended pulps would be caused by the increased activity of very fine particles.

Surprisingly enough, in these experiments sampling did not seem to introduce any appreciable error. Apparently the half-dozen crystals used, which were all from Violamac, and all selected by their regular shape, absence of twins, and straightness of axes, were very similar in chemical properties. From all crystals used there were a few very high results which were considered to be due to fragments falling under the rotor and being ground up to give a large increase in surface area.

In an industrial application, control by diffusion through the gas-liquid interface would be easily possible with fine particles and inadequate aeration. Even more likely, in fairly strong caustic (which would be necessary in a batch process) would be control by diffusion through the films at the solid-liquid interface. Motion of the particle would be controlled by the laws of viscous flow, and it would not be possible to get out of this range. As was seen on page 24 this would mean control by diffusion through the film about the particle.

#### Mechanism of the Reaction in 0.5 Normal Sodium Hydroxide

According to Eyring<sup>16</sup> a reaction of a gas at a surface may be separated into five steps, the slowest of

<sup>16</sup> Glasstone, S., Laidler, K., and Eyring, H., The Theory of Rate Processes, McGraw-Hill Book Co. Inc., New York and London, 1941.



which will determine the rate of the over-all process. The steps are:

1. Transport of the reactants to the surface.
2. Adsorption of the reactants.
3. Reaction on the surface
4. Desorption of the products.
5. Transport of the products from the surface.

Using this classification for the pressure oxidation of galena, the experiments with agitation indicate that control must be by steps 2, 3, or 4. It is also known that the rate is proportional to the square root of the oxygen partial pressure, that a negative potential on the galena increases the rate, and that the activation energy is low.

Stenhouse<sup>17</sup> found in the oxidation of pyrite that the rate of oxidation of iron depended on the square root of the partial pressure of oxygen, but that at low pressures the rate of oxidation of sulphur depended on the first power of the partial pressure of oxygen. In other work of the department on aqueous oxidation, polythionates formed could be explained by the initial formation of  $\text{SO}_2$ , which would give dependency on the first power of the oxygen partial pressure, if this were the rate-controlling step. At low pH, the oxidation of sulphur is slow or incomplete and apparently sulphur is liberated to form globules of the element<sup>18</sup>. In Mr. Stenhouse's work, and generally observed

<sup>17</sup> Stenhouse, J. F., *ibid.*

<sup>18</sup> McIntosh, R. B., *ibid.*

in aqueous oxidation, it is found that the activation energy for the oxidation of metals is lower than that for sulphur. For these reasons the rate-controlling step in this reaction, where no new phase appeared at the boundary between galena and solution, will be considered to involve only the oxidation of lead.

For the rate to be proportional to the square root of the partial pressure of oxygen there are two possibilities for the actual mechanism:

1. Adsorption is rapid but dissociation is slow.
2. The reaction involving dissociation is rapid, but the fraction of the sites involved is small. This follows from the Langmuir isotherm:

$$\frac{x}{1-x} = ap^{\frac{1}{2}}$$

where x is the fraction of the sites involved

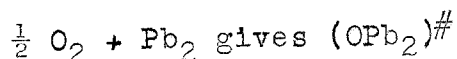
a is a constant

p is the oxygen partial pressure

when x is small and  $1 - x$  approaches 1.

#### Mechanism I

For the first mechanism, consider the reaction:



where  $Pb_2$  represents two adjacent sites and  $(OPb_2)^{\#}$  the activated complex. The rate equation for this reaction is:

$$\text{rate (in molecules cm}^{-2} \text{ sec}^{-1}) = c_{O_2}^{\frac{1}{2}} c_{Pb} \frac{kT}{h} \frac{f^{\#}}{f_{O_2}^{\frac{1}{2}} f_{Pb}} \exp. -H^{\#}/RT$$

where  $c_{O_2}$  is the concentration of oxygen in solution

$c_{Pb}$  is the concentration of sites

$k$  is Boltzmann's constant

$h$  is Planck's constant

$T$  is the absolute temperature

$f^\#$ ,  $f_{O_2}$ , and  $f_{Pb}$  are the partition functions of the activated complex, of oxygen in solution, and of the sites, respectively, for a standard state of one molecule per  $cm^3$  or  $cm^2$

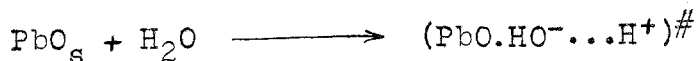
$R$  is the gas constant

$H^\#$  is the enthalpy of activation

The rate on the basis of this mechanism has been worked out, using available data, and gives a value which is 23,500 times as fast as the experimental value. The calculations are given in Appendix B.

#### Mechanism II

In the second case above, the rate controlling step is one which follows chemisorption, and it was postulated that it was desorption accompanied by hydration of  $PbO$ , to give after ionization  $HPbO_2^-$  ion. This would explain the effect of potential as aiding in desorption, by repelling the anion. The rate controlling step would be:



and the rate equation would be:

$$\text{rate} = c_{PbO} c_{H_2O} \frac{kT}{h} \frac{f^\#}{f_{PbO} f_{H_2O}} \exp. -H^\#/RT$$

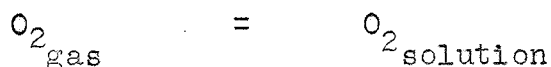
where  $c_{H_2O}$  is the concentration of water

$c_{PbO}$  is the concentration of PbO sites

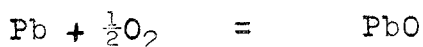
$f_{H_2O}$  is the concentration partition function of liquid water

and the other symbols have the same significance as previously

By substitution of quantities from the equilibria:



and



the rate equation may be written

$$\text{Rate} = c_{O_{2\text{gas}}}^{\frac{1}{2}} c_{Pb} c_{H_2O} \frac{kT}{h} \frac{f_{H_2O}^{\#}}{f_{O_2}^{\frac{1}{2}} f_{Pb} f_{H_2O}} \exp. -(H_1 - H_2 - H^{\#})/RT$$

where  $H_1$  is the enthalpy of solution of oxygen in the aqueous medium

$H_2$  is the enthalpy of the chemisorption of atomic oxygen

$H^{\#}$  is the enthalpy of activation

The term  $(\frac{H_1}{2} + H_2 + H^{\#}) + RT$  is equal to the experimental value of activation energy,  $E$ .

$H_1$  is negative and is of the order of 100 calories per mole, by calculation from data in International Critical Tables.

$H_2$  corresponds to dissociation and chemisorption of oxygen to a metal surface. The reaction is probably slightly exothermic.

This means that  $H^{\#}$  equals  $E + \frac{100}{2} - H_2^{\frac{RT}{2}}$ , and

therefore that  $H^\#$  may be considerably larger than  $E$ .

On calculating the rate from the above expression, surprisingly good agreement with experiment was achieved. The calculations are given in Appendix C.

By this model, the activation energy for the dissociation and adsorption of oxygen to the surface must be low. It has been found in the adsorption of hydrogen on nickel or platinum, activation energies of the order of 5 kilocalories were observed. Polanyi<sup>19</sup> explains this by considering the metal surface to be highly degenerate, thus rounding off the peak corresponding to the activation energy and reducing its value.

There is a possibility that part of the effect of potential may be in increasing the hydrogen-ion concentration. It is known from Geffcken's data that hydroxyl has a depressing effect on solubility of oxygen in water, but that hydrogen-ion has little effect.

These effects could be evaluated experimentally by measuring the activation energy with applied potential. If there were no change in activation energy, then the effect would only be on the temperature independent term, through increase in oxygen concentration; whereas if the effect is on desorption there would be a decrease in the experimental activation energy.

<sup>19</sup> Polanyi, M., Catalytic Activation of Hydrogen, The Scientific Journal of the Royal College of Science, Vol. VII, 1937.

### Mechanism III

A third possibility is a reaction analagous to the corrosion of a metal or alloy, with the metal tending to react with hydrogen-ion and being depolarized by the dissolved oxygen. That is, in terms of cells, the presence of the oxygen-hydroxyl half-cell is necessary to raise the emf sufficiently to cause reaction. The kinetics of such a picture is not clear enough to attempt evaluation of sulphide oxidation on these terms.

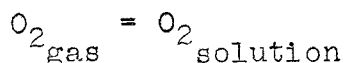
It is realized that these three mechanisms are by no means exhaustive, that there are other possibilities. However, Mechanism II does explain the observed effects, and the rate deduced from it by the theory of absolute reaction rates checks with the observed rate. It remains to consider Mechanism II with regard to variables not included in the restricted situation treated above.

#### Consideration of Mechanism II with Respect to the Remaining Variables

##### 1 Agitation and Concentration of Sodium Hydroxide

These variables appear inseparable and will be treated together.

It is observed that the rate falls with caustic concentration in a manner that appears to roughly conform to the square root of the falling oxygen solubility. The general effect of caustic concentration on the rate of the reaction would be by displacement of the equilibrium:



to the left. Although the activity of oxygen can be said to remain the same when the temperature and pressure of the gas are the same, but caustic concentration different, nevertheless the change in the activity coefficient of the oxygen would be reflected by a change in the activity coefficient of  $\text{PbO}$  or activated complex in the same direction. This would have the result of making the rate proportional to concentration rather than activity.

There is a further complication of viscosity here, however, and reaction rates are seen to vary with agitation. This is explained by the mechanical picture of stagnant films about particles moving relative to a fluid. The film resistance is considered to be high enough that it takes control of the reaction, by virtue of being the slowest of the five steps listed above. It is not known conclusively whether control is by diffusion of reactants in or of products out from the interface.

## 2 Effect of Silicate-Ion

Silicate-ion apparently reacts with macroscopic coatings of oxide but not with the oxygen chemisorbed to the surface. It is not understood why this should be so, unless reaction with silicate-ion is dependent on hydration.

## 3 Effect of Substituting Sodium Acetate for Sodium Hydroxide

The results of this substitution were abortive, as stated previously.

#### 4 Effect of Change in Surface Area

Although not considered as a variable, the surface area was noted to change, mainly by formation of etchmarks consisting of intersecting lll planes. Apparently this has no effect on the rate. This may be for two reasons:

1. The surface becomes covered with pits in the initial stages of the reaction, but this is concealed by the build-up of oxygen concentration, marked by the toe of the rate curve.
2. The rates on lll planes are slower by a factor which compensates exactly for the increase in area.

Pits may be caused by differences in activity between different parts of the crystal. Etchmarks are a well-known phenomenon, used in geology for symmetry determinations on mineral crystals.

#### Conclusions

The use of a cathode-ray polarograph as a method of measuring the rate of oxidation of galena immersed in a solution, under oxygen pressure, is satisfactory for measuring the rate of solution of lead. It gives no indication of the rate of oxidation of sulphur, but as no separate phase appeared and no polythionates were detected, undoubtedly the rate in terms of formation of sulphate would have been identical with that in terms of solution of lead.



This technique could be applied profitably to the measurement of rates of corrosion under extreme conditions of temperature and pressure of all metals, alloys, or minerals where a soluble, reducible or oxidizable product is formed. It is restricted in that it cannot be used in very concentrated solutions of the ion or molecule being measured, and interference by impurities may also render it inoperative.

In any commercial application of aqueous oxidation, a cathode-ray polarograph would be a very useful control instrument for measuring concentration of oxygen in solution. Such information might be vital to efficient operation of the process.

Even in fused-salt electrolysis one can see possible uses for a device patterned on this, in either research or plant operation.

It is not possible from the experimental results here obtained to decide whether rate of oxidation of lead or of sulphur controls the over-all rate. From other considerations it is thought that lead is involved in the rate-controlling step.

In high caustic concentrations, rate is found to be controlled by diffusion through stagnant films about the particle.

Under reaction control, rate of solution of lead is proportional to the square root of the oxygen partial pressure. The activation energy is 6820 calories per mole. A negative

potential applied to the crystal profoundly increased the rate. It is not known whether this increase in rate is due to repulsion of  $\text{HPbO}_2^-$  or to the increased solubility of oxygen in the absence of hydroxyl-ion. The former appears to be most probable.

Three possible mechanisms for the reaction were suggested.

Mechanism I, control by the dissociation of oxygen at the surface was found to give too high a calculated rate. Mechanism III, modelled on a corrosion picture, was not verified as no method of calculation from fundamental data appeared to be available.

In Mechanism II the rate-controlling step consisted of desorption with hydration. The rate calculated on this basis from fundamental data using the experimental value of activation energy was  $4 \times 10^{15}$  molecules  $\text{cm}^{-2} \text{sec}^{-1}$  under certain conditions, compared to an experimental value of  $2.55 \times 10^{15}$ . This was considered an excellent check. It is realized the uncertainties in the partition function of the activated state, and in the number of sites available for reaction, are such that so close an agreement must be considered a coincidence.

No experimental data conflicted with the picture from Mechanism II, although it is of course possible that there is an equally plausible, alternative model which would also fit the observations.

## Appendix A

## Assay of Solution by the Molybdate Method

## (Gravimetric)

The basic solution was made just acid to litmus with nitric acid, then slightly basic by the addition of ammonium acetate--usually about five grams. The solution was then heated to boiling and filtered. To the boiling filtrate was added 40 ml. of ammonium molybdate solution for each 0.1 g of lead present. After boiling a few minutes the solution was allowed to stand, then filtered and washed with hot water containing 2% ammonium nitrate. The residue was ignited at dull red heat, cooled, and weighed as  $\text{PbMoO}_4$ .

$$\text{PbMoO}_4 \times 0.5643 = \text{Pb}$$

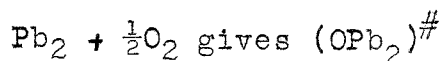
## Ammonium Molybdate Solution

Dissolve 4 g of the salt per litre of water plus 10 ml acetic acid.

## Appendix B

## Calculation of Rate from Mechanism I

From the reaction:



the rate equation is given by:

$$\text{rate (molecules cm}^{-2} \text{ sec}^{-1}) = c_{\text{O}_2}^{\frac{1}{2}} c_{\text{Pb}} \frac{kT}{h} \frac{f^{\#}}{f_{\text{O}_2}^{\frac{1}{2}} f_{\text{Pb}}} \exp. -H^{\#}/RT \quad (1)$$

The solution of oxygen is considered to reach equilibrium.

$$\text{Then, } \frac{\text{Conc. of oxygen in liquid}}{\text{Conc. of oxygen in gas phase}} = \frac{f_{\text{O}_2}(\text{liquid})}{f_{\text{O}_2}(\text{gas})} \exp. -H_1/RT$$

where  $f$  represents the designated partition functions

$H_1$  is the enthalpy of solution

Substituting for  $c_{\text{O}_2}$  in (1), and cancelling  $f_{\text{O}_2}$  liquid,

$$\begin{aligned} \text{rate} &= c_{\text{O}_2 \text{ gas}}^{\frac{1}{2}} c_{\text{Pb}} \frac{kT}{h} \frac{f^{\#}}{f_{\text{O}_2 \text{ gas}}^{\frac{1}{2}} f_{\text{Pb}}} \exp. -(H_1/2 + H^{\#})/RT \\ &= e c_{\text{O}_2 \text{ gas}}^{\frac{1}{2}} c_{\text{Pb}} \frac{kT}{h} \frac{f^{\#}}{f_{\text{O}_2 \text{ gas}}^{\frac{1}{2}} f_{\text{Pb}}} \exp. -E/RT \end{aligned} \quad (2)$$

Experimental results are conveniently available for 400°K.

In this analysis concentration partition functions based on a standard state of one molecule per square centimetre or per cubic centimetre were used. Choice of this standard state was purely a matter of convenience. The resulting partition functions are very large numbers because of this choice.

The concentration partition function of gaseous oxygen is:

$$\text{Translation... } \frac{(2\pi mkT)^{3/2}}{h^3} = 2.73 \times 10^{26}$$

$$\text{Rotation..... } \frac{(8\pi^2 IkT)}{h^2} = 190$$

Vibration..... approximates 1

where I is the moment of inertia of the oxygen molecule

m is the mass of the oxygen molecule

the other symbols have the usual significance.

$$\text{Then } f_{O_2 \text{ gas}} = 5.2 \times 10^{28}$$

$$c_{O_2 \text{ gas}} = \frac{6.02 \times 10^{23}}{22400} \times \frac{273}{400} = 1.83 \times 10^{19} \text{ molecules cm}^{-3}$$

$$c_{Pb} = 7 \times 10^{14} \text{ sites cm}^{-2}$$

$$k, \text{ Boltzmann's constant} = 1.38 \times 10^{-16} \text{ erg deg}^{-1}$$

$$h, \text{ Planck's constant} = 6.62 \times 10^{-27} \text{ erg sec}$$

e is the base for natural logarithms, 2.72

E is the experimental activation energy, 6820 cal mol<sup>-1</sup>

$$f^{\#} = f_{Pb} \text{ and both approximate 1}$$

On substituting these numerical values,

$$\text{rate} = \frac{2.72 \times (1.83 \times 10^{19})^{1/2} \times 7 \times 10^{14} \times 1.38 \times 10^{-16} \times 400 \times 1 \times e^{-\frac{6820}{2(400)}}}{6.62 \times 10^{-27} \times (5.2 \times 10^{28})^{1/2} \times 1}$$

$$= 6.0 \times 10^{19} \text{ molecules cm}^{-2}$$

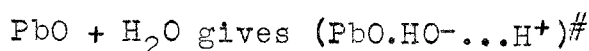
$$\text{The observed rate is } 4.1 \times 10^{-9} \times 6.02 \times 10^{23} = 2.55 \times 10^{15} \text{ molecules cm}^{-2}$$

It is seen that the calculated rate is 23,500 times too large.

## Appendix C

## Calculation of Rate from Mechanism II

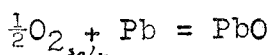
If the rate-controlling step is desorption of the PbO, with accompanying hydration:



The following reactions will have reached equilibrium:

$$\text{O}_{2\text{gas}} = \text{O}_{2\text{solution}} \quad (1)$$

and



As in Appendix B 
$$c_{\text{O}_{2\text{soln}}} = c_{\text{O}_{2\text{gas}}} \frac{f_{\text{O}_{2\text{soln}}}}{f_{\text{O}_{2\text{gas}}}} \exp. -H_1/RT$$

As regards (2) 
$$c_{\text{PbO}} = c_{\text{Pb}} c_{\text{O}_{2\text{soln}}}^{1/2} \frac{f_{\text{PbO}}^{1/2}}{f_{\text{Pb}} f_{\text{O}_{2\text{soln}}}} \exp. -H_2/RT$$

where  $H_2$  is the enthalpy of reaction

Then 
$$c_{\text{PbO}} = c_{\text{Pb}} c_{\text{O}_{2\text{gas}}}^{1/2} \frac{f_{\text{PbO}}^{1/2}}{f_{\text{Pb}} f_{\text{O}_{2\text{gas}}}} \exp. -(\frac{H_1}{2} + H_2)/RT$$

And rate = 
$$c_{\text{O}_{2\text{gas}}}^{1/2} c_{\text{H}_2\text{O}} c_{\text{Pb}} \frac{kT}{h} \frac{f^\#}{f_{\text{O}_{2\text{gas}}}^{1/2} f_{\text{H}_2\text{O}} f_{\text{Pb}}} \exp. -(\frac{H_1}{2} + H_2 + H^\#)/RT$$

or, expressing enthalpies as an experimental activation energy,

rate = 
$$c_{\text{O}_{2\text{gas}}}^{1/2} c_{\text{H}_2\text{O}} c_{\text{Pb}} \frac{kT}{h} \frac{f^\#}{f_{\text{O}_{2\text{gas}}}^{1/2} f_{\text{H}_2\text{O}} f_{\text{Pb}}} \exp. -E/RT$$

It is seen that this expression differs from equation (2) of Appendix B by a factor  $\frac{c_{\text{H}_2\text{O}}}{f_{\text{H}_2\text{O}}}$ .

$$c_{\text{H}_2\text{O}} = \frac{6 \times 10^{23}}{18} \text{ molecules cm}^{-3}$$

## Calculation of Concentration Partition

## Function of Liquid Water

$$S_{H_2O \ 298.1^\circ K} = 16.75 \text{ E.U. mole}^{-1} \text{ (Hougan and Watson)}^{20}$$

$$\text{Change in } S_{H_2O \ 298.1^\circ K - 400^\circ K} = 2.38 \text{ E.U. mole}^{-1} \text{ (Kelley)}^{21}$$

$$\text{Then } S_{H_2O \ 400^\circ K} = 19.1 \text{ E.U. mole}^{-1}$$

To change from the standard state of liquid water to a standard state of one molecule per  $\text{cm}^3$ , dilute the water ideally to one molecule per  $\text{cm}^3$ .

$$S = R \ln \frac{6 \times 10^{23}}{18} = 103 \text{ E.U. mole}^{-1}$$

Then the entropy in a state of one molecule per  $\text{cm}^3 =$

$$122.1 \text{ E.U. mole}^{-1}$$

$$f_{H_2O} = e^{-\frac{122.1}{R}} = 5 \times 10^{26}$$

$$\text{Rate from Appendix B} = 6 \times 10^{19} \text{ molecules cm}^{-3} \text{ sec}^{-1}$$

$$\text{Rate for this model} = 6 \times 10^{19} \times \frac{6 \times 10^{23}}{18} \times \frac{1}{5 \times 10^{26}} =$$

$$4 \times 10^{15} \text{ molecules cm}^{-3} \text{ sec}^{-1}$$

which approximately checks with the experimental value of  $2.55 \times 10^{15}$ .

There are two uncertainties in this calculation of the rate.  $c_{Pb}$ , the concentration of Pb sites available for reaction, may be increased by roughening of the surface, or reduced by poisoning.  $f^\#$ , the partition function of the

20 Hougan, O. A., and Watson, K. M., Chemical Process Principles, Part II, John Wiley & Sons Inc., New York, 1947.

21 Kelley, K. K., Contributions to the Data on Theoretical Metallurgy X, Bulletin 476, United States Government Printing Office, Washington, 1949.

activated complex, may have a vibration partition function of some magnitude, but probably not greater than 10.



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