A METHOD OF STUDYING INVOLVED EQUILIBRIA AND ITS APPLICATION TO METALLURGICAL PROCESSES

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Introduction.

The chemical reactions which the metallurgist meets often constitute complex transformations, resulting from the mingling of several more or less distinct reactions. The calculation of these "involved equilibria" (to use the term 'équilibrès enchevêtrés' due to P. Montagne) is often laborious.

The method of studying these equilibria of which we shall here indicate the broad outline is based on the fact that the variable factors which characterise each of these equilibria may be divided into two groups; two of these factors, which are the same for all equilibria, are considered as independent variables, and their values are plotted respectively as ordinates and abscissae on a two-dimensional diagram; the other factors are considered as parameters. The characteristics of the equilibrium of each of the reactions can then be represented in the diagram by a family of lines of which each corresponds to a determined value of the parameter.

If the characteristic equilibria of different reactions are also represented on the same diagram, which may express a given chemical system, an intermingling of many families of lines is obtained; these form a picture which may be used for the study of the resultant of the reactions which it is possible to produce in the system under consideration. By a judicious choice of the two independent variables it is often possible to express the equilibria by families of straight (or nearly straight) lines parallel to each other; the construction of the equilibrium diagram is then quite simple.

As standard examples, we shall rapidly review several cases relating to systems of increasing complexity, composed of 1, 2, and 3 constituents respectively, being the systems "oxygen," "carbon-oxygen," "zinc-oxygen," and "zinc-carbon-oxygen"; we shall also have something to say on the systems "hydrogen-oxygen," "sulphur-oxygen," and "iron-chlorine." Firstly, we shall recall several kinds of diagrams which are obtained if the logarithm of the equilibrium constant of a reaction is plotted as the ordinates, and the reciprocal of the absolute temperature as abscissae.

(a) Scheffer's Rule.

It is well-known that, as shown by Scheffer in 1913, the effect of temperature $T$ on the equilibrium constant $K$ of most reactions may usually be represented at normal temperatures for these experiments by expressions of the simple type:

$$ \log K = \frac{A}{T} + B \quad (4) $$

These expressions are usually obeyed just as well as the more complicated relations which were in universal use in 1913; the influence of the heat of reaction $\Delta H$ as a function of $T$ is generally so small that for nearly all equilibria the error caused by neglecting it is less than the experimental errors.
It follows that in a diagram where $K$ is plotted as ordinates and $1/T$ as abscissae, the characteristics of the above-mentioned equilibria are represented by a straight, or nearly straight line (see Fig. 1). The slope of this straight line, $A$, (or of a tangent at a point on this line) is a measure of the heat of reaction at constant pressure, $\Delta H$, and the reaction is exothermic or endothermic (in the sense which corresponds to the disappearance of the substances whose pressure appears in the numerator of the equilibrium constant) according to whether the line is ascending or descending; the ordinate at the origin measures the entropy of the reaction $\Delta S$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Scheffer's Rule.}
\end{figure}

(b) **Trouton's Rule and the Le Chatelier-Matignon Rule.**

Trouton's rule states that when a liquid is evaporated the ratio of the latent heat of evaporation $\Delta H$ (expressed in calories per gram molecule) to the absolute temperature of the boiling-point at a pressure of 1 atm., $\Delta H/T$, is often approximately equal to 21. It is easy to show that this is the same as saying that at the boiling-point at 1 atm., the entropy of evaporation is approximately 21 cal./° C., i.e., for this temperature the tangent to the vapour pressure curve makes an ordinate at the origin of approximately $21/4.575 = 4.6$, if this curve is plotted as log $p$ against $1/T$ (see Fig. 2).

Similarly the Le Chatelier-Matignon rule states that in certain cases, and notably in the case of reactions involving only a single gaseous component, the heat of reaction $\Delta H$ in calories per gram molecule of vapour divided by the absolute temperature at which the pressure of the vapour is equal to 1 atm. (this temperature is called the
“inversion temperature”), i.e., $\Delta H / T$, is often approximately 32. This is the same as saying that at the point corresponding to $\log p = 0$, the tangent to the equilibrium curve makes an ordinate at the origin equal to $32 / 4.575 = 7.0$. The calculation of the inversion temperature, which is often made use of in metallurgy, is only permissible when this condition is fulfilled (see Fig. 3).

**One-Component Systems**

**The System “Oxygen.”**

If ordinary diatomic oxygen, $O_2$, is heated, it decomposes at high temperatures according to the reaction:

$$O_2 \rightleftharpoons 2O$$

and the condition at equilibrium may, between 1,500° and 5,000° K., be expressed fairly closely by the relation:

$$\log \frac{p_{O_2}}{p_{O_2}} = \frac{26670}{T} - 7.06$$

which, for this temperature range, bears out the results of Johnston & Wheeler with satisfactory accuracy.

This relation may be written in the two following forms, considering the functions $\log p$ and $1/T$ as independent variables:
In a two-dimensional diagram in which values of log $P_{o_2}$ are plotted as ordinates and $1/T$ as abscissa, these two conditions for equilibrium may be expressed respectively by two families of straight lines symmetrical about the line from the figure zero ordinate (see Fig. 4. For the first family each line corresponds to a value of the pressure of monatomic oxygen; for the second family each line corresponds to the same value of the ratio of the partial pressures of $O_2$ and $O$.

It is easy to trace the isobar for which the sum of the partial pressures has the same value from points on this diagram. By reading off the temperature at which the 1 atm. isobar crosses the lines of family (b) (of which each line corresponds to a value determined by the degree of dissociation $x = \frac{2P_0}{(P_{o_2} + 2P_0)}$, it is readily seen on this figure that if diatomic oxygen is heated under a pressure of 1 atm., the degree of dis-

\[
\log P_{o_2} = \frac{26670}{T} - 7.06 + 2 \log P_0 \quad \text{(a)}
\]

\[
\log P_{o_2} = \frac{26670}{T} + 7.06 + 2 \log \frac{P_{o_2}}{P_0} \quad \text{(b)}
\]
The degree of dissociation into monatomic oxygen has the following values at different temperatures:

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>2,137</th>
<th>2,659</th>
<th>3,355</th>
<th>4,097</th>
<th>4,996</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of dissociation %</td>
<td>0.5</td>
<td>4.7</td>
<td>33.3</td>
<td>83.4</td>
<td>99.0</td>
</tr>
</tbody>
</table>

The conditions for stability of ozone (O₃) have also been represented in Fig. 4, according to the relation:

\[ \log P_{O_3} = \frac{7511}{T} + 3.54 + \log P_{O_2} \]

which expresses the results of Davis & Johnston (7) between 1,000° and 5,000° K. It is readily deduced from this figure that the maximum amount of ozone formed by simple heating of diatomic oxygen at 1 atm. pressure will be obtained for those points on the 1 atm. isobar where its tangent is parallel to the lines of family (c) which is about 3,300° C.; this maximum content of ozone, which will be determined by the value of those lines of family (c) which pass through this point, corresponds to a pressure of approximately 10⁻⁶ atm., i.e., about 2 mg. per cubic metre (at 0° C. and 760 mm. Hg.).
Two-Component Systems.

System "Carbon-Oxygen."

The two-component system "carbon-oxygen" is composed particularly of the following substances:

- Gaseous O, O₂, and O₃;
- Solid carbon (C, C₂, C₃);
- Gaseous CO and CO₂.

The conditions for the stability of gaseous CO and CO₂, as well as for solid carbon, may ordinarily be expressed by relations such as the following, due to Rey(7), which are entirely satisfactory at temperatures between 800° and 2,000° K.

\[
\begin{align*}
(\text{P}_{\text{CO}})^2 \cdot \text{P}_{\text{O}_2} &= \frac{29360}{\text{T}} + 8.96 \quad (\text{a}) \\
\frac{\text{P}_{\text{CO}}}{\text{P}_{\text{CO}_2}} &= \frac{9080}{\text{T}} + 9.30 \quad (\text{b}) \\
\text{P}_{\text{O}_2} &= \frac{20280}{\text{T}} - 0.34 + \log \text{P}_{\text{CO}_2} \quad (\text{c})
\end{align*}
\]

In order to study the aggregate of the equilibria which may be the basis of the system "carbon-oxygen," we shall modify the method of expressing these conditions for equilibria in the way which has been shown, wherever possible, i.e., in terms of the same two independent variables \( \log \text{P}_{\text{O}_2} \) and \( 1/\text{T} \), and we shall consider the other variables as parameters.

Thus we obtain the following relations, valid between 800° and 2,000° K:

\[
\begin{align*}
2\text{CO} + \text{O}_2 &= 2\text{CO}_2 : \log \text{P}_{\text{O}_2} = \frac{29360}{\text{P}_{\text{CO}}^2} + 8.96 + 2 \log \frac{\text{P}_{\text{CO}}}{\text{P}_{\text{CO}_2}} \quad (\text{e}) \\
2\text{C} + \text{O}_2 &= 2\text{CO} : \log \text{P}_{\text{O}_2} = \frac{11200}{\text{T}} - 9.64 + 2 \log \text{P}_{\text{CO}} \quad (\text{c}) \\
\text{C} + \text{O}_2 &= \text{CO}_2 : \log \text{P}_{\text{O}_2} = \frac{20280}{\text{T}} - 0.34 + \log \text{P}_{\text{CO}_2} \quad (\text{d})
\end{align*}
\]

Each of these three relations for equilibrium may be expressed in a graph (\( \log \text{P}_{\text{O}_2} \) against \( 1/\text{T} \)) by a family of straight lines. Such lines are drawn in Fig. 5, where not only are the equilibrium conditions of gaseous C and C₂ represented, but also the conditions for monatomic oxygen already considered in Fig. 4. For every point in this figure, the ratios of the equilibrium pressures of CO and CO₂ are indicated by the values of those lines of family (e) which pass through this point. In the presence of solid carbon, the partial pressures of CO₂, CO, C, and C₂ are indicated by the values of the lines of families (d), (c), (a), and (b) respectively.

Similarly the isobars for which solid carbon is stable under different pressures of CO₂ + CO + C + C₂ have been plotted in Fig. 5; these isobars limit the "region of stability" of solid carbon under the different pressures considered; the region of stability of solid carbon under a total pressure due to the four gases of 1 atm. has been shown shaded. The lines (e) and (f) of zero value separate the regions where the predominant gases are CO₂, CO, and C + C₂ respectively.

Fig. 5 gives a composite picture of the circumstances under which the different possible reactions in a chemical system containing only carbon and oxygen can occur. If it is remembered that a system will be more oxidising insofar as the point representing it is higher on the graph, and that it will occur at a higher temperature as its point is situated more towards the right-hand side, a quantitative expression may readily be derived from this diagram of the phenomena which govern the action of oxygen and of the temperature on the carbon; by oxidation at a lower temperature, i.e., on the
left-hand side of the graph, the carbon tends to be converted into gaseous $\text{CO}_2$; appreciable quantities of $\text{CO}$ appear when the first of the lines of family (e) is reached, for which the proportion of $\text{CO}$ is 1%, i.e., at temperatures above a limiting value which varies from 400° to 700° C. according to the pressure; above 700° to 1,500° C. nearly all the carbon is converted into $\text{CO}$; above 3,000° to about 7,000° it appears as mona-
tomic and diatomic oxygen vapour. Solid carbon cannot be stable in the presence of traces of free oxygen, except perhaps at high pressures from 100 to 1,000 atm., and at temperatures of about 7,000° to 10,000° C., when the diagram shows that, if a certain amount of extrapolation of the lines is not too invalid, the gas can contain 0.005 to 0.01% of monatomic oxygen.

In connexion with Boudouard’s equilibrium, Fig. 5 enables one readily to draw Fig. 6, which represents the influence of the temperature on the equilibrium \( \text{CO}_2 + \text{C} = 2\text{CO} \) for different total pressures of \( \text{CO} + \text{CO}_2 \), by means of plotting points along the isobars.

![Fig. 6. — Equilibrium \( \text{CO}_2 + \text{C} = 2\text{CO} \) under different pressures.]

In connexion with the dissociation of \( \text{CO}_2 \), the family of lines (j) has been drawn in Fig. 5, which, showing the condition \( P_{\text{CO}} = 2P_{\text{O}_2} \) in the case of the equilibrium \( 2\text{CO}_2 = 2\text{CO} + \text{O}_2 \), correspond to the conditions in which the dissociation of \( \text{CO}_2 \) proceeds exclusively according to this reaction on the absence of any other forms of carbon or oxygen. It is clearly seen that the temperatures for which the degree of dissociation has the value of 1% will be in the neighbourhood of 1,450° C. at 0.01 atm., 1,650° at 1 atm., and 1,950° at 100 atm. respectively, and this is in agreement with the values given in the literature. At temperatures of the order of 2,000° to 3,000° C., an appreciable proportion of monatomic oxygen appears; a dissociation according to \( \text{CO}_2 = \text{CO} + \text{O} \) is then superimposed on the dissociation \( 2\text{CO} = 2\text{CO}_2 + \text{O}_2 \), and becomes preponderant at temperatures of the order of 4,000° to 8,000° C. At still higher temperatures, at which the thermodynamic data are insufficiently known, there is probably a dissociation of \( \text{CO} \) with formation of monatomic oxygen and carbon vapour.

System “ Zinc-Oxygen.”

Fig. 7 represents the equilibria of the system “zinc-oxygen.” The following substances are considered:
- Gaseous O and \( \text{O}_2 \);
- solid, liquid, and gaseous zinc;
- solid \( \text{ZnO} \),

and the following conditions of equilibrium are assumed:

\[
2\text{Zn (s)} + \text{O}_3 = 2\text{ZnO (s)} : \log P_{\text{O}_2} = -\frac{34900}{T} + 8.70 \quad (c)
\]
$2\text{Zn}(1) + \text{O}_2 = 2\text{ZnO}(s): \log P_{\text{O}_2} = -\frac{35970}{T} + 10.24$ (d)

Fig. 7.—Equilibrium of the system "zinc-oxygen."
2Zn(g) + O₂ = 2ZnO(s) : log $P_{O_2} = \frac{48520}{T} + 20.902 - \log P_{Zn}$

So far as the condensed phases which make up this system are concerned, the diagram represents the regions of stability of solid and liquid zinc and solid zinc oxide. The isobars are drawn, along which liquid zinc and solid ZnO are stable in the presence

Fig. 8.—Equilibrium of the system "hydrogen-oxygen."
of gaseous atmospheres containing oxygen and/or zinc vapour under a fixed total pressure of $P_{O_2} + P_{Zn}$, and the "region" in which these substances are stable in the presence of atmospheres at a total pressure of 1 atm. has been shaded.

It is to be noted that these isobars become progressively curved inwards in the neighbourhood of the line (f) along which the partial pressures of oxygen and zinc

Fig. 9.—Equilibrium of the system "sulphur-oxygen"
vapour are equal, their orientation changes sharply at their intersection with line (d) along which the composition of the basic substances is modified (transformation of ZnO to Zn). In linear diagrams of this kind, such changes of orientation of the isobars have the following wholly general significance: (11), a progressive curve inwards always corresponds to a progressive modification of the composition of one of the reacting phases (in the present case it is the composition of the gaseous phase which is modified; in other cases it may be that of a solid or liquid solution); a sharp curve inwards always corresponds to a sharp change in the composition of one of the reacting phases, i.e., to the appearance and/or disappearance of a condensed phase.

It must also be pointed out that, in general, the existence of a vertical isobar (parallel to the ordinate axis) indicates the formation of a gaseous substance without liberation or fixation of a constituent the pressure of which is shown by its ordinate (i.e., oxygen in the present example). In the case of binary mixtures, which we are here considering, this can only correspond to phenomena of simple evaporation; for example the evaporation of zinc at the lower right-hand side of Fig. 7, and the evaporation of carbon at the lower right-hand side of Fig. 5; evaporation of sulphur at the lower part of Fig. 9; evaporation of water in the middle of Fig. 8; evaporation of iron and of ferrous chloride at the right and towards the middle respectively of Fig. 10.

On the other hand, the existence of an oblique isobar indicates the formation of a gaseous substance with the fixation or liberation of the constituent whose pressure is shown by the ordinate; for example the transformation of solid ZnO into zinc vapour and oxygen at the upper right-hand side of Fig. 7; the transformation of solid carbon
into gaseous CO and CO₂ with fixation of oxygen in the centre of Fig. 5; the transformation of liquid sulphur into gaseous SO₂ with fixation of oxygen towards the middle of Fig. 9; the transformation of solid and liquid iron into gaseous FeCl₃ and of solid and liquid FeCl₂ into gaseous Fe₂Cl₆, respectively in the two middle regions of Fig. 10.

It follows that, as in the case of ZnO and similarly for CdO and HgO, when the region of stability of an oxide exhibits isobars the lower part of which are oblique, it is certain that this oxide is decomposed by heat. It is thus easy to draw a line at the edge of the diagram which shows the conditions of equilibrium of the gaseous atmosphere resulting from this decomposition, and thus allows of the rapid graphical study of the conditions under which this decomposition is possible. For example, in Fig. 7, line (g) shows the condition \( P_{Zn} = 2P_{O_2} \) which occurs when ZnO decomposes, in the absence of other derivatives of zinc and/or oxygen, according to the reaction

\[ 2ZnO (s) = 2Zn (g) + O_2. \]

The values of the abscissa of the points of intersection of this line (g) with the different isobars indicate the temperatures for which the decomposition pressure of ZnO has fixed values; it is seen, for example, that the decomposition pressure of ZnO will be approximately 0·01 atm. at about 1,500° C.

Figs. 3, 9, and 10 represent the equilibrium diagrams relating to the three binary systems ("hydrogen-oxygen," "sulphur-oxygen," and "iron-chlorine"). Such diagrams would be very useful to metallurgists. We shall not analyze them here, as this would enlarge the limits of our treatment too much.

**Three-Component Systems.**

**System "Zine-Carbon-Oxygen."**

If Figs. 5 and 7, relating to the systems "carbon-oxygen" and "zinc-oxygen" respectively, are superimposed, a picture is obtained which represents the conditions of equilibrium of all the substances which are being considered in the construction of the two figures, i.e.:

- Gaseous O, O₂, and O₃;
- solid carbon, gaseous C and C₂;
- gaseous CO and CO₂;
- solid, liquid, and gaseous zinc;
- solid ZnO.

Since the ternary system "zinc-carbon-oxygen" under consideration includes also zinc, carbonate, ZnCO₃ at the exclusion of carbide, carbonyl, and solid or liquid solutions of carbon, this picture will be complete only if a representation of the conditions of stability of ZnCO₃, which are unfortunately little known, is added.

In order to fix our ideas, we shall neglect, as a first approximation, the probable formation of solid solutions between ZnCO₃ and ZnO, and we shall provisionally assume that the decomposition pressure of ZnCO₃ according to the reaction

\[ ZnCO_3 = ZnO + CO_2 \]

can be expressed quantitatively by the relation

\[ \log P_{CO_2} = \frac{8080}{T} + 14·18 \]

which, between 279° and 297° C., closely follows the results of Centnerszwer(1). Fig. 11 is thus obtained, which constitutes the equilibrium diagram of the system "zinc-carbon-oxygen."

So far as the condensed phases are concerned, carbon can only be stable under line (d); between this line (d) on the one part, and the lines (b) and (c) on the other, carbon can co-exist with ZnO, insofar as the total pressure of CO₂ + CO + Zn (g) contained in the gaseous atmosphere cannot be lower than a pressure of the value shown on the isobars. Below lines (b) and (c), zinc oxide is reduced to solid and liquid metallic zinc.
respectively, without that the carbon ceases to be stable. Above line (d), carbon is no longer stable, and according to whether the pressure of CO$_2$ in the reacting atmosphere is lower or higher than the value shown on the isobars, it will be transformed by oxidation into gaseous CO$_2$ or into ZnCO$_3$ resulting from the fixation of CO$_2$ by ZnO.

Amongst the problems for the rapid study of which Fig. 11 may be found useful,
is that of the reduction of zinc oxide by carbon. It may readily be shown that the conditions under which this reduction is possible are indicated by the line (m), for which the partial pressures of CO and zinc vapour are equal, and that these conditions thus correspond to the case where reduction proceeds exclusively according to the reaction

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

without formation of \( \text{CO}_2 \). By reading off the simultaneous values along this line of the total pressures of CO, \( \text{CO}_2 \), and zinc vapour (indicated by the values of the different isobars), the temperature (from the abscisses), and the partial pressures of CO, \( \text{CO}_2 \), and zinc vapour (read respectively from scales (e), (f), and (k)), the following values of the conditions for the reduction of \( \text{ZnO} \) by carbon are obtained:

<table>
<thead>
<tr>
<th>(1/T \times 10^3)</th>
<th>(\log P_{\text{CO}})</th>
<th>(P_{\text{Zn}})</th>
<th>(P_{\text{ZnO}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-065</td>
<td>26-12</td>
<td>22-97</td>
<td>19-74</td>
</tr>
<tr>
<td>0-958</td>
<td>0-01</td>
<td>0-1</td>
<td>1</td>
</tr>
<tr>
<td>0-850</td>
<td>666</td>
<td>771</td>
<td>903</td>
</tr>
<tr>
<td>CO content %</td>
<td>49-7</td>
<td>49-7</td>
<td>49-7</td>
</tr>
<tr>
<td>(\text{CO}_2) content %</td>
<td>0-6</td>
<td>0-6</td>
<td>0-6</td>
</tr>
<tr>
<td>Zn content %</td>
<td>49-7</td>
<td>49-7</td>
<td>49-7</td>
</tr>
</tbody>
</table>

The presence of a little \( \text{CO}_2 \) shows, as is confirmed by experiment, that the reduction of \( \text{ZnO} \) is not only performed according to the reaction

\[ C + \text{ZnO} = \text{CO} + \text{Zn}, \]

as we have provisionally assumed here, but wholly according to the two simultaneous reactions

\[ \text{ZnO} + C = \text{Zn} + \text{CO}, \]
\[ 2 \text{ZnO} + C = 2 \text{Zn} + \text{CO}_2. \]

The proportion of zinc vapour in the atmosphere thus does not vary according to the relation \( P_{\text{Zn}} = P_{\text{CO}} \), but according to \( P_{\text{Zn}} = P_{\text{CO}} + 2 P_{\text{CO}_2}. \)

It follows that the characteristics of the atmosphere are not indicated in Fig. 11 by line (m) (for which \( P_{\text{Zn}} = P_{\text{CO}} \)), but by another line situated very slightly above line (m). The correction which results from this modification hardly affects the values found above for the reduction temperatures of \( \text{ZnO} \); the composition of the gas, slightly modified, becomes as follows:

| CO content % | 49-1 |
| \(\text{CO}_2\) content % | 0-6 |
| Zn content % | 50-3 |

These values, as well as those which have been found further above, and which relate to the reduction of \( \text{ZnO} \), are in agreement with those which have been obtained previously on this subject by Decroly(13) and by Meunier(14).

Both Decroly and Meunier also studied the conditions under which the reduction of \( \text{ZnO} \) by carbon can give rise directly to liquid zinc. These conditions are represented in Fig. 11 as well as in Fig. 12, which shows a part of Fig. 11 on an enlarged scale, by the portion of line (c) (relating to the equilibrium between \( \text{ZnO} \) (s) and \( \text{Zn} \) (l)), situated above the point where this line meets the line, situated very slightly below line (m), which represents the gaseous atmospheres for which \( P_{\text{Zn}} = P_{\text{CO}} + 2 P_{\text{CO}_2}. \)

The values of the pressures and temperatures beyond which the direct formation of liquid zinc is possible will thus be those which correspond to the point of contact of the two lines; these are respectively:

| Temperature | 1049°C C. |
| Pressure | 7-5 atm. |
The gaseous atmosphere then has the following composition:

- CO content %: 49.3
- CO₂ content %: 0.7
- Zn content %: 50.0

These values are also in agreement with those established by Decroly and by Meunier.

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**Fig. 12.**—Equilibrium of the system “zinc-carbon-oxygen” (detail).

**The Phase Rule.**

The phase rule, which has rendered considerable service to the study of chemical equilibria, has completely merited the respect and recognition of every metallurgist.
However, when chemical problems are studied with the aid of diagrams such as those we have here presented, there is no need for the phase rule: it is no longer necessary to devote oneself to classical research into the number of phases \( v \) and the number of independent constituents \( c \) in order to determine the degree of freedom of the system \( v = c + 2 - f \). This degree of freedom is, in effect, automatically obtained by simple consideration of the graphical representation. Every line in the representation corresponds to a univariant system, except those which are affected by a parameter which depends on an algebraic function of the partial pressures of two gases other than that substance of which the partial pressure is shown as the ordinate (e.g., \( O_2 \) or \( Cl_2 \)); in this case the system is divariant. It follows from this that except for those curves which are affected by such a parameter:

- a point corresponds to an invariant system,
- a line corresponds to a univariant system,
- a family of lines corresponds to a divariant system.

For those lines which are affected by a parameter which depends on the ratio of the partial pressures of two gases other than the substance considered for the ordinates (e.g., for lines of family (e) in Fig. 5, of which the parameter is \( \frac{P_{CO}}{P_{CO}} \)):

- a point corresponds to a univariant system,
- a line corresponds to a divariant system,
- a family of lines corresponds to a trivariant system.

For example:

1. In the case of Fig. 7 relating to the binary system "zinc-oxygen":
   - (a) The point where lines (a), (b), and (c) meet (three condensed phases of solid and liquid Zn, solid ZnO, and a gaseous phase) corresponds to an invariant equilibrium \( v = 2 + 2 - 3 = 1 \).
   - (b) The line (c) (two condensed phases of liquid Zn and solid ZnO, and a gaseous phase) corresponds to a univariant equilibrium \( v = 2 + 2 - 4 = 0 \).
   - (c) The family of lines (k) relating to the pressure of zinc vapour (1 phase of solid ZnO and a gaseous phase) corresponds to a divariant equilibrium \( v = 2 + 2 - 2 = 2 \).

2. In the case of Fig. 5 relating to the binary system "carbon-oxygen":
   - (a) The family of lines (c) relating to the pressure of CO (1 phase of solid carbon and a gaseous phase) corresponds to a divariant equilibrium \( v = 2 + 2 - 2 = 2 \).
   - (b) The family of lines (e) relating to the ratio of the pressures of \( CO_2 \) and CO (only one gaseous phase) corresponds to a trivariant equilibrium \( v = 2 + 2 - 1 = 3 \).

3. In the case of Fig. 11 relating to the ternary system "zinc-carbon-oxygen":
   - (a) The point where lines (a), (b), and (c) meet (four condensed phases of solid carbon) liquid and solid zinc, and solid ZnO, and a gaseous phase) corresponds to an invariant equilibrium \( v = 3 + 2 - 5 = 0 \).
   - (b) The family of isobars, for instance in the portion between lines (c) and (d), (two condensed phases of solid ZnO and solid carbon, and a gaseous phase) corresponds to a divariant equilibrium \( v = 3 + 2 - 3 = 2 \).

In conclusion, two more remarks may be added.

1. This technique of studying gaseous equilibria is obviously applicable to homogeneous as well as to heterogeneous systems. It can easily be modified for the study of reactions which occur in solution(18).

2. The diagrams which are presented here differ markedly from those to which we are accustomed, and their appearance is generally disconcerting because of this.

It is often difficult to investigate high-temperature equilibria at pressures far removed from 1 atm., and in any case the determination of the equilibrium composition of a reacting mixture is dependent on the rate of reaction being appreciable, especially when no catalyst for the reaction is known. This present method often enables avoidance of such difficulties; equilibria which may be investigated
experimentally can be used to elucidate those which are not, and all the equilibria of the simultaneous reactions occurring in a complex system may be expressed on a single diagram. Facility in the use of reciprocal and logarithmic scales is soon attained and these diagrams then become very easy to interpret. From the point of view of instruction, such representations can help towards knowledge and understanding; from the point of view of pure or applied research they can provide a means of guiding the worker in a useful direction.

We are envisaging the publication of books of such diagrams as relate to certain families of chemical systems; because of the particularly great interest in oxidation reactions the first of these books will relate to "Pressures of oxygen of oxides".

REFERENCES.


4. A and B are both constants of which the values are given by the enthalpy of the reaction $\Delta H$ (or heat of reaction at constant pressure) and by the entropy of reaction $\Delta S$ in the relations:

$$A = \frac{-\Delta H}{4.575} \quad \text{and} \quad B = \frac{\Delta S}{4.575}$$

The relation $\log K = \frac{\Delta H}{4.575T} + \frac{\Delta S}{4.575}$ can then be written as:

$$\log K = \frac{\Delta H}{4.575T} + \frac{\Delta S}{4.575}$$


7. Ibid., Erg. III, 2612.

8. We are here considering carbon only in the form of graphite.


11. It must be remembered that the slope of the isobars, as that of all other lines of the diagram, measures the heat of reaction at constant pressure for the transformation which corresponds to this isobar, evaluated for 1 gm. mol. of diatomic oxygen.


Independently of us, J. Gillis has established "diagrams of sensitivity" for the study of analytical chemistry, which, as in the diagrams which we have used, employ several logarithmic scales. The technique of construction and use of these diagrams is described in the two papers:


Comment.

In 1946 it was my good fortune to meet Dr. Pourbaix when he was visiting England, and to compare the methods of attack on a number of similar problems that we had worked out independently in wartime isolation. Although our respective diagrams have a somewhat different basis, their applications in the study of metallurgical processes are closely related. But, whereas my main concern has been to compare the affinities of the various metals, Dr. Pourbaix has been interested in a more detailed examination of the variation of the affinities of individual metals over a wider range of conditions, extending to temperatures at which the dissociation of gases such as CO and oxygen may become
significant. It has been a great pleasure to see the elegant methods of representation that he has evolved, and to hear his clear exposition of the interpretation and use of the diagrams exhibited.

H. J. Ellingham.

Comment.

Mr. Trombe signale une expérience qu’il a effectué sur la distillation du carbone.

Une surface de graphite, chaufferée dans l’air au foyer d’un four solaire, se creuse très rapidement et se dépouse, latéralement à la surface focale, de longues grappes de carbone distillé. La combustion simultanée paraît très faible ; Mr. Trombe demande à Mr. Pourbaix si la dissociation de l’oxyde de carbone vers 1,000°C. peut être responsable en partie de la faible combustion observée.

Réponse.

Le carbone se vaporise vers 5,000°C. sous une pression de 1 atm., avec formation de vapeur de carbone $C_1$ et $C_2$, mono- et biatomic. A ces températures, l’oxygène $O_2$ est presque totalement dissocié avec formation de $O_1$, monoatomique, et le CO commence à se décomposer en vapeur de carbone et en $O_1$; le taux de cette décomposition atteindrait 50% vers 10,000°C.

Il est donc probable que la destruction de graphite constatée au four solaire résulte à la fois d’une distillation du carbone et d’une combustion partielle du carbone avec formation de CO, la fraction de carbone enlevée par distillation étant d’autant plus forte que la température est plus élevée.

M. Pourbaix.

Comment.

I must apologise for speaking again this morning. I want just to point out that Dr. Pourbaix is going shortly to publish a book giving the detail of his very ingenious method of mapping chemical equilibrium data.

The best feature of this method is probably the possibility of starting with several diagrams of simple systems and superposing them to obtain a picture of even very intricate equilibria.

M. Rey.

(Professor, Paris School of Mines.)