ZINC SMELTING FROM A
CHEMICAL AND THERMODYNAMIC VIEWPOINT

BY

C. G. MAIER
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<td></td>
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ZINC SMELTING FROM A CHEMICAL AND THERMODYNAMIC VIEWPOINT

By C. G. MAIER

INTRODUCTION

The fundamental chemistry of zinc smelting, especially that part dealing with the chemical reduction of the zinc-oxide content of a roasted zinc ore, has been discussed by metallurgists in some detail, but, in the light of present knowledge, unsatisfactorily. A considerable portion of the information available has been qualitative, or quantitative in a sense that could not be interpreted chemically. A number of attempts to elucidate the physical chemistry of zinc oxide reduction have been based upon unsubstantiated and, as is now known, incorrect equilibrium data.

To write upon the chemistry of zinc smelting at this time, when electrolytic methods for the production of zinc metal from ore are becoming increasingly widespread, may seem a belated effort. So, for example, C. A. Hansen, in the communicated discussion of an article by the author, writes as follows:

I do not think that the fundamental chemistry of the thermal reduction processes is as important to-day as it was some years ago, and for reasons that are purely economic ones. A few years ago the world consumed some 1,200,000 tons of zinc annually, practically all of it retort-process zinc. A negligible fraction of this total, some 20,000 to 30,000 tons, was of specially high grade, and this represented something like the limiting quantity available from especially suitable ores. By reason of its scarcity it commanded a premium of some 30 per cent in market value. To-day, with a production of something like 1,500,000 tons of zinc, rather more than 10 per cent of the total is electrolytic zinc, comparable in purity with the high-grade retort zinc. Electrolytic plants are being built, or planned for erection in the immediate future, in America, in Germany, and in Belgium, which will double the output of electrolytic zinc. The premium for high-grade zinc is bound to diminish to the banishing point, but by reason of its greater purity the high-grade zinc will command a preferred market; retort zinc may then well be penalized—a sort of negative premium due to changed standards. The thermal process is not well adapted to the production of pure zinc from other than pure ores, although lower temperature reduction may reduce the lead content of zinc made from leady ores.

Secondly, the world does not lack sufficient reserves of zinc ore, and we are not at all likely to suffer from a zinc famine. But the world does lack sufficient reserves of the type of lead ores which have yielded our principal supplies of lead, and the more important lead-ore reserves are in the form of complex ores in which the zinc content is comparable with, or greater than, the lead content. An insistent demand for lead will tend to the commercializing of the complex ores, and both zinc and lead will be recovered; it is quite possible that zinc will become more and more a by-product of the lead smelter. It seems to me that the wet

1 Work on manuscript completed October, 1929.
3 Consulting engineer, General Electric Co.
processes are more flexibly adaptable to these complex ores than is any thermal reduction zinc process.

Thirdly, the quantity of labor required for the production of retort zinc is at least three times that required for an equivalent production of electrolytic zinc, even though the comparison is based upon high zinc tenor concentrates and coal-fired primary power stations, conditions in every way more favorable to the retort process. In respect to skilled labor requirements, the comparison is still less favorable to the retort plant. The working conditions for skilled labor are less strenuous and less disagreeably uncomfortable in the electrolytic refining plant than they are in the retort plant. The labor requirements in the retort plant have not changed materially in two generations; the labor requirements in one large electrolytic plant are nearly 30 per cent less than they were five years ago, at which time the comparative data indicated 18 man-hours per ton of retort zinc as against 6 man-hours for electrolytic zinc.

Until the retort is displaced, there is little likelihood of any material reduction in labor requirements, and while processes are now in course of development which may eventually do away with the retort, still no substitute for the retort has yet proved commercially attractive.

The critic thus outlines the conditions the zinc-smelting industry must presently meet and now confronts to preserve its identity in the face of electrolytic competition and by-product zinc metal. No one will doubt but that zinc will be smelted continuously for many years to come, but if the smelting industry is to remain profitable its methods must become more efficient from the standpoint of conservation of energy and labor. These considerations mean the better use of fuel and large-size direct-acting reduction units. It is in just these latter directions that a precise knowledge of chemical fundamentals may be expected to define the limits of imaginative possible projects; and if the smelting industry is not too moribund to use the excellent chemical data that now exist, it can not fail to improve the practice of smelting and may even attain that recurrent goal of the zinc metallurgist, the so-called direct smelting of zinc to liquid metal. Quantitative physical chemistry is now able to point out under what conditions and by what means this is a physical possibility.

The significance of these data are to be made clear in this publication; it then becomes the part of the practical zinc metallurgist to select those facts that may be used in a commercial way.

The Bureau of Mines, at its Pacific Experiment Station, has for some time been engaged in a study of the reduction chemistry of metallurgically important oxides, and zinc oxide was among the first of the number. The fundamental theoretical, and especially thermodynamic results of this work on zinc oxide have been described in a series of published articles, but these publications did not develop the application of the data obtained to zinc smelting. In a later publication the use of the new results as regards reduction by gaseous materials only was briefly discussed.

The present work proposes to show, with some detail, the application of newly recalculated theoretical data to the general chemistry of zinc reduction in smelting. It is not its purpose to invent new zinc-smelting processes. Because the reduction of zinc oxide is both practically and theoretically a reversible process such data as free energies of formation, which are unfortunately still merely abstract

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generalizations to many otherwise highly competent metallurgists, are tremendously important and practical matters. These data exist, and if they have not been used it may be because the way has seemed too involved and impractical. That it is not so the reader may discover.

In the articles mentioned above the thermodynamic determinations and calculations were purposely made as thorough and extensive as possible. These determinations showed the discrepancies and errors of previous work, especially as to reduction equilibria, and no attempt at application was made until sufficient conclusions had been reached by diverse methods adequately to substantiate the results. The theoretical thermodynamic results on zinc oxide are condensable into a value of free energy of formation of the material, but it was not until four independent methods were shown to give concordant values that it was decided enough work had been done to justify an attempt to apply the data. Although such meticulous duplication of methods may seem academic to the practical metallurgist, the wide divergences of previous equilibrium data necessitated a high degree of certitude if new and critical conclusions were to be drawn. Moreover, whereas the duplication of methods for free-energy determination of zinc oxide incidentally served to indicate the applicability and probable accuracy of various methods that might be selected for further work on other oxides, and in this sense have had an exploratory value for future work, for the present purpose the multiplicity of results on zinc oxide primarily is useful to enable definitive calculation to be made of the statics of zinc reduction.

The metallurgist engaged in zinc smelting is interested chiefly in the dynamics of zinc reduction; that is to say, in tonnage and production. When dynamic chemical studies of the subject have been made in the past they have served only approximate and empirically direct purposes. It is not strange, in the absence of good data on the chemical limits which equilibrium determinations define, that the process of zinc smelting as a problem in chemical reaction rates has not received adequate scientific attention. The present work does not offer new quantitative experimental data on reaction rates; but an effort will be made to show how such results, if obtained, should be interpreted and how they might be of practical value in smelting. The manner in which information on the statics of reduction may be used in certain cases to study a dynamic process is also disclosed.
Part I. THERMODYNAMIC PROPERTIES OF ZINC AND ITS COMPOUNDS

In the following pages of this part the effort is made to collect and correlate all available significant thermodynamic data for zinc and its metallurgically important compounds. There are considered here only the intrinsic properties of pure materials, to serve as reference points for later applications. As nearly as possible, the order outlined is maintained as follows:

1. Specific heats at low temperatures.
   (a) Compressibility and thermal expansiveness and atomic volume.
   (b) Entropy calculated from specific heats.
2. Specific heats at high temperatures.
3. Sublimation and vapor pressures.
4. Thermal data.
   (a) Heats involved in change of state—sublimation, fusion, vaporization.
   (b) Heats of formation of compounds.
   (c) Free energies of formation of compounds.
5. Correlation of heats, free energies, and entropies.

The reader not interested in sources of data or in the precision of the methods used may wish to omit this section. For convenience in reference, Tables 13 to 16 summarize the results and may be found at the end of this section.

METALLIC ZINC

ALLOTROPY

Before proceeding to specific information on the properties of zinc the question of its possible existence in several allotropic states must be considered. The very extensive literature on this subject is extraordinarily contradictory, nor would its complete reproduction here be significant. Earlier experimenters have usually reported transitions near 170° and 320° C., but more recent observers have usually failed to find definite evidence for these changes, perhaps because metal of extreme purity has recently become more readily obtainable. That the physical properties of commercial zinc and even metal of good purity undergo marked changes in this temperature range is well known.
### Table 1.—Investigations on allotropy of zinc

<table>
<thead>
<tr>
<th>Year</th>
<th>Investigator</th>
<th>Reference</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1920</td>
<td>Bingham</td>
<td>(1)</td>
<td>Mechanical and physical</td>
<td>Evidence for allotropy.</td>
</tr>
<tr>
<td>1922</td>
<td>Losana</td>
<td>(2)</td>
<td>Conductivity</td>
<td>174° and 322°.</td>
</tr>
<tr>
<td>1923</td>
<td>Owen and Preston</td>
<td>(3)</td>
<td>X-ray analysis</td>
<td>1 allotrope suggested.</td>
</tr>
<tr>
<td>1924</td>
<td>Eastman, Williams, and Young</td>
<td>(4)</td>
<td>Specific heat</td>
<td>None.</td>
</tr>
<tr>
<td>1924</td>
<td>Behrens and Drucker</td>
<td>(5)</td>
<td>…… do ……</td>
<td>Do.</td>
</tr>
<tr>
<td>1925</td>
<td>Stockdale</td>
<td>(6)</td>
<td>Differential e. m. f.</td>
<td>315°.</td>
</tr>
<tr>
<td>1925</td>
<td>Pierce, Anderson, and Dyck</td>
<td>(7)</td>
<td>X-ray analysis</td>
<td>None.</td>
</tr>
<tr>
<td>1925</td>
<td>Freeman, Sellers, and Brandt</td>
<td>(8)</td>
<td>Mechanical, electrical, and X-ray</td>
<td>Do.</td>
</tr>
<tr>
<td>1927</td>
<td>Petrenko</td>
<td>(9)</td>
<td>Microscopic</td>
<td>300.</td>
</tr>
<tr>
<td>1928</td>
<td>Van de Putte and Thyssen</td>
<td>(10)</td>
<td>Expansion</td>
<td>None.</td>
</tr>
</tbody>
</table>


The published work prior to 1920 has been fully summarized by Miss Bingham (see Table 1, footnote 1) and need not be reproduced here. The important investigations since then are listed in Table 1. The results of careful X-ray analyses should be the most conclusive evidence concerning allotropy; and the conclusions of Pierce, Anderson, and Van Dyck and of Freeman, Sellers, and Brandt, who undoubtedly worked on material of extraordinarily high purity (and in the latter case on metal which had not been subject to mechanical strains) may be accepted as proving the absence of allotropism in pure metal.

**Specific Heats at Low Temperatures**

Data obtained by various investigations prior to 1924 have been summarized by Behrens and Drucker (see Table 1, footnote 5), who include the figures of Behn, Schimpf, Nernst, Pollitzer, and Griffiths.

The low-temperature results of these latter investigators were used by Lewis, Gibson, and Latimer for the calculation of atomic entropies. The more recent figures obtained by Clusius and Hartec proceed to much lower temperatures and furnish very complete results from 12° K to room temperature. All of the important

data are plotted in Figure 1, curve A, and with the exception of the results of Schimpf are satisfactorily concordant. The figures of Schimpf and Behn are derived from mean specific heats over considerable temperature ranges and need not be considered to throw any doubt upon the probably precise work of Clusius and Harteck. From the "smoothed" curve the figures of Table 2 were obtained, giving the specific heat of pure zinc at 10° intervals at all lower temperatures. On curve B are plotted with an enlarged scale the experimental results obtained by Clusius and Harteck below 30° K. This portion of the curve obeys accurately the \( T^3 \) law of Debye.

Table 2.—Gramatomic specific heat of zinc at low temperatures, \( C_p \)

<table>
<thead>
<tr>
<th>Temperature, °K.</th>
<th>Log T</th>
<th>( C_p )</th>
<th>Temperature, °K.</th>
<th>Log T</th>
<th>( C_p )</th>
<th>Temperature, °K.</th>
<th>Log T</th>
<th>( C_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0</td>
<td>0.060</td>
<td>110</td>
<td>2.414</td>
<td>4.795</td>
<td>210</td>
<td>2.3222</td>
<td>5.77</td>
</tr>
<tr>
<td>20</td>
<td>1.3010</td>
<td>0.421</td>
<td>120</td>
<td>2.0792</td>
<td>4.965</td>
<td>220</td>
<td>2.3424</td>
<td>5.82</td>
</tr>
<tr>
<td>30</td>
<td>1.4771</td>
<td>1.163</td>
<td>130</td>
<td>2.1133</td>
<td>5.120</td>
<td>230</td>
<td>2.3617</td>
<td>5.86</td>
</tr>
<tr>
<td>40</td>
<td>1.6221</td>
<td>2.005</td>
<td>140</td>
<td>2.1401</td>
<td>5.250</td>
<td>240</td>
<td>2.3802</td>
<td>5.90</td>
</tr>
<tr>
<td>50</td>
<td>1.6960</td>
<td>2.735</td>
<td>150</td>
<td>2.1701</td>
<td>5.390</td>
<td>250</td>
<td>2.3977</td>
<td>5.94</td>
</tr>
<tr>
<td>60</td>
<td>1.7782</td>
<td>3.290</td>
<td>160</td>
<td>2.2041</td>
<td>5.46</td>
<td>260</td>
<td>2.4150</td>
<td>5.97</td>
</tr>
<tr>
<td>70</td>
<td>1.8451</td>
<td>3.715</td>
<td>170</td>
<td>2.2304</td>
<td>5.54</td>
<td>270</td>
<td>2.4314</td>
<td>6.00</td>
</tr>
<tr>
<td>80</td>
<td>1.9031</td>
<td>4.070</td>
<td>180</td>
<td>2.2555</td>
<td>5.61</td>
<td>280</td>
<td>2.4472</td>
<td>6.02</td>
</tr>
<tr>
<td>90</td>
<td>1.9542</td>
<td>4.300</td>
<td>190</td>
<td>2.2788</td>
<td>5.67</td>
<td>290</td>
<td>2.4624</td>
<td>6.06</td>
</tr>
<tr>
<td>100</td>
<td>2.0000</td>
<td>4.585</td>
<td>200</td>
<td>2.3010</td>
<td>5.72</td>
<td>298.1</td>
<td>2.4744</td>
<td>6.08</td>
</tr>
</tbody>
</table>

Compressibility, Expansion, and Atomic Volume

Although the data above are entirely adequate for the calculation of entropy, without the necessity of calculating \( C_p \) for extrapolation, using coefficients of expansion and compressibility, available data for these quantities are included here for the sake of completeness.
The work of Lindemann, leading to mean values of the coefficient over rather wide temperature ranges is less extensive than that of more recent investigators. By far the best results have been obtained by Dorsey and Grüneisen and Goens. The data of these investigators are plotted on Figure 2. Grüneisen and Goens had available a single crystal, and their results are unusually complete.

Curve A of the figure shows the coefficient parallel to the crystal axis, and C that perpendicular to the axis. Curve B represents \(1/3 (\alpha_1 + 2\alpha_1)\), corresponding to the heterogeneous axes represented by crystal aggregates such as were used by Dorsey. From the smoothed curve of \(\dot{\beta}\) the figures of Table 3 were taken.

**Table 3.**—Coefficient of linear expansion of zinc

<table>
<thead>
<tr>
<th>Temperature, °K.</th>
<th>Temperature, °C.</th>
<th>Coefficient of expansion, (\alpha \times 10^4)</th>
<th>Temperature, °K.</th>
<th>Temperature, °C.</th>
<th>Coefficient of expansion, (\alpha \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>-50</td>
<td>30.6</td>
<td>100</td>
<td>-173</td>
<td>23.3</td>
</tr>
<tr>
<td>273</td>
<td>0</td>
<td>30.1</td>
<td>90</td>
<td>-223</td>
<td>15.5</td>
</tr>
<tr>
<td>200</td>
<td>-73</td>
<td>25.9</td>
<td>25</td>
<td>-248</td>
<td>9.0</td>
</tr>
<tr>
<td>150</td>
<td>-123</td>
<td>27.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is evident from the chart that the results of Dorsey agree well near ordinary temperatures but are somewhat low at lower temperatures. Because Grüneisen and Goens used single crystals their work is undoubtedly to be considered more satisfactory, especially so since Dorsey records his results on zinc as erratic.

The compressibility of zinc has been measured by Richards,\(^1\) by Adams, Williamson, and Johnston,\(^2\) and by Lussana.\(^3\) Richards gives for the average compressibility, \(K\), per megabar between 100 and 500 megabars, \(K = 1.5 \cdot 10^{-6}\). (The megabar used by the American workers is approximately 1 atmosphere. 1 megabar = 10\(^6\) dynes per square centimeter = 0.987 atmosphere.) A slight extrapolation of Lussana’s data results in \(K = 2.16 \cdot 10^{-6}\) at zero pressure, per atmosphere pressure. The results of Adams, Williamson, and Johnston are undoubtedly the most precise available:

\[
K \text{ per megabar at } 0^\circ = 1.74, K \text{ at } 10,000 \text{ megabars} = 1.43
\]

For purposes of thermodynamic calculation the figure 1.74 per megabar is adequate.

Many rather discordant values for the density of zinc have been summarized by Mellor,\(^4\) but we shall select the recent results of Hoffman and Stahl,\(^5\) who worked with zinc which had been accurately analyzed: Zn, 99.882 per cent; Pb, 0.033 per cent; Cd, 0.065 per cent; Fe, 0.020 per cent; Sn, 0 per cent; Cu, 0 per cent. The density at 0\(^\circ\) referred to water at its maximum density was 7.158 (vacuum basis) and for liquid zinc, 6.684 (in air) at 463\(^\circ\) C.

The atomic volume, \(V\), at 0\(^\circ\) is then 9.132 c. c. per gram atom and for liquid zinc, 9.780 at 463\(^\circ\).

**CALCULATION OF ENTROPY**

From the thermodynamic relationship

\[
C_p - C_v = \frac{9\alpha^2 \beta VT}{\beta}
\]

where \(C_p\) is the specific heat at constant pressure, \(C_v\) that at constant volume, \(\alpha\) the linear coefficient of thermal expansion, \(T\) the absolute temperature, and \(\beta\) the coefficient of compressibility, and from the specific figures above, \(C_p - C_v\) is calculated to be 0.28 calorie per gram atom at 273\(^\circ\) K., but only 0.001 at 30.3\(^\circ\) K.

Clusius and Hartecck had 18 experimental points below this temperature. For their 18 points the difference between the specific heat at constant pressure and at constant volume is obviously negligible, and the Debye \(T^3\) law may be applied directly. In fact the lower points, as plotted in Figure 3, show almost exact concordance when the theoretical Debye curve is superimposed thereon.

For the purpose of reestimating the atomic entropy of zinc the curve of Figure 3 is drawn in a \(C_p - \log T\) chart, using the “smoothed”

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\(^3\) Lussana, S., Proprietà termiche dei solide e dei liquidi: Nuovo Cimento (C), vol. 7, 1919, p. 355.
points from Figure 1. The area under the curve from log $T = 1.200$ ($T = 15.85$) to log $T = 2.4744$ ($T = 298$), marked A on the chart, was estimated by count and planimeter to be 9.924 entropy units. The 18 points on the curve obeying the Debye $T^3$ law show an average value for $\beta \nu$ (the Bebye function parameter) of 205.5, which enables the area under the $C_p - \log T$ curve below log $T = 1.200$ (shown shaded), to be calculated from the tables of Simou. 22

Since $\frac{\beta \nu}{T}$ at log $T = 1.2$ is 12.96, the entropy from thence to 0° K. is 0.071, and the total entropy at 298° K. is $9.924 + 0.071 = 9.995$. The even figure 10.00 will be used in future calculations. Lewis,

**Figure 3.**-Logarithmic specific-heat curve of zinc metal at low temperatures: A, Directly determined entropy; B, part for which entropy is determined by extrapolation of the Debye curve

Gibson, and Latimer gave 9.83, based on less extensive data. The figure 10.00 is thought to be correct to 0.1 unit.

**SPECIFIC HEATS AT HIGH TEMPERATURES**

In a previous publication (see footnote 5, first citation, p. 2) the specific heat of solid zinc at elevated temperatures was taken from the results of Eastman, Williams, and Young. 23 Since that time there have appeared the published results of Umino, 24 as well as the direct measurements of true specific heat of Behrens and Drucker (see Table 1, footnote 5), who also summarized previous results of some

---

other workers. Awberry and Griffiths\textsuperscript{25} have recently reported results upon the heat content of the solid and liquid metal. In the summary of Behrens and Drucker (see Table 1, footnote 5) are included the results of Schubel\textsuperscript{26} and Jaeger and Diesselhorst.\textsuperscript{27} There remain to be considered also the figures of Wüst, Meuthen, and Durer,\textsuperscript{28} of Itaka,\textsuperscript{29} and of Gaede\textsuperscript{30} as comprising fairly recent work.

The above authors who have measured total heat content have not used a similar basis (that is, 0°, 18°, 20°, etc.), nor do the methods used for deriving true specific heats from total heats seem to be directly comparable; in fact, the method is often not mentioned. For the purpose of making such a comparison the original results of Umino, Eastman, Awberry and Griffiths, Schubel, Itaka, and Wüst have been recalculated to a comparable basis of total heats from 0° C. The true specific heat determinations of Behrens and Drucker may be adequately expressed by a quadratic for the range 0–200° C.

\[ C_p = 6.03 + 1.5 \times 10^{-2} t + 3 \times 10^{-4} t^2, \]

where \( C_p \) is the specific heat per gram atom and \( t \) the temperature in degrees centigrade. In order to include these data the quadratic was integrated to total heats and calculated at 100° intervals, a reversal of the usual procedure. All of these data have been plotted on the chart of Figure 4, where the line S shows the heat content from 0° C. of the solid and line L that of liquid zinc.

In the case of the solid there is evident a very substantial agreement in heat content from 0° C. to the melting point (419.5°) of all experimenters except Wüst and Awberry and Griffiths, who agree with each other but with none of the other workers. The individual points of these latter experimenters are, however, far from consistent in themselves, and certain of their results practically coincide with the other work. The excessive curvature upon approaching the melting points of the results of Wüst and Griffiths would seem to indicate impure samples, but the latter claims to have used electrolytic zinc of high purity. Itaka admittedly used impure zinc. In the author's opinion, the weight of evidence favors the results of the other workers, which practically agree with the figures of Eastman, Williams, and Young. The analytic expression of these latter authors might well be chosen as final, except for the fact that a slight adjustment is required to fit their results to the more extensive and probably more accurate low-temperature data. Thus the true specific heat at 0° C. is calculated from Eastman at 5.92 per gram atom, whereas from Table 2 the figure should be 6.01, and Behrens and Drucker had 6.03. It has been assumed therefore that curve S of Figure 4, representing the concordant data for solid zinc, could be expressed by the function \( H_e = 6.01t + bt^2 \), where \( H_e \) is the heat content per gram atom from 0° C. Per gram, \( h_e = 0.0919 + t + bt^2 \), and the figure \( b = 2.02 \times 10^{-5} \) is cal-

culated from the heat content at the melting point = 42.13 calories. Then $B$ is $2.64 \cdot 10^{-3}$ and

$$C_p(zn) = 5.29 + 2.64 \cdot 10^{-3}T$$

when the temperature is expressed as absolute centigrade temperature. A 3-coefficient formula is not justified by the available data.

For liquid zinc the available data are very discordant, particularly at the lower temperatures. Since the results of Umino are in excellent agreement for solid zinc and since his figures are most consistent in themselves for the liquid they are accepted as the best available. The expression $C_p(zn) = 7.40 + 1.15 \cdot 10^{-3}t$, or $C_p(zn) = 7.09 + 1.15 \cdot 10^{-3}T$

![Figure 4](image)

**Figure 4.** Heat contents of zinc metal at high temperatures: Curve $S$, data of solid zinc to melting point; curve $L$, of liquid zinc. Heat contents are all from $0^\circ$ C. $\bigcirc$ Umino, $\bigcirc$ Eastman, Williams, and Young, $\bigcirc$ Awberry and Griffiths, $+$ Schubel, $\times$ Behrens and Drucker, $\ast$ Hata, $\wedge$ Wust, $\ast$ Braune

is valid for these results from the melting point to $850^\circ$ C. A figure used previously by the author was $C_p(zn) = 7.24$ from Braune, but a more critical examination of Braune’s experimental results does not seem to the author to justify the conclusion of a constant specific heat of liquid zinc, as was claimed. The present expression for liquid zinc becomes $C_p = 7.88$ at the melting point.

According to Cooke the vapor density of zinc indicated that it is a monatomic gas, and as such its specific heat may be taken as independent of the temperature and equal to five calories per gram atom.

---

The available data on the vapor pressures of liquid zinc are more extensive and more accurate than for those of solid zinc and will be considered first. In a previous publication (see footnote 5, first citation, p. 2) the author recalculated the data then available (1925) for thermodynamic consistency. The newly determined figures for the specific heats of zinc liquid and solid require some change to be made in these calculations. The methods used are identical, except as noted, with the previous work, and involve the calculation of the $\Sigma$ function

$$
\Sigma = -R \ln K + \Delta r_{\Gamma} \ln T + 1/2 \Delta \Gamma_{\eta} T + 1/6 \Delta \Gamma_{\eta} T^2
$$

where $R$ is the gas constant, $K$ the vapor pressure in atmospheres, and the $\Gamma$ terms the coefficients of the change of specific heat expressed as a quadratic. Because of considerable variations in the figures available for the heat of fusion of zinc thermodynamic consistency was obtained in the previous work by using the Sackur equation with Lewis's version of the Tetrode constant for the calculation of the entropy of the gas.\(^{33}\)

This procedure gave rise to thermodynamically consistent expressions for the vaporization and sublimation of zinc but violated the principle that the vapor pressures of solid and liquid must be equal at the melting point. The new expressions for specific heat obtained in the preceding sections enable a more adequate and satisfactory interpretation of the available experimental results on vapor pressure to be obtained, with equal thermodynamic consistency, but lead to results not completely in agreement with the Sackur equation for the entropy of zinc vapor. That the vapor pressure of solid and liquid is equal at the melting point seems a more definite and certain physical limitation than the implications of the Sackur equation. Any deviation of zinc vapor from the behavior of a perfect gas would not account for more than small variations of 0.1 or 0.2 entropy unit, but such gases as hydrogen and the alkali-metal vapors are known to require correction terms in the Sackur equation because of peculiarities disclosed by their band spectra.\(^{34}\) This matter should be investigated for zinc. Rodebush and Dixon\(^ {35}\) obtained satisfactory check with the Sackur equation by choosing the specific heats of Wüst and Iitaka for the liquid metal, but those of Eastman, Williams, and Young for the solid. If the former investigators had incorrect data for the solid, as now seems likely, the choice of these data for the liquid does not seem rational. Tolman\(^ {36}\) calculated the entropy of the gas from the vapor pressure of the solid only, using the results of Egerton\(^ {47}\) but a consideration of all these data does not lead to a definite slope for the vapor pressure when plotted as $\log K$ vs. $\frac{1}{T}$.

In this work the application of the Sackur equation will be ignored, and reliance placed on actual experimental data.


\(^{47}\) Egerton, A. C., The Vapor Pressure of Zinc, Cadmium, and Mercury: Phil. Mag., ser. 6, vol. 33, 1917, p. 38.
In Figure 5 the line L shows the sigma function for the data of Braune,38 Rodebusch and Dixon,39 Jenkins,40 and Greenwood,41 plotted against reciprocal temperatures. In the reaction

\[ \text{Zn}(l) = \text{Zn}(g) \]  \hspace{1cm} \text{(Reaction 1)}

\[ C_{p,\text{Zn}(l)} = 5.0, \]

\[ C_{p,\text{Zn}(g)} = 7.09 + 1.15 \cdot 10^{-3}T \]

\[ \Delta C_p = -2.09 - 1.15 \cdot 10^{-3}T \]

and \[ \Sigma = -1.9885 \ln p - 2.09 \ln T - 0.575 \cdot 10^{-3}T \]

The figures of Braune, Jenkins, and Greenwood extend from a vapor pressure of 1 mm. to 53 atmospheres and include 25 experimental determinations. Rodebusch and Dixon had 30 points from 8 mm. to 49 mm. vapor pressure, of which only selected alternate values are plotted on Figure 5 because many points are very close together. It is evident that a straight line adequately expresses the data, and the slope = \( \Delta H_\theta \) is +31,087 calories per gram atom. The calculation of the integration constant \( I \) for the above reaction as the difference between \( \Sigma \) and \( \frac{\Delta H_\theta}{T} \) leads to results that are summarized in Table 4.

**Table 4.—Integration constant of free energy of zinc vaporization**

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Method</th>
<th>Number of points</th>
<th>( I )</th>
<th>A. D. of M.</th>
<th>Weight factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Braune</td>
<td>Inert gas</td>
<td>5</td>
<td>-41.876±</td>
<td>0.044</td>
<td>23</td>
</tr>
<tr>
<td>Do</td>
<td>B. P.</td>
<td>7</td>
<td>-41.813±</td>
<td>0.007</td>
<td>143</td>
</tr>
<tr>
<td>Greenwood</td>
<td>B. P. (high pressure)</td>
<td>4</td>
<td>-42.001±</td>
<td>0.184</td>
<td>5</td>
</tr>
<tr>
<td>Jenkins</td>
<td>Manometric</td>
<td>9</td>
<td>-41.852±</td>
<td>0.030</td>
<td>53</td>
</tr>
<tr>
<td>Rodebusch and Dixon</td>
<td>B. P.</td>
<td>30</td>
<td>-41.837±</td>
<td>0.018</td>
<td>77</td>
</tr>
<tr>
<td>Weighted mean</td>
<td></td>
<td></td>
<td>-41.837±</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

38 See footnote 31.
39 See footnote 35.
ZINC SMELTING

In this table the weight factor for the calculation of the weighted mean was taken, perhaps somewhat arbitrarily, as the reciprocal of the average deviation from the mean of the results of individual investigators.

Then the free energy of zinc vaporization from the liquid state becomes:

$$\Delta F^o_{298} = -RT \ln p = 31.087 + 2.09 \ T \ln T + 0.575 \cdot 10^{-3} T^2 - 41.84 \ T$$ (Equation 1)

$$\Delta F^o_{298} = +22.216$$

and

$$\log p_{(s)} = 9.1373 - \frac{6.7895}{T} - 1.051 \log T - 1.255 \cdot 10^{-4} T$$ (Equation 2)

In continuation of these calculations, for the reaction

$$Zn_{(s)} \rightarrow Zn_{(l)}$$ (Reaction 2)

$$C_p(Zn_{(s)}) = 7.09 + 1.15 \cdot 10^{-3} T$$

$$C_p(Zn_{(l)}) = 5.29 + 2.14 \cdot 10^{-3} T$$

$$\Delta C_p = 1.80 - 1.49 \cdot 10^{-3} T$$

$$\Delta H_T = \Delta H_s + 1.80 \ T - 0.745 \cdot 10^{-3} T^2$$ (Equation 3)

From the accepted curves for heat content of solid and liquid zinc plotted on Figure 4 the latent heat of fusion is 24.09 calories per gram, or at the melting point

$$\Delta H_{982.5} = 1575 \ \text{calories}$$

Substituting $$T = 692.6$$ in equation (3),

$$\Delta H_s = 685, \ \text{and} \ \Delta F^o_{982.5} = 0 = 6.85 - 1.80 \ T \ln T + 0.745 \cdot 10^{-3} T^2 + 1 T$$

$$I = 10.268$$

and the free energy of melting of zinc is

$$\Delta F^o_T = 685 - 1.80 \ T \ln T + 0.745 \cdot 10^{-3} T^2 + 10.27 \ T$$ (Equation 4)

$$\Delta F^o_{298} = +755$$

By the addition of equations (1) and (4) the theoretical vapor pressure of solid zinc may be obtained:

$$Zn_{(s)} \rightarrow Zn_{(l)}$$

$$\Delta F^o_{298} = 31.087 + 2.09 \ T \ln T + 0.575 \cdot 10^{-3} T^2 - 41.84 \ T$$

$$Zn_{(s)} = Zn_{(l)}$$

$$\Delta F^o_T = 685 - 1.80 \ T \ln T + 0.745 \cdot 10^{-3} T^2 + 10.27 \ T$$

$$Zn_{(l)} = Zn_{(s)}$$ (Reaction 3)

$$\Delta F^o_T = 31.772 + 0.29 \ T \ln T + 1.32 \cdot 10^{-3} T^2 - 31.57 \ T$$

$$\Delta F^o_{298} = +22.917$$ (Equation 5)

This equation may now be compared to the actual measurements of Egerton. For this comparison the vapor pressure of liquid zinc at the melting point was calculated from equation (2) by substitution of $$T = 692.6$$, whence $$\log p = -3.7379$$, and this is also the vapor pressure of solid zinc at the melting point.

$$\Sigma_{(s)} = -R \ln p - 0.29 \ln T - 1.32 \cdot 10^{-4} T$$

is then calculated for the solid as $$+14.3038$$ and is shown as the square inclosed point at the bottom of line S of Figure 5. Proceeding
from this point the line S was then drawn with a slope $\Delta H_e = 31.772$. The other points indicated represented $E_0$ calculated from Egerton’s actual experimental data. It is evident that the line thus drawn accurately expresses Egerton’s values at the higher pressures (lower points on the curve), and the discrepancy at the lower temperatures is not more than might be expected from the experimental difficulties of his determinations. These calculations complete the correlation of specific heats, heats of fusion, and vapor and sublimation pressures, and involve no discrepancies except those referring to the use of the Sackur equation for the entropy of the vapor.

Equation (2) enables calculation to be made of the vapor pressures of liquid zinc, representing rationally averaged results of the different investigators. Similarly, equation (5) may be transformed to the expression for sublimation,

$$\log p_v = 6.8948 - \frac{6.939.0}{T} - 0.1458 \log T - 2.883 \cdot 10^{-4} T$$  \hspace{1cm} \text{(Equation 6)}$$

Such calculated average values of vapor and sublimatic pressure are presented in Table 5. With the exception of the extrapolated first figures at room temperatures the limits of the table cover no more than experimentally investigated ranges of vapor pressure.

<table>
<thead>
<tr>
<th>State</th>
<th>Temperature</th>
<th>Log vapor pressure (atmospheres)</th>
<th>Vapor pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C.</td>
<td>°K.</td>
<td>At.</td>
</tr>
<tr>
<td>Solid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>298.1</td>
<td>-16.8263</td>
<td>1.49 $\cdot 10^{-11}$</td>
</tr>
<tr>
<td>300</td>
<td>473.1</td>
<td>-8.2687</td>
<td>5.03 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>350</td>
<td>573.1</td>
<td>-6.9176</td>
<td>1.21 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>400</td>
<td>623.1</td>
<td>-5.7505</td>
<td>1.66 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>450</td>
<td>673.1</td>
<td>-4.6266</td>
<td>1.48 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>500</td>
<td>723.1</td>
<td>-3.5478</td>
<td>9.54 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>550</td>
<td>773.1</td>
<td>-2.7774</td>
<td>1.83 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>600</td>
<td>823.1</td>
<td>-1.9367</td>
<td>1.45 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>650</td>
<td>873.1</td>
<td>-1.8987</td>
<td>3.55 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>700</td>
<td>923.1</td>
<td>-1.4500</td>
<td>7.38 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>750</td>
<td>973.1</td>
<td>-1.1231</td>
<td>1.26 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>800</td>
<td>1023.1</td>
<td>-0.6230</td>
<td>3.94 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>850</td>
<td>1,073.1</td>
<td>-0.2540</td>
<td>5.57 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>900</td>
<td>1,123.1</td>
<td>-0.0244</td>
<td>9.48 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>950</td>
<td>1,173.1</td>
<td>0.0000</td>
<td>1.000</td>
</tr>
<tr>
<td>1,000</td>
<td>1,223.1</td>
<td>+1.3882</td>
<td>1.543</td>
</tr>
<tr>
<td>1,050</td>
<td>1,273.1</td>
<td>+1.813</td>
<td>2.406</td>
</tr>
<tr>
<td>1,100</td>
<td>1,323.1</td>
<td>+1.2982</td>
<td>5.280</td>
</tr>
<tr>
<td>1,150</td>
<td>1,373.1</td>
<td>+1.0136</td>
<td>10.318</td>
</tr>
<tr>
<td>1,200</td>
<td>1,423.1</td>
<td>+1.1731</td>
<td>18.210</td>
</tr>
<tr>
<td>1,250</td>
<td>1,473.1</td>
<td>+1.2411</td>
<td>30.284</td>
</tr>
<tr>
<td>1,300</td>
<td>1,523.1</td>
<td>+1.2952</td>
<td>46.903</td>
</tr>
</tbody>
</table>

| Solid and liquid at melting point |            |                                  |                |              |
| Liquid                        |             |                                  |                |              |
| 450                           | 723.1       | -3.3478                          | 4.49 $\cdot 10^{-4}$ | 341 |
| 500                           | 773.1       | -2.7774                          | 1.67 $\cdot 10^{-3}$ | 1.37 |
| 550                           | 823.1       | -2.2890                          | 5.20 $\cdot 10^{-3}$ | 4.00 |
| 600                           | 873.1       | -1.8987                          | 1.45 $\cdot 10^{-3}$ | 11.00 |
| 650                           | 923.1       | -1.4500                          | 3.55 $\cdot 10^{-4}$ | 26.97 |
| 700                           | 973.1       | -1.1231                          | 7.38 $\cdot 10^{-4}$ | 59.47 |
| 750                           | 1,023.1     | -0.6230                          | 1.26 $\cdot 10^{-3}$ | 123.1 |
| 800                           | 1,073.1     | -0.2540                          | 3.94 $\cdot 10^{-4}$ | 234.5 |
| 850                           | 1,123.1     | -0.0244                          | 5.57 $\cdot 10^{-4}$ | 423.5 |
| 900                           | 1,173.1     | 0.0000                           | 9.48 $\cdot 10^{-4}$ | 720.2 |
| 950                           | 1,223.1     | +1.3882                          | 1.000 |
| 1,000                         | 1,273.1     | +1.813                          | 1.543 |
| 1,050                         | 1,323.1     | +1.2982                          | 2.406 |
| 1,100                         | 1,373.1     | +1.0136                          | 5.280 |
| 1,150                         | 1,423.1     | +1.1731                          | 10.318 |
| 1,200                         | 1,473.1     | +1.2411                          | 18.210 |
| 1,250                         | 1,523.1     | +1.2952                          | 30.284 |
| 1,300                         | 1,573.1     | +1.2952                          | 46.903 |

| Normal boiling point         |             |                                  |                |              |
| Liquid under pressure        |             |                                  |                |              |
| 905.4                        | 1,178.5     | .0000                            | 1.000 |
| 950                           | 1,228.5     | +1.8822                          | 1.543 |
| 1,000                        | 1,278.5     | +1.813                          | 2.406 |
| 1,050                        | 1,328.5     | +1.2982                          | 5.280 |
| 1,100                        | 1,378.5     | +1.0136                          | 10.318 |
| 1,150                        | 1,428.5     | +1.1731                          | 18.210 |
| 1,200                        | 1,478.5     | +1.2411                          | 30.284 |
| 1,250                        | 1,528.5     | +1.2952                          | 46.903 |

### THERMAL DATA ON METALLIC ZINC

The acceptance of the free-energy equations (1) and (5) for the vaporization and sublimation of zinc fix the acceptable values for heats of vaporization, sublimation, and fusion.
Thus from equation (1) the heat of vaporization is:

\[ \Delta H_T = 31,087 - 2.09 T - 0.575 \times 10^{-3} T^2 \]
\[ \Delta H_{298} = +30,411 \]  

(Equation 7)

and from equation (5) the heat of sublimation is

\[ \Delta H_T = 31,772 - 0.29 T - 1.32 \times 10^{-3} T^2 \]
\[ \Delta H_{298} = +31,569 \]  

(Equation 8)

and for fusion

\[ \Delta H_T = 685 + 1.80 T - 0.745 \times 10^{-3} T^2 \]
\[ \Delta H_{298} = +1,156 \]
\[ \Delta H_{602.8} = +1,575 \text{ or } 24.09 \text{ per gram} \]  

(Equation 9)

In the absence of direct determinations of heats of vaporization and sublimation the figures above may be considered the best available. In the case of fusion, the value 24.09 calories per gram represents the selected comparison of heat-content determinations, but it is of interest to compare the results of indirect methods. Honda and Ishigaki have reviewed and recalculated data on the determination of heat of fusion from the depression of the melting point and have made a few new determinations. The figures in Table 6 were taken from that source. The range of heats of fusion from 24.1 to 27.1 confirms the specific heat values chosen in a previous part of this work to within the experimental limitations of the indirect method, although these results cannot be taken as definitive determination of the heat of fusion.

<table>
<thead>
<tr>
<th>Source</th>
<th>Solute metal</th>
<th>Type of melting curve</th>
<th>Depression for 1 gram atom of solute, °C.</th>
<th>Heat of fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selected</td>
<td>Mg</td>
<td>Simple eutectic</td>
<td>5.98</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>do</td>
<td>5.83</td>
<td>25.1</td>
</tr>
<tr>
<td>Honda</td>
<td>Cd</td>
<td>do</td>
<td>6.05</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td>TI</td>
<td>do</td>
<td>5.36</td>
<td>27.1</td>
</tr>
<tr>
<td>Heycock and Neville and Honda</td>
<td>Ag</td>
<td>Solid solution</td>
<td>5.54</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>do</td>
<td>5.53</td>
<td>26.5</td>
</tr>
</tbody>
</table>

**ZINC OXIDE**

**ALLOTROPY**

There are no indications of allotropic modifications of zinc oxide. De Forcrand concluded that polymerization of zinc oxide took place at high temperatures, his evidence being based upon variations of the heat of solution of the oxide in acid when it was ignited for varying periods of time. More recent investigators have been unable to confirm these observations, and it is assumed that any changes occurring are of no thermodynamic importance.

Specific Heats at Low Temperatures

Available data on the specific heats at low temperatures of zinc oxide are represented by the figures of Parks, Millar, and Clusius and Hartec. All of these results have been plotted on Figure 6, curve L. It is apparent from this chart that the results of Clusius and Hartec are in general somewhat higher than those of Parks and Millar, who agree well. The former authors note, however, that these results on zinc oxide were among the first obtained, with an apparatus that had a bad cooling rate at low temperatures. For these reasons the “smoothed” curve has been drawn with special reference to the work of the latter investigators, and the results of the former are used only to facilitate extrapolation at the lower temperatures.

Table 7 gives the specific heats below room temperature at 10° intervals down to 30° K., as obtained from this “smoothed” curve.

Table 7.—Low-temperature specific heats of zinc oxide

<table>
<thead>
<tr>
<th>Temperature, ° K.</th>
<th>log T</th>
<th>C_p/F. W.</th>
<th>Temperature, ° K.</th>
<th>log T</th>
<th>C_p/F. W.</th>
<th>Temperature, ° K.</th>
<th>log T</th>
<th>C_p/F. W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30...</td>
<td>1.4771</td>
<td>[0.54]</td>
<td>130...</td>
<td>2.1139</td>
<td>5.48</td>
<td>230...</td>
<td>2.3617</td>
<td>8.50</td>
</tr>
<tr>
<td>40...</td>
<td>1.6021</td>
<td>1.12</td>
<td>140...</td>
<td>2.1461</td>
<td>5.86</td>
<td>240...</td>
<td>2.3802</td>
<td>8.72</td>
</tr>
<tr>
<td>50...</td>
<td>1.6990</td>
<td>1.78</td>
<td>150...</td>
<td>2.1761</td>
<td>6.24</td>
<td>250...</td>
<td>2.3977</td>
<td>8.92</td>
</tr>
<tr>
<td>60...</td>
<td>1.7732</td>
<td>2.28</td>
<td>160...</td>
<td>2.2041</td>
<td>6.68</td>
<td>260...</td>
<td>2.4150</td>
<td>9.12</td>
</tr>
<tr>
<td>70...</td>
<td>1.8451</td>
<td>2.92</td>
<td>170...</td>
<td>2.2304</td>
<td>6.92</td>
<td>270...</td>
<td>2.4314</td>
<td>9.30</td>
</tr>
<tr>
<td>80...</td>
<td>1.9031</td>
<td>3.40</td>
<td>180...</td>
<td>2.2553</td>
<td>7.22</td>
<td>280...</td>
<td>2.4472</td>
<td>9.45</td>
</tr>
<tr>
<td>90...</td>
<td>1.9542</td>
<td>3.84</td>
<td>190...</td>
<td>2.2788</td>
<td>7.50</td>
<td>290...</td>
<td>2.4624</td>
<td>9.62</td>
</tr>
<tr>
<td>100...</td>
<td>2.0000</td>
<td>4.26</td>
<td>200...</td>
<td>2.3010</td>
<td>7.78</td>
<td>300...</td>
<td>2.4744</td>
<td>9.75</td>
</tr>
<tr>
<td>110...</td>
<td>2.0414</td>
<td>4.68</td>
<td>210...</td>
<td>2.3222</td>
<td>8.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120...</td>
<td>2.0792</td>
<td>5.08</td>
<td>220...</td>
<td>2.3424</td>
<td>8.25</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

46 See footnote 13.
The compressibility of zincite (natural zinc oxide) was given by Madelung and Fuchs as $0.77 \cdot 10^{-6}$ megabars per square centimeter, and according to Fizeau the linear coefficient of expansion is $3.16 \cdot 10^{-6}$. The density of zincite was given by Blake as 5.684. The volume of a gram formula weight of zinc oxide is therefore 11.48 c. c. Recent data on the expansion and density of zinc oxide seem to be lacking, but the figures as given will serve adequately for calculation of the difference between specific heats at constant volume and pressure.

**Calculation of Entropy**

If the above figures are applied to the formula

$$C_p - C_v = \frac{9\alpha^2 VT}{\beta}$$

$$C_p - C_v = 0.098 \text{ calorie per degree at } 300^\circ \text{ K.}$$

Similarly, according to Simon

$$C_p - C_v = aC_v^2T,$$

where $a$ is a constant nearly independent of the temperature, the equation serving to calculate $C_p - C_v$ at lower temperatures, when measured data in this range are lacking. Thus, it is found that for zinc oxide $a$ is $3.4 \cdot 10^{-6}$ and $C_p - C_v$ is calculated at $100^\circ \text{ K.}$ as 0.006 calories per formula weight. At still lower temperatures the difference between $C_p$ and $C_v$ obviously becomes negligible.

On plotting the "smoothed" data on a $C_p - \log T$ chart, as is done in Figure 7, it is found that the results below $100^\circ \text{ K.}$ may be expressed by a simple Debye curve with a value of $\beta\nu = 283$. The shaded extrapolated area under the curve below $\log T = 1.5$ is then found in a manner similar to that of zinc to have an area of 0.23 entropy unit. The unshaded area directly determined from thence to $298^\circ \text{ K.}$ (log $T = 2.4744$) is 10.21 entropy units, and the entropy of zinc oxide at $298^\circ \text{ K.}$ is 10.44, a result only slightly higher than that calculated by Parks (10.4). This figure is thought to be correct to within 0.2 entropy unit.

**Specific Heats at High Temperatures**

In a previous publication the results of White on the specific heats of zinc oxide at high temperatures were reported, and from data on four mean specific heats ($25^\circ - 700^\circ$, $900^\circ$, $1,100^\circ$, $1,300^\circ$; 11.693, 11.929, 12.156, 12.369, respectively) the general equation

$$C_p(ZnO) = 9.96 + 2.98 \cdot 10^{-2}T - 3.87 \cdot 10^{-7}T^2$$

was derived. This, however, leads to a calculated value of 10.82 calories per mol at $298^\circ$, whereas from Table 7 the true figure should

---

be near 9.75. At the time this formula was derived the low-temperature measurements leading to the result 9.75 were not available. Because there is still considerable curvature in the specific heat curve near room temperature it is hardly to be expected that such an extrapolation should be entirely consistent.

Besides the results of White there are available for zinc oxide only the older figures of Magnus \(^{53}\) and of Regnault.\(^{54}\) In a manner exactly similar to that used for zinc these data have all been recalculated to a comparable basis of heat content from 0° C. and in this form are plotted on curve H of Figure 6. If, then, the heat content is

\[ H_e = at + bt^2 + ct^3 \]

\(a\) must, from Table 7, be equal to 9.35. If now the coefficients \(b\) and \(c\) are calculated from the points at 700° and 1,300° C. (the limits of White’s experiments) the expression

\[ H_e = 9.35t + 4.34 \cdot 10^{-3}t^2 - 1.574 \cdot 10^{-6}t^3 \]  

(Equation 10)

is obtained. The line drawn on the chart represents this function, and it is immediately clear that it accurately fits the points near 100° of

---


Regnault and Magnus and somewhat less closely approximates the upper figures of Magnus at 259° and 550° C.

**Table 8.—Heat content of zinc oxide from 0° C.**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Observed heat content, calories</th>
<th>Observer</th>
<th>H⁺ per formula</th>
<th>Temperature, °C</th>
<th>Observed heat content, calories</th>
<th>Observer</th>
<th>H⁺ per formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>983.7</td>
<td>Regnault</td>
<td></td>
<td>700</td>
<td>8,132</td>
<td>White</td>
<td>8,132</td>
</tr>
<tr>
<td>99</td>
<td>995.3</td>
<td>Magnus</td>
<td></td>
<td>900</td>
<td>10,677</td>
<td>do</td>
<td>16,753</td>
</tr>
<tr>
<td>259</td>
<td>2,886</td>
<td>do</td>
<td></td>
<td>1,100</td>
<td>13,306</td>
<td>do</td>
<td>13,443</td>
</tr>
<tr>
<td>550</td>
<td>6,039</td>
<td>do</td>
<td></td>
<td>1,300</td>
<td>16,009</td>
<td>do</td>
<td>16,009</td>
</tr>
</tbody>
</table>

Because the heat-content curve obviously has a point of inflection, the $T^3$ term is essential for expression of the data, in contrast to those for zinc metal. The formula fits White’s data to better than 1 per cent and seems the only satisfactory interpretation of the entire sets of figures. The accuracy of the experimental results hardly justifies a $T^n$ term, which would be necessary to obtain closer approximation of the formula to White’s middle results.

By differentiation of equation (10) and substitution of $t = (T - 273.1)$, there is obtained the expression for the specific heat of zinc oxide at high temperatures

$$C_p(znO) = 6.63 + 11.26 \times 10^{-3}T - 4.722 \times 10^{-6}T^2$$

(Equation 11)

valid at least up to 1,600° K.

**SUBLIMATION AND VAPOR PRESSURES**

Pure zinc oxide does not seem to melt below its sublimation point. No satisfactory determinations of sublimation pressures have been made, although a number of investigations of the volatility of zinc oxide have been made. The most recent of these are the experiments of Feiser, who has reviewed previous work.

Feiser unfortunately does not give experimental data but shows a vapor-pressure curve derived by an indirect method of doubtful accuracy. From this chart the figures for temperature and sublimation pressure of Table 9 were taken.

**Table 9.—Supposed sublimation pressure of zinc oxide**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$1/T \times 10^8$</th>
<th>Sublimation pressure, mm.</th>
<th>Log sublimation pressure, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C.</td>
<td>°K.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,350</td>
<td>1,623</td>
<td>6.16</td>
<td>0.45</td>
</tr>
<tr>
<td>1,400</td>
<td>1,673</td>
<td>5.98</td>
<td>1.2</td>
</tr>
<tr>
<td>1,450</td>
<td>1,723</td>
<td>5.80</td>
<td>3.5</td>
</tr>
<tr>
<td>1,500</td>
<td>1,773</td>
<td>5.64</td>
<td>13</td>
</tr>
</tbody>
</table>

When these data are plotted as log $p$ vs. $\frac{1}{T}$, the figures show considerable curvature, and it is impossible to estimate even an approximate value for heat of sublimation. Feiser estimated the sublimation temperature at 1,800° to 1,850° by analogy with cadmium oxide, but this seems a somewhat questionable procedure. The sublimation pressure of zinc oxide is a matter of some technical importance and should be investigated further.

**THERMAL DATA ON ZINC OXIDE**

In a recent publication the author reviewed the status of investigations on the heat of formation of zinc oxide and reported new experimental work that served to enable a definitive value to be adopted. For dry oxide the result $\Delta H_{298} = -83,156$ was found; for wet oxide, $-83,200$. In another place (see footnote 45) the free energy of formation of the oxide from cell measurements was shown to be $\Delta F^{\circ}_{298} = -75,930$. For comparison, the free energy may be calculated from the entropies obtained in the earlier part of this publication. Thus, for the reaction

$$\text{Zn}(s) + \frac{1}{2}\text{O}_2 = \text{ZnO}(s)$$

the entropies are 10.00, 24.52, 10.44

$$\Delta S = -24.08$$

and since

$$\Delta F = \Delta H - T\Delta S$$
$$\Delta F = -83,156 - 298.1(-24.08)$$
$$\Delta F^{\circ}_{298} = -75,979$$

Lewis and Randall gave 24.0 for the entropy of $\frac{1}{2}\text{O}_2$, but the figure used represents the most probable value on the basis of recent determinations and calculations of W. F. Giauque and Johnston. The agreement between the free energy determined from cell measurements and that from the heat of formation and entropy is well within the estimated probable error of the calorimetric work on zinc oxide, which was thought to be about 50 calories.

As final correlation between thermal data there remains only recalculation of experiments described in the work upon reduction equilibria (see footnote 52, p. 18), using the equations now thought most valid for specific heats of metal and oxide and vapor pressure of the liquid metal. The sigma function plot method is again used for these newer calculations.

It seemed expedient to adopt for these new calculations the figures derived by Eastman for carbon monoxide and dioxide. Thus for

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56 Maier, C. G., The Heat of Formation of Zinc Oxide. (In course of publication.)
the reaction
\[ \text{ZnO(s)} + \text{CO(g)} = \text{Zn(g)} + \text{CO}_2(g) \] 

(Reaction 4)

\[ C_{p(\text{CO}_2)} = 7.70 + 5.30 \cdot 10^{-3}T - 0.83 \cdot 10^{-6}T^2 \]

\[ C_{p(\text{Zn(s)})} = 5.00 \]

\[ C_{p(\text{ZnO})} = 6.63 + 11.26 \cdot 10^{-3}T - 4.722 \cdot 10^{-6}T^2 \]

\[ C_{p(\text{CO})} = 6.76 + 0.61 \cdot 10^{-3}T + 0.13 \cdot 10^{-6}T^2 \]

\[ \Delta C_p = -0.69 - 6.57 \cdot 10^{-5}T + 3.76 \cdot 10^{-6}T^2 \]

\[ \Sigma = -R \ln \left[ \frac{p_{\text{Zn}}}{p_{\text{CO}_2}} \right] - 0.69 \ln T - 3.285 \cdot 10^{-3}T + 0.6287 \cdot 10^{-6}T^2 \]

*Figure 8.* Sigma function plot for reduction of zinc oxide by carbon monoxide

where \( p_{\text{Zn}} \) is the vapor pressure of liquid zinc in atmospheres, calculated from equation (2) (p. 14), and the ratio \( \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \) is that obtained directly from the experimental results.

In Figure 8 are plotted the values of \( \Sigma \) vs. \( \frac{1}{T} \) for the 18 experimental points of Maier and Ralston’s work as cited in footnote 52. The data are also recorded in Table 10.
<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>Temperature, °K.</th>
<th>Log ( \frac{p_{CO}}{p_{CO}} )</th>
<th>Log vapor pressure ( Zn )</th>
<th>( \Sigma )</th>
<th>( \frac{1}{T} \cdot 10^4 )</th>
<th>( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1................</td>
<td>825.3</td>
<td>-3.2620</td>
<td>-2.2584</td>
<td>18.357</td>
<td>12.117</td>
<td>-39.074</td>
</tr>
<tr>
<td>2................</td>
<td>867.1</td>
<td>-3.1073</td>
<td>-1.8897</td>
<td>15.835</td>
<td>11.533</td>
<td>-38.828</td>
</tr>
<tr>
<td>3................</td>
<td>900.5</td>
<td>-2.9215</td>
<td>-1.3088</td>
<td>12.536</td>
<td>10.746</td>
<td>-38.397</td>
</tr>
<tr>
<td>5................</td>
<td>966.3</td>
<td>-2.8164</td>
<td>-1.1477</td>
<td>10.818</td>
<td>10.349</td>
<td>-38.233</td>
</tr>
<tr>
<td>6................</td>
<td>988.1</td>
<td>-2.7550</td>
<td>-1.0053</td>
<td>9.825</td>
<td>10.120</td>
<td>-38.141</td>
</tr>
<tr>
<td>7................</td>
<td>1,015.1</td>
<td>-2.6153</td>
<td>-0.8382</td>
<td>8.549</td>
<td>9.851</td>
<td>-38.342</td>
</tr>
<tr>
<td>8................</td>
<td>1,029.3</td>
<td>-2.4976</td>
<td>-0.7540</td>
<td>7.385</td>
<td>9.715</td>
<td>-38.601</td>
</tr>
<tr>
<td>9................</td>
<td>1,033.4</td>
<td>-2.5690</td>
<td>-0.7299</td>
<td>7.590</td>
<td>9.676</td>
<td>-38.271</td>
</tr>
<tr>
<td>10................</td>
<td>1,034.6</td>
<td>-2.6002</td>
<td>-0.7221</td>
<td>7.697</td>
<td>9.665</td>
<td>-38.112</td>
</tr>
<tr>
<td>11................</td>
<td>1,035.9</td>
<td>-2.5835</td>
<td>-0.7157</td>
<td>7.583</td>
<td>9.653</td>
<td>-38.169</td>
</tr>
<tr>
<td>12................</td>
<td>1,072.9</td>
<td>-2.4789</td>
<td>-0.5110</td>
<td>5.842</td>
<td>9.321</td>
<td>-38.337</td>
</tr>
<tr>
<td>13................</td>
<td>1,073.3</td>
<td>-2.4347</td>
<td>-0.5078</td>
<td>5.854</td>
<td>9.316</td>
<td>-38.301</td>
</tr>
<tr>
<td>14................</td>
<td>1,074.2</td>
<td>-2.4371</td>
<td>-0.5029</td>
<td>5.839</td>
<td>9.308</td>
<td>-38.276</td>
</tr>
<tr>
<td>15................</td>
<td>1,078.1</td>
<td>-2.4227</td>
<td>-0.4827</td>
<td>5.671</td>
<td>9.275</td>
<td>-38.296</td>
</tr>
<tr>
<td>16................</td>
<td>1,109.3</td>
<td>-2.2440</td>
<td>-0.3229</td>
<td>4.041</td>
<td>9.015</td>
<td>-38.387</td>
</tr>
<tr>
<td>17................</td>
<td>1,113.6</td>
<td>-2.2774</td>
<td>-0.3003</td>
<td>4.080</td>
<td>8.978</td>
<td>-38.473</td>
</tr>
<tr>
<td>18................</td>
<td>1,119.7</td>
<td>-2.2533</td>
<td>-0.2715</td>
<td>3.821</td>
<td>8.931</td>
<td>-38.599</td>
</tr>
</tbody>
</table>

Average = -38.26

1 Omitted from average.

The line representing these points on the sigma function chart is drawn with a slope of \( \Delta H_0 = 47,397 \), which is consistent with the following heats of formation of the reacting materials.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_{f0} )</th>
<th>Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>-83,313</td>
<td>Maier.1 (See footnote 56).</td>
</tr>
<tr>
<td>CO</td>
<td>-26,330</td>
<td>Eastman (from Roth and Naepe).</td>
</tr>
<tr>
<td>CO2</td>
<td>-94,270</td>
<td>Do.</td>
</tr>
<tr>
<td>Zn(g)</td>
<td>+31,576</td>
<td>Maier. (See equation 8, p. 16).</td>
</tr>
<tr>
<td>Reaction</td>
<td>+46,909</td>
<td></td>
</tr>
</tbody>
</table>

1 The value for zinc oxide is not a calorimetric result. The heat of formation of zinc oxide is given in footnote 55 as \( \Delta H_{f0} = -83,210 \), but this figure is based on the heat of formation of water used by Lewis and Randall, \( \Delta H_{f0} = -83,270 \). The recent values of Roth, as reported in Landolt-Börnstein, 1st Ergänzungsband, 5th ed., Julius Springer, Berlin, 1927, p. 809, are some 60 calories higher. Since Eastman used Roth's results for carbon monoxide and dioxide it seems logical to call the calorimetric heat of formation of the oxide \( \Delta H_{f0} = -83,270 \) at 298°. This is, within the probable experimental error of the calorimetric work, comparable to the 83,313 at 18°. The slope \( \Delta H_0 = 47,397 \) is selected primarily to fit the actual reduction data, and since the free energy so calculated coincides with the probably more accurate free energy obtained from electro-motive force measurements, it seems better to throw the error into the heat of formation rather than to the free energy.

It is apparent that this line adequately represents the data except for the points at the ends of the line, where the experimental error was known to be exaggerated.

Omitting the obviously discordant values of \( I \) from points 1, 2, 8, and 16, 17, 18 the average for the integration constant of the free-energy equation is \( I = -38.26 \pm 0.07 \), and the standard free-energy equation for reaction (4) is

\[
\Delta F^0_T = 47,397 + 0.69 \cdot T \ln T + 3.285 \cdot 10^{-4} T^2 - 0.627 \cdot 10^{-4} T^3 - 38.26 T 
\]  
(Equation 12)

\[
\Delta F_{298} = -37,453
\]

From the free energy of reaction (4) at 298° K, the free energy of formation of the oxide may be calculated from the following data.
The free energy of zinc oxide thus obtained checks almost exactly with \(-75,930\) obtained from electromotive force determinations and differs only 42 calories from the figure obtained from the third law, \(-75,970\), although the former figure should be \(-75,900\) if Eastman's (see p. 23) newly calculated value for the free energy of water is accepted. The reader may note an apparent inconsistency, in that in calculating the entropy the heat of formation of zinc oxide was taken as 83,156; but for the calculation above, 83,200, the two figures represent those obtained calorimetrically for dry and wet oxide respectively. It was shown experimentally that the heat of wetting of the oxide sample used was nearly equal to this difference. The difference may be ascribed to surface energy. Because the usual "dry-process" or "wet-process" oxide is of extreme fineness it may not be surprising that a formula weight should have 50 calories surface energy. At elevated temperatures and particularly in the presence of equilibrium concentrations of CO and CO₂ the oxide shrinks, grain growth occurs, and it is logical to use the "wet-oxide" value for calculations at high temperatures. Lewis and Randall 89 have discussed this matter of surface energy. Zinc seems one of the few substances for which the effect is sufficiently great to be detectable by calorimetric methods. Either value of \(\Delta H\) for ZnO will lead to satisfactorily consistent check of the third law with equilibrium and electromotive force data to within 0.3 entropy unit for zinc oxide, and it seems justifiable to conclude that systems of zinc metal or zinc oxide may now be known thermodynamically with a higher precision than most other materials and that considerable confidence may be placed in suitable calculations from the data given.

**ZINC SULPHIDE**

**ALLOTROPY**

Zinc sulphide exists in two crystalline forms, the cubic sphalerite and the hexagonal wurtzite. The latter mineral is not a common form, and there are practically no thermodynamic data available for it. In this work zinc sulphide will be considered only as sphalerite. The specific heat data of Bornemann and Hengstenberg 83 indicate that the anomalies observed in the heat contents near 720° C. are dependent upon impurities (iron?) in the blende and disappear with increasing purity of sample.

---

Specific Heats at Low Temperatures

Available determinations of the specific heat of zinc sulphide below room temperature consist of a few points near liquid hydrogen temperatures by Günther \(^{61}\) and the more extensive measurements of Clusius and Harteeck. (See footnote 13, p. 5.) The complete data are plotted on Figure 9, curve T. Günther's results are practically ignored in drawing the "smoothed" curve, from which the figures of Table 31 were taken. The experimental points do not extend above 200° K. for these investigators, and the upper part of the curve is extrapolated to pass through points above room temperature, discussed in the next section. Because of this extrapolation the calculations of entropy to follow will be somewhat less certain than for zinc metal or oxide.

Compressibility, Expansion, and Atomic Volume

Madelung and Fuchs (see footnote 48, p. 18) gave the compressibility of zinc blende 1.28 \(\times\) 10\(^{-6}\) megabars per square centimeter, and this constitutes the only available measurement. The coefficient of thermal expansion was given by Kopp\(^{62}\) as 3.6 \(\times\) 10\(^{-5}\) between 15° and 47° C., but Fizeau (see footnote 49, p. 18) gave 6.7 \(\times\) 10\(^{-5}\) at 40°. It is probable that the latter figure is the more nearly correct one. Madelung and Fuchs gave 4.0904–4.0946 (4.0915 average) for the density at 0° C., and this does not differ greatly from that of Allen and Crenshaw. \(^{63}\) Accepting the former average, the volume of 97.37 grams of ZnS is 23.80 c. c.

---


CALCULATION OF ENTROPY

Using methods similar to those for zinc oxide, it may be calculated that
\[
C_v - C_p (\text{zns}) = \frac{9 \cdot (6.7 \cdot 10^{-6})^2 - 23.80 - 313}{1.28 \cdot 10^{-6}} \quad \text{c. c. atmosphere per degree}
\]
\[
= 0.057 \quad \text{caloric per degree at } 313^\circ \text{K.}
\]

By analogy with the oxide, the negligible difference between \( C_p \) and \( C_v \) at lower temperatures is confirmed.

When the data of Table 11 are plotted as \( C_p = C_v \) vs. log \( T \), as is done in “Log” of Figure 9, it is found that the lower part of the curve is accurately expressed by a Debye curve of modulus \( \beta \nu = 213.0 \). The entropy of the shaded portion of the curve below log \( T = 1.5 \) to absolute zero is then found to be \( S = 0.470 \), using Simon’s tables (footnote 22, p. 9) as before. By direct measurement the remainder of the curve up to log \( T = 2.4744 \) (\( T = 298.1 \)) is 12.45 entropy units, and the entropy of zinc sulphide is \( S_{298} = 12.92 \). The error due to extrapolation from 200° K. to 298° K. may be as great as 0.5 entropy unit.

**Table 11.—Specific heat of zinc sulphide at low temperatures**

<table>
<thead>
<tr>
<th>Temperature, ( ^\circ \text{K.} )</th>
<th>log ( T )</th>
<th>( C_v )</th>
<th>Temperature, ( ^\circ \text{K.} )</th>
<th>log ( T )</th>
<th>( C_v )</th>
<th>Temperature, ( ^\circ \text{K.} )</th>
<th>log ( T )</th>
<th>( C_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.</td>
<td>1.3010</td>
<td>0.39</td>
<td>120.</td>
<td>2.0792</td>
<td>6.95</td>
<td>220.</td>
<td>2.3424</td>
<td>9.82</td>
</tr>
<tr>
<td>30.</td>
<td>1.4771</td>
<td>1.11</td>
<td>130.</td>
<td>2.1139</td>
<td>7.44</td>
<td>230.</td>
<td>2.3617</td>
<td>9.97</td>
</tr>
<tr>
<td>40.</td>
<td>1.6021</td>
<td>1.96</td>
<td>140.</td>
<td>2.1461</td>
<td>7.88</td>
<td>240.</td>
<td>2.3802</td>
<td>10.11</td>
</tr>
<tr>
<td>50.</td>
<td>1.6960</td>
<td>2.75</td>
<td>150.</td>
<td>2.1701</td>
<td>8.35</td>
<td>250.</td>
<td>2.3977</td>
<td>10.24</td>
</tr>
<tr>
<td>60.</td>
<td>1.7782</td>
<td>3.45</td>
<td>160.</td>
<td>2.2041</td>
<td>8.85</td>
<td>260.</td>
<td>2.4150</td>
<td>10.36</td>
</tr>
<tr>
<td>70.</td>
<td>1.8451</td>
<td>4.10</td>
<td>170.</td>
<td>2.2304</td>
<td>9.84</td>
<td>270.</td>
<td>2.4314</td>
<td>10.48</td>
</tr>
<tr>
<td>80.</td>
<td>1.9031</td>
<td>4.73</td>
<td>180.</td>
<td>2.2553</td>
<td>9.08</td>
<td>280.</td>
<td>2.4363</td>
<td>10.51</td>
</tr>
<tr>
<td>90.</td>
<td>1.9542</td>
<td>5.32</td>
<td>190.</td>
<td>2.2788</td>
<td>9.28</td>
<td>290.</td>
<td>2.4472</td>
<td>10.58</td>
</tr>
<tr>
<td>100.</td>
<td>2.0000</td>
<td>5.88</td>
<td>200.</td>
<td>2.3010</td>
<td>9.47</td>
<td>298.1</td>
<td>2.4624</td>
<td>10.68</td>
</tr>
<tr>
<td>110.</td>
<td>2.0414</td>
<td>6.43</td>
<td>210.</td>
<td>2.3222</td>
<td>9.63</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**SPECIFIC HEATS AT HIGH TEMPERATURES**

Available data on the specific heat of zinc sulphide at high temperatures are meager. Bornemann and Hengstenberg (see footnote 60, p. 24) have summarized previous measurements, including the results of Lindner, whose publication was not available. The heat contents on a 0°–5° C. basis have been calculated as in earlier parts of this work, and the results plotted as curve \( H_e \) of Figure 9. Bornemann and Hengstenberg’s results are accepted as the best presently available. They used a sample of “Annam blende” containing 66.29 per cent Zn, 32.88 per cent S, 0.25 per cent Fe, 0.08 per cent Cu, and 0.30 per cent SiO₂. Correction has been made for the silica. The previously mentioned discontinuity between 700° and 800° C. is hardly perceptible on this scale chart, and the curve of heat content has been drawn to ignore any supposed effect in this range, as it is probably less than the experimental error. The analytic expression

\[
H_e (\text{per g formula}) = 0.10801 t + 5.21 \cdot 10^{-5} t^2 - 3.14 \cdot 10^{-6} t^3 \]  \hspace{1cm} (Equation 13)

conforms with the specific heat 10.51 per formula weight obtained at 273.1° K. (0° C.) from the low-temperature chart and expresses the data to about 2 per cent. Then

\[
H_e (\text{per g zns}) = 10.51 t + 5.07 \cdot 10^{-4} t^2 - 3.06 \cdot 10^{-6} t^3
\]

By differentiation, and substitution of \( t = T - 273.1 \) there is obtained expression
\[
C_v(T) = 7.05 + 15.15 \cdot 10^{-3}T - 9.17 \cdot 10^{-4}T^2 
\] (Equation 14)
valid from room temperature to 1,000° C. and probably not more than 5 per cent in error at 1,500°.

**Sublimation and Vapor Pressures; Melting Point**

No quantitative data on sublimation or the vapor pressure of zinc sulphide exist. Mellor \(^{64}\) says, "Many have observed that the sublimation temperature or temperature at which zinc sulphide volatilizes is near 1,000°." The experimental difficulties in avoiding chemical oxidation or reduction, or thermal dissociation, would seem to cast doubt upon this observation, even though the names of "many" were recorded. It is worth record that Tiede and Schleede \(^{65}\) were able to melt zinc sulphide at 1,800° to 1,900° C. under 100 to 150 atmospheres of nitrogen, with the formation of wurtzite on cooling. In a later part of this publication the dissociation of zinc sulphide will be discussed from a practical point of view. (See p. 89.)

**Thermal Data on Zinc Sulphide**

Available data on the heat of formation of zinc sulphide are: Berthelot,\(^{66}\) 43,000 calories; Thomsen,\(^{67}\) 39,570 calories; and Mixter,\(^{68}\) 41,300 calories. Although direct comparison of the methods used by these experimenters does not permit choice of the best result, it can be shown by indirect methods that the figure of Berthelot is probably the best. Thus, from the measurements of the solubility of zinc sulphide in acids of various concentrations measured by Glixelli,\(^{69}\) Bruner and Zawadzki\(^{70}\) were able to determine the solubility product of zinc sulphide as \(1.1 \cdot 10^{-24}\), when concentrations are expressed in mols per liter. Then for the reaction
\[
\text{ZnS}(s) = \text{Zn}^{++} + \text{S}^{--}
\] (Reaction 5)
\[
\Delta F_{298} = -RT \ln[\text{Zn}^{++}] [\text{S}^{--}]
\]
\[
= -1.9885.291 \cdot 2.3026 \cdot \log (1.1 \cdot 10^{-24})
\]
\[
= +31,900 \text{ calories.}
\]

Lewis and Randall give for the free energy of formation of zinc ion \(-34,984 \text{ calories and for sulphide ion +23,450, whence the free energy of zinc sulphide is calculated to be -43,450 calories. For the entropies of the reaction}
\[
\text{Zn} + \text{S}_{(c)} = \text{ZnS}
\]
\[
10.00 \quad 7.6 \quad 12.92 \quad \Delta S = -4.68
\]


\(^{66}\) Berthelot, M., Sur les principes generaux de la thermochimie: Douzieme memoire; Etudes et experiences sur les sulfures; Ann. chim. phys., sec. 6, Vol. 4, 1877, p. 137.

\(^{67}\) Thomsen, J., Thermochemistry (Burke): Longmans, Green & Co., London, 1908, p. 309.


the figures in a previous part of this paper are combined with the entropy of sulphur from Lewis and Randall. Then in the equation

\[ \Delta F = \Delta H - T \Delta S \]

\[ -43,450 = \Delta H - (-1,400) \]

\[ \Delta H = -44,850 \]

In the above calculations the difference in temperature between the reference point of Lewis and Randall (25° C.) and the experimental temperature (18°) has been ignored; and it is, moreover, improbable that the solubility determination should give the more precise figure for \( \Delta H \). It seems expedient, therefore, to adopt Berthelot's figure \( \Delta H = -43,000 \) for zinc sulphide and calculate

\[ \Delta F^0_{298°} (ZnS) = -41,600 \]

The experiments of Jellinek and Zakowski \(^{71}\) do not permit the calculation of an independent result of free energy.

There remain to be derived the standard free energy equation of formation of zinc sulphide, according to the reaction

\[ Zn(s) + S_{(s)} = ZnS \]  

(Reaction 6)

\[ C_{p\text{ZnS}} = 7.05 + 15.15 \cdot 10^{-3}T - 9.17 \cdot 10^{-7}T^2 \]

\[ C_{pS_{(s)}} = 4.12 + 4.7 \cdot 10^{-3}T \]

\[ C_{pZn_{(s)}} = 5.29 + 2.64 \cdot 10^{-3}T \]

\[ \Delta C_p = -2.36 + 7.81 \cdot 10^{-3}T - 9.17 \cdot 10^{-7}T^2 \]

\[ \Delta H_T = -42,637 - 2.36T + 3.91 \cdot 10^{-3}T^2 - 3.06 \cdot 10^{-7}T^2 \]

(Industrial 15)

\[ \Delta F^0_T = -42,637 + 2.36T \ln T - 3.91 \cdot 10^{-3}T^2 + 1.53 \cdot 10^{-7}T^3 - 9.14T \]

(Industrial 16)

**ZINC CARBONATE**

Thermodynamic data on zinc carbonate or the mineral smithsonite are meager, and only a brief review will be undertaken. No specific heats at low temperatures, from which the entropy can be calculated, are available. Lindner (see footnote 64, p. 27) measured the specific heats up to 400° C., which is near the decomposition temperature of the carbonate. Figure 10 shows the data. The results are moderately well expressed by the equation

\[ H_c(\text{per gram}) = 0.154t + 5 \cdot 10^{-5}t^2 \]

whence

\[ C_p(ZnCO_3) = 15.85 + 12.54 \cdot 10^{-3}T \]

(Equation 17)

valid to the decomposition temperature.

Quantitative determinations of the dissociation of zinc carbonate do not seem to have been made. Adequate thermal data are, however, available for zinc carbonate. Berthelot \(^{72}\) gave for the heat of


formation from the elements 194,200 calories. Recently Roth and Chall \(^\text{73}\) determined the heats of solution of zinc carbonate, oxide, and metal in 2 normal hydrochloric acid at 50° C., and from these data and the heat of formation of carbon dioxide it is possible to

![Heat-content curve for zinc carbonate](image)

**Figure 10.—Heat-content curve for zinc carbonate**

calculate a similar value, \(\Delta H_{328} = -194,120\). Therefore in the reaction

\[
\text{Zn} + \text{C} + \frac{3}{2} \text{O}_2 = \text{ZnCO}_3
\]

(Reaction 7)

\[
C_v(\text{Zn}) = 5.29 + 2.64 \cdot 10^{-3}T
\]

Authority: This publication (p. 28)

\[
C_v(\text{C}) = 1.22 + 4.89 \cdot 10^{-3}T - 1.11 \cdot 10^{-4}T^2
\]

Eastman. (See footnote 58.)

\[
C_v(\text{O}_2) = 9.75 + 1.50 \cdot 10^{-3}T
\]

Do.

\[
C_v(\text{ZnCO}_3) = 15.85 + 12.54 \cdot 10^{-3}T
\]

This publication.

\[
\Delta C_v = -0.41 + 3.51 \cdot 10^{-3}T + 1.11 \cdot 10^{-4}T^2
\]

\[
\Delta H_T = -194,180 - 0.41T + 1.755 \cdot 10^{-3}T^2 + 0.37 \cdot 10^{-5}T^3
\]

(Equation 18)

\[
\Delta H_{328} = -194,136
\]

These results agree almost exactly with those of Berthelot. Furthermore, Smith \(^{74}\) made accurate measurements of the solubility of zinc carbonate in solutions of carbonic acid from 4 to 40 atmospheres pressure at 25° C., which show little variation of the equilibrium constant over this range. Thus

\[
K = \frac{\alpha[Zn(HCO_3)]^2}{\sqrt{H_2CO_3}} = 3.36 \cdot 10^{-3}
\]

where \(\alpha\) is the dissociation of zinc bicarbonate assumed equal to that of zinc chloride. The solubility product of zinc carbonate \(K_3 = [Zn^{++}][CO_3^{--}]\) is then related to \(K\) by the expression

\[
K_3 = \frac{K^3(K_1)}{K_1}
\]

where \(K_1\) and \(K_2\) are the first and second dissociation constants of carbonic acid. Lewis and Randall give for these \(K_1 = 350 \cdot 10^{-7}, K_2 = 3.7 \cdot 10^{-11}\), whereas \(K_3 = 1.605 \cdot 10^{-11}\), \(\log K_3 = -10.794; -RT\ln K_3 = \Delta F = +14,733\). For the reaction

\[
ZnCO_3 = Zn^{++} + CO_3^{--} + \Delta F,
\]

\[x = -34,984 - 125,760 + 14,733,
\]

\[x = -175,477
\]

Furthermore, since \(\Delta F = \Delta H - T\Delta S\), for the reaction

\[
Zn + C + \frac{3}{2}O_2 \rightarrow ZnCO_3 + \Delta S
\]

\[10.00 \quad 1.3 \quad 73.65x - 62.6
\]

\[x = S_{298}^{0}(ZnCO_3) = 22.4
\]

The standard free-energy equation for the formation of zinc carbonate from its elements may now be derived on the basis of equation 18, as

\[
\Delta F_{298}^{0} = -194,180 + 0.41 TlnT - 1.76 \cdot 10^{-3}T^2 - 1.85 \cdot 10^{-7}T^3 + 60.95T \quad (\text{Equation 19})
\]

**Zinc Silicates**

With the exception of heats of formation there are practically no thermodynamic data on the zinc silicates. The former figures were obtained by Mulert \(^{75}\) with only moderate precision. Thus he estimated from Kopp's rule that the specific heat of the orthosilicate \(Zn_2SiO_4\) is 0.14 calorie per gram = 31.2 per formula weight. Similarly the specific heat of the metasilicate \(ZnSiO_3\) is 0.16 calorie per gram = 22.6 per formula weight. Furthermore, he gives the following thermal data:

Reaction 8. \(-2ZnO + SiO_2\) (amorphous) \(\rightarrow\) \(Zn_2SiO_4\) (glassy) \(\Delta H_{298} = 23,740\).

Reaction 9. \(-2ZnO + SiO_2\) (amorphous) \(\rightarrow\) \(Zn_2SiO_4\) (crystalline) \(\Delta H_{298} = 14,700\).

Reaction 10. \(-ZnO + SiO_2\) (amorphous) \(\rightarrow\) \(ZnSiO_3\) (crystalline) \(\Delta H_{298} = -2,490\).


Since Kopp's rule was used to calculate the specific heats $\Delta C_p$ is assumed zero in these reactions.

The mineral calamine is a hydrated zinc silicate, with considerable uncertainty as to silicate degree. Mulert attempted some work on hydrous-zinc silicates, but the differences in heat of solution between this and true metasilicate were within his experimental error. His results are probably not better than 5 per cent accuracy, and the figures reported are in consequence only valid for very rough calculations. The results serve to show, however, that metasilicate will not behave very differently from zinc oxide in reduction reactions.

**ZINC SULPHATE**

Although zinc sulphate is not directly smelted, as one of the possible products of roasting of blende and as an important material in the hydrometallurgy of zinc, its thermodynamic properties have considerable interest. For zinc sulphate and its hydrated salts, there is a very considerable body of thermodynamically usable data, much of the work having been stimulated by the former use of the Clark cell as an electromotive force standard; but, as will be pointed out, there are notable discrepancies in the available information.

**FORMS OF ZINC SULPHATE**

There exist at least three well-defined hydrates of zinc sulphate, although more have been reported in older work. There also may be two allotrophic forms of the anhydrous salt, although thermodynamically the data are explained on the supposition of a basic salt. The hydrate forms that seem to have the best evidence of existence are the ones with 1, 6, and 7 formula weights of water per formula weight of anhydrous salt. The heptahydrate is stable up to 39.0° C., the hexahydrate from thence to about 70° C., and the monohydrate to nearly 300°. The vapor pressures of water above pairs of these salts have been determined, and the data have been reviewed by Wilson, but a discussion of the results as summarized by Wilson follows best a summary of the available specific heat and thermal data.

**SPECIFIC HEATS AT LOW TEMPERATURES**

Specific heat measurements at low temperatures of the heptahydrate have been made by Pollitzer and by Jackson. At higher temperature there are available only the results of Rolla and Accame, Schottky, and the very old figures of Pape.

The low-temperature results for ZnSO$_4$·7H$_2$O have been plotted on Figure 11. The estimation of entropy is somewhat inaccurate, since the high-heat capacity even at the temperatures of liquid hydrogen prevents the direct use of the Debye function extrapolation.

---

81 Pape, C., über die specifische Wärme wasserfreier und wasserhaltiger schwefelsaurer Salze: Poggendorf's Ann., vol. 120, 1863, p. 337.
In order to be able to apply the Debye curve the values of \( \frac{C_p}{4} \) per mole have been plotted, and it is then possible to fit a Debye curve of parameter \( \beta \nu = 175 \); this being equivalent to saying that the total specific heat is the sum of four equal functions of that parameter. The entropy below \( \log T = 1.5 \) is then found by the tables to be 0.774 and the entropy per mole, 2.98. The area under the curve from \( \log T = 1.5 \) to \( \log T = 2.4744 \) (\( T = 295.1 \)) is directly determined at 89.75 entropy units, and the total \( \Delta S_{298}^o = 92.7 \). Because these measurements were early ones and not of the precision that is now obtainable experimentally, the error may be as great as 1 or 2 entropy units.

![Figure 11](image_url)

**Figure 11.**—Thermodynamic data on zinc sulphate. Main curve shows specific heat of the heptahydrate at low temperatures as a function of logarithmic temperature. Curve \( C_p/4 \) is quarter value of specific heats at lower temperatures, where the Debye function is approximately fitting. Shaded area is the extrapolated area used for calculating entropy by the Debye function. Upper curve represents the thermal decomposition equilibrium constant for anhydrous sulphate as a function of reciprocal temperature.

The specific heats of the various hydrate forms near room temperature are summarized in Table 12.

**Table 12.**—Specific heats of zinc sulphate and its hydrates

<table>
<thead>
<tr>
<th>Salt</th>
<th>( C_p ) per formula weight</th>
<th>Temperature, °C.</th>
<th>Observer</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄</td>
<td>28.1</td>
<td>22-100</td>
<td>Pape.</td>
</tr>
<tr>
<td>ZnSO₄·1 H₂O</td>
<td>34.7</td>
<td>9</td>
<td>Rolla and Accent.</td>
</tr>
<tr>
<td>ZnSO₄·6 H₂O</td>
<td>98.8</td>
<td>9</td>
<td>Do.</td>
</tr>
<tr>
<td>ZnSO₄·7 H₂O</td>
<td>93.4</td>
<td>9</td>
<td>Do.</td>
</tr>
<tr>
<td>ZnSO₄·7 H₂O</td>
<td>96.4</td>
<td>25</td>
<td>Figure 11.</td>
</tr>
</tbody>
</table>
THERMAL DATA AND FREE ENERGIES

Thomson's figures for the heats of hydration of zinc sulphate can not be much in error, even though he reports figures for several hydrates that do not exist. Mellor 82 has incorrectly reported Thomson's figures, and included the results of Favre and Valson 83 as representing a formula weight, when they are actually per equivalent and are not comparable until multiplied by 2.

The heat of formation of the anhydrous salt from its elements according to Berthelot 84 is 229,600, but this was corrected by De Forcrand 85 to 230,910. Thomson's figure for the formation of zinc sulphate from oxygen and sulphur dioxide is 158,990, which combined with the figure selected by Lewis and Randall for SO₂, gives 228,000 for the formation from the elements. It is known, however, that Thomson's measurements on zinc oxide involved here were 2,200 calories too high, so that if this be applied as a correction, Thomson's figure should be 230,200.

Table 13 summarizes the thermal data and shows the values selected for use.

<table>
<thead>
<tr>
<th>Material</th>
<th>Produced from</th>
<th>Heat evolved at 18° or 10°C.</th>
<th>Observer</th>
<th>Selected value ΔH₂₉₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄</td>
<td>Zn, S, O</td>
<td>Calories 220,600</td>
<td>Berthelot</td>
<td>-230,000</td>
</tr>
<tr>
<td>ZnSO₄·H₂O</td>
<td>ZnSO₄·H₂O (l)</td>
<td>8,484</td>
<td>De Forcrand</td>
<td>-8,550</td>
</tr>
<tr>
<td>ZnSO₄·3H₂O</td>
<td>ZnSO₄·3H₂O (l)</td>
<td>22,694</td>
<td>Thomsen (corr.)</td>
<td>-11,000</td>
</tr>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>ZnSO₄·7H₂O (l)</td>
<td>22,720</td>
<td>Thomsen</td>
<td>-23,000</td>
</tr>
</tbody>
</table>

With this background of information the thermal decomposition of the hydrates may be more closely considered. From Wilson's table the partial pressure of water vapor above the heptahydrate at 25° C. is taken as 13.6 mm. = 0.0179 atmosphere, representing a number of concordant determinations. Then for the reaction

\[ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O} (g) \]

\[ \Delta F_{298} = -RTlnp \]

\[ = +2,386 \text{ calories} \]

As an independent check the cell measurements of Cohen and Inouye 86 may be considered. They found that a zinc amalgam electrode in contact with the heptahydrate compared to a similar electrode in the hexahydrate had an electromotive force of 6.03

millivolts at 25° C. and 1 atmosphere pressure. Then for the reaction:

\[ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O} (l) \]

\[ \Delta F_{298} = -NFE = 2 \times 23,074 \times 0.00603 = 278 \text{ calories} \]

To render this comparable with the previous equation there must be added \( \text{H}_2\text{O} (l) = \text{H}_2\text{O} (g) \) \( \Delta F_{298} = 2,053 \); \( 2,053 + 278 = 2,331 \) calories compared to 2,386 by direct measurement. The direct result, \( \Delta F_{298} = 2,386 \), will be taken for calculation.

Similarly, for the reaction

\[ \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} = \text{ZnSO}_4 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O} (g) \]

\[ p = 13.0 \text{ mm. (from Wilson's table)} \]

\[ \Delta F_{298} = 5 \times 2,412 = +12,060 \text{ calories} \]

In this case data for check other than vapor-pressure measurements are not available, but the concordance in experimental results indicated by Wilson’s table does not lead to much doubt as to the results obtained.

For the final step of dehydration represented by reaction \( \text{ZnSO}_4 \cdot 1\text{H}_2\text{O} = \text{ZnSO}_4 + \text{H}_2\text{O} (g) \) the data are not so reliable. From Wilson’s table the partial pressure of water vapor over the monohydrate was given by Müller-Erzbach as 0.5 mm., whereas Foote and Scholes \(^{57}\) reported 1.0 mm. However, Lescoeur \(^{88}\) reported a vapor pressure of 162 mm. at 174.5° C. For present purposes the reaction above may be written as the sum of the following:

\[ \text{ZnSO}_4 \cdot \text{H}_2\text{O} = \text{ZnSO}_4 + \text{H}_2\text{O} (l) \text{ (Reaction 12)} \quad \Delta H_{298} = 8,550 \text{ (Table 13)} \]

\[
\begin{align*}
\text{H}_2\text{O} (l) & = \text{H}_2\text{O} (g) \\
\text{ZnSO}_4 \cdot \text{H}_2\text{O} & = \text{ZnSO}_4 + \text{H}_2\text{O} (g) \\
C_p & = 34.7 \\
& = 28.1 \\
& = 8.5 \\
\Delta H_v & = +18,444 \\
\Delta F_{298} & = 18,444 - 1.9 T \ln T + IT
\end{align*}
\]

For 1 mm. at 25° C. \( \Delta F_{298}^0 = +3,934 \), but for Lescoeur's results,

\[ \Delta F_{298}^{0,4} = -4.578 \cdot 447.6 \log_{760} 162 \]

\[ = +1,375 \]

\[ I = -26.52 \]

\[ \Delta F_{298} = +8,300 \]

The great discrepancy between the two values of \( \Delta F_{298}^0 \) could not be explained by possible uncertainties in the specific heats involved. To decide between these values recourse may be had to the data of Friedrich and Blicke,\(^{89}\) who made a study of the thermal effects involved upon heating zinc sulphate. A sudden absorption of heat occurred in this work beginning at 275° C., reaching a maximum at


300°. The weight changes showed water to be given off in this range. If it be assumed that the pressure of water vapor above the monohydrate was 1 atmosphere at 275°, then

$$\Delta F_{148}^0 = 0 = 18,444 - 1.9 T \ln T + IT$$

$$I = -21.69$$

$$\Delta F^o_{298} = +8.754$$

This confirms the magnitude of Lesceour's figure. The figure $\Delta F^o_{298} = +8.754$ will be selected for the present use.

In the work of Foote and Scholes the change of concentration of the absolute alcohol used when saturated with the monohydrate of zinc sulphate amounted to only a few tenths of 1 per cent, and the vapor-pressure curve was ill defined at the end. Unless quite extraordinary precautions are taken against accidental absorption of water and in the estimation of the water content of the alcohol, it seems improbable that this method could furnish satisfactory results upon materials of very low water-vapor tension, such as zinc monohydrate.

If now the free energy of the reaction $ZnSO_4 \cdot 7H_2O = ZnSO_4 + 7H_2O(g)$ (reaction 11) is obtained by the addition of the similar reactions for the three hydrates,

$$\Delta F^o_{298} = +2,386 + 12,060 + 8,754$$

$$= +23,200$$

The heat of reaction (11) is the negative heat of hydration $\Delta H_{298} = 23,000$ plus the heat of vaporization of 7 formula weights of water, $7 \times 10,450 + 96,150$ calories in total. Since

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

$$\Delta S = \frac{96,150 - 23,200}{298.1}$$

$$= +244.7$$

For calculation of the entropy and free energy of anhydrous sulphate there is still needed the entropy of water vapor at 25° C. The entropy of liquid water is obtainable from the tables of Simon as 15.80. Furthermore, for the reaction

$$H_2O(l) = H_2O(g)$$

$$\Delta H_{298} = 10,450$$

$$\Delta F_{298} = 2,053$$

$$\Delta S = \frac{10,450 - 2,053}{298.1}$$

$$= +28.15$$

and the entropy of water vapor is $S^o_{298} = 15.82 + 28.15 = 43.95$.

---

Referring again to reaction 11,
\[
\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = \text{ZnSO}_4 + 7\text{H}_2\text{O} \quad (g)
\]
\[
S^\circ_{298} = 92.7 \times 307.7 \quad \Delta S = 244.7
\]
\[
X = S^\circ_{298} (\text{ZnSO}_4) = 29.7
\]
Then finally for the formation of anhydrous zinc sulphate there is obtained:
\[
\text{Zn}(s) + 8(rh) + 2 \text{O}_2 = \text{ZnSO}_4(\text{anhyd}) \quad \text{(Reaction 13)}
\]
\[
\begin{array}{ccc}
C_p & 6.1 & 5.5 & 13.6 & 28.1 & \Delta C_p = +2.9 \\
S^\circ_{298} & 10.0 & 7.6 & 98.1 & 29.7 & \Delta S = -86.0
\end{array}
\]
\[
\Delta H^\circ_{298} = -230,000 = \Delta H^\circ_\circ + 2.9T
\]
\[
\Delta H^\circ_\circ = -230,870
\]
\[
\Delta F^\circ_{298} = -230,000 - 298.1(-86.0)
\]
\[
\Delta F^\circ_{298} = 204,350
\]
\[
= -230,870 - 2.9T \ln T + 105.5T
\]
\[
I = +105.5
\]
\[
\Delta F^\circ_\circ = -230,870 - 2.9T \ln T + 105.5T \quad \text{(Equation 20)}
\]

There remains to be accomplished a comparison of these figures obtained solely from low-temperature experiments with the results of experiments at high temperatures. The equilibrium pressures of the dissociation of zinc sulphate have been measured by Wöhler and Plüddemann. These authors by an ingenious method determined the total gas pressure, consisting of a presumably equilibrium mixture of SO\(_3\), SO\(_2\), and O\(_2\), produced by heating the sulphate, but did not determine the composition of the gas. If it is assumed that equilibrium in the reaction
\[
\text{SO}_3 = \text{SO}_2 + 1/2\text{O}_2 \quad \text{(Reaction 14)}
\]
was reached in these experiments, the gas compositions may be calculated. If \(p\) is the total pressure of the evolved gas, and \(p_{\text{SO}_3}\), \(p_{\text{SO}_2}\), and \(p_{\text{O}_2}\) the partial pressures of sulphur trioxide, sulphur dioxide, and oxygen, then
\[
p = p_{\text{SO}_3} + p_{\text{SO}_2} + p_{\text{O}_2}
\]
Furthermore, from the stoichiometric relations,
\[
p_{\text{SO}_2} = 2p_{\text{O}_2}
\]
and finally, from the equilibrium expression for reaction (14)
\[
K_{14} = \frac{(p_{\text{SO}_3})(p_{\text{O}_2})^{1/2}}{p_{\text{SO}_2}}
\]
By combination
\[
p = \frac{0.707}{K_{14}} (p_{\text{SO}_3})^{3/2} + 1.5 p_{\text{SO}_2} \quad \text{(Equation 21)}
\]

\(K_{14}\) is calculated from the free-energy equation of Lewis and Randall for the reaction and equation (21) is solvable by graphic methods.


when \( p \) is known. From the result for \( p_{SO_2} \) oxygen is immediately known as \( \frac{p_{SO_2}}{2} \) and \( p_{SO_3} \) is the difference between \( p \) and the sum of sulphur dioxide and oxygen pressures.

The hypothetical reaction for the dissociation of zinc sulphate is

\[
\text{ZnSO}_4(s) = \text{ZnO}(s) + \text{SO}_2(g)
\]

(Reaction 15)

where \( K_{15} = p_{SO_3} \).

Table 14 shows the figures obtained by the above calculations from Wöhler and Plüddemann's experimental results. The two final columns furnish figures which may be plotted, as is done in the upper left corner of Figure 11, which shows \( \log K_{15} \) vs. \( \frac{1}{T} \).

Table 14.—Dissociation of zinc sulphate (data of Wöhler and Plüddemann)

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature, °C</th>
<th>( p_0 ), observed atmosphere</th>
<th>( 1/K_{15} )</th>
<th>( p_{SO_2} ) atmosphere</th>
<th>( p_{SO_3} = K_{15} ) atmospheres</th>
<th>Temperature, °K</th>
<th>( \frac{1}{T} \times 10^4 )</th>
<th>( \log p_{SO_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>575</td>
<td>0.0066</td>
<td>3.478</td>
<td>0.0040</td>
<td>6.10^4</td>
<td>945</td>
<td>10.55</td>
<td>-3.222</td>
</tr>
<tr>
<td>2</td>
<td>690</td>
<td>0.0079</td>
<td>2.885</td>
<td>0.0049</td>
<td>5.2.10^4</td>
<td>963</td>
<td>10.38</td>
<td>-3.294</td>
</tr>
<tr>
<td>3</td>
<td>720</td>
<td>0.0316</td>
<td>2.630</td>
<td>0.0368</td>
<td>3.4.10^4</td>
<td>993</td>
<td>10.07</td>
<td>-2.468</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>0.0902</td>
<td>1.444</td>
<td>0.1623</td>
<td>1.065.10^4</td>
<td>1,023</td>
<td>9.75</td>
<td>-1.951</td>
</tr>
<tr>
<td>5</td>
<td>775</td>
<td>0.1474</td>
<td>1.108</td>
<td>0.0852</td>
<td>1.96.10^4</td>
<td>1,048</td>
<td>9.54</td>
<td>-1.708</td>
</tr>
<tr>
<td>6</td>
<td>800</td>
<td>0.2487</td>
<td>.861</td>
<td>0.1438</td>
<td>3.3.10^4</td>
<td>1,073</td>
<td>9.32</td>
<td>-1.481</td>
</tr>
</tbody>
</table>

It will be noted that the three upper points lie nearly upon a straight line (slope \( \Delta H = +47,200 \)), as is required by theory, but the lower points are erratic. This is partly explained by the second thermal point in the work of Friedrich and Blicke (see footnote 89, p. 34), who found a supposed transition point in zinc sulphate at 740° C. \( T = 1,013°, \frac{1}{T} = 9.87 \times 10^{-4} \). The break in the curve of Wöhler and Plüddemann confirms the discontinuity observed, and their data extrapolated to this point show a result \( K_{15} = -2.06 \), which may be considered a significant point, since at this temperature the free energies of the forms of zinc sulphate stable at high and low temperatures must be equal if the break is actually due to a transition.

That reaction (15) does not represent the true state of dissociation of the supposed \( \alpha \) form of zinc sulphate (that stable to 740°) can readily be shown by the calculation of the value of \( K_{15} \) at the transition point, using the previously given figures for the free energy and heat of formation of zinc sulphate. It is true that no adequate specific heats at high temperatures are available for zinc sulphate and sulphur trioxide. In the former case there is only the mean value for 22° to 100° C. For a similar range of temperature the mean specific heat of zinc oxide is 10.2. For sulphur trioxide it may be assumed, as Lewis and Randall have done with marked success for the dissociation of sulphur trioxide to dioxide and oxygen, that the specific heat of the
trioxide is identical with the sum of $\text{SO}_2 + 1/2 \text{O}_2 = 12.6$ over this same range. Then $\Delta C_p$ for this hypothetical reaction is $-5.3$.

$$a\text{ZnSO}_4 = \text{ZnO} + \text{SO}_4(g) \text{ (hypothetical)}$$

$C_p$ 28.1 10.2 12.6 $\Delta C_p = -5.3$

$\Delta H_{298} = -230,000 - 83,200 - 91,600 \text{ (Lewis and Randall)}$ $\Delta H_{298} = +55,200$

$\Delta H_o = +56,700$

$\Delta F_{298} = -204,350 - 75,930 - 85,890 \text{ (Lewis and Randall)}$ $\Delta F_{298} = 42,430$

$\Delta F_{o,T} = 56,700 + 5.3 \ln T - 78.1 T \text{ (hypothetical)}$

$\Delta F_{1,015} = 14,700$

$\log K_{15(1,015)} = -3.17$

The discrepancy disclosed here between the actual $K_{15} = -2.06$, and the calculated $K_{15} = -3.17$ is too great to be ascribable to uncertainties of specific heats.

Friedricks and Blick (see footnote 89, p. 34) showed, however, that a basic sulphate of zinc was formed which had the composition of $3\text{ZnO} \cdot 2\text{SO}_3$. If it is tentatively assumed that the reaction for Wöhler and Plüddemann’s upper three points was actually

$$1/2(3\text{ZnO} \cdot 2\text{SO}_3) = 3/2\text{ZnO} + \text{SO}_3 \quad \text{(Reaction 16)}$$

the peculiarities of the system immediately become explicable. The former authors are emphatic in reporting that weight changes did not take place at 740° and that the basic sulphate did not dissociate until 930° C., yet this apparent discrepancy may have been due to the rapid heating rate in their experiments (10° in 15 to 20 seconds) as compared with the approximately static conditions of the latter experiments. It is certain that under Wöhler and Plüddemann’s conditions dissociation took place below 740°.

In reaction (16) it may further be assumed from stochiometry that $\Delta C_p$ is two-thirds of the $\Delta C_p$ of hypothetical reaction (15) and that the observed heat $\Delta H = +47,200$ (from the slope of the upper line) is correct at the middle temperature (775° C. = 1,048° K.). This allows for a slight curvature.

Then

$$47,000 = \Delta H_o - 3.5T$$

$\Delta H_o = 50,820$

$\Delta H_{298} = 49,780$

The heat of formation of $1/2 \ (3\text{ZnO} \cdot 2\text{SO}_3)$ from reaction (16) is

$$\Delta H_{298} = -(3/2 \cdot 83,200 + 91,600 + 49,780) = -266,180$$

and per formula weight

$$\Delta H_{298}(3\text{ZnO} \cdot 2\text{SO}_3) = -532,360$$
THERMODYNAMIC PROPERTIES OF ZINC AND ITS COMPOUNDS

If log $K_{15(1,012)} = -2.06$, then $\Delta F^0_{1,013} = +9,550$ calories; and

$$9,550 = 50,820 + 3.5 T \ln T + I T$$

$I = -65.0$

$$\Delta F^0_T = 50,820 + 3.5 T \ln T - 65.0 T \quad \text{(Equation 22)}$$

$$\Delta F^0_{298} (3ZnO \cdot 2SO_3) = -474,340$$

Below 740°, according to this hypothesis, the reaction is

$$3ZnSO_4 = 3ZnO \cdot 2SO_3 + SO_3 \quad \text{(Reaction 17)}$$

$$\Delta H_{298} = -3 \times 230,000 - 532,360 - 91,600 = 66,040 = \Delta H_a - 1.8 T$$

$$\Delta H_a = 71,700$$

$$\Delta F^0_{298} = -3 \times 204,350 - 474,340 - 85,890 = 52,820$$

Then

$$\Delta F^0_{298} = 52,820 = 71,700 + 1.87 \ln T + I T$$

$I = -73.6$

$$\Delta F^0_T = 71,700 + 1.8 T \ln T - 73.6 T \quad \text{(Equation 22)}$$

As final check on the validity of these assumptions and calculations, if $T = 1,013$ is substituted, $\Delta F^0_{1,013} = +9,710$, compared with the observed 9,550, which must be considered a remarkable degree of concordance.

In conclusion, the question as to whether or not there is a true transition in zinc sulphate at 740° must be left in abeyance until more complete data are available. The thermodynamics of zinc sulphate decomposition is adequately consistent if it is assumed that up to 740° C. on slow heating, basic sulphate is formed, but above that only oxide. Rapid heating results in mixtures with indefinite composition but with definite thermal phenomena.

SUMMARY

For convenience of reference the following tables summarize the results obtained in this section.

**Table 15.—Specific heats**

[Quadratic equations of the form $C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2$]

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Gamma_0$</th>
<th>$\Gamma_1 \times 10^3$</th>
<th>$\Gamma_2 \times 10^2$</th>
<th>Temperature range of actual determinations, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (solid)</td>
<td>5.29</td>
<td>+2.64</td>
<td></td>
<td>0 to 419.5.</td>
</tr>
<tr>
<td>Zn (liquid)</td>
<td>7.02</td>
<td>+1.18</td>
<td></td>
<td>419.5 to 850.</td>
</tr>
<tr>
<td>Zn (gas)</td>
<td>6.00</td>
<td>+11.26</td>
<td>-47.22</td>
<td>0 to 1,300.</td>
</tr>
<tr>
<td>ZnO</td>
<td>7.05</td>
<td>+15.15</td>
<td>-9.17</td>
<td>0 to 1,000.</td>
</tr>
<tr>
<td>ZnS</td>
<td>15.85</td>
<td>+12.54</td>
<td></td>
<td>0 to 400. Kopp's rule.</td>
</tr>
<tr>
<td>ZnSO3</td>
<td>31.2</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>ZnSO4·H2O</td>
<td>96.5</td>
<td></td>
<td></td>
<td>0 to 20.</td>
</tr>
<tr>
<td>ZnSO4</td>
<td>28.1</td>
<td></td>
<td></td>
<td>0 to 100.</td>
</tr>
</tbody>
</table>
Table 16.—Standard entropies, heats of formation, and free energies

<table>
<thead>
<tr>
<th>Substance</th>
<th>$S_{298}$</th>
<th>$\Delta H_{298}$</th>
<th>$\Delta F_{298}$</th>
<th>Reference points of $\Delta H$ and $\Delta F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (solid)</td>
<td>10.00 ± 1</td>
<td>0</td>
<td>$+755 ±53$</td>
<td>Zn (solid), Do.</td>
</tr>
<tr>
<td>Zn (liquid)</td>
<td>11.29 ± 2</td>
<td>+1,141 ±50</td>
<td>+22,917 ±50</td>
<td></td>
</tr>
<tr>
<td>Zn (gas)</td>
<td>38.92 ± 2</td>
<td>+31,698 ±50</td>
<td>+75,300 ±60</td>
<td>Zn, $\frac{1}{2}$ O$_2$.</td>
</tr>
<tr>
<td>ZnO</td>
<td>10.44 ± 2</td>
<td>-83,260 ±60</td>
<td>-75,930 ±60</td>
<td>Zn, $\frac{1}{2}$ O$_2$.</td>
</tr>
<tr>
<td>ZnS</td>
<td>12.92 ± 5</td>
<td>-43,000 ±500</td>
<td>-41,600 ±500</td>
<td>Zn, S($\sigma$), Zn, C, $\frac{3}{2}$ O$_2$.</td>
</tr>
<tr>
<td>ZnCO$_3$ (crystalline)</td>
<td>22.4 ±1</td>
<td>-194,180 ±300</td>
<td>-175,477 ±500</td>
<td></td>
</tr>
<tr>
<td>ZnS$_2$O$_5$ (crystalline)</td>
<td>92.7 ±1</td>
<td>-230,000 ±500</td>
<td>-294,350 ±500</td>
<td>ZnS, S($\sigma$), 2O$_2$.</td>
</tr>
<tr>
<td>ZnSO$_4$ (anhydrous)</td>
<td>29.7 ±1</td>
<td>-532,360 ±500</td>
<td>-474,340 ±500</td>
<td>ZnS, S($\sigma$), $\frac{9}{2}$ O$_2$.</td>
</tr>
<tr>
<td>ZnO · 2SO$_3$</td>
<td>79.1 ±2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 17.—Standard free-energy equations of formation

$$[\Delta F^0_f = \Delta H_f + A \ln T + BT^2 + CT^3 + \ldots + D/T]$$

<table>
<thead>
<tr>
<th>Substances</th>
<th>Reference</th>
<th>$\Delta H^0_f$</th>
<th>$A$</th>
<th>$B \times 10^6$</th>
<th>$C \times 10^6$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(gas)</td>
<td>Zn (g)</td>
<td>+31,772</td>
<td>0.29</td>
<td>+1.98</td>
<td>-13.77</td>
<td>0.24</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn (l)</td>
<td>+31,087</td>
<td>2.09</td>
<td>+7.67</td>
<td>+10.27</td>
<td>1.84</td>
</tr>
<tr>
<td>Zn (liquid)</td>
<td>Zn (s)</td>
<td>+685</td>
<td>1.80</td>
<td>+7.45</td>
<td>+33.79</td>
<td>0.26</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn (s), $\frac{1}{2}$ O$_2$</td>
<td>-83,593</td>
<td>-8.1</td>
<td>-6.0</td>
<td>+2.62</td>
<td>+33.79</td>
</tr>
<tr>
<td>Zn (gaseous), CO$_2$</td>
<td>ZnO (s), CO</td>
<td>+47,397</td>
<td>6.99</td>
<td>+3.285</td>
<td>-0.63</td>
<td>-9.14</td>
</tr>
<tr>
<td>ZnS$_2$</td>
<td>Zn (s), S ($\sigma$)</td>
<td>-42,637</td>
<td>2.36</td>
<td>-3.91</td>
<td>+1.53</td>
<td>-0.91</td>
</tr>
<tr>
<td>ZnCO$_3$</td>
<td>Zn (s), C ($\sigma$), $\frac{3}{2}$ O$_2$</td>
<td>-194,180</td>
<td>4.1</td>
<td>-1.76</td>
<td>-1.85</td>
<td>+60.95</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>Zn (s), S ($\sigma$), 2O$_2$</td>
<td>-230,870</td>
<td>-2.9</td>
<td>+1.8</td>
<td>-78.6</td>
<td>-105.5</td>
</tr>
<tr>
<td>(ZnO · 2SO$_3$) , SO$_3$</td>
<td>ZnSO$_4$</td>
<td>+71,700</td>
<td>+1.8</td>
<td>+7.0</td>
<td>-130.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 18.—Vapor pressures of solid and liquid zinc

\[
\text{Zn(l) } \log p_{\text{atmos.}} = 9.1373 - \frac{6789.5}{T} - 0.1051 \log T - 1.255 \times 10^{-4} T
\]

\[
\log p_{\text{pm}} = 11.9181 - \frac{6789.5}{T} - 0.1051 \log T - 1.255 \times 10^{-4} T
\]

\[
\text{Zn(s) } \log p_{\text{atmos.}} = 6.8948 - \frac{6939.0}{T} - 0.1458 \log T - 2.883 \times 10^{-4} T
\]

\[
\log p_{\text{pm}} = 9.7756 - \frac{6939.0}{T} - 0.1458 \log T - 2.883 \times 10^{-4} T
\]

In Table 15, which shows the specific heats above room temperature chosen for zinc and its metallurgically important compounds, the temperature intervals over which the determinations were made have been indicated. The author has at times not hesitated to use such expressions for purposes of extrapolation. Wherever calculated results are obtained by such practice the limitations of accuracy involved must not be forgotten.

Similarly, in Table 16, where are shown entropies, heats of formation, and free energies at 25°C, effort has been made to indicate the probable uncertainty. For zinc metal in its various forms and for zinc oxide sufficient correlation of thermodynamic results was possible to justify the belief that the possible errors indicated actually
represent the extent to which possible future more accurate
determinations may coincide. For the remaining materials such
comparisons were not possible, and the actual error may contain
unestimated errors in calorimetric determinations.

Table 17 shows only the standard free-energy equations of forma-
tion, and the reader should note that in the use of these equations
for the calculation of other reactions care should be taken that con-
sistent values of specific heat are selected. For example, if it is
desired to calculate the reaction ZnCO₃ = ZnO + CO₂, the specific heat
for the carbon dioxide must be taken in accordance with the accepted
value of Eastman and not from Lewis and Randall.

The vapor-pressure equations of Table 18 represent the "best"
average of the various investigations and cover a very wide range
of temperatures. No hesitation need be felt in applying these equa-
tions for any temperature range up to 1,500° C.
Part II. ZINC OXIDE AND CARBON

"TEMPERATURE OF REDUCTION"

The reduction of zinc oxide by carbon is the only important method of zinc pyrometallurgy at present. Many attempts have been made to investigate directly the conditions under which carbon will reduce zinc oxide. Although such tests serve to indicate the qualitative facts, because of the nature of the reactions taking place they are inherently unsuited for accurate quantitative data. The results obtained depend on reaction rates and the sensitiveness of the criterion used. Chiefly, such experiments have attempted to measure the temperature at which carbon begins to reduce zinc oxide. An excellent résumé of such work is given by Zeller and O'Harra. Since this bulletin may not be available to some readers, the results of previous investigations reviewed in it are summarized in Table 19.

Table 19.—Temperature of reduction of zinc oxide by carbon

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Reference</th>
<th>Method</th>
<th>Results, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hempel</td>
<td>(o)</td>
<td>Direct</td>
<td>910 to 1,300.</td>
</tr>
<tr>
<td>Frost</td>
<td>(e)</td>
<td>Heating in bomb.</td>
<td>1,075</td>
</tr>
<tr>
<td>Schappaus and Longwitz</td>
<td>(e)</td>
<td>Direct</td>
<td>910</td>
</tr>
<tr>
<td>Boudouard</td>
<td>(e)</td>
<td>Direct</td>
<td>1,125</td>
</tr>
<tr>
<td>Johnson</td>
<td>(e)</td>
<td>Zinc flame at outlet</td>
<td>1,010 to 1,120.</td>
</tr>
<tr>
<td>Doelitz and Graumann</td>
<td>(e)</td>
<td>Sugar carbon+ZnO in Na</td>
<td>890</td>
</tr>
<tr>
<td>Sickly and Clayton</td>
<td>(e)</td>
<td>Direct</td>
<td>900 to 950.</td>
</tr>
<tr>
<td>Bodenstein and Schubart</td>
<td>(e)</td>
<td>do</td>
<td>1,012</td>
</tr>
<tr>
<td>Doelitz, Graumann, Bodenstein and Schubart</td>
<td>(e)</td>
<td>Calculated</td>
<td>780</td>
</tr>
<tr>
<td>Fulton</td>
<td>(o)</td>
<td>Gas evolution</td>
<td>910 to 980.</td>
</tr>
<tr>
<td>Lemarchand</td>
<td>(o)</td>
<td>Calculated</td>
<td>762 to 1,058.</td>
</tr>
<tr>
<td>Pirroni</td>
<td>(o)</td>
<td>Calculated</td>
<td>826</td>
</tr>
</tbody>
</table>

The causes for the wide discrepancy in the above figures have been variously ascribed to differences in physical form of the zinc oxide and carbon. Only Bodenstein and Schubart seem to have realized clearly that the pressure of the gas phase affected the results; only Zeller and O’Harra have understood clearly that “The equilibrium temperature of the reaction can not vary unless the different forms of zinc oxide and carbon are truly allotropic modifications.” Confusion has resulted from failure to distinguish between chemically static and dynamic systems of zinc oxide and carbon.

The complete reaction taking place in a zinc retort may be written

\[(x+2y)\text{ZnO} + (x+y)\text{C} = (x+2y)\text{Zn} + x\text{CO} + y\text{CO}_2\]  \hspace{1cm} (Reaction 1)

but this formulation does not clarify the analysis of the conditions of the reaction; it merely reiterates that carbon and zinc oxide, when heated together, produce certain, generally indeterminate, amounts of zinc vapor, carbon monoxide, and carbon dioxide. Reaction (1) is obviously the sum of

\[x\text{ZnO} + x\text{C} = x\text{Zn} + x\text{CO}\] \hspace{1cm} (Reaction 1a)

\[2y\text{ZnO} + y\text{C} = 2y\text{Zn} + y\text{CO}_2\] \hspace{1cm} (Reaction 1b)

yet these reactions certainly do not express consecutive steps of combination, and do not have any relationship to the actual mechanism of zinc oxide reduction. If the reduction of zinc oxide takes place by direct action between solid oxide and carbon, as some metallurgists believe, all attempts to measure the “temperature of reduction” have been concerned only with the question of the temperature at which the reaction rate becomes measurable according to whatever method was used. Nevertheless it is certain that no amount of continued heating at a definite pressure will cause gas-free carbon to reduce zinc continuously below certain temperatures. Moreover, at higher temperatures where the reaction takes place at any definite pressure either zinc oxide or carbon, or both, disappear from the system. Then without resorting to the occasionally obscuring terminology of the phase rule it is apparent that if the pressure is fixed; that is, if a system containing zinc oxide and carbon is vented at a definite pressure, a condition of equilibrium can exist at only one temperature. Below this temperature reduction by carbon does not take place, and above it continuous reaction takes place; that is, the system above is unstable as far as chemical equilibrium is concerned and from the phase-rule standpoint is invariant.

To this point of the consideration only those ideas have been expressed that must have been implicit in any attempt to find a “temperature of reduction.” So far metallurgists are in substantial agreement, except only the small minority that still believes direct reduction by carbon is important. However, these thoughts recorded above must have been entirely implicit, for the conclusion to which they clearly lead has seldom been expressed. Since in an unstable system the constitution found by chemical analysis at any time is determined by chemical reaction rates it is certain that any experiment based upon continuous reaction with carbon depends for its results upon reaction rates and can not be interpreted to determine the “equilibrium temperature.” In consequence, the true equilib-
rium temperature, meaning that single temperature at which, when
the pressure on the system is predetermined, zinc oxide and carbon
may exist in chemical equilibrium, can best be determined by indirect
methods, especially thermodynamic calculations.

**MECHANISM OF REDUCTION OF ZINC OXIDE BY CARBON**

To calculate by thermodynamic means the temperatures at which
continuous reduction of zinc oxide by carbon becomes possible at
specified pressures it is necessary for the mechanism of zinc reduc-
tion by carbon to be known. There is only one mechanism consistent
with the experimental facts discussed above. Since it is the mech-
anism usually advanced by those who have studied the reduction it
will be accepted here without attempt at justification (other than
mention of its obvious suitability in fitting the known facts of reduc-
tion), because it consists of steps that have been investigated sep-
arately and are now well known thermodynamically. In accepting
the implication of this mechanism conclusions need not be based on
fancy or hypothesis, but may now be checked by comparison with
actual data. Moreover, this mechanism has been directly tested by
Bodenstein\(^2\) and now rests upon a secure foundation of experimental
facts.

The acceptable theory of mechanism divides the action of reduction
into two steps, the first of which is expressed by the reaction

\[
\text{ZnO} + \text{CO} = \text{Zn(gas)} + \text{CO}_2 \quad (\text{Reaction 2})
\]

but the carbon-dioxide content of the gaseous products is limited at
high temperatures by the second step:

\[
\text{C} + \text{CO}_2 = 2\text{CO} \quad (\text{Reaction 3})
\]

**THERMODYNAMICS OF ZINC OXIDE REDUCTION BY CARBON**

Reaction (2) was the subject of the experimental work described
in footnote 5, Part 1, page 2, where the accuracy of the data is con-
sidered in detail. Although the actual equilibrium data were obtain-
able only over the range from 550° to 850° C. the results were con-
forced independently by thermodynamic means, and the standard
free energy for reaction (2) may be used for extrapolation without fear
as to the essential correctness of the results, although obviously minor
inaccuracies may be found when the range of extrapolation is great,
especially in the high-temperature range.

As a first step in the use of the free-energy equation for reaction (2),

\[
\Delta F^\circ_T = 47,397 + 0.69 T \ln T + 3.285 \cdot 10^{-3} T^2 - 0.627 \cdot 10^{-6} T^3 - 38.26 T \quad (\text{Equation 1})
\]

a series of suitable values of \( T = ^\circ \text{C.} + 273 \) may be substituted in the
above equation and \( \Delta F^\circ \) calculated for the selected temperatures.
From \( \Delta F^\circ \) the corresponding equilibrium constants are given by the
solution of the general equation

\[
\Delta F^\circ = -RT \ln K = -4.5787 T \log K
\]

In Table 20 are recorded the figures for free energies and equilibrium constants calculated in this way over the temperature range from 427° to 1,527° C. for each 100°.

The figures of Table 20 have no special intrinsic interest and are significant especially because they allow calculation of gas concentrations at equilibrium in the first step of metallurgical zinc reduction; that is, reaction (2).

To derive gas compositions from the values of $K_2$ shown in Table 20, some assumption must be made as to the conditions of the reacting system. For example, reaction (2) shows an increase in the number of moles of gas between the right and left side of the equation, and gas compositions will depend upon the total pressure in the system. As the first limitation of the determination of gas concentrations, let

$$p_{CO} + p_{Zn} + p_{CO_2} = P$$

where $P$ is the total pressure on a system containing solid zinc oxide, gaseous carbon monoxide, dioxide, and zinc at equilibrium. Furthermore, let the assumption be made that only pure carbon monoxide has been admitted to the system and that the amounts of zinc vapor and carbon dioxide are only those produced by the reaction of reduction. Then a stoichiometric relationship must exist, expressed by the equation $p_{Zn} = p_{CO_2}$. Mechanically, these limitations correspond to a container with zinc oxide, evacuated at the start, but with carbon monoxide admitted until the pressure builds up to a final value, $P$, the pressure at which the system is vented. It is evident that other conditions might be chosen. For example, a definite pressure of carbon monoxide might be the starting point of the reaction, with the final pressure determined by the extent of the reaction. The conditions as chosen will be the most useful in the analysis to follow, and other results may be derived by simple calculations from the values obtained.

### Table 20.—Free energies and equilibrium constants for the reaction ZnO + CO = Zn (gas) + CO₂

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Δ$F^{\circ}$</th>
<th>Log $K_1$</th>
<th>$K_1$ (atmospheres)</th>
<th>Temperature, °C.</th>
<th>Δ$F^{\circ}$</th>
<th>Log $K_1$</th>
<th>$K_1$ (atmospheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>427</td>
<td>+25,174</td>
<td>-7.8544</td>
<td>1.396·10⁻⁴</td>
<td>1,027</td>
<td>+8,265</td>
<td>-1.3835</td>
<td>4.088·10⁻²</td>
</tr>
<tr>
<td>527</td>
<td>+22,290</td>
<td>-6.0769</td>
<td>8.377·10⁻⁷</td>
<td>1,127</td>
<td>+5,550</td>
<td>-8.9638</td>
<td>1.362·10⁻¹</td>
</tr>
<tr>
<td>627</td>
<td>+19,391</td>
<td>-4.7056</td>
<td>1.970·10⁻⁴</td>
<td>1,227</td>
<td>+2,851</td>
<td>-4.1518</td>
<td>3.845·10⁻¹</td>
</tr>
<tr>
<td>727</td>
<td>+16,561</td>
<td>-3.0169</td>
<td>2.415·10⁻⁴</td>
<td>1,327</td>
<td>+1,156</td>
<td>-2.0229</td>
<td>9.487·10⁻¹</td>
</tr>
<tr>
<td>827</td>
<td>+13,766</td>
<td>-2.7331</td>
<td>1.849·10⁻³</td>
<td>1,427</td>
<td>-2,506</td>
<td>+3.3219</td>
<td>2.099</td>
</tr>
<tr>
<td>927</td>
<td>+11,003</td>
<td>-2.0025</td>
<td>9.943·10⁻³</td>
<td>1,527</td>
<td>-5,175</td>
<td>+3.6279</td>
<td>4.245</td>
</tr>
</tbody>
</table>

The gas compositions at equilibrium may now be calculated by solving the simultaneous equations consisting of the two above, and as third the formal equilibrium expression

$$\frac{p_{Zn}}{p_{CO}} = K_2$$

The solution of these simultaneous equations is

$$p_{Zn} = -K_2 \pm \sqrt{PK_2 + K_2^2}$$  (± sign only is valid here)

$$p_{CO} = p_{Zn}$$

$$106847° - 30 = 4$$
The percentage composition of the gas phases, as calculated from
the values of $K_{(2)}$ given in Table 20, and with the assumption of values
of $P$ of 0.01, 0.1, 1.0, 10.0, and 100.0 atmospheres pressure are recorded
in Table 21 for a number of temperatures covering the range from
reduction of zinc oxide in retort practice to the condensation point.
The results are shown graphically in Figure 12, in which isobaric
lines are plotted on the temperature-composition diagram. Discussion
of the implications of Table 21 is deferred until the second step
of the mechanism of zinc reduction has been considered. It should
be clearly understood that the gas compositions given are not those
from an actual retort. It is of interest, however, to note the extent
to which pressure inhibits the reaction as measured by zinc-vapor
content of the final gas.

Table 21.—Gas composition at various final pressures for the reaction $\text{ZnO} + \text{CO} = \text{Zn(gas)} + \text{CO}_2$

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$P=0.01$ atmosphere</th>
<th>$P=0.1$ atmosphere</th>
<th>$P=1$ atmosphere</th>
<th>$P=10$ atmospheres</th>
<th>$P=100$ atmospheres</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn or CO₂</td>
<td>CO</td>
<td>Zn or CO₂</td>
<td>CO</td>
<td>Zn or CO₂</td>
</tr>
<tr>
<td>427</td>
<td>0.12</td>
<td>99.76</td>
<td>0.04</td>
<td>99.92</td>
<td>0.01</td>
</tr>
<tr>
<td>627</td>
<td>4.25</td>
<td>91.50</td>
<td>1.38</td>
<td>97.74</td>
<td>1.45</td>
</tr>
<tr>
<td>727</td>
<td>13.31</td>
<td>73.38</td>
<td>4.60</td>
<td>96.64</td>
<td>1.53</td>
</tr>
<tr>
<td>827</td>
<td>28.32</td>
<td>43.36</td>
<td>11.67</td>
<td>81.26</td>
<td>4.12</td>
</tr>
<tr>
<td>927</td>
<td>41.6</td>
<td>16.8</td>
<td>24.15</td>
<td>61.70</td>
<td>9.03</td>
</tr>
<tr>
<td>1,027</td>
<td>47.2</td>
<td>5.6</td>
<td>35.07</td>
<td>68.86</td>
<td>16.54</td>
</tr>
<tr>
<td>1,127</td>
<td>49.5</td>
<td>1.0</td>
<td>43.2</td>
<td>13.6</td>
<td>29.75</td>
</tr>
<tr>
<td>1,227</td>
<td>50</td>
<td>Neg.</td>
<td>47.5</td>
<td>5.0</td>
<td>34.58</td>
</tr>
<tr>
<td>1,327</td>
<td>50</td>
<td>Neg.</td>
<td>49.3</td>
<td>4.4</td>
<td>41.1</td>
</tr>
<tr>
<td>1,427</td>
<td>50</td>
<td>Neg.</td>
<td>45.1</td>
<td>4.8</td>
<td>45.1</td>
</tr>
<tr>
<td>1,527</td>
<td>50</td>
<td>Neg.</td>
<td>47.7</td>
<td>4.6</td>
<td>35.4</td>
</tr>
</tbody>
</table>
Having defined the limits of the first step of metallurgical zinc reduction, the significance of the second step is to be considered. The reaction
\[ \text{C} + \text{CO}_2 = 2\text{CO} \] (Reaction 3)
is commonly called the "producer-gas" reaction, and the equilibria involved have been investigated many times. Eastman has reviewed the available information and adopts the expression for the standard free energy of this reaction
\[
\Delta F^o_{\text{r}} = -39,810 - 10.04 T \ln T + 15.32 \cdot 10^{-3}T^2 - 4.231 \cdot 10^{-5}T^3
+ 6.048 \cdot 10^{-10}T^4 + 17.12 T
\] (Equation 2)
\[ \Delta F_{298} = 29,115 \]

Since it was shown in Part I of this report that Eastman's calculations for carbon monoxide and dioxide are superior to Lewis and Randall's selection of the data it will be preferable to use this expression, rather than that of Lewis and Randall. The latter is based on the less accurate first series of Rhead and Wheeler.

In Table 22 are given figures for the free energy and equilibrium constant of the producer-gas reaction, as derived from Eastman's equation. The value of \( K_3 \) is obviously the ratio \( \frac{(\text{P}_{\text{CO}})^2}{\text{P}_{\text{CO}_2}} \), in atmospheres.

<table>
<thead>
<tr>
<th>Temperature, ( ^\circ \text{C.} )</th>
<th>( \Delta F^o )</th>
<th>Log ( K_3 )</th>
<th>( K_3 )</th>
<th>Temperature, ( ^\circ \text{C.} )</th>
<th>( \Delta F^o )</th>
<th>Log ( K_3 )</th>
<th>( K_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>527.</td>
<td>+7.702</td>
<td>-2.1026</td>
<td>7.896 \cdot 10^{-3}</td>
<td>1.127</td>
<td>-17.308</td>
<td>2.7000</td>
<td>501.2</td>
</tr>
<tr>
<td>627.</td>
<td>+3.473</td>
<td>-8.428</td>
<td>1.430 \cdot 10^{-1}</td>
<td>1.227</td>
<td>-21.395</td>
<td>3.1151</td>
<td>1,303.5</td>
</tr>
<tr>
<td>727.</td>
<td>-4.906</td>
<td>+1.594</td>
<td>1.443</td>
<td>1.327</td>
<td>-25.462</td>
<td>3.4756</td>
<td>2,986.5</td>
</tr>
<tr>
<td>827.</td>
<td>-9.062</td>
<td>1.6030</td>
<td>44.60</td>
<td>1.527</td>
<td>-33.524</td>
<td>4.0676</td>
<td>6,174.6</td>
</tr>
<tr>
<td>927.</td>
<td>-13.196</td>
<td>2.2169</td>
<td>164.78</td>
<td>1.627</td>
<td>-37.511</td>
<td>4.3118</td>
<td>20,502</td>
</tr>
</tbody>
</table>

Values for gas compositions corresponding to equation (3), starting with pure carbon dioxide and ending at definite final pressures, could be calculated from the values of \( K_3 \) in the same manner as was done for the initial reduction step, but such values are not directly comparable with the concentrations obtained for the latter reaction. Reaction (3) involves an increase of the number of moles between the right and left sides of the equation, and compositions accordingly depend on the total pressure. Compositions determined for reaction (3), ending at 1 atmosphere final pressure, are not comparable to compositions determined for the same final pressure in reaction (2), because the zinc vapor is a diluent for reaction (3) and is present in too large amounts under conditions of actual reduction to be negligible. For example, O'Harra has plotted curves showing the per

cent of carbon dioxide for reduction reaction (2) and producer-gas reaction (3), "at 1 atmosphere pressure," and from the intersection of the superposed curves finds $850^\circ$ is the critical temperature where "at lower temperatures the concentration of carbon dioxide in equilibrium with solid carbon is greater than the concentration that can exist in equilibrium with zinc." That the actual values of carbon dioxide content given by O’Harra for the reduction reaction are in error by more than 1,000 per cent depends upon an unsatisfactory method of experimentation; but that the intersection of the two curves should have significance as plotted is an error of principle, because pressure and composition changes due to the presence of zinc vapor have been neglected.

**COMPARISON OF ACTUAL AND THEORETICAL CARBON-DIOXIDE CONTENT IN RETORT GASES**

Before proceeding to correct calculation of the temperatures which are "invariant" when the final pressure is fixed it is important for the reaction rates of equations (2) and (3) to be considered. In their first series of experiments at 1 atmosphere pressure Rhead and Wheeler found the gas compositions to be those shown in Table 23, but the reaction was slow at the lower temperatures and did not become moderately rapid until temperatures over 1,000° had been reached. This is in marked contrast to the reaction of zinc oxide reduction by carbon monoxide, which is rapid at $600^\circ$ to $700^\circ$ and only becomes slow below about $550^\circ$ C. At the temperatures of actual retort smelting of zinc, which may be taken as being between 1,100 and $1,300^\circ$ C, in ordinary practice, the zinc oxide reduction reaction is intrinsically more rapid than its physical limitations; that is, it is limited by gas diffusion rates. The work of Rhead and Wheeler proves that although the producer-gas reaction becomes moderately rapid at these temperatures it does not have the speed of the reduction step. The chemical situation in a zinc retort, as regards carbon-dioxide content, is a balance between opposing tendencies. Reduction tends to increase the carbon-dioxide content to a value corresponding to the reduction equilibrium composition, about 32 per cent CO$_2$ at $1,200^\circ$ C. (see Table 21), but the producer-gas reaction tends to reduce the carbon-dioxide content to less than 0.06 per cent. (The limit is less than 0.06, because the carbon-monoxide content of the gas is less than 100 per cent minus the carbon-dioxide content.) The actual carbon-dioxide content must be between the limits of the reduction reaction and the producer-gas reaction.

**Table 23.—Summary of measurements of Rhead and Wheeler (from Lewis and Randall) for the reaction C+CO$_2$=2CO at 1 atmosphere total pressure**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>CO$_2$</th>
<th>CO</th>
<th>Temperature °C</th>
<th>CO$_2$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>6.23</td>
<td>93.77</td>
<td>1,100</td>
<td>0.15</td>
<td>99.85</td>
</tr>
<tr>
<td>900</td>
<td>2.22</td>
<td>97.78</td>
<td>1,200</td>
<td>.66</td>
<td>99.94</td>
</tr>
<tr>
<td>1,000</td>
<td>.59</td>
<td>98.41</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

If the reduction reaction is intrinsically rapid, compared to the producer-gas step, the question may be asked as to why the fast step does not determine the carbon-dioxide content, which is usually
about 1 per cent in retort gases. First examining the premises of the
deductions: Is it certain that the reduction step is the more rapid
reaction? Rather definite data exist, which apply here. The total
rate of zinc reduction, including both steps, must be determined by
the slow step, and any change made in the conditions of the reaction
which apply only to the rapid reaction will be without effect upon
the final rate. In the paper of Zeller and O’Harra (see footnote 1,
p. 42) are given graphs showing the rates of reduction, with both
graphite and anthracite, of various forms of zinc oxide. The varieties
upon which experiments were performed included C. P. wet-process
oxide, C. P. dry process, ignited C. P. oxide, roasted sphalerite, and
calcined smithsonite, and of these various forms only calcined smith-
sonite showed a difference greater than the probable inaccuracy of
the rate determination. The conclusion may be drawn from these
experiments (excluding the effect with smithsonite) that only an
extraordinary variation of properties of the oxide can cause the reduc-
tion step to become intrinsically as slow as the producer gas step and
that the rate of reduction is dependent upon the second step.

The low carbon-dioxide content of retort gases must then be ex-
plained on some other basis. A number of possible factors may
enter. The usual practice in smelting is to use a large excess of
reducing fuel, partly to keep the charge from becoming too dense
during heating, but primarily because such practice has been found
necessary to get good operating speed of distillation, completeness of
reduction, and elimination of blue powder. Moreover, the customary
use of a blanket of reducing material near the mouth of the retort
causes the effluent gases to be subject to the producer-gas reaction
without a possibility of the zinc-oxide reduction step, spatially
separated from it, taking place.

Even though the specific reaction rate of the reduction step is
apparently greater than that of the second step the actual total rate
in a retort may not be markedly different because of concentration
effects acting through the mass-action law and because of the varia-
tion of relative surface of zinc oxide and carbon, a changing factor
throughout the distillation. For example, a high carbon-dioxide con-
tent in the retort would decrease the speed of the reduction step, but
increase the producer gas step. Actually, little is known concerning
the carbon-dioxide content of the gas in the retort.

Various analyses which have been reported are probably very far
from representing the facts in the retort, largely because of changes of
composition which take place when a gas containing zinc vapor and
carbon dioxide is cooled. Since the reduction reaction is rapid even
at 700° C. the gas in the retort may have a relatively high carbon-
dioxide content at 1,200° C.; but by the time it is cooled to 700°,
even in the absence of the reducing blanket of the retort, nearly all
of the carbon-dioxide should disappear, as is indicated by the results
shown in Table 21. For example, the figures quoted by Hoffman 6
from the work of Fischer are quite erratic: 0.48 per cent CO₂ at the
beginning of distillation; 9.06 per cent, 0.11 per cent, and 1.10 per cent
at various intermediate stages of the reduction; and 0.82 per cent just
before the end of distillation. The nitrogen content of these samples
was low; the highest value being 1.01 per cent, corresponding to the

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9.06 per cent CO₂, and in no case great enough to explain the high
CO₂ by oxidation through the leakage of air into the retort. Other
analyses by Mühlaeuser 7 show an average carbon-dioxide content
over the distillation period of about 1.5 to 0.8 per cent CO₂, but in
this case considerable nitrogen was present, so that interpretation of
the results is difficult.

The conclusions that may be taken from these figures are limited
by the factor of reversibility of the reduction discussed above. It
seems then that the actual carbon-dioxide content of the gas in the
retort has not been determined. This situation is very unfortunate,
because a knowledge or determination of the composition would enable
a sound estimate of the activity of the reducing agent to be made.
By the term “activity” is not meant the function used by physical
chemists to designate the relative fugacity, but rather a vaguer term
to indicate the effectiveness of the reducing agent, involving many
physical factors affecting its speed of reaction, such as porosity,
degree of subdivision or surface per unit mass, and whatever other
factors may enter into the limitation of chemical rates. According
to this criterion an active reducing carbon would be one maintain-
ing a low carbon-dioxide content in the retort, and the extent to
which the carbon-dioxide content approached the limiting value fixed
by the producer-gas equilibrium would be a quantitative measure of
the quality of the reducer with greater scientific and technical signifi-
cance than any comparison of smelting rates with different kinds of
reducing fuel. The selection of an active reducer should allow the
use of less excess fuel for distillation, and experimental work to find
methods of actually analyzing the gases without change of composition
is earnestly commended to zinc metallurgists as a probably truly
definitive control method.

If, however, no blue powder was formed during the cooling of the
retort gas by the reversal of the reduction reaction, no greater carbon-
dioxide content of the gas than is shown in the cooled samples could
have existed at the high temperature. Then, since during the normal
period of distillation in the best practice (that is, apart from the
beginning and end of the reduction) very little blue powder is actually
formed, the conclusion is inescapable that the true carbon-dioxide
content is closer to the producer-gas step than to that required by
the reduction equilibrium. It must be concluded that the only
alternatives are either that the fuel blanket is entirely responsible
for the low carbon-dioxide content of the samples analyzed, or that
although at temperatures of 1,100° or thereabouts there is good reason
to believe that the reduction step is the faster reaction, at higher
temperatures the rate of the producer-gas step may increase dispro-
portionately and result in approximately equal rates for both. Then
the process of actual distillation is analagous to the “steady state”
obscured in work on reaction rates in aqueous solvents, when two
simultaneous or consecutive reactions, whose rates are of the same
order of magnitude, compete for a common constituent.

Probably the real truth lies between these divergent alternatives,
and both factors are important. It is too much to say that a dis-

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7 Mühlaeuser, Otto, Ueber die während der Reduktion der Röstblende aus den Zink muffeln entweich-
crepancy in the theory does exist, but it is nevertheless true that adequate data are lacking. Experimental work on the subject would be tremendously significant for zinc smelting. The actual carbon-dioxide content of the smelting gases will be considered again in a later part of this publication.

"INARIANT" TEMPERATURES OF ZINC REDUCTION

Returning now to the question of the mechanism of reduction of zinc oxide by carbon and the calculation of those temperatures at which carbon may be in equilibrium with the same gas compositions as zinc vapor, it is apparent that, if the reduction reaction is the rapid step, the carbon-dioxide content of the system is determined by it. Supposing that the carbon dioxide and monoxide as thus determined are of such magnitude as to exceed the equilibrium constant of the producer gas reaction \( \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \) no disappearance of carbon dioxide will occur, but carbon monoxide will tend to dissociate. If, however, the concentrations are such as to make \( \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \) less than the equilibrium constant, carbon dioxide will disappear more or less slowly through the producer-gas reaction, and the reduction will be continuous. The significance of the "temperature of reduction" of zinc oxide by carbon is now made clear. At lower temperatures than the equilibrium temperature for a given pressure it is not strictly true that no reduction of zinc oxide by carbon occurs but only that the reduction is very slow and does not result in a continuous production of zinc; when vented at a definite pressure, because the pressure developed will be less than the venting pressure. At higher temperatures the corresponding equilibrium pressure is greater than the venting pressure, and continuous disappearance of zinc oxide and carbon occurs under the driving force of the difference between the pressure that should obtain at equilibrium and the pressure at which venting takes place. This latter step may still be very slow near the temperature of continuous reduction. If an inert gas is passed over carbon and zinc oxide, continuous reduction should occur at all temperatures, but the result obtained depends on reaction rates. From this point of view all the classical experiments on the temperature of reduction, with the exception of those of Bodenstein and Schubart,\(^8\) have been concerned only with the measurement of a rate, and the temperature of reduction obtained depended upon the sensitivity of the method. The pressure work of Bodenstein and Schubart perhaps would have given correct results had the pressure of zinc in their system been fixed or determined. (For a detailed criticism of these results see footnote 5, Part I, p. 2.)

To calculate the temperature of continuous reduction in a correct manner the following condition may be imagined. Carbon monoxide is admitted to an evacuated system containing zinc oxide at various

temperatures until the total pressure builds up to a definite value and equilibrium concentrations are obtained. Carbon is then admitted to the system. From the content of carbon monoxide and dioxide determined by the zinc oxide-carbon monoxide reduction, an apparent value of \( \frac{p_{\text{CO}^2}}{p_{\text{CO}_2}} = K'_(3) \) is calculated, and the results are plotted.

On the same chart the true value of \( K_(3) \) is plotted as a function of temperature. Where the lines of apparent value cross the line of true \( K_(3) \) equilibrium for both steps of the mechanism discussed above may exist, and carbon introduced at this point (temperature) would neither be used up nor increased in amount.

In Table 24 are collected calculated values of true and apparent equilibrium constants, as designated above. The method of obtaining true \( K_(3) \) has already been discussed. Values of apparent \( K_(3) \) are equal to the ratio \( p_{\text{CO}^2}:p_{\text{CO}_2} \), obtained from the data of Table 21, where \( p_{\text{CO}} = P \) times \( \frac{\text{per cent CO}}{100} \), and \( p_{\text{CO}_2} = P \) times \( \frac{\text{per cent CO}_2}{100} \). The values of Table 24 are shown graphically in Figure 13. In order to avoid plotting a wide range of numbers, the plot is made for log \( K \) vs. \( T \), which does not give the straight line of a log \( K \) vs. \( \frac{1}{T} \) plot but results in only slight curvature and has the advantage that \( T \) may be read directly without conversion from reciprocal values.
Table 24.—True and apparent equilibria corresponding to $K_3$

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>True log $K_3$</th>
<th>$P=0.01$ atmosphere</th>
<th>$P=0.1$ atmosphere</th>
<th>$P=1.0$ atmosphere</th>
<th>$P=10$ atmosphere</th>
<th>$P=100$ atmosphere</th>
<th>$P=1,000$ atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K'_3$</td>
<td>Log $K'_3$</td>
<td>$K'_3$</td>
<td>Log $K'_3$</td>
<td>$K'_3$</td>
<td>Log $K'_3$</td>
<td>$K'_3$</td>
</tr>
<tr>
<td>597...</td>
<td>-2.103</td>
<td>1.059</td>
<td>-0.360</td>
<td>7.01</td>
<td>+0.846</td>
<td>1.755</td>
<td>+0.340</td>
</tr>
<tr>
<td>627...</td>
<td>-3.843</td>
<td>1.693</td>
<td>-0.964</td>
<td>1.111</td>
<td>-1.066</td>
<td>2.71</td>
<td>-0.871</td>
</tr>
<tr>
<td>727...</td>
<td>+1.159</td>
<td>1.755</td>
<td>+0.244</td>
<td>61.4</td>
<td>+1.788</td>
<td>228.1</td>
<td>+2.460</td>
</tr>
<tr>
<td>827...</td>
<td>+2.975</td>
<td>2.000</td>
<td>+2.340</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>927...</td>
<td>1.640</td>
<td>2.400</td>
<td>+2.864</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,027...</td>
<td>2.217</td>
<td>2.555</td>
<td>+3.115</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,127...</td>
<td>2.700</td>
<td>2.711</td>
<td>+3.476</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,227...</td>
<td>3.115</td>
<td>2.864</td>
<td>+3.791</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,327...</td>
<td>3.476</td>
<td>2.864</td>
<td>+3.968</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,427...</td>
<td>3.791</td>
<td>2.864</td>
<td>+4.172</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,527...</td>
<td>4.068</td>
<td>2.864</td>
<td>+4.312</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
<tr>
<td>1,627...</td>
<td>4.312</td>
<td>2.864</td>
<td>+4.312</td>
<td>28.42</td>
<td>1.454</td>
<td>2.423</td>
<td>3.388</td>
</tr>
</tbody>
</table>

By reading the points of intersection from a larger-scale chart than is shown in Figure 13, figures for the temperatures of continuous reduction of zinc oxide by carbon at various restraining pressures were obtained. They are summarized and recorded in Table 25. The data for the value at 1,000 atmospheres given in Table 24 represent the limit of extrapolation, which seems justifiable, as this point may be of doubtful accuracy. The calculations are dependent upon adherence of the gases to the perfect gas law, and there is no doubt that this condition would not hold at 1,000 atmospheres, even though the temperature is high.

Table 25.—Temperatures of continuous reduction of zinc oxide by carbon

<table>
<thead>
<tr>
<th>Venting pressure, $P$ atmospheres</th>
<th>Log $P$</th>
<th>Temperature of continuous reduction, °C.</th>
<th>Venting pressure, $P$ atmospheres</th>
<th>Log $P$</th>
<th>Temperature of continuous reduction, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-2</td>
<td>687.5</td>
<td>0.1</td>
<td>-1</td>
<td>587</td>
</tr>
<tr>
<td>1.0</td>
<td>-1</td>
<td>753</td>
<td>1.0</td>
<td>0</td>
<td>1,000</td>
</tr>
</tbody>
</table>
Part III. DIRECT SMELTING FOR LIQUID ZINC AND THE ZINC BLAST FURNACE

HISTORICAL ATTEMPTS AT DIRECT SMELTING

There have been a number of ambitious attempts to smelt zinc oxide directly to liquid zinc in a blast furnace under rather high pressures. The problem of direct smelting has, curiously enough, recurred almost cyclically at 10-year intervals. According to Hoffman (footnote 6, Pt. II, p. 49):

In 1896 Lungwitz proposed to smelt oxidized zinc ore under a pressure of 30 to 45 pounds per square inch, which was to prevent the volatilization of zinc. Barus had found that zinc boiled at 1,034° C. under a pressure of 20 pounds, and at 1,500° C. under one of about 741 pounds. Early experiments were unsuccessful. The process was tried again at Warren, N. H., in 1906, in a furnace which was air-tight at 80 pounds pressure, but failed again.

In 1916 Woolsey McA. Johnson, as reported in Metallurgical and Chemical Engineering, made comments so interesting and instructive that two full paragraphs are quoted here:

With knowledge of these factors, we could operate the furnace (at Warren, N. H.) with some degree of certainty. There was raised, however, the question of the "law of partial pressures." For liquefying any vapor, the full pressure of the vapor must exist next to the surface of the liquid. Now, in the furnace operations at Warren, for each cubic foot of zinc vapor there were some 9 cubic feet of indifferent gases, carbon monoxide and nitrogen, sweeping through the melting zone. Accordingly, should any zinc be liquefied, it would be evaporated by this sweep unless the pressure were ten (9 + 1) times as large as had been considered and calculated. The condition was analogous to a steam condenser with too much air in the system. The point was brought out in discussion, but it was decided to start at any rate. It was found later that it militated strongly against the success of the Lungwitz process.

The emphasis on the above sentence is that of the present author. Apparently, there was a theoretical prophet present at this discussion, but his advice seems to have been overridden by the practical metallurgists who had not learned the economy of deriving theoretical information from theoretical research. Further the commentator says:

We can thus chronicle the last and most serious attempt to make spelter in the blast furnace. The work was done with elaborateness, without regard to expense, and with all possible engineering care. It can be concluded that inherent metallurgical difficulties prevented the success of this scheme, and will prevent that of any other similar scheme. In short, while a brilliant attempt had attained some success in working out apparently insuperable practical details to a certain degree the law of partial pressures attacked the very heart of the process and made it faulty in theory.

In 1926 the proposal to smelt zinc in the blast furnace was again submitted to the staff of the Berkeley station of the Bureau of Mines as a problem that might be elucidated by the theoretical work that had been performed there. It seems justifiable to consider the matter here in some detail, in order that the fundamental limitations

---

of such attempts may be clearly understood in the future. It is indeed theoretically possible to smelt zinc directly to liquid under pressure, though the "militation" of the "law of partial pressures" may not be considered as serious to-day as the effect of pressure itself upon the reduction. The early experimenters had good qualitative knowledge, but they lacked quantitative knowledge and the theoretical though precise thermodynamic methods that might have saved many thousands of misspent dollars.

CONDITIONS FOR PRODUCTION OF LIQUID ZINC

Table 25 shows that the temperature of continuous reduction of zinc oxide by carbon rises rapidly with increased venting pressure. That the critical temperature of theoretically continuous reduction must be exceeded in any practical zinc-smelting operation using carbonaceous fuel directly is obvious; if liquid zinc is to be produced as well, still another limitation of conditions must be considered coincidentally with the invariant points.

Two conditions for the direct production of liquid zinc may now be considered. In the first of these, carbon monoxide from an external source might be pumped into a gas-tight retort at various pressures and temperatures, and the data now available may be so dealt with as to show the temperatures and pressures at which liquid zinc will begin to condense. In the second case a sealed retort, in which the pressure may build up owing to the reaction between zinc oxide and carbon, may be imagined. To determine the properties of the second system, an equivalent but somewhat different actual scheme will be considered, the details of which will be given after the first case has been dealt with.

CASE I. LIQUID ZINC BY REDUCTION WITH CARBON-MONOXIDE GAS

Let there be imagined a system containing at the start only zinc oxide, to which carbon monoxide is admitted at various temperatures, until the pressure at equilibrium becomes certain fixed values. The partial pressure of zinc vapor is then calculable in accordance with the methods given in the first part of this publication. If these values are charted on a plot containing also the vapor-pressure curve of liquid zinc the intersections of the partial pressure curves with the vapor-pressure line will indicate those temperatures at which zinc must begin to condense at the pressure chosen. The data from which such a chart may be constructed are given in Table 26, and the chart itself is shown in Figure 14. Here again the data have been plotted as log $p_{Zn}$ vs $T$ to shorten the ordinate scale and to obtain lines of less curvature than the direct plot of pressure. Line L shows the vapor pressure of liquid zinc and the lines marked with numerals the partial pressures of zinc at the various total pressures enumerated. In making the calculations for these data no corrections have been made for the deviation of the gases from the perfect gas law or for the change of vapor pressure with external pressure. These factors would produce some differences, especially in the curves for high pressures, but it is probable that the error so produced would be equivalent to not more than a few degrees of temperature.
### Table 26.—Partial and vapor pressures of zinc

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>Log $V$, $P$, Zn (l) atmosphere</th>
<th>$P=0.01$</th>
<th>$P=0.1$</th>
<th>$P=1$</th>
<th>$P=10$</th>
<th>$P=50$</th>
<th>$P=100$</th>
<th>$P=250$</th>
<th>$P=400$</th>
</tr>
</thead>
<tbody>
<tr>
<td>419.5</td>
<td></td>
<td>-3.373</td>
<td>-3.564</td>
<td>-3.736</td>
<td>-2.523</td>
<td>-2.100</td>
<td>-1.356</td>
<td>-1.200</td>
<td></td>
</tr>
<tr>
<td>527</td>
<td></td>
<td>-1.840</td>
<td>-2.869</td>
<td>-2.367</td>
<td>-1.854</td>
<td>-1.514</td>
<td>-1.398</td>
<td>-1.398</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>-1.840</td>
<td>-2.869</td>
<td>-2.367</td>
<td>-1.854</td>
<td>-1.514</td>
<td>-1.398</td>
<td>-1.398</td>
<td></td>
</tr>
<tr>
<td>627</td>
<td></td>
<td>-2.875</td>
<td>-2.334</td>
<td>-1.815</td>
<td>-1.310</td>
<td>-0.959</td>
<td>-0.824</td>
<td>-0.824</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>-2.875</td>
<td>-2.334</td>
<td>-1.815</td>
<td>-1.310</td>
<td>-0.959</td>
<td>-0.824</td>
<td>-0.824</td>
<td></td>
</tr>
<tr>
<td>827</td>
<td></td>
<td>-5.10</td>
<td>-2.547</td>
<td>-1.925</td>
<td>-1.385</td>
<td>-0.873</td>
<td>-0.519</td>
<td>-0.366</td>
<td>-0.168</td>
</tr>
<tr>
<td>827</td>
<td></td>
<td>-5.10</td>
<td>-2.547</td>
<td>-1.925</td>
<td>-1.385</td>
<td>-0.873</td>
<td>-0.519</td>
<td>-0.366</td>
<td>-0.168</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td>-0.23</td>
<td>-2.318</td>
<td>-1.617</td>
<td>-1.044</td>
<td>-0.514</td>
<td>-0.094</td>
<td>+0.084</td>
<td>+1.195</td>
</tr>
<tr>
<td>927</td>
<td></td>
<td>-0.23</td>
<td>-2.318</td>
<td>-1.617</td>
<td>-1.044</td>
<td>-0.514</td>
<td>-0.094</td>
<td>+0.084</td>
<td>+1.195</td>
</tr>
<tr>
<td>1,000</td>
<td></td>
<td>+3.81</td>
<td>-2.326</td>
<td>-1.455</td>
<td>-0.782</td>
<td>-0.222</td>
<td>+0.387</td>
<td>+0.500</td>
<td>+0.602</td>
</tr>
<tr>
<td>1,027</td>
<td></td>
<td>+3.81</td>
<td>-2.326</td>
<td>-1.455</td>
<td>-0.782</td>
<td>-0.222</td>
<td>+0.387</td>
<td>+0.500</td>
<td>+0.602</td>
</tr>
<tr>
<td>1,127</td>
<td></td>
<td>+7.23</td>
<td>-2.305</td>
<td>-1.364</td>
<td>-0.589</td>
<td>+0.921</td>
<td>+0.642</td>
<td>+0.756</td>
<td>+0.869</td>
</tr>
<tr>
<td>1,200</td>
<td></td>
<td>+7.23</td>
<td>-2.305</td>
<td>-1.364</td>
<td>-0.589</td>
<td>+0.921</td>
<td>+0.642</td>
<td>+0.756</td>
<td>+0.869</td>
</tr>
<tr>
<td>1,227</td>
<td></td>
<td>+1.264</td>
<td>-2.301</td>
<td>-1.323</td>
<td>-0.461</td>
<td>+0.208</td>
<td>+0.975</td>
<td>+1.079</td>
<td></td>
</tr>
<tr>
<td>1,300</td>
<td></td>
<td>+1.264</td>
<td>-2.301</td>
<td>-1.323</td>
<td>-0.461</td>
<td>+0.208</td>
<td>+0.975</td>
<td>+1.079</td>
<td></td>
</tr>
<tr>
<td>1,327</td>
<td></td>
<td>+1.453</td>
<td>-2.301</td>
<td>-1.301</td>
<td>-0.346</td>
<td>+0.357</td>
<td>+1.269</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,400</td>
<td></td>
<td>+1.453</td>
<td>-2.301</td>
<td>-1.301</td>
<td>-0.346</td>
<td>+0.357</td>
<td>+1.269</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,427</td>
<td></td>
<td>+1.453</td>
<td>-2.301</td>
<td>-1.301</td>
<td>-0.346</td>
<td>+0.357</td>
<td>+1.269</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From a study of the curves of Figure 14, it is immediately apparent that the partial-pressure curves for 1 atmosphere or less do not inter-

![Figure 14](image-url)

**Figure 14.**—Graphical determination of liquid zinc formation from zinc oxide and carbon monoxide: L, Vapor pressure of zinc; P lines, isobars of partial pressures of P atmospheres. Temperatures of intersection are shown by dotted lines.
Table 27.—Critical temperatures for the production of liquid zinc by CO under pressure

<table>
<thead>
<tr>
<th>Final gas pressure at equilibrium = P (atmospheres)</th>
<th>Log P</th>
<th>Temperature at which liquid zinc forms, °C.</th>
<th>Final gas pressure at equilibrium = P (atmospheres)</th>
<th>Log P</th>
<th>Temperature at which liquid zinc forms, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-2</td>
<td>&lt;M. P.</td>
<td>100</td>
<td>2.000</td>
<td>818</td>
</tr>
<tr>
<td>.1</td>
<td>-1</td>
<td>&lt;M. P.</td>
<td>150</td>
<td>2.176</td>
<td>914</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>&lt;M. P.</td>
<td>250</td>
<td>2.362</td>
<td>1,050</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>514</td>
<td>400</td>
<td>2.622</td>
<td>1,263</td>
</tr>
<tr>
<td>50</td>
<td>1.699</td>
<td>704</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The reaction velocity of reduction of zinc oxide by carbon monoxide is rapid at about 700° C. and from Table 27 it is evident that a pressure of 50 atmospheres or approximately 750 pounds per square inch would result in the production of some liquid zinc. However, gases containing the equilibrium concentration of carbon dioxide and saturated at this temperature with zinc vapor would have to be removed from the system, so that it is probable that only a relatively small portion of the total zinc reduced would appear as liquid zinc.

CASE II. LIQUID ZINC BY CARBON REDUCTION

If the system considered in Case I had the zinc oxide removed and a small amount of carbon introduced into it and if the temperature were above the temperature of continuous reduction the carbon-dioxide content would be decreased to that corresponding to the producer-gas equilibrium; and if one deals only with temperatures above 1,100° C. this content would be negligible. Such gas, again coming into contact with zinc oxide, would reduce more zinc, and the zinc content would be increased. This process may be imagined to be repeated indefinitely, until a final maximum concentration of zinc results. The gases so produced will carry much more zinc vapor than is shown by the gas compositions of Table 21, Part II, and the pressures required to condense zinc will be much lower at any given temperature than for the first case.

To get a mechanical picture of such a process a column of alternate layers of carbon and zinc oxide, starting with carbon, may be imagined. Into this column, which is maintained at some constant exit pressure and average temperature, a small amount of oxygen is admitted. In the first carbon layer carbon monoxide is formed, and in the first zinc-oxide layer the gas composition will be that given by the data of Table 28. In the second carbon layer more CO is formed, and with enough layers the ultimate composition will be reached. The general solution of the determination of the changes taking place at any layer will be made. It is necessary to assume that the transit of gas through each layer is so slow that equilibrium is reached each time. The further assumption will be made that the carbon-dioxide content in each carbon zone is negligible compared to the carbon.
monoxide and zinc content. At each layer the calculations will be referred to 1 mole of carbon-monoxide gas.

Let \( r = \text{ratio moles Zn gas} \) \text{ vol. per cent Zn gas}
\( \text{moles CO gas} \) \text{ vol. per cent CO gas}
in the \( n \)th carbon zone;

Let \( P = \text{total pressure on the system} \);

Let \( x = \text{the proportion of CO reacting in the} \ n \text{th zinc layer, the one following the} \ n \text{th carbon.} \)

Then \( 1-x = \text{moles of CO remaining after the} \ n \text{th zinc equilibrium,} \)
\( x = \text{moles of CO}_2 \text{ formed,} \)
\( x = \text{moles of new zinc vapor formed,} \)
\( r+x = \text{total zinc after the} \ n \text{th zinc equilibrium,} \)
\( r+x+x+1-x = 1+r+x = \text{total number of moles after the} \ n \text{th zinc equilibrium.} \)

From these values
\[
p_{Zn} = \left(\frac{r+x}{1+r+x}\right)P
\]
\[
p_{CO_2} = \left(\frac{x}{1+r+x}\right)P
\]
\[
p_{CO} = \left(\frac{1-x}{1+r+x}\right)P
\]

From the equilibrium expression
\[
K_x(\theta) = \frac{p_{Zn} \cdot P_{CO_2}}{p_{CO}}
\]
\[
k_{p}(\theta) = \left(\frac{r+x}{1+r+x}\right)P \cdot \left(\frac{x}{1+r+x}\right)P
\]

Solving for \( x \)
\[
x = -\frac{r}{2} + \sqrt{\frac{K}{P}} \left(1+r\right) \left(\frac{x}{1+r+x}\right)P \]
Equation 1

When \( x \) is determined its values may be reintroduced into the above equations to solve for \( P_{Zn}, P_{CO_2}, \) and \( P_{CO}, \) or directly into the mole fractions for each gas to give percentage composition directly. Furthermore, if at the \( n \)th zinc step the carbon dioxide content is \( A_n \) parts by volume, when the carbon dioxide is reduced in the \( n+1 \) carbon zone 2 volumes of carbon monoxide are produced for each volume of carbon dioxide reacting, and the percentage of zinc (which is an inert gas in this step) will be decreased in the ratio \( \frac{1}{1+A_n} \), or the Zn content of the \( n+1 \) step = \( \frac{P_{Zn(n)}}{1+A_n} \).

As a specific example, the condition at 1,227° C. and 1 atmosphere pressure has been calculated step by step for a number of layers. The results are collected in Table 28. Inspection of the first seven
rows of figures indicates that the values of $r$ are approaching unity as a limit, and indeed this might have been predicted. Although the reaction $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ does not represent a complete reaction, because carbon dioxide is always present, its formulation nevertheless indicates that the limiting ratio of zinc to carbon monoxide is mole per mole, and this must be true for any condition where the carbon-dioxide content is negligible compared to the carbon monoxide. Then without going through the actual steps, equation (1) may be applied with the value $r = 1$, to determine limiting values wherever the carbon-dioxide content may be considered negligible. Such values are collected in Table 29 for temperatures from 1,127° C. to 1,527° C. and 1, 10, and 100 atmospheres. The minimum zinc content and the maximum carbon-monoxide content, if determined by a limiting carbon step, would each be 50 per cent ($r = 1$), but the minimum carbon dioxide was determined by substituting the value $p_{\text{CO}} = 0.5P$ in the expression $K_{p(3)} = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$ and solving for $P_{\text{CO}_2}$.

**Table 28.—Progressive changes of gas composition in the ZnO--C system at 1,227° C. and 1 atmosphere**

<table>
<thead>
<tr>
<th>$n =$ No. of zone</th>
<th>$z =$ conversion of CO</th>
<th>Zinc layer</th>
<th>Carbon layer</th>
<th>$r =$ (moles Zn) / (moles CO) in nth carbon layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn(n)</td>
<td>CO</td>
<td>Zn(n) / (1 + A)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Per cent</td>
<td>Per cent</td>
<td>Per cent</td>
</tr>
<tr>
<td>1.</td>
<td></td>
<td>34.58</td>
<td>34.58</td>
<td>30.84</td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td>44.72</td>
<td>25.62</td>
<td>29.66</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>49.73</td>
<td>21.94</td>
<td>28.33</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>53.70</td>
<td>19.98</td>
<td>27.32</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>54.52</td>
<td>18.86</td>
<td>26.62</td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td>55.75</td>
<td>18.12</td>
<td>26.13</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td>56.50</td>
<td>17.65</td>
<td>25.84</td>
</tr>
<tr>
<td>8.</td>
<td></td>
<td>58.50</td>
<td>16.60</td>
<td>25.05</td>
</tr>
<tr>
<td>9 = limit.</td>
<td></td>
<td>39.93</td>
<td>55.23</td>
<td>16.60</td>
</tr>
</tbody>
</table>

The results summarized in Table 29 are of considerable interest, for they apply not only to a blast furnace with oxygen blast but also to a retort as now used. After a large number of steps (that is, as $n$ approaches infinity) the original oxygen used to start the series will have become engulfed in so large an amount of gas produced from the solid materials that its content will be negligible. The small variation between maximum and minimum possible values of zinc content of the gas with the change of temperature and pressure is striking. Moreover, since pressure affects the two steps of the reduction in the opposite sense as far as carbon-dioxide content is concerned, in the values at high pressure (100 atmospheres) the curious condition is found that the zinc step permits only a lower carbon-dioxide content than the producer-gas step. This can only mean that the limiting value $r = 1$ (that is, the "steady state" corresponding to $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ with $\text{CO}_2$ negligible) can only be attained below certain limiting values of total pressure.
Table 29.—Limiting values of gas composition in the system ZnO—C

\[ P=1 \text{ ATMOSPHERE} \]

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( x_n )</th>
<th>Max. Zn</th>
<th>Log ( p_{zn} )</th>
<th>Max. ( \text{CO}_2 )</th>
<th>Min. ( \text{CO} )</th>
<th>Min. ( \text{CO}_2 )</th>
<th>Log ( p_{co2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,127.0</td>
<td>0.200</td>
<td>54.55</td>
<td>-0.293</td>
<td>9.09</td>
<td>36.36</td>
<td>0.0499</td>
<td>-3.310</td>
</tr>
<tr>
<td>1,227.0</td>
<td>.396</td>
<td>58.35</td>
<td>-0.334</td>
<td>16.69</td>
<td>25.05</td>
<td>.0192</td>
<td>-3.717</td>
</tr>
<tr>
<td>1,327.0</td>
<td>.606</td>
<td>61.62</td>
<td>-0.210</td>
<td>23.24</td>
<td>15.14</td>
<td>.0084</td>
<td>-4.076</td>
</tr>
<tr>
<td>1,427.0</td>
<td>.767</td>
<td>63.90</td>
<td>-0.195</td>
<td>27.72</td>
<td>8.38</td>
<td>.0041</td>
<td>-4.387</td>
</tr>
<tr>
<td>1,527.0</td>
<td>.866</td>
<td>65.15</td>
<td>-0.186</td>
<td>30.27</td>
<td>4.38</td>
<td>.0021</td>
<td>-4.678</td>
</tr>
</tbody>
</table>

\[ P=10 \text{ ATMOSPHERE} \]

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( x_n )</th>
<th>Max. Zn</th>
<th>Log ( p_{zn} )</th>
<th>Max. ( \text{CO}_2 )</th>
<th>Min. ( \text{CO} )</th>
<th>Min. ( \text{CO}_2 )</th>
<th>Log ( p_{co2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,127.0</td>
<td>0.0265</td>
<td>50.65</td>
<td>0.705</td>
<td>1.31</td>
<td>48.04</td>
<td>0.4990</td>
<td>-1.310</td>
</tr>
<tr>
<td>1,227.0</td>
<td>.0700</td>
<td>51.70</td>
<td>0.714</td>
<td>3.38</td>
<td>44.92</td>
<td>.1918</td>
<td>-1.717</td>
</tr>
<tr>
<td>1,327.0</td>
<td>.1510</td>
<td>53.35</td>
<td>0.729</td>
<td>7.02</td>
<td>39.43</td>
<td>.0837</td>
<td>-2.676</td>
</tr>
<tr>
<td>1,427.0</td>
<td>.2722</td>
<td>56.00</td>
<td>0.748</td>
<td>12.02</td>
<td>31.98</td>
<td>.0460</td>
<td>-2.387</td>
</tr>
<tr>
<td>1,527.0</td>
<td>.4205</td>
<td>58.67</td>
<td>0.768</td>
<td>17.36</td>
<td>23.97</td>
<td>.0214</td>
<td>-2.678</td>
</tr>
</tbody>
</table>

\[ P=100 \text{ ATMOSPHERE} \]

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( x_n )</th>
<th>Max. Zn</th>
<th>Log ( p_{zn} )</th>
<th>Max. ( \text{CO}_2 )</th>
<th>Min. ( \text{CO} )</th>
<th>Min. ( \text{CO}_2 )</th>
<th>Log ( p_{co2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,127.0</td>
<td>0.0035</td>
<td>50.10</td>
<td>1.700</td>
<td>0.17</td>
<td>49.73</td>
<td>4.990</td>
<td>0.698</td>
</tr>
<tr>
<td>1,227.0</td>
<td>.0088</td>
<td>50.18</td>
<td>1.700</td>
<td>0.29</td>
<td>49.53</td>
<td>1.918</td>
<td>2.383</td>
</tr>
<tr>
<td>1,327.0</td>
<td>.0188</td>
<td>50.52</td>
<td>1.703</td>
<td>0.53</td>
<td>48.55</td>
<td>.907</td>
<td>-0.976</td>
</tr>
<tr>
<td>1,427.0</td>
<td>.0400</td>
<td>51.02</td>
<td>1.708</td>
<td>1.96</td>
<td>47.02</td>
<td>.405</td>
<td>-3.877</td>
</tr>
<tr>
<td>1,527.0</td>
<td>.0760</td>
<td>51.83</td>
<td>1.715</td>
<td>3.66</td>
<td>44.49</td>
<td>.214</td>
<td>-6.788</td>
</tr>
</tbody>
</table>

These values of limiting pressures for the steady state may be derived as follows:

The limiting values of per cent zinc and per cent carbon monoxide in gas from the last carbon zone are both 50 per cent (where \( n \) is large according to the discussion above); then

\[
\frac{(p_{co2})^2}{p_{co2}} = K_{(z)}
\]

\[
p_{co2} = \left(\frac{p_{co2}}{K_{(z)}}\right)^2; \quad \text{and since } p_{co} = 0.50 \, P
\]

\[
p_{co2} = \frac{p^2}{4K_{(z)}}
\]

Applying this value of \( p_{co2} \) and the limiting values of \( p_{zn} = p_{co} \) to the reduction equilibrium

\[
\frac{p_{zn} \cdot p_{co2}}{p_{co}} = K_{(z)}
\]

\[
p_{co2} = K_{(z)}
\]

Eliminating \( p_{co2} \),

\[
P = 2\sqrt{K_{(z)} \cdot K_{(z)}}
\]

Values of limiting pressure calculated from the above equation, for various temperatures, are recorded in Table 30. Coincidentally with these values the temperatures and pressures at which liquid zinc would begin to condense from the steady-state composition of gas are of great interest. The solution of this problem can be made by
converting the maximum zinc concentrations given in Table 28 to partial pressures, that is, \( p_{zn} = \text{per cent Zn times } P \), and plotting upon the same chart as the vapor-pressure curve for liquid zinc. However, at the temperatures of intersection the value of maximum concentration of zinc is very close to the minimum value of 50 per cent, and no significant error will be introduced by reading directly the values of temperature from the vapor-pressure chart corresponding to half the total pressure. Actual values so read are shown in Table 31. For a more precise statement see Part II.

**Table 30.**—Limiting values of pressure above which gas from the \( n = \) carbon step can not produce zinc in the \( n = +1 \) zinc step

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
<th>( P ) (atmosphere)</th>
<th>Log ( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>827</td>
<td>1.849-10^-1</td>
<td>6.435</td>
<td>0.2942</td>
<td>-0.0310</td>
</tr>
<tr>
<td>927</td>
<td>6.943-10^-1</td>
<td>5.184</td>
<td>1.3532</td>
<td>0.0246</td>
</tr>
<tr>
<td>1,027</td>
<td>4.088-10^-4</td>
<td>5.188</td>
<td>5.188</td>
<td>0.7150</td>
</tr>
<tr>
<td>1,127</td>
<td>1.362-10^-1</td>
<td>510.2</td>
<td>16.526</td>
<td>1.2181</td>
</tr>
<tr>
<td>1,227</td>
<td>3.845-10^-4</td>
<td>1,303.6</td>
<td>44.78</td>
<td>1.6569</td>
</tr>
<tr>
<td>1,327</td>
<td>9.487-10^-5</td>
<td>106.5</td>
<td>2.0273</td>
<td></td>
</tr>
<tr>
<td>1,427</td>
<td>2.099</td>
<td>6.174.5</td>
<td>227.8</td>
<td>2.3572</td>
</tr>
<tr>
<td>1,527</td>
<td>4.245</td>
<td>11.684</td>
<td>446.8</td>
<td>2.6479</td>
</tr>
</tbody>
</table>

**Table 31.**—Temperatures at which liquid zinc condenses from "steady state" gas compositions

<table>
<thead>
<tr>
<th>( P = ) total pressure, atmospheres</th>
<th>Log ( P )</th>
<th>Partial pressures ( Zn = p_{zn} )</th>
<th>Log ( p_{zn} )</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.3010</td>
<td>0.25</td>
<td>-0.6029</td>
<td>752</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>0.50</td>
<td>-0.3010</td>
<td>840</td>
</tr>
<tr>
<td>2.0</td>
<td>+0.3010</td>
<td>1.0</td>
<td>0.3090</td>
<td>995</td>
</tr>
<tr>
<td>5.0</td>
<td>+0.9900</td>
<td>2.5</td>
<td>+1.3990</td>
<td>1,004</td>
</tr>
<tr>
<td>10.0</td>
<td>1.0</td>
<td>5.0</td>
<td>+1.9900</td>
<td>1,091</td>
</tr>
<tr>
<td>20.0</td>
<td>1.3010</td>
<td>10.0</td>
<td>+1.9900</td>
<td>1,192</td>
</tr>
<tr>
<td>50.0</td>
<td>1.9900</td>
<td>25.0</td>
<td>+1.9900</td>
<td>1,351</td>
</tr>
<tr>
<td>100.0</td>
<td>2.00</td>
<td>50.0</td>
<td>+1.9900</td>
<td>1,515</td>
</tr>
</tbody>
</table>

**CONSTITUTION DIAGRAM OF ZINC OXIDE-CARBON SYSTEM**

A stability diagram may be constructed from selected portions of the data above. Figure 15 has been drawn with temperatures as ordinates and the logarithms of total pressure as abscissas, the logarithmic rather than direct plot of the abscissas being chosen to condense the chart. Curve A represents the values shown in Table 25, Part II; curve B was drawn from the data of Table 27, Part III; curve C from Table 31, Part III; and curve D from Table 30, Part III. These curves are boundaries to the fields of pressure and temperature, which have a certain definite significance with respect to zinc-smelting processes.

Curve A is the locus of the invariant points discussed in the first part of this publication. An analogy with a simpler system may be of value in making clear the physical and chemical implications of the results. A similarity exists between the chemical invariance expressed by curve A and the physical invariance of a system of liquid in equilibrium with its vapor. To cause liquid to evaporate continuously at a given pressure the temperature must be maintained an infinitesimal amount above the temperature at which the vapor...
pressure of the liquid is equal to the external pressure. In like manner, curve A is the boiling-point curve of the system zinc oxide, carbon, carbon monoxide, and carbon dioxide, and the temperature at any fixed pressure must be held infinitesimally higher than A to cause continuous distillation of zinc. Another way of stating the significance of curve A is that only at the pressures and temperatures so indicated may zinc vapor, solid zinc oxide, solid carbon, carbon monoxide, and carbon dioxide exist in equilibrium with each other.

In a similar manner curve B is the curve of "dew point" in the system containing zinc vapor, zinc liquid, carbon monoxide, and carbon dioxide in contact with zinc oxide and represents the only conditions of pressure and temperature where the above materials may be in equilibrium. To produce liquid zinc by gaseous reduction with carbon monoxide, the pressure must be greater than the values shown by B. Curves A and B refer to formal equilibrium conditions only and have only theoretical significance with respect to the steady state of zinc reduction as actually carried on in practice. The intersection of curves A and B is the quadruple point Q and shows the only set of conditions where zinc vapor, zinc liquid, zinc oxide, carbon, carbon monoxide, and carbon dioxide may all be in equilibrium with each other. Such a system has zero degrees of freedom, according to the phase-rule formulation. The quadruple point is then approximately located at 1,500° C, and approximately 12,000 pounds per square inch pressure, a condition of no practical interest from the standpoint of zinc metallurgy.

Curve C is the apparent dew-point curve for the steady-state condition, and pressures must be greater than those given to-condense liquid zinc from the gases at the \( n = \infty \) step of the hypothetical layer.
system discussed above. Similarly, curve D is the limit of continuous reduction under steady-state conditions, and pressures must be less than those shown if continuous formation of zinc under steady-state conditions is to be obtained. Curves C and D intersect at a temperature of about 1,070° C. and 8.3 atmospheres pressure or about 120 pounds per square inch. That part of curve C below curve D has no significance because the limiting values of gas composition corresponding to the steady state would not be reached, and the results here are hypothetical. The shaded area above the intersection, between curves C and D, represents the conditions where liquid zinc could be produced by the use of pressure under steady-state conditions.

From another point of view, it may be considered that curves A and B represent conditions in our layer system at \( n = 1 \), and curves C and D show the limits when \( n = \infty \). It is obvious that intermediate values of \( n \) might be of interest, with zones of stability between the two sets. The calculation of such intermediate conditions may be made in a similar manner, but further data will not be included here. With a rapid rate of distillation in an actual retort it seems certain that the analogy of the layer system will not hold completely, because equilibrium conditions may not be attained and diffusion rates prevail. We are incompetent to deal with the system away from equilibrium conditions until such time as the chemical dynamics of the reaction mechanism may have been worked out.

In an earlier part of this publication, the desirability of determining the actual carbon-dioxide content of retort gases was pointed out. Although the physical-chemical theory of the dynamics of zinc reduction is not at present worked out the extent to which the limits imposed by equilibrium are actually approached in smelting may be determined by the comparison of such results, if obtained, with the data of Table 28. To facilitate such comparison and to show graphically the limiting values of gas composition which may be expected, Figure 16 has been prepared, showing the possible ranges of variation.
of composition at 1 atmosphere pressure. The diagram is self-
explanatory and shows directly the fields of composition within which
the zinc vapor, carbon monoxide, and carbon dioxide content must
lie at the steady state.

The limiting conditions which have been determined by the above
thermodynamic treatment do not account for the effect of available
heat supply. It is possible that smelting rates in actual practice may
be limited by the rate at which heat may be supplied to meet the
endothermic requirements of the reduction reaction. The data given
would apply to a closed system to which heat was applied from an
external source or internally by other means than combustion at a
rate faster or equal to the thermal requirements of the equilibria
involved. In a blast furnace for zinc the effort is made to supply this
heat by burning excess fuel, but this results in the dilution of gases
mentioned in the quoted report of Johnston's remarks. It is plain
that the dilution of gases, which is entailed by the use of air, is
unfavorable to any attempt to reach the ideal conditions delineated
by the calculations made. It is also apparent that if enriched air or
oxygen was used a much better approach to the ideal conditions
described above would be attained. From this point of view, it
seems possible that despite the quoted remarks of Johnston the last
word on direct smelting for liquid zinc in the blast furnace may not
have been said, if, in the future, it should ever become economically
easible to supply cheap oxygen.
Part IV. A THERMALLY "IDEAL" ZINC-SMELTING CYCLE

HIGH TEMPERATURES OF ZINC RETORTS

The reader of the preceding pages must have realized by now that one implication of the acceptance of the mechanism of zinc reduction as discussed in a quantitative way is that the whole necessity for the high temperatures used in present retort smelting of zinc is based upon the need of completing the producer-gas step. If this is true the theorist, impatient with any process that is theoretically irrational, will find it difficult to accept the present retorts as a suitable or efficient means of carrying out the reduction reaction. Since the reduction step is rapid at much lower temperatures than the second step some theoretical advantage might ensue from an actual separation in practice between the chemically consecutive parts of the reduction.

The yields which may be obtained by the use of carbon monoxide as reducer, as illustrated by the data of Table 21, are indeed much lower than had been indicated by previous incorrect data upon the reduction reaction. Nevertheless, they are not such as to preclude the use of carbon monoxide as a reducer, provided some suitable means of obtaining the latter is available. It seems worth while to discuss from a theoretical point of view the sequence of reactions that would make this possible.

The amount of reducing fuel used in retort smelting is customarily many times that required by the stoichiometric relationships of the reduction reactions, nor does this fuel furnish its available heat directly for reduction except to the extent of a small portion of the total heat available or required. The heat of the reaction $C + \frac{1}{2}O_2 \rightarrow CO$ is approximately 29,000 calories at ordinary temperatures, but for the reaction $C + O_2 \rightarrow CO_2$ there are available 94,300 calories per mole; and for every pound of fuel burned in the retort more than two-thirds of its heat is wasted, as far as thermal efficiency is concerned, although, as previously explained, the excess serves a necessary purpose in the reduction process. Any attempt to recover in an unburned form the carbon monoxide that issues from a retort is obviously beset by serious practical difficulties, dependent upon the nature of the smelting process and the containers used. Nevertheless, it seems strange that a more serious attempt has not been made to find a method of zinc smelting in which only carbon dioxide should leave the process, thus utilizing the total heat of combustion of carbon.

"IDEAL" CYCLE

In its simplest configuration such a thermally ideal process could be constructed of five units: (1) A reducer in which zinc oxide, preheated to a suitable temperature ($900^\circ$ minimum) was treated with carbon monoxide gas; (2) a "producer" in which the exit gases of the reducer would pass over incandescent carbon ($1,100^\circ$ minimum);
(3) a condenser in which the zinc content of the exit gas would be recovered; (4) heat interchangers of a number of possible configurations; and (5) a gas container for temporary storage of carbon monoxide. This process would be of the intermittent continuous type. During a portion of the period air would be blown into the producer, preferably preheated by having been previously used to cool the condenser, and all products of combustion would be vented to the atmosphere after recovery of available heat in the interchanges. In the second stage air would be excluded, and carbon monoxide from the storage would pass first through a preheater which might be part of (4) or a separate unit, then proceed to the reducer, producer, and condenser in series, to return to the container augmented in volume by the chemical reactions in the reducer and producer, which together are a source of carbon monoxide.

Since the invention of a zinc-smelting process is no part of the paper no attempt will be made to describe machinery or practical arrangements by which such a cycle might be carried out, but some calculations will be made to indicate the chemical conditions that must be met. The reader should note, however, that with the exception of the "reducer," no new type of metallurgical machine is involved.

GAS COMPOSITIONS OF "IDEAL" CYCLE

Depending on the temperature the gas issuing from the reducer will have certain compositions, but at all times the zinc-vapor content must remain below 50 per cent, the stoichiometric limit. As the basis of calculation it will be sufficient for the present purpose to assume five compositions of the reducer-gas content and three temperature conditions of the producer. These are designated in Table 32.

Table 32.—Assumptions of conditions in reducer and producer of the "ideal" cycle

<table>
<thead>
<tr>
<th>Notation adopted</th>
<th>CO</th>
<th>CO₂</th>
<th>Zn</th>
<th>Required temperature of exit gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Per cent</td>
<td>Per cent</td>
<td>Per cent</td>
<td>°C.</td>
</tr>
<tr>
<td>Case 1</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>941</td>
</tr>
<tr>
<td>Case 2</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>1,067</td>
</tr>
<tr>
<td>Case 3</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>1,175</td>
</tr>
<tr>
<td>Case 4</td>
<td>20</td>
<td>40</td>
<td>40</td>
<td>1,307</td>
</tr>
<tr>
<td>Case 5</td>
<td>10</td>
<td>45</td>
<td>45</td>
<td>1,425</td>
</tr>
</tbody>
</table>

Table 32.—Assumptions of conditions in reducer and producer of the "ideal" cycle

<table>
<thead>
<tr>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case A</td>
</tr>
<tr>
<td>Case B</td>
</tr>
<tr>
<td>Case C</td>
</tr>
</tbody>
</table>

The general solution of the determination of gas compositions at 1 atmosphere pressure is as follows:

Let \( a = \) proportional part by volume of CO₂ to start in the producer, and

\( b = \) proportional part by volume of CO to start.

Then \( 1 - (a + b) = \) proportional part by volume of Zn vapor.

Also let \( x = \) proportional part of original CO₂ reacting.
Suppose the start is made with 1 mole of original gas, of composition \(a\), \(b\), and \(1-(a+b)\) parts carbon dioxide, carbon monoxide, and zinc, then

\[
\begin{align*}
(1-x)\ a &= \text{moles CO}_2 \text{ at end of producer reaction}, \\
2\ xa+b &= \text{moles CO at end of producer reaction}, \\
1-(a+b) &= \text{moles Zn at end of producer reaction}, \\
a-xa+2xa+b+1-a-b &= 1+xa \text{ are the total moles after reaction.}
\end{align*}
\]

Then the final concentration of gas from the producer, if equilibrium is obtained, will be

\[
\begin{align*}
P_{\text{CO}_2} &= \frac{(1-x)\ a}{1+xa} \\
P_{\text{CO}} &= \frac{2\ xa+b}{1+xa} \\
P_{\text{Zn}} &= \frac{1-(a+b)}{1+xa} \\
\text{and } K_\omega &= \frac{(2xa+b)^2}{(1+xa)(1-x)\ a}
\end{align*}
\]

By applying the above equations the compositions of gas that would exist at the entrance to the condenser under ideal conditions may be calculated.

By the substitution of numerical values for \(a\), \(b\), and \(K_\omega\) the last equation given is solvable for \(x\), as the first step in the general solution of the problem, but this leads to an unwieldy quadratic for \(x\) requiring tedious calculations. The reader may note, however, that under all practical conditions (that is above 1,000° for the producer-gas reaction) the value of \(x\) so obtained will be near unity. Without appreciable error unity may be substituted for \(x\) in the expressions \((2xa+b)\), and \((1+xa)\), whence there is obtained

\[
\begin{align*}
K_\omega &= -\frac{(2a+b)^2}{(1+a)a(1-x)} \\
x &= 1 - \frac{(2a+b)^2}{K_\omega a(1+a)} = 1 - \frac{1}{K_\omega a(1+a)}
\end{align*}
\]

This latter form is sufficiently precise for the present use and greatly simplifies the calculations.

Results of these approximate calculations for the conditions selected in Table 32 are recorded in Table 33. In this table the condition combination 1A indicates that the reducer gives gas compositions of Case I, corresponding to an exit temperature of 941° C., and that the producer is at 1,027° C., case A.
TABLE 33.—Gas compositions at producer exit in “ideal” cycle

<table>
<thead>
<tr>
<th>Combination of conditions</th>
<th>X—proportional conversion</th>
<th>CO₂ in exit gas</th>
<th>Zn in exit gas</th>
<th>CO in exit gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducer</td>
<td>Producer</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>0.94485</td>
<td>0.502</td>
<td>9.19</td>
</tr>
<tr>
<td>1</td>
<td>B</td>
<td>0.93903</td>
<td>0.655</td>
<td>90.4</td>
</tr>
<tr>
<td>1</td>
<td>C</td>
<td>0.98583</td>
<td>0.015</td>
<td>90.9</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>0.97472</td>
<td>0.412</td>
<td>82.9</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>0.9502</td>
<td>0.653</td>
<td>83.2</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>0.99333</td>
<td>0.111</td>
<td>83.3</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>0.8445</td>
<td>0.359</td>
<td>75.6</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>0.98803</td>
<td>0.454</td>
<td>76.3</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>0.95068</td>
<td>0.009</td>
<td>76.9</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>0.98116</td>
<td>0.310</td>
<td>71.1</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>0.98833</td>
<td>0.039</td>
<td>71.4</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>0.99917</td>
<td>0.008</td>
<td>71.4</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>0.98609</td>
<td>0.289</td>
<td>68.7</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>0.98682</td>
<td>0.035</td>
<td>69.0</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>0.99975</td>
<td>0.007</td>
<td>69.0</td>
</tr>
</tbody>
</table>

CONDENSATION AND REOXIDATION

Considering in detail the results of the calculations recorded in Table 33, it will be of interest to determine the temperature of reoxidation and of condensation of zinc as the gas compositions given are cooled in the condenser. To determine the reoxidation point, the value of \( K_{\rho(2)} = \frac{P_{\text{Zn}} \cdot P_{\text{CO}_2}}{P_{\text{CO}}} \) is calculated from the composition given and the corresponding temperature read from a chart of log \( K_{\rho(2)} \) vs. \( T \) as determined from the data of Table 20. The dew point is determined similarly by interpolation on the vapor-pressure curve of liquid zinc. Table 34 gives the results of these calculations.

TABLE 34.—Reoxidation and dew points of condenser gas in “ideal” cycle

<table>
<thead>
<tr>
<th>Combination of conditions</th>
<th>Calculated ( K_0 )</th>
<th>Log ( K_\rho )</th>
<th>Apparent reoxidation temperature, °C.</th>
<th>Log ( p_{\text{Zn}} )</th>
<th>Zinc dew point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducer</td>
<td>Producer</td>
<td>( 10^{-4} )</td>
<td>( 10^{-4} )</td>
<td>( 10^{-3} )</td>
<td>( 10^{-3} )</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>5.05</td>
<td>-3.397</td>
<td>761</td>
<td>-1.041</td>
</tr>
<tr>
<td>1</td>
<td>B</td>
<td>6.31</td>
<td>-4.200</td>
<td>767</td>
<td>1.672</td>
</tr>
<tr>
<td>1</td>
<td>C</td>
<td>1.30</td>
<td>-4.886</td>
<td>715</td>
<td>1.615</td>
</tr>
<tr>
<td>1</td>
<td>D</td>
<td>8.30</td>
<td>-3.981</td>
<td>753</td>
<td>785</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>1.01</td>
<td>-3.940</td>
<td>1.096</td>
<td>1.673</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>2.20</td>
<td>-4.857</td>
<td>1.333</td>
<td>800</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>1.08</td>
<td>-2.966</td>
<td>800</td>
<td>710</td>
</tr>
<tr>
<td>2</td>
<td>D</td>
<td>1.35</td>
<td>-3.870</td>
<td>753</td>
<td>1.259</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>2.71</td>
<td>-4.569</td>
<td>1.440</td>
<td>800</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>1.25</td>
<td>-2.903</td>
<td>800</td>
<td>710</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>1.50</td>
<td>-3.807</td>
<td>753</td>
<td>1.259</td>
</tr>
<tr>
<td>3</td>
<td>D</td>
<td>3.21</td>
<td>-4.495</td>
<td>1.447</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>1.30</td>
<td>-2.886</td>
<td>800</td>
<td>710</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>1.72</td>
<td>1.711</td>
<td>1.171</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>2.24</td>
<td>1.474</td>
<td>800</td>
<td></td>
</tr>
</tbody>
</table>

1 Fictitious results when zinc condenses.

Study of the results of Table 34 immediately shows that the A conditions all indicate a reoxidation temperature above the dew point, and the equilibria would require zinc oxide to be formed by the
reversal of reactions before any liquid zinc was produced resulting in the inevitable formation of chemical blue powder. In the B and C conditions, however, a considerable portion of the zinc will always be condensed before any reoxidation takes place.

To calculate the actual portion of the zinc which would be condensed before reoxidation in the B and C conditions of Table 34, it is necessary to account for the changes produced when liquid zinc appears in the system. The figures of Table 33 show reoxidation temperatures for a definite content of zinc vapor corresponding to the resulting composition of the producer reaction; but as the temperature drops when liquid zinc is present in the system, as in a condenser, the temperatures so obtained are no longer correct because the zinc-vapor content now is determined by the vapor pressure of the liquid metal and decreases as the temperature drops. The previous assumption, with absence of liquid, involves constant gas composition.

In a later part of the publication the general solution of this problem is considered (see p. 77). The ratio $\frac{P_{CO_2}}{P_{CO}}$, which does not change until reoxidation takes place, is the deciding factor.

This conclusion implies that the rate of the dissociation of carbon monoxide according to the reaction $2CO = CO_2 + C$ is much slower than the reoxidation reaction, an experimental observation discussed in more detail in connection with blue-powder formation.

Table 35 gives the necessary data for estimation of true reoxidation temperatures obtained from Table 32. The values for the percentage of zinc recovered before reoxidation, as given in the last column, were corrected for the change in a given volume of the carbon monoxide, due to the condensation of zinc from it.

The data given show that for the B and C conditions a satisfactory recovery of liquid zinc without formation of oxide should be possible if equilibrium can be reached in the producer and reducer of the ideal cycle. This necessity for reaching equilibrium prevents any prophecy from being made as to the capacity of the suppositious "ideal" cycle; but at these temperatures it is known that reaction velocities of both steps of the method are moderately rapid, and there is no doubt but that equilibrium will be reached with a slow enough gas velocity over the zinc oxide and carbon.

Table 35.—Reoxidation temperatures and unoxidized zinc recovery below the dew point in "ideal" cycle

<table>
<thead>
<tr>
<th>Combination of conditions</th>
<th>$\frac{P_{CO_2}}{P_{CO}}$</th>
<th>Log $\left(\frac{P_{CO_2}}{P_{CO}}\right)$</th>
<th>True re-oxidation temperature, °C.</th>
<th>Vapor pressure of Zn at reoxidation point, atmospheres</th>
<th>Zn removed before reoxidation, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B</td>
<td>6.9 - 10^{-4}</td>
<td>-3.16</td>
<td>609</td>
<td>0.0172</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>1.4 - 10^{-4}</td>
<td>-3.85</td>
<td>451</td>
<td>0.0105</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>6.4 - 10^{-4}</td>
<td>-3.19</td>
<td>603</td>
<td>0.013</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>5.9 - 10^{-4}</td>
<td>-3.89</td>
<td>475</td>
<td>0.0098</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>1.2 - 10^{-4}</td>
<td>-3.23</td>
<td>594</td>
<td>0.0132</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>5.5 - 10^{-4}</td>
<td>-3.92</td>
<td>470</td>
<td>0.0076</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>1.1 - 10^{-4}</td>
<td>-3.96</td>
<td>4.4</td>
<td>0.0113</td>
</tr>
<tr>
<td>8</td>
<td>C</td>
<td>5.3 - 10^{-4}</td>
<td>-3.28</td>
<td>585</td>
<td>0.0017</td>
</tr>
<tr>
<td>9</td>
<td>B</td>
<td>1.0 - 10^{-4}</td>
<td>-4.00</td>
<td>458</td>
<td>0.0056</td>
</tr>
</tbody>
</table>
THERMAL REQUIREMENTS OF "IDEAL" CYCLE

The question of the endothermic heat of reaction as affecting the results of the "ideal" cycle remains to be considered. Although the use of thermal calculations will be complicated here the fact that rather complete data are available justifies some simple estimates. As the simplest possible assumption, consider 1 mole of carbon monoxide gas at a temperature $T_A$, which reacts with a determinable amount, which shall be called $y$ moles, of zinc oxide at an initial temperature $T_B$, the system reaching a final temperature $T_Y$, also determinable. The number of moles of zinc oxide, $y$, is just that needed to supply the equilibrium composition of the resultant gas at a temperature $T_Y$. Now the endothermic heat of reduction—equation (1)—may be obtained from the free-energy equation (12), Part I, and may be written:

$$\Delta H^\circ_T = +47,397 - 0.697T - 3.285 \times 10^{-5}T^3 + 1.254 \times 10^{-7}T^3$$  \hspace{1cm} (Equation 1)$$

Then the mean heat of reduction between the temperatures $T_B$ and $T_Y$, which we will designate by $f(T_Y)$, is

$$f(T_Y) = \frac{1}{T_B - T_Y} \int_{T_B}^{T_Y} \Delta H_T dT,$$

or

$$f(T_Y) = \frac{1}{T_B - T_Y} [47,397(T_B - T_Y) - 0.345(T_B^2 - T_Y^2) - 1.095 \times 10^{-5}(T_B^3 - T_Y^3) + 0.313 \times 10^{-6}(T_B^4 - T_Y^4)]$$

$$= 47,397 - 0.345(T_B + T_Y) - 1.095 \times 10^{-5}(T_B^2 + T_B T_Y + T_Y^2) + 0.313 \times 10^{-6}(T_B^3 + T_B^2 T_Y + T_B T_Y^2 + T_Y^3)$$  \hspace{1cm} (Equation 2)$$

Furthermore, the heat available for supplying endothermic reaction is given by the difference in heat contents of the carbon monoxide used. The specific heat of carbon monoxide will be taken as

$$C_p = 6.76 + 0.61 \times 10^{-3}T + 0.13 \times 10^{-5}T^2$$

where

$$H_T = \int_0^T C_p dT$$

$$H_T = 6.76T + 0.305 \times 10^{-3}T^2 + 0.43 \times 10^{-5}T^3$$

and if the drop of temperature of the carbon monoxide is considered in two steps, a justifiable assumption since the heat is independent of the path, 1 mole drops from $T_A$ to $T_B$, but $(1 - y)$ moles drop from $T_B$ to $T_Y$, and if the heat available is $H_A$,

$$H_A = 6.76(T_A - T_B) + 0.305 \times 10^{-3}(T_A^2 - T_B^2) + 0.43 \times 10^{-7}(T_A^3 - T_B^3) + (1 - y)[6.76(T_B - T_Y) + 0.305 \times 10^{-3}(T_B^2 - T_Y^2) + 0.43 \times 10^{-7}(T_B^3 - T_Y^3)],$$

$$= 6.76(T_A - T_B) + 0.305 \times 10^{-3}(T_A^2 - T_B^2) + 0.43 \times 10^{-7}(T_A^3 - T_B^3) - y[6.76(T_B - T_Y) + 0.305 \times 10^{-3}(T_B^2 - T_Y^2) + 0.43 \times 10^{-7}(T_B^3 - T_Y^3)].$$

Let

$$F(T_Y) = 6.76(T_A - T_Y) + 0.305 \times 10^{-3}(T_A^2 - T_Y^2) + 0.43 \times 10^{-7}(T_A^3 - T_Y^3)$$

and

$$F'(T_Y) = 6.76(T_B - T_Y) + 0.305 \times 10^{-3}(T_B^2 - T_Y^2) + 0.43 \times 10^{-7}(T_B^3 - T_Y^3).$$
Equating the heat absorbed by the reaction with the available heat

\[ yf(T_v) = F(T_v) - yF'(T_v) \]  \hspace{1cm} \text{(Equation 3)}

and

\[ y = \frac{F(T_v)}{f(T_v) + F'(T_v)} \]  \hspace{1cm} \text{(Equation 4)}

Furthermore, \( y \) may be related to \( T_y \) by the equilibrium constant \( K_{2y} \) corresponding to the reduction reaction. If the start of the reduction reaction is made with 1 mole of carbon monoxide after reaction there will be \( 1 - y + y + y = 1 + y \) gaseous moles, and the percentage of zinc after reaction is \( 100 \cdot \frac{y}{1+y} \). The percentage may be read from Table 21 for any specific value of \( T_y \) and \( y \) calculated. If, now, the values of \( y \) as calculated from the thermal data are plotted as a function of \( T_y \), and upon the same chart the curve of \( y \) as calculated from equilibria is superimposed, the intersection of the two curves must represent the value of composition and temperature of the system after reaction.

Only two examples illustrative of this simple system will be given here.

**EXAMPLE A**

\( T_A \) is assumed = 1,527° C. = 1,800° K.
\( T_B \) is assumed = 1,027° C. = 1,300° K.

Probable values of \( T_v \) will be covered by the range 927°, 1,027°, and 1,127° C. Table 36 shows the calculated results obtained in the section covered by \( A \). If the calculated figures for \( y \) from thermal data and from equilibria are plotted (chart not reproduced) it is found that the intersection lies at \( T_v = 936° \) C., \( y = 0.1060 \).

**EXAMPLE B**

Similarly, suppose that the start is made with the zinc oxide 200° hotter; that is,

\( T_A = 1,527° \) C. = 1,800° K.
\( T_B = 1,227° \) C. = 1,500° K.

Table 36 shows the results in this case in the section covered by \( B \) in the first column. When the concomitant values of \( y \) are plotted, the intersection is found at \( T_v = 933 \), \( y = 0.1037 \), a result differing only slightly from that for example \( A \). At first sight the obvious conclusion of these calculations, that an increase of zinc oxide temperature actually decreases the yield, seems startling but is explained by the fact that the available heat of the carbon monoxide is thus greatly decreased, whereas the equilibrium requires such low values for \( y \) that compensation can not be gained for the loss. Conversely, since the mean heat of reduction over the range \( T_B \) to \( T_v \) varies only slightly, to get high yields for the sort of system described in these examples the maintenance of a high-temperature difference between the incoming carbon monoxide and the reacting zinc oxide is essential. However, the condition where only \( y \) moles of zinc oxide would be subjected to the treatment of 1 mole of carbon monoxide is one that would be of little or no practical importance, and its discussion here serves only to illustrate the principles involved.
From a practical point of view conditions which are of interest result from further generalization of these calculations. Let it be supposed that 1 mole of carbon monoxide comes into contact with \( m + y \) moles of zinc oxide, of which \( y \) moles react completely. Then there will be available the difference in heat content between the temperatures \( T_B \) and \( T_y \) furnished by \( m \) moles of zinc oxide; and this, added to the available heat in the carbon monoxide, will materially improve possible recoveries and conversion yields.

The specific heat of zinc oxide is given by the expression

\[
C_p(znO) = 6.63 + 11.26 \cdot 10^{-2} T - 4.722 \cdot 10^{-4} T^2
\]

The available heat is

\[
H_A(znO) = \int_{T_y}^{T_B} C_p \, dt = F''(T_y)
\]

\[
F''(T_y) = 6.63 (T_B - T_y) + 5.63 \cdot 10^{-3} (T_B^2 - T_y^2) - 1.574 \cdot 10^{-4} (T_B^3 - T_y^3)
\]

(Equation 4)

Then equation (3) becomes

\[
yf(T_y) = F(T_y) - yF''(T_y) + mF'''(T_y)
\]

\[
y = \frac{F(T_y) + mF''(T_y)}{F(T_y) + F''(T_y)}
\]

(Equation 5)

By the use of equation (5) the figures in Table 37 have been calculated, showing \( y \) for a number of assumed values of \( m \). Figure 17 shows these numbers as derived from thermal data, compared with the function \( y \) as obtained from equilibrium, the latter being shown as the curve \( e \). The intersections of \( e \) with the individual lines corresponding to each value of \( m \) give the final result of temperature and conversion in the "ideal" cycle. In the lower part of the figure the lines for examples A and B show the percentages of zinc in the gas obtained from the reducer in a single step, when the mass factor \( m \) is varied. These data are also summarized in Table 38.

Table 36.—Thermal quantities in solutions for examples A and B

<table>
<thead>
<tr>
<th>Example</th>
<th>( T_y ) °C.</th>
<th>( f(T_y) )</th>
<th>( F'(T_y) )</th>
<th>( F''(T_y) )</th>
<th>( y ) from thermal data</th>
<th>Final Zn, per cent</th>
<th>( y ) from equilibrium data</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>927</td>
<td>43,847</td>
<td>4,781</td>
<td>+772</td>
<td>0.1072</td>
<td>9.03</td>
<td>0.0993</td>
</tr>
<tr>
<td></td>
<td>1,027</td>
<td>43,763</td>
<td>4,099</td>
<td>0</td>
<td>0.0917(3)</td>
<td>16.54</td>
<td>19.69</td>
</tr>
<tr>
<td>B</td>
<td>927</td>
<td>43,575</td>
<td>4,781</td>
<td>-783</td>
<td>0.0754(4)</td>
<td>25.75</td>
<td>0.3465</td>
</tr>
<tr>
<td></td>
<td>1,027</td>
<td>43,393</td>
<td>4,099</td>
<td>1,574</td>
<td>0.0992</td>
<td>16.54</td>
<td>19.69</td>
</tr>
<tr>
<td></td>
<td>1,027</td>
<td>42,211</td>
<td>3,227</td>
<td>701</td>
<td>0.0733</td>
<td>25.75</td>
<td>0.3465</td>
</tr>
</tbody>
</table>

Table 37.—Conversions from thermal data in the general solution for examples A and B, \( m = 0 \)

<table>
<thead>
<tr>
<th>Example</th>
<th>( T_y ) °C.</th>
<th>( F''(T_y) )</th>
<th>( y ) at ( m = 0 )</th>
<th>( y ) at ( m = 1 )</th>
<th>( y ) at ( m = 5 )</th>
<th>( y ) at ( m = 10 )</th>
<th>( y ) at ( m = 20 )</th>
<th>( y ) at ( m = 50 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>927</td>
<td>1,333</td>
<td>0.1072</td>
<td>0.1370</td>
<td>0.2565</td>
<td>0.4059</td>
<td>0.7047</td>
<td>1.0009</td>
</tr>
<tr>
<td></td>
<td>1,027</td>
<td>-1,322</td>
<td>0.0917</td>
<td>0.0117</td>
<td>0.0917</td>
<td>-2.358</td>
<td>-5.827</td>
<td>-1.4697</td>
</tr>
<tr>
<td>B</td>
<td>927</td>
<td>2,625</td>
<td>0.0992</td>
<td>0.1475</td>
<td>0.3810</td>
<td>0.6729</td>
<td>1.2567</td>
<td>3.0080</td>
</tr>
<tr>
<td></td>
<td>1,027</td>
<td>1,303</td>
<td>0.0733</td>
<td>0.1050</td>
<td>0.2214</td>
<td>0.3685</td>
<td>0.6656</td>
<td>1.5540</td>
</tr>
</tbody>
</table>
The latter curves show that a fair concentration of zinc vapor could be obtained in the "ideal" cycle, at not excessive tempera-
tures, and the specific values given, although they apply only for the chosen values of $T_A$ and $T_B$, nevertheless would be useful if an actual reducer was being designed. The value $m + y$ represents the number of moles of zinc oxide which must be treated by 1 mole of carbon.
monoxide to get the stated final temperatures and compositions per "blow." Therefore, if the capacity of a given installation is predetermined the value of \( m \) will allow calculation of the mass of zinc oxide which must be maintained in the reducer.

**SIGNIFICANCE OF "IDEAL" CYCLE**

The calculations which have been made are not intended to embody recommendations for the details of a zinc-smelting process. It is the purpose to show thermodynamically that it is chemically possible to devise a "paper" process which rejects only carbon dioxide and is therefore thermally as efficient as any process using carbon as reducer could possibly be. Moreover, the thermal requirements of the endothermic zinc-reduction reaction did not preclude the storage of sufficient heat in the reactants themselves to yield adequate conversions (but lower than in present retorts).

The zinc content of the gaseous phase issuing from the reducer will be low, and to produce zinc metal further difficulties enter in the condensation from low zinc content gas. It is conceivable that if such a process should be attempted for actual zinc production one of two alternatives would have to be adopted. The zinc content of the exit gas from the reducer might be removed without further temperature drop, as, for example, by solution in liquid lead, from which the zinc metal might be recovered by liquidation or distillation. Under these circumstances reoxidation and the formation of blue powder on cooling would be prevented. The second alternative would be to pass the exit gases from the reducer through a bed of incandescent carbon at the same or higher temperature. The carbon-dioxide content of the gas would then disappear, but further dilution of the gas would ensue, inasmuch as each volume of carbon-dioxide produces two volumes of carbon-monoxide. Table 39 shows the final zinc concentrations which would be obtained if such a scheme was used.

<table>
<thead>
<tr>
<th>( m )</th>
<th>Example A</th>
<th></th>
<th>Example B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn in gas from reducer</td>
<td>Zn in gas to condenser</td>
<td>Zn in gas from reducer</td>
<td>Zn in gas to condenser</td>
</tr>
<tr>
<td>Per cent</td>
<td>Per cent</td>
<td>Per cent</td>
<td>Per cent</td>
</tr>
<tr>
<td>0.</td>
<td>9.38</td>
<td>8.73</td>
<td>9.43</td>
</tr>
<tr>
<td>1</td>
<td>11.11</td>
<td>10.00</td>
<td>14.14</td>
</tr>
<tr>
<td>5</td>
<td>13.48</td>
<td>11.88</td>
<td>22.18</td>
</tr>
<tr>
<td>10</td>
<td>14.53</td>
<td>12.69</td>
<td>26.14</td>
</tr>
<tr>
<td>20</td>
<td>15.30</td>
<td>13.34</td>
<td>29.37</td>
</tr>
<tr>
<td>50</td>
<td>16.02</td>
<td>13.80</td>
<td>32.00</td>
</tr>
<tr>
<td>( \infty )</td>
<td>16.54</td>
<td>14.19</td>
<td>34.58</td>
</tr>
</tbody>
</table>

It is apparent that under typical conditions of use the maximum zinc content of gas from the thermally ideal cycle would be not much more than half that from a zinc retort as now used. From a practical viewpoint the thermodynamic possibilities of the zinc blast furnace using oxygen seem more attractive.
Part V. REOXIDATION AND BLUE POWDER FORMATION

CHEMICAL SOURCES OF BLUE POWDER

When heating of a charge is begun in a zinc retort water and volatile hydrocarbons are present in the exit gases and produce some blue powder. For the greater and more important part of the reduction the gases from the retort consist only of zinc vapor, carbon monoxide, and carbon dioxide, in amounts determined by various factors enumerated in previous parts of this work. In this report and for most practical purposes it suffices to consider only the questions of the oxidation of zinc by carbon monoxide, and especially by carbon dioxide.

ZINC AND CARBON MONOXIDE

Zinc is a moderately strong basic metal. By analogy with the alkaline earth and alkali metals, which are known to reduce carbon monoxide at elevated temperatures, zinc also might be expected to reduce carbon monoxide. The reaction has been written:

\[ \text{Zn}(g) \text{ or Zn}(l) + \text{CO} = \text{ZnO} + \text{C} \]  

(1)

This equation is obviously the reversal of the steady-state condition of continuous reduction and involves the reversal of the producer-gas reaction

\[ 2\text{CO} = \text{CO}_2 + \text{C} \]  

(2)

Equation (1) is then not a complete reaction, since carbon dioxide is omitted, and equilibrium can not be attained at any pressures and temperatures except those of the invariant points determined in Part II. (See p. 51.) At 1 atmosphere pressure equilibrium is possible only at 857° C. The mechanism of reaction (1) then consists of the consecutive or simultaneous reactions

\[ 2\text{CO} = \text{CO}_2 + \text{C} \]

\[ \text{CO}_2 + \text{Zn} = \text{ZnO} + \text{CO} \]

Of these the first is known to be slow below about 1,100° C., but the second is perceptible above 300° C. and is very rapid above about 550° C. Then the rate at which zinc is oxidized by carbon is determined by the slow step, the reversal of the producer-gas reaction, or the dissociation of carbon monoxide.

Reference to the gas composition of Table 22 (producer-gas reaction) shows that large amounts of carbon dioxide would be present in the equilibrium mixture at temperatures below 850° C., but it is also known that below 850° the rate of dissociation becomes increasingly slow, and in the absence of a very active catalyst months or even years might be necessary to reach the equilibrium concentration. It is, of course, possible to write the free-energy equation of reaction (1) in a purely formal way; but, in view of the above facts, this does
not furnish us with new results, because reaction rates are not as yet predictable from free-energy quantities. The result of such calculations would show that at low temperatures carbon monoxide should nearly disappear, according to the reaction written, but it is not necessary actually to make such calculations in order to see that this must be true. It is known that the dissociation of carbon monoxide would furnish, at temperatures below 850°, many times the carbon-dioxide content which could be in equilibrium with zinc oxide and carbon monoxide. The question as to whether or not reaction (1) is technically important as a source of blue powder in zinc condensation devolves then upon the question of what materials are catalysts. It has been known for a long time that iron is a catalyst for the dissociation of carbon monoxide, and may be responsible for the formation of soot in the iron blast furnace. The mechanism given will then require iron also to be a catalyst for the reduction of carbon monoxide by zinc. Furthermore, it is interesting, and perhaps important to know whether the surfaces of liquid zinc or of solid zinc oxide are also surface catalysts.

R. W. Millar ¹ of the Berkeley station of the Bureau of Mines, has investigated the catalytic action of several materials in a semi-quantitative way, and a brief résumé of his results are of interest here.

The materials investigated as catalysts were iron, alumina, fire brick containing iron oxide and freed from iron, zinc oxide, and liquid zinc. Blank experiments were made in which no catalyst material was used. Of these materials only iron and the fire brick containing iron were active enough as catalysts so that they definitely could be shown to have catalytic effect. Data in footnote 5, Part I, show, however, that under some circumstances a mixture of zinc oxide and metallic zinc, and especially a zinc surface, have some noticeable catalytic effect but that the rate of reaction is less than 1/100 of that of the zinc oxide reduction at the same temperature.

The reduction of carbon monoxide by zinc is then a thermodynamically possible and necessary reaction at temperatures below 850° C., but the rate is so slow as to be of negligible practical importance in the absence of active catalysts. It is worth noting, however, that the iron content of clays used in condensers might have some practical importance. The matter has been further discussed by Millar.²

ZINC AND CARBON DIOXIDE

Practical experience in zinc smelting is in accord with the above reasoning, confirming the importance of reoxidation of zinc by carbon dioxide as the only important source of chemical blue-powder formation.

The fundamental principle for discussion of chemical blue-powder formation may be given as follows: If, upon cooling a gas consisting of zinc vapor, carbon monoxide, and carbon dioxide no reoxidation can take place through reversal of the reduction reaction $\text{Zn(g)} + \text{CO}_2 = \text{ZnO} + \text{CO}$ above the temperature of the dew point of the zinc vapor, then the metal will begin to condense without fouling and blue-powder formation will be minimized.

² Millar, R. W., Condenser Materials and Blue Powder in Zinc Smelting: Min. and Met., vol. 9, 1928, p. 395.
Because the reduction of zinc oxide by carbon monoxide is rapid compared to the reduction of carbon dioxide by carbon at all temperatures below 1,000° C. and probably also at high temperatures it may be assumed that any portion of gas, after leaving a particle of zinc oxide, is in equilibrium with it and should react reversibly as soon as it cools. If, however, this portion of gas has the last contact with carbon and if the temperature is over 1,000° C. it may be assumed that the carbon-dioxide content is that appertaining to the producer-gas reaction. The latter condition is obviously the only one of practical interest. In Part III it was shown that the ensuing gas compositions may be used in the equilibrium constant for the reduction reaction to calculate the temperature at which this gas would be in equilibrium condition; similarly it was shown that the zinc dew point may be calculated from the known vapor pressure of zinc and the gas composition. In actual cases the dew point may be either above or below the equilibrium or reoxidation temperature. If the dew point is the lower, only blue powder could form. When, however, zinc begins to condense at temperatures above the reoxidation point the apparent reoxidation temperatures so obtained are no longer correct because a decreasing zinc-vapor content ensues, which permits a greater content of carbon dioxide to be present at any temperature. Above the dew point the zinc content of the gas is unchanged, since no reaction is occurring, but below this temperature the partial pressure of zinc is determined by the vapor pressure of the liquid metal. If one substitutes \( \frac{v \cdot p_{Zn}}{p_{CO}} \) for the partial pressure in the equilibrium expression and solves for the ratio \( \frac{p_{CO_2}}{p_{CO}} \), there is obtained

\[
\frac{v \cdot p_{Zn}}{p_{CO}} \cdot \frac{p_{CO_2}}{p_{CO}} = K(2) 
\]

The reoxidation point for those conditions where condensation begins before reoxidation occurs may then be determined by plotting values of \( \frac{K(2)}{v \cdot p_{Zn}} \) vs. temperature, or better \( \log \left( \frac{K(2)}{v \cdot p_{Zn}} \right) \) vs. temperature, and reading from it the temperature corresponding to any value of \( \frac{p_{CO_2}}{p_{CO}} \) as determined by gas composition. Table 40 shows such values at 100° intervals from 427° to 1,127° C., which more than covers the range of possible condensation temperatures.

In Figure 18, curve A, are plotted the figures for \( \log \left( \frac{K_2}{v \cdot p_{Zn}} \right) = \log \left( \frac{p_{CO_2}}{p_{CO}} \right) \) against the temperature. Table 40 and Figure 18 are generally useful to determine reoxidation temperatures for any given gas composition when liquid zinc is present. In the greater number of practical cases, however, one has no direct means of analyzing actual retort or other gas containing zinc vapor without the possibility of reversal during analysis. The use of the chart and Table 40 will be limited by this physical difficulty.

106847°—30—6
Table 40.—Reoxidation points for systems containing liquid zinc

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Log ( K_1 )</th>
<th>Log ( v_p.253 )</th>
<th>Log ( K_2 )</th>
<th>Log ( v_p.253 )</th>
<th>( K_2 ) for ( p_{CO} ) at ( p_{CO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>427</td>
<td>-7.8543</td>
<td>-3.6401</td>
<td>-4.2142</td>
<td>6.105 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>527</td>
<td>-6.0709</td>
<td>-2.5012</td>
<td>-3.5577</td>
<td>2.657 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>627</td>
<td>-4.7056</td>
<td>-1.6245</td>
<td>-3.1017</td>
<td>7.915 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>727</td>
<td>-3.6169</td>
<td>-3.9056</td>
<td>-2.6384</td>
<td>2.658 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>827</td>
<td>-2.7331</td>
<td>-5.096</td>
<td>-2.2505</td>
<td>4.350 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>927</td>
<td>-2.0025</td>
<td>+.0090</td>
<td>-2.0061</td>
<td>8.030 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>1,027</td>
<td>-1.3885</td>
<td>+.4787</td>
<td>-1.0572</td>
<td>1.350 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>1,127</td>
<td>-0.0538</td>
<td>+.8054</td>
<td>-1.0712</td>
<td>2.130 \times 10^{-4}</td>
<td></td>
</tr>
</tbody>
</table>

Another view of the problem seems somewhat more pertinent for practical application. The temperature of the blanket of carbon in a retort may be measured without serious difficulty. Assuming that the gases there reach equilibrium with the carbon, what relationship exists between the blanket temperature and the temperature of reoxidation in the condenser?

Table 41.—Blanket temperatures and reoxidation temperatures

<table>
<thead>
<tr>
<th>Blanket temperature, °C</th>
<th>Log ( p_{CO} )</th>
<th>Reoxidation temperature, °C</th>
<th>Log ( p_{CO} )</th>
<th>Reoxidation temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,027</td>
<td>-2.2169</td>
<td>1776.5</td>
<td>-1.5179</td>
<td>1,125</td>
</tr>
<tr>
<td>1,127</td>
<td>-2.7000</td>
<td>1060</td>
<td>-2.0010</td>
<td>966</td>
</tr>
<tr>
<td>1,227</td>
<td>-3.1151</td>
<td>557</td>
<td>-2.4161</td>
<td>808</td>
</tr>
<tr>
<td>1,327</td>
<td>-3.4156</td>
<td>493</td>
<td>-2.7766</td>
<td>703</td>
</tr>
<tr>
<td>1,427</td>
<td>-3.7906</td>
<td>444.5</td>
<td>-3.0916</td>
<td>624</td>
</tr>
<tr>
<td>1,527</td>
<td>-4.0976</td>
<td>468</td>
<td>-3.3986</td>
<td>566</td>
</tr>
<tr>
<td>1,627</td>
<td>-4.3118</td>
<td>461.28</td>
<td>-3.6126</td>
<td>521</td>
</tr>
</tbody>
</table>

1 Below melting point.
From the producer-gas reaction

\[ \text{C} + \text{CO}_2 = 2\text{CO} \quad \text{(Reaction 3, Part II)} \]

the equilibrium expression \( \frac{p_{\text{CO}_2}}{p_{\text{CO}_2}} = K_3 \). It has been previously shown that in all cases where the gases are in contact with carbon as a last step, the carbon monoxide and zinc (g) content approach 50 per cent of the effluent gases. Then if \( P \) is the total pressure, \( p_{\text{CO}} = 0.5 \ P \) may be used for the carbon monoxide, without appreciable error. Further,

\[
\frac{p_{\text{CO}}}{p_{\text{CO}_2}} = \frac{K_3}{0.5P} = 2K_3
\]

\[
\log \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \log P - \log K_3 - 0.3010 \quad \text{(Equation 1)}
\]

The values of \( \log \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \) calculated from this equation may be transformed to reoxidation temperatures by interpolation on curve A, Figure 17. The reader should note that although \( p_{\text{CO}} \) could have been completely eliminated from equation (1) the given form is superior.

The ratio \( \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \) will not change with the temperature, even if zinc vapor is condensed, as long as no reoxidation occurs, whereas the actual value of \( p_{\text{CO}_2} \) will increase as zinc condenses.

The curves showing the relationship between blanket temperature and reoxidation temperature are also charted on Figure 17, where curves 1 and 10 show the results for these respective numbers of atmospheric pressure. To avoid oxidation the condensation temperature must lie above these curves. It is of interest to note that for low temperatures the condensation temperatures are high, and this condition authenticates further the previous assertion that high temperatures in retort smelting are required to complete the producer-gas reaction. It is evident that the blanket temperature must also be high for the same intrinsic reason, here pertinent to the avoidance of blue-powder formation. Furthermore, the higher the pressure the higher must be the condensation temperature. Condensation temperatures must be as low as possible to secure the maximum degree of condensation. The charts show the theoretical limits that must be attained.
Part VI. METHANE AS REDUCER FOR ZINC OXIDE

GASEOUS REDUCTION OF ZINC

In a previous publication\(^1\) the author pointed out that present reduction practice is essentially dependent upon reduction by gas (CO), and this viewpoint has been enlarged by the thermodynamic calculations of the present work. Methane can be shown to have great theoretical advantages for zinc reduction, and in fact such proposals as that of the Coley process\(^2\) seem based upon an unconscious recognition of such advantages. The "nascent" form of carbon supposed to be responsible for the reduction of zinc oxide in this process, according to the theory advanced in the patent specifications, seems an unsatisfactory and unnecessary hypothesis. Part II has shown that the temperatures where graphitic carbon may continuously reduce zinc oxide are accurately calculable. The free energy of "amorphous" carbon is probably less than 2,000 calories greater than that of graphitic carbon.\(^3\)

Had an attempt been made to introduce this value, the difference in the calculations of this report would have been in the nature of a small percentage difference. The zinc reduction itself involves a free-energy change some twenty times greater than the difference between graphitic and amorphous carbon. (The possible variation in behavior between various types of carbon has not previously been considered in this work. Graphitic carbon is the type for which precise thermodynamic data are available. The matter does not enter in discussion of the reduction reaction proper, \(\text{ZnO} + \text{CO} = \text{Zn}(g) + \text{CO}_2\), since the effect of the form of carbon involved in the heats and free energies of formation of carbon monoxide and dioxide is avoided because of the presence on opposite sides of the equation of identical atomic amounts of combined carbon. The reaction \(\text{C} + \text{CO}_2 = 2\text{CO}\) will, on the contrary, be influenced by the form of carbon to the small extent mentioned.)

PRODUCTS OF METHANE REDUCTION OF ZINC

Zinc oxide and methane, if permitted to react at elevated temperatures, could produce, besides zinc vapor, either carbon monoxide or dioxide, either hydrogen or water vapor, or mixtures of these gases. Methane itself is unstable and dissociates at high temperatures, the reaction rate becoming appreciable though slow about 750° C. According to Coward and Wilson\(^4\) the equilibrium mixture contains 2.5 per cent methane and 97.5 per cent hydrogen at 850° C, where the dissociation still requires a catalyst for obtaining good reaction rates.

If methane should have significance as a reduction medium for zinc oxide, it will be because of the possibility of reduction with high yield at lower temperatures than reduction by carbon, carbon monoxide, or hydrogen. At temperatures below 1,000° C. it may be shown that the amount of carbon dioxide in equilibrium with zinc oxide and carbon monoxide is low, as well as the amount of water vapor in equilibrium with zinc oxide and hydrogen. It also seems probable that, with a sufficient surface of oxide exposed to the action of methane, the zinc oxide may be reduced faster than carbon is formed by dissociation of methane. If these steps of reasoning are admitted the reduction reaction may be considered to be substantially

$$\text{ZnO} + \text{CH}_4 = \text{Zn(gas)} + \text{CO} + 2\text{H}_2$$

(Reaction 1)

Interest in the thermodynamic properties of the reaction is based upon the very considerable difference in specific heat between the sides of the reaction. This large difference means that the heat of the reaction and the free-energy change are very sensitive to increase in temperature. These facts are disclosed by the specific figures below.

**THERMODYNAMIC PROPERTIES OF METHANE**

For reaction (1) above, accurate free energies of formation and heats of formation are available for all the reactants and products, with the exception of methane itself. Lewis and Randall have calculated the heat of formation and free energy of formation of methane, and Randall and Mohammad have recently reviewed all available data on this subject. They give for the reaction

$$\text{C (graph)} + 2\text{H}_2 = \text{CH}_4$$

(Reaction 2)

$$\Delta F^o_{298} = -11,573$$

$$\Delta H_{298} = -16,963$$

There is, however, an unexplained discrepancy in connection with these figures. If the entropy of methane is calculated from the data for reaction (2)

$$\Delta S = \frac{-16,963 - (-11,573)}{298}$$

$$= -18.1$$

Lewis and Randall estimated the entropy of graphitic carbon at 25° to be 1.3, and Giauque has recommended that the entropy of hydrogen be taken as 31.25. Substituting the above results in reaction (2) the entropy of methane from these data should be 45.7, but this figure does not agree with the entropy of methane as derived by other methods.

Low-temperature specific-heat determinations on solid and liquid methane have been made by Eucken and Karwat, and determinations

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on the gas at low temperatures have been made by Heuse, Giacomini, and Millar. Furthermore, Karwat has measured the heat of fusion and the vapor pressure of solid methane. The vapor pressure of liquid methane, from which the heat of vaporization of the liquid may be obtained, has been measured by Stock, Henning, and Kuss.

Extrapolation of the specific heat of the solid is somewhat uncertain because the heat capacity is still 5.27 per mol at 28.65° K. It can be shown, however, that if the Debye function applies to the lowest temperature point the entropy up to that point is 5.51 units. If, however, it is assumed that the empirical expression \( C_p = AT^B \) holds the entropy becomes 6.65 units at 28.65° K. It is apparent that the first estimate is lower than the truth, the second greater, and the average 6.1 can not be in error by more than \( \pm 0.6 \) unit. Further estimates of entropy may then be made as follows:

<table>
<thead>
<tr>
<th>From, °K</th>
<th>Form</th>
<th>To, °K</th>
<th>Units</th>
<th>From, °K</th>
<th>Form</th>
<th>To, °K</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Solid</td>
<td>28.65</td>
<td>6.1</td>
<td>111.8</td>
<td>Liquid-vapor</td>
<td>111.8</td>
<td>22.5</td>
</tr>
<tr>
<td>28.65</td>
<td>do</td>
<td>90.3</td>
<td>9.0</td>
<td>111.8</td>
<td>Gas</td>
<td>298.1</td>
<td>7.52</td>
</tr>
<tr>
<td>90.3</td>
<td>Solid-liquid</td>
<td>90.3</td>
<td>2.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90.3</td>
<td>Liquid</td>
<td></td>
<td>2.56</td>
<td></td>
<td></td>
<td>298.1</td>
<td>50.6</td>
</tr>
</tbody>
</table>

1 Melting point.
2 Boiling point.

The difference between this figure, 50.6, and that calculated from equilibria, 45.7, is too great to be explained by the somewhat unsatisfactory nature of the specific heat data. Furthermore, by a study of the comparisons involved in certain organic compounds involving the methyl group, Kelley has estimated (for the purpose of this work) that by analogy the entropy of methane should be 49.5 and the free energy, \(-12,200\). The heat of formation on this basis would be \( \Delta H_{298} = -16,460 \). For the data of these estimates the reader is referred to the paper by Parks, Kelley, and Huffman. There is, then, good agreement between the values for entropy derived directly and indirectly from specific heat measurements but differing from those from equilibria. It seems impossible to straighten out these difficulties until more experimental work has been done on methane; for the present purpose the best that can be done is to calculate the results on the basis of each set of values.

**CALCULATION OF METHANE REDUCTION OF ZINC OXIDE**

Data required for the calculation of methane reduction, not already given in this publication, are the specific heats of hydrogen and

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methane. The most critical estimates available are those of Eastman.

Referring again to probable reduction reaction (1) with methane, the following summary may be made for the specific heats.

\[
C_p(Zn \text{ gas}) = 5.0
\]

\[
C_p(CO) = 6.76 + 0.606 \cdot 10^{-3}T + 0.13 \cdot 10^{-6}T^2
\]

\[
C_p(2H_2) = 13.70 + 0.56 \cdot 10^{-3}T + 0.44 \cdot 10^{-6}T^2
\]

Sum of products = \[
25.46 + 1.166 \cdot 10^{-3}T + 0.57 \cdot 10^{-6}T^2
\]

\[
C_p(CH_4) = 5.90 + 9.60 \cdot 10^{-3}T
\]

\[
C_p(ZnO) = 6.63 + 11.26 \cdot 10^{-3}T - 4.722 \cdot 10^{-6}T^2
\]

Sum of reactants = \[
12.53 + 20.86 \cdot 10^{-3}T - 4.722 \cdot 10^{-6}T^2
\]

\[
\Delta C_p \text{ by difference} = 12.93 - 18.69 \cdot 10^{-3}T + 5.29 \cdot 10^{-6}T^2
\]

The heats of formation and free energies at \(25^\circ C\) may further be summarized:

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta H_m)</th>
<th>(\Delta F_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (gas)</td>
<td>+31,569</td>
<td>+22,917</td>
</tr>
<tr>
<td>CO</td>
<td>−26,313</td>
<td>−32,265</td>
</tr>
<tr>
<td>(2H_2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Products</td>
<td>+5,256</td>
<td>−9,348</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>−16,963 or −16,460</td>
<td>−11,573 or −12,200</td>
</tr>
<tr>
<td>ZnO</td>
<td>−83,313</td>
<td>−75,928</td>
</tr>
<tr>
<td>Reactants</td>
<td>−100,276 or −99,773</td>
<td>−87,501 or −88,128</td>
</tr>
<tr>
<td>Reaction by difference</td>
<td>+105,532 or +105,029</td>
<td>+78,153 or +78,780</td>
</tr>
</tbody>
</table>

From these data there are derived two alternative free-energy equations for reaction (1):

\[
\Delta F^\circ_T = +102,464 - 12.93 T \ln T + 9.35 \cdot 10^{-3}T^2 - 0.88 \cdot 10^{-6}T^3 - 10.53 T
\]

(Equation A)

or

\[
\Delta F^\circ_T = +101,962 - 12.93 T \ln T + 9.53 \cdot 10^{-3}T^2 - 0.88 \cdot 10^{-6}T^3 - 6.75 T
\]

(Equation B)

The reader will note that the value of \(I\) is small and that the decrease of \(\Delta F^\circ\) from a large positive to a smaller or negative value at increased temperatures will depend almost entirely upon the large coefficient of the \(T \ln T\) term.

It is known that at high temperatures considerable amounts of carbon dioxide or water might be present in the products of methane reduction, in consequence of which the use of the simple reaction (1) would no longer be justified. It suffices, therefore, to calculate the free energy of the reaction over a temperature range from 527\(^\circ\) to 927\(^\circ\) C. as convenient selected limits. Assuming that reaction (1) is the predominant reaction in this range, the gas concentrations may

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be readily calculated, using the ordinary methods of solution based on the constitution equations as follows:

\[ K'' = \frac{p_{\text{CH}_4}^2 \cdot p_{\text{CO}} \cdot p_{\text{Zn}}}{p_{\text{CH}_4}} \text{ from equilibrium} \]

\[ p_{\text{CH}_4} + p_{\text{Zn}} + p_{\text{CO}} + p_{\text{H}_2} = 1 \text{ (atmosphere). Total pressure at end of reaction.} \]

\[ p_{\text{CO}} = p_{\text{Zn}} \] from stoichiometric relationships, if the reaction is started with pure
\[ p_{\text{H}_2} = \frac{1}{2} p_{\text{Zn}} \] methane.

**Table 42.—Calculated free energies and equilibrium constants \((K''_T)\) for the reaction \(\text{ZnO} + \text{CH}_4 = \text{Zn(gas)} + \text{CO} + 2\text{H}_2\)**

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>Equation (A)</th>
<th>Equation (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta F^o)</td>
<td>(\log K''_A)</td>
</tr>
<tr>
<td>527</td>
<td>500</td>
<td>30,749</td>
</tr>
<tr>
<td>627</td>
<td>900</td>
<td>21,127</td>
</tr>
<tr>
<td>727</td>
<td>1,000</td>
<td>11,501</td>
</tr>
<tr>
<td>827</td>
<td>1,100</td>
<td>1,883</td>
</tr>
<tr>
<td>927</td>
<td>1,200</td>
<td>-7,720</td>
</tr>
</tbody>
</table>

These equations may be reduced to the form

\[ p_{\text{Zn}} = \frac{1}{4} \cdot \frac{p_{\text{Zn}}^4}{K''} \]

which is best solved by trial substitution. Table 43 shows the results obtained by such processes for both the A and B free-energy equations. It seems significant that the zinc-vapor content of the final gas increases rapidly to its maximum value of 25 per cent in a relatively short temperature range as compared to the action of carbon monoxide on zinc oxide. The reason for this behavior, as has been pointed out before, is the large coefficient of the \(T \ln T\) term, which comes back to the great difference in heat capacity of products and reactants. At low temperatures zinc oxide should be reduced less readily by methane than by carbon monoxide, but a relatively moderate increase in temperature causes the \(T \ln T\) term to become the predominant one in the free-energy summation.

**Table 43.—Gas concentrations calculated for the reaction \(\text{ZnO} + \text{CH}_4 = \text{Zn(gas)} + \text{CO} + 2\text{H}_2\)**

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Equation (A)</th>
<th>Equation (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn or CO</td>
<td>(%)</td>
</tr>
<tr>
<td>527</td>
<td>50.56</td>
<td>1.12</td>
</tr>
<tr>
<td>627</td>
<td>5.56</td>
<td>7.13</td>
</tr>
<tr>
<td>727</td>
<td>13.66</td>
<td>27.32</td>
</tr>
<tr>
<td>827</td>
<td>24.19</td>
<td>48.38</td>
</tr>
<tr>
<td>927</td>
<td>24.985</td>
<td>49.97</td>
</tr>
</tbody>
</table>
It must not be forgotten that these calculations are to some extent purely formal and the supposition must not be made that the reaction takes place according to the assumed formulation. It is certain, however, that other reactions may take place. The important ones to be considered are the deposition of carbon by dissociation of methane, the reduction of zinc oxide by carbon monoxide, and the reduction of the oxide by hydrogen. Each of these may be considered from the point of view of equilibria or from that of reaction rate.

It would not be consistent to utilize the free-energy equation of Randall and Mohammad for the calculation of methane dissociation, as these investigators have used specific heat data somewhat different from those accepted for this work. It may be assumed, however, that the results for $\Delta F^0$ and $\Delta H$ calculated to 298° $K$ represent the best figures now available, and a new free-energy equation must be derived which will be consistent with the present calculations in the specific heat terms. Thus the data for the reaction

$$C_{\text{graphitic}} + 2H_2 = CH_4, \quad K'''' = \frac{p_{CH_4}}{p_{H_2}^2}$$

may be summarized

$$
C_p(\text{CH}_4) = 5.90 + 9.60 \cdot 10^{-3} T \\
C_p(\text{graphitic}) = 1.22 + 4.89 \cdot 10^{-3} T - 1.11 \cdot 10^{-4} T^2 \\
C_p(\text{H}_2) = 13.70 + 0.56 \cdot 10^{-3} T + 0.44 \cdot 10^{-4} T^2 \\
\text{Reactants: } 14.92 + 5.45 \cdot 10^{-3} T - 0.67 \cdot 10^{-4} T^2
$$

$$\Delta C_p \text{ by difference} = -9.02 + 4.15 \cdot 10^{-3} T + 0.67 \cdot 10^{-4} T^2$$

$$\Delta F^0_T = -\frac{14,446(A)}{14,011(B)} + 9.02 T \ln T - 2.075 \cdot 10^{-3} T^2 - 0.11 \cdot 10^{-4} T^3 - \frac{41.06(A)}{44.68(B)} T$$

The alternative figures marked (A) and (B) refer to the two sets of data for methane as previously discussed. From these free-energy equations the true equilibrium constant for the synthesis of methane from its elements may be calculated. The designation "true" does not refer here to factual truth, for the uncertainty in the methane reaction is obvious, but rather to distinguish the constant so obtained in comparison with an apparent equilibrium (untrue) constant which would be obtained by calculating the ratio $\frac{p_{CH_4}}{p_{H_2}^2}$ using the previously arrived at concentrations of CH$_4$ and H$_2$ obtained from the calculations with zinc-oxide reduction by methane. The first constant has been designated as $K''''_A$, or $K''''_B$, with the subscript letter referring to the free-energy equation from which it was derived. Similarly, the apparent constant may be designated as $K^{000}_A$, or $K^{000}_B$. It will be more suitable to express these constants as logarithms than as absolute numbers.

In Table 44 are recorded calculated values of "true" and "apparent" equilibrium constants for the reaction C+2H$_2$=CH$_4$, as indicated above. These data are charted on Figure 19, where the values of log $K^{000}_A$ and log $K''''_A$ are shown as a function of temperature by full lines, and log $K^{000}_B$ and log $K''''_B$ by dotted lines. It is evident that these lines for conditions A and B intersect at a tem-
perature of approximately 870° C. At lower temperatures the apparent equilibrium constant is higher than the true, which can only mean that below this temperature carbon might be formed by direct dissociation of methane from the concentrations of the final gas as derived from the reaction \( \text{ZnO} + \text{CH}_4 = \text{Zn(gas)} + \text{CO} + 2\text{H}_2 \). Above this temperature carbon should not be formed.

**Table 44.** "True" and "apparent" equilibria corresponding to \( \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} \)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Equation (A)</th>
<th>Equation (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C.</td>
<td>°K.</td>
<td>( K_{oo}^A )</td>
</tr>
<tr>
<td>527</td>
<td>800</td>
<td>7.780</td>
</tr>
<tr>
<td>627</td>
<td>900</td>
<td>168</td>
</tr>
<tr>
<td>727</td>
<td>1,000</td>
<td>6.06</td>
</tr>
<tr>
<td>827</td>
<td>1,100</td>
<td>1.139</td>
</tr>
<tr>
<td>927</td>
<td>1,200</td>
<td>.0028</td>
</tr>
</tbody>
</table>

The conclusion has been stated conditionally, for reasons that become evident upon somewhat closer examination of the conditions of the above reaction. Let it be supposed that methane is permitted
to react with zinc oxide at 1 atmosphere final pressure and at 827° C. Then, according to this reasoning, after the primary reduction of zinc oxide by the methane, the residual methane may dissociate further to give carbon and hydrogen. Such an increase of hydrogen may now be supposed to cause reversal of the reduction reaction and formation of methane. The ultimate status of the reaction, as far as equilibria are concerned, is then a condition of continuous dissociation of methane occurring until true equilibria concentration for the methane synthesis is obtained. Whether such a sequence would actually be obtained will depend upon chemical reaction rates. Methane synthesis is known to be a slow reaction, but nothing is known concerning the rate of the primary reduction reaction with methane. That an investigation of this matter should prove profitable seems obvious.

There is still another aspect of this matter that needs consideration. It has been shown that carbon monoxide reacts rapidly with zinc oxide, and some reaction must occur between the carbon monoxide supposed to have been first formed and the zinc oxide of the system. The original premise was that the content of carbon dioxide from this source was negligible. This amount can be calculated. The equilibrium constant

$$K_2 = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$$

has been given for various temperatures in Table 20. From the stoichiometric relations of the methane-reduction reaction as written $P_{\text{Zn}} = P_{\text{CO}}$, then $P_{\text{CO}_2} = K_2$. Furthermore, from the gas compositions of Table 20 and the value of $P_{\text{CO}_2} = K_2$ the temperatures of continuous reduction of zinc oxide by carbon, which might be formed by methane dissociation, may be estimated for the present system. As in the procedure described in Part II the solution of the problem consists of plotting the apparent value of $K_2 = \frac{P_{\text{CO}}}{P_{\text{CO}_2}}$ (producer-gas reaction) obtained from these concentrations, for comparison with the true value of $K_2$ as obtained from Table 21. Table 45 shows the figures so obtained for the gas concentrations given by the (A) formula.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Zn(gas) or CO</th>
<th>CO₂</th>
<th>“Apparent” $K_2 = \frac{P_{\text{CO}}}{P_{\text{CO}_2}}$</th>
<th>“True” $K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>527</td>
<td>0.56</td>
<td>0.000008</td>
<td>37.4</td>
<td>0.00079</td>
</tr>
<tr>
<td>627</td>
<td>3.56</td>
<td>0.00007</td>
<td>64.3</td>
<td>0.144</td>
</tr>
<tr>
<td>727</td>
<td>13.65</td>
<td>0.0242</td>
<td>77.0</td>
<td>1.44</td>
</tr>
<tr>
<td>827</td>
<td>24.19</td>
<td>0.185</td>
<td>31.6</td>
<td>9.44</td>
</tr>
<tr>
<td>927</td>
<td>24.985</td>
<td>0.364</td>
<td>6.3</td>
<td>44.6</td>
</tr>
</tbody>
</table>

Table 45.—Carbon monoxide and dioxide in methane reduction of ZnO

When the figures of the last two columns are plotted (chart not shown) the intersection is found to be approximately 870° C. This temperature is the invariant point not only for the methane system, but also for the ZnO—CO—CO₂ system when the zinc vapor and carbon monoxide are determined by the methane reduction.

The water-vapor content of the gas will be of the same order of magnitude as the carbon dioxide and need not be calculated separately.
SIGNIFICANT FACTORS IN METHANE REDUCTION

It has been shown that, because of the great difference in heat capacity between reactants and products in the reaction

$$\text{ZnO} + \text{CH}_4 = \text{Zn(gas)} + \text{CO} + 2\text{H}_2$$

it should be thermodynamically possible to carry on the reduction of zinc oxide by methane at temperatures considerably lower than in present retort practice. Below 870° C., however, elementary carbon may be formed by dissociation of methane, if the system can approach equilibrium for this latter reaction. This carbon would not react further with zinc oxide continuously below this temperature. Near this critical temperature the amount of carbon dioxide in the gaseous products of the reaction may confidently be expected to be not over 0.5 per cent, whereas the stoichiometric limit of zinc-vapor content is 25 per cent. Because this carbon dioxide and an analogous water-vapor content could not readily be removed the product of methane reduction will always be subject to some reoxidation on cooling and condensation, but the net amount of oxide so formed should be small. The use of methane should be very suitable for the manufacture of zinc dust. Data need to be obtained on reaction rates in the zinc oxide-methane system to ascertain whether the reactions theoretically postulated may actually predominate.
Part VII. ZINC SULPHIDE IN SMELTING

ROASTING OF BLENDE

If the reaction for the roasting of blende is written

$$2\text{ZnS} + 2\text{O}_2 = 2\text{ZnO} + \text{SO}_4$$  \hspace{1cm} (Reaction 1)

it must be admitted that this reaction is probably completely irreversible as written under any condition of practical interest for pressure, temperature, and concentration. The reaction itself is probably the net result of consecutive reactions, nevertheless the mechanism is not certainly known. It may be postulated that separate reactions involved are

$$\text{ZnS} + 2\text{O}_2 = \text{ZnSO}_4$$  \hspace{1cm} (Reaction 2)

$$\text{ZnSO}_4 = \text{ZnO} + \text{SO}_3$$, and  \hspace{1cm} (Reaction 3)

$$\text{SO}_3 = \text{SO}_2 + \frac{1}{2} \text{O}_2$$  \hspace{1cm} (Reaction 4)

Of these reactions, No. (2) seems irreversible; the remaining reactions are definitely known to be reversible. The thermodynamics of reaction (3) has been discussed in connection with the free energy of zinc sulphate in Part I.

From the standpoint of reaction rate little may be said concerning the three latter reactions, except that reaction (2) is probably the slowest and actually determines the roasting rate, reaction (4) may be of intermediate speed, and reaction (3) is known to be rapid. Except for those portions in which the stability of the sulphate is important, the whole problem of roasting is one of reaction rate far from equilibrium conditions, and application of thermodynamic data does not lead to significant considerations.

ZINC SULPHIDE AND OXIDE

The reaction between cuprous sulphide and oxide goes nearly to completion at slightly elevated temperatures and was at one time used commercially as a method of copper smelting. The reaction may be responsible, at least to a considerable degree, for the formation of elementary copper in the present practice of converting copper mattes. The analogous reaction for zinc,

$$2\text{ZnO} + \text{ZnS} = 3\text{Zn(g)} + \text{SO}_3$$  \hspace{1cm} (Reaction 5)

has often been proposed by inventors as a possible means for direct reduction of zinc without using reducing carbon. In this instance thermodynamic data available suffice to predict approximately the
conditions under which the reaction might have practical interest. The figures may be summarized as follows:

\[ C_p(3\text{Zn gas}) = 15.0 \]

\[ C_p(\text{SO}_2) = 7.70 + 5.30 \cdot 10^{-2}T - 0.83 \cdot 10^{-8}T^2 \quad \text{Source: Monatomic gas.} \]

Products

\[ 22.70 + 5.30 \cdot 10^{-2}T - 0.83 \cdot 10^{-8}T^2 \quad \text{Eastman.} \]

\[ C_p(2\text{ZnO}) = 13.26 + 22.52 \cdot 10^{-2}T - 4.722 \cdot 10^{-6}T^2 \quad \text{Part I.} \]

\[ C_p(\text{ZnS}) = 7.05 + 15.15 \cdot 10^{-2}T - 0.917 \cdot 10^{-6}T^2 \quad \text{Do.} \]

Reactants

\[ 20.31 + 37.67 \cdot 10^{-2}T - 5.64 \cdot 10^{-6}T^2 \]

\[ \Delta C_p \text{ by difference} = 2.39 - 32.37 \cdot 10^{-2}T + 4.81 \cdot 10^{-6}T^2 \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_{298} )</th>
<th>Source</th>
<th>( \Delta F_{298} )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Zn (gas)</td>
<td>+93,617</td>
<td>Part I.</td>
<td>+68,751</td>
<td>Part I.</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>-69,000</td>
<td>Lewis and Randall</td>
<td>-69,600</td>
<td>Lewis and Randall</td>
</tr>
<tr>
<td>Products</td>
<td>+24,617</td>
<td></td>
<td>-909</td>
<td></td>
</tr>
<tr>
<td>2ZnO</td>
<td>-106,626</td>
<td>Part I.</td>
<td>154,890</td>
<td>Part I.</td>
</tr>
<tr>
<td>ZnS</td>
<td>-43,000</td>
<td>Do.</td>
<td>-41,600</td>
<td>Do.</td>
</tr>
<tr>
<td>Reactants</td>
<td>-299,400</td>
<td></td>
<td>-193,490</td>
<td></td>
</tr>
<tr>
<td>For the reaction by difference</td>
<td>+231,243</td>
<td></td>
<td>+192,551</td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta F^\circ_T = +234,923 - 2.39 \cdot T \ln T + 16.18 \cdot 10^{-2}T^2 - 0.80 \cdot 10^{-6}T^3 - 133.6 \cdot T \]

The free-energy equation so obtained may be solved at various temperatures. For the present purpose it will suffice to obtain \( \Delta F^\circ \) at 727° C. and 1,227° C., these temperatures representing approximately those of a zinc condenser and a zinc retort. It is found that \( \Delta F^\circ_{1,000} = +100,193 \), log \( K_{1,000} = -21.90 \), and \( \Delta F^\circ_{1,500} = 42,000 \), log \( K_{1,500} = -6.11 \). The corresponding values of \( K \) are 1.25 \cdot 10^{-22} at 1,000° and 7.76 \cdot 10^{-7} at 1,500° K. If no other gases than those produced by the reaction are present the stoichiometric relationships require that \( p_{\text{Zn}} = 3p_{\text{SO}_2} \). From the equilibrium expression

\[ K = p_{\text{Zn}}^3 \cdot p_{\text{SO}_2} = \frac{1}{3} p_{\text{Zn}}^4, \]  
where \( p_{\text{Zn}} = \sqrt[3]{K} \)

Numerically it is found that the partial pressure of zinc which can exist in the system described is less than 4.4 \cdot 10^{-6} atmospheres below 727° C. and only 0.039 atmosphere at 1,227° C.

Although the above calculations can not be more than approximations, because of the uncertainties and assumptions made in deriving the thermodynamic data they do show clearly the course of reaction (5). At low temperatures the reaction has a large positive free energy in the direction written, and zinc must reduce sulphur dioxide nearly completely to zinc sulphide and oxide. At 727° the reaction is still largely backward, and no appreciable amounts of zinc vapor can exist in equilibrium with sulphur dioxide. At 1,227°, as in an actual zinc retort, it seems highly probable that the reaction should occur as written to a small degree. Although the reaction may proceed, the resulting products on being cooled in the condenser would immediately revert to zinc oxide and sulphide. If the gas
was passed through a blanket of reducing carbon the $\text{SO}_2$ would be reduced to sulphur vapor, but this also would cause zinc sulphide to reappear in the condenser. In this instance the dissociation of zinc sulphide would have to be considered.

Nothing is known concerning rates in reaction (5), but since in the forward direction as written the rate must depend on the interaction at the common surface of two solids we may be sure it will be slow at any temperatures below which the vapor pressures of the solids become inappreciable, certainly so below $1,000^\circ$ or $1,100^\circ$ C.

As far as the practical use of reaction (5) is concerned the conclusion is that it may be responsible for the formation of some zinc vapor at temperatures above $1,100^\circ$ C, but that it would not be usable from a practical point of view, unless some means of removing sulphur vapor or sulphur dioxide from the system at the temperature of reduction was available and at best would require much higher temperatures than the reduction of oxide by carbon. It is also probable that the presence of sulphur vapor in retort practice is more deleterious than the presence of oxidizing vapors, such as carbon dioxide or water vapor, and may be an important source of undesired blue powder.
CONCLUSIONS

The foregoing pages of thermodynamic calculations relating to zinc smelting have been assembled to show the incisive and critical potentialities of this modern tool of the metallurgist. They have been written from a synthetic rather than analytic viewpoint. From certain general thermodynamic principles and methods and a few moderately precise data no hesitation has been felt in building a somewhat complex structure of inherent physicochemical limitations and possibilities in zinc reduction. To the practicing metallurgist the structure may seem inverted and top-heavy. Indeed, it must not be supposed that actual smelting processes necessarily attain or embody these limits. Nevertheless, in spite of avoidance of the minutiae of zinc smelting in this attempt the conclusions are in themselves rigorous. Whatever uncertainty there may be as to the data used need not prove disturbing; the important fact is that once the data are available they may be applied in truly simple ways to critical discussion of actual practical operations, and whatever changes may be necessary when better data become available will be changes of degree rather than kind.

The process of zinc reduction is one in which a particularly wide series of applications of thermodynamic data may be made; in fact, these chemical and thermodynamic methods are the only ones sufficiently fundamental and general to supply certain types of information. It has been shown that such a simple fact as the "temperature of reduction" of zinc oxide by carbon is only approximated to a few hundred degrees by direct experimental methods but is precisely calculable from thermodynamic data. Many variations might be tried in the actual smelting of zinc in retorts, but the constitution diagram of the zinc-oxygen-carbon system could never be derived from the results. Whether or not a zinc blast furnace may produce liquid zinc depends on this constitution diagram. A knowledge of the system derived from thermodynamic data may allow a zinc blast furnace to be designed, but the expensive attempts at the empirical construction of such a metallurgical instrument have in the past not only lead to the erroneous conclusion that it was physically impossible to produce liquid zinc directly but they have even failed to furnish unequivocal information concerning those fields of temperature, pressure, or concentration of reducing gases which might prohibit or permit the desired end. In contrast a few simple thermodynamic calculations furnish an answer of beautiful clarity and definiteness.

Even a Maxwellian demon might find difficulty in separating the constituents of the gas phase in an operating zinc retort. If thermodynamic methods do not enable the precise gas composition to be predicted because these contents depend on reaction rates, nevertheless they show exactly the limits within which these concentrations must lie. Where, if not to thermodynamic calculations, must one go to find reliable information concerning the thermal requirements of zinc reduction or the energy efficiency of a retort? Discussion of the formation of blue powder is only pertinent if the effect of the new phase—liquid zinc—is quantitatively brought into confirmed information on reduction equilibria in the gas phase. These and many other answers to vexing practical problems are constructible by the theoretical methods that have been given. In contrast, there are
very definite limitations in the thermodynamic method. It is futile to discuss equilibria based on the formal free-energy change of a reaction which may not actually proceed at a measurable rate or the effects of which may be nullified by more rapid predominating reactions. Thermodynamic investigations are the exordium upon which the final design of sound knowledge of this smelting process must be based.

The author of this work would be seriously at fault did he not point out the degree of uncertainty that may be involved in the formal use of standard free-energy equations. To determine the free energy of formation of such a material as zinc oxide at any definite temperature, as for example at 25° C., to within an uncertainty of 250 calories, requires a considerable refinement of experimental method. The authentication of such a result has, in this case at least, obviously required painstaking and laborious correlation of all available quantitative thermodynamic data. If such a result is transformed to 1,000° C. in the formal way, such an error may produce a minimum difference in calculated free energy in that the logarithm of the difference is \[ \frac{250}{2.303RT} \] where \( R \) is the gas constant, \( T \) the absolute temperature, and 2.303 the conversion factor of natural and Briggsian logarithms. If \( S \) is this difference then \( \log S = 0.04 \), \( S = 1.095 \), and this number represents the ratio of the correct to calculated value of an equilibrium constant which might be derived from the calculated free energy. In other words, the error involved under these conditions is 9.5 per cent.

Sometimes the difference in free energy of different forms of the same material may be considerable; the case of graphitic and amorphous carbon has been discussed, and it was pointed out that this difference might involve some 2,000 calories. In this case \( \log S = 0.437 \) at 1,000°, and \( S = 6.4 \). The purely formal error in equilibrium constant would then be sixfold. This error would not, however, necessarily be involved in the calculation of the constitution diagram or other derived information as long as the calculation was consistently carried out. Uniformity of results in such an instance would be secured by the modification of each free-energy quantity involving carbon, as, for example, the free energies of formation of carbon monoxide, carbon dioxide, methane, and others.

An error of 9.5 per cent may seem extraordinarily large in comparison with the few tenths per cent uncertainty in the weight or analysis of a slab of zinc metal. In comparison with the more than hundredfold error that existed in the best equilibrium measurements available before exact thermodynamic methods of investigation were used the newer data may be considered remarkably precise.

The practice and empiricism of hundreds of years of zinc smelting have brought little change in practical methods of reduction. Present activity in the attempts to develop new and better smelting processes bears eloquent witness to the fact that the industry has realized the deficiency of its present practices. If progress is to be made in the future, it must rest upon a sound and inclusive knowledge of the chemistry of the process. The goal may be reached most surely and expeditiously by careful, thermodynamic methods of study.