



Metal-Metal Oxide-Hydrogen Atmosphere Chart for Brazing or Bright Metal Processing

The dew point-temperature, metal-metal oxide equilibrium diagram is revised based on the latest thermodynamic data and is expanded to include curves for additional metals

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SYNOPSIS. Reducing of metallic oxides by furnace atmospheres is a fundamental requirement for atmosphere brazing and other bright processing operations. The dew point-temperature, metal-metal oxide equilibrium diagram presented by W. H. Chang in 1956 has been revised, updated, expanded, and recalculated using the latest thermodynamic data. The newly presented diagram includes equilibrium curves for 20 metallic elements and gives information on 13 additional elements.

Practical use of the diagram requires that:

1. When dealing with an alloy, the most stable oxide forming element should be identified.
2. A somewhat lower than the equilibrium dew point than that indicated on the diagram is required in practice.
3. A continuous flow of hydrogen is required in practice.

The dew point of hydrogen is, in effect, a measure of oxygen content. It has been found in practice that flowing atmospheres of inert gases having similar total oxygen content, and also continually pumped vacuum give results similar to those of hydrogen.

Thermochemical calculations were based on data from the 1967 edition of *Metalurgical Thermochemistry* (Kubaschewski & Evans). The calculations are based on the free energies of the metal oxidation reaction, and of the hydrogen oxidation reaction, applying Van't Hoff's equilibrium box

experiment fundamentals results in each calculated equilibrium dew point.

Introduction

Furnace brazing, bright annealing, sintering, and all other metallurgical processes, where metallic oxides are reduced in hydrogen atmospheres, require a fundamental knowledge of the factors involved in the oxide reducing process. The ability of pure hydrogen to reduce the oxides on the surfaces of metals and alloys is determined by three basic factors:

1. The temperature.
2. Oxygen content of the hydrogen (measured as dew point.)
3. The pressure of the gas.

Most applications are at a pressure of one atmosphere; therefore, only two variable factors remain—temperature and dew point. The diagram presented in Fig. 1 is a plot of the dew point at which the oxide and the metal are in equilibrium at various temperatures. The twenty curves shown in this diagram define the equilibrium conditions for the twenty pure metal-metal oxide systems. The position of 13 additional elements whose curves fall outside the chart is also indicated. The oxide chosen for the calculation of this diagram represents the most difficult to reduce oxide of each metal.

The metal-metal oxide equilibrium curves (Fig. 1) slope upward and to the right for each metal. The region above and to the left of each curve represents conditions that are oxidizing for that metal. All points below and to the right of each curve cover the conditions required for reducing the oxides. The diagram therefore illustrates that the higher the processing temperature, the higher the dew point (or oxygen content) that can be used for any particular metal. Or, in other words, a given purity of hydrogen becomes progressively more reducing at progressively higher temperatures.

Use of the Diagram

Use of this diagram for practical purposes requires, first, that the correct curve be selected. When processing an alloy, the element having the most stable oxide (farthest to the right) is the governing curve. *Example:* When processing chromium stainless steels, the Cr_2O_3 curve applies since chromium oxides are more stable than those of iron or nickel. Generally, it has been found that, when the most difficult-to-reduce constituent of an alloy is present in more than about 1% (atomic percentage), a continuous film of its oxide is formed and its curve therefore is applicable. Alloys having progressively

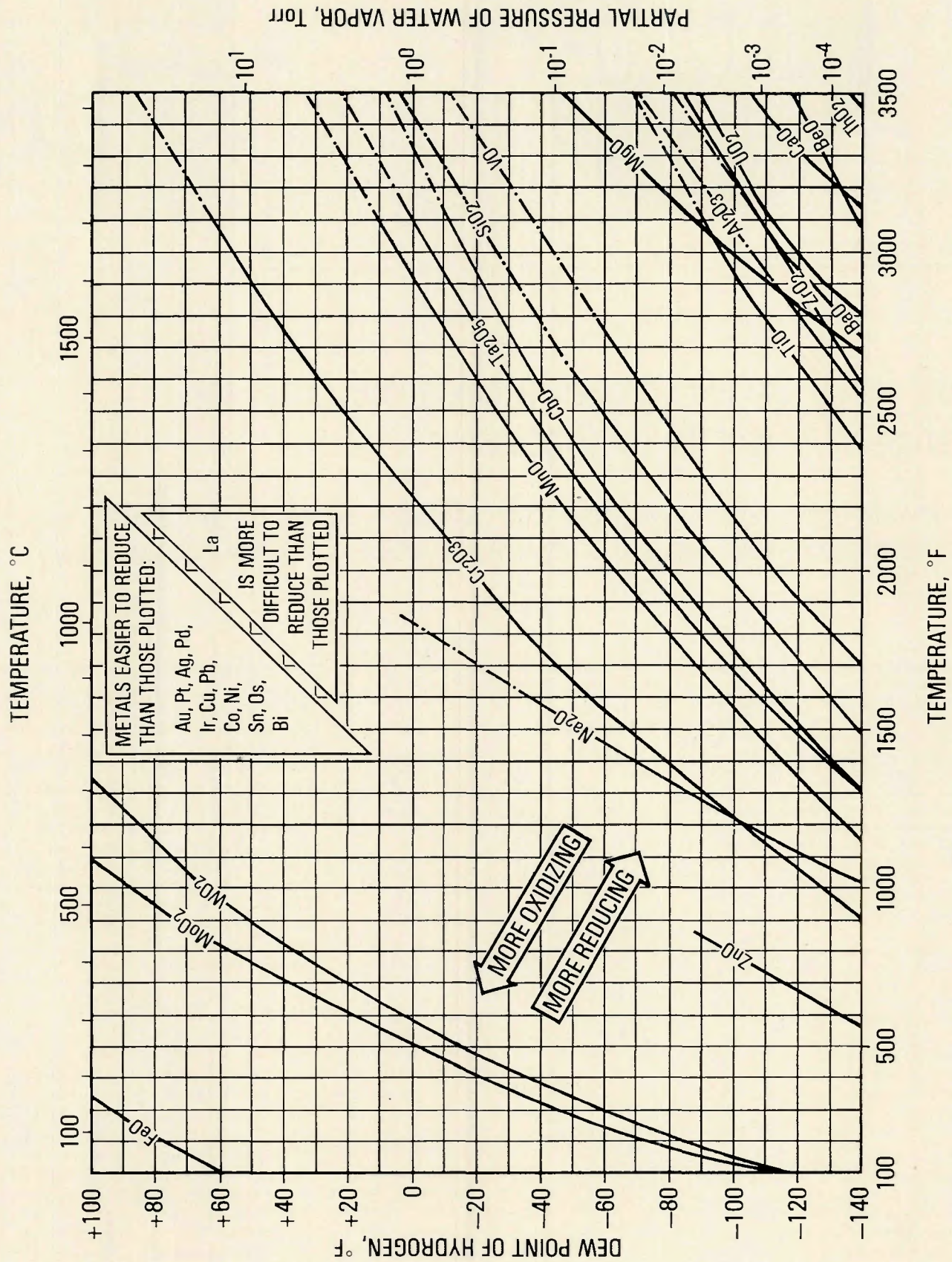


Fig. 1—Metal-metal oxide equilibria in pure hydrogen atmospheres

lower than 1 atomic-percent concentration of the most stable oxide former appear to lie progressively closer to the curve of the next most stable oxide former.

In practice it has been found necessary to use hydrogen that has a somewhat lower dew point than that indicated by the curve for any given metal. This is in part due to the fact that the surface becomes oxidized during heating until the temperature is reached that corresponds to the equilibrium temperature for that dew point. The reduction of these oxides formed during heating requires that sufficient time be allowed at conditions sufficiently below, or to the right of the equilibrium curve. It is also necessary in practice to provide a continuous flow of hydrogen into the work zone during the processing to maintain the necessary atmosphere purity at the metal surface. Figure 2 shows an instrument of a type for measuring the dew point of hydrogen.

It has also been found in practice that inert gases, of similar oxygen content and if flowed continually through the work zone, give similar results as hydrogen atmosphere. A continuously pumped vacuum roughly equivalent to the partial pressure of water vapor as presented on the right hand ordinate of Fig. 1 also gives similar results in practice.

Since the equilibrium diagram is presented only for H_2/H_2O atmospheres, all the oxygen (O_2) in the hydrogen atmospheres must be converted to H_2O before the dew point is determined.

Special caution is indicated when dealing with metals having a high affinity for H_2 . Pure metals or alloys composed principally of Ti, Zr, Hf, Ta, Cb (Nb), and certain others will immediately react with H_2 at sufficiently high temperatures, forming hydrides, or dissolving hydrogen in the base metal.

History

In 1956 Dr. W. H. Chang published a paper in the WELDING JOURNAL entitled "A Dew Point-Temperature Diagram for Metal-Metal Oxide Equilibria in Hydrogen Atmospheres."¹ The paper included thermochemical equilibrium calculations necessary for obtaining the diagram, the interpretation of the diagram, and finally, the diagram itself. In later years Dr. Chang's diagram was reproduced in many handbooks, monographs and papers as the best available source of information for metallurgists dealing with hydrogen atmospheres. More recently, in the *Welding Handbook* (American Welding Society, 5th Edition, 1964) and in the *Metals Handbook* (American Society for Metals, 8th Edition, 1964) this equilibrium diagram has been repro-

duced again, with some minor changes.

The last two editions of the *Brazing Manual* (AWS, 1955 and 1963) have adopted another, somewhat more complicated diagram—"Equilibrium Relationships in Controlled Atmospheres."² In this diagram the equilibrium curves are presented for two atmospheres:

1. Hydrogen with varying $\log P_{H_2O}/P_{H_2}$ ratios.
2. For some carbon dioxide-carbon monoxide mixtures.

The *Brazing Manual* diagram has been taken over, with some minor changes from the Armour Research Foundation Report, "Literature Review and Industrial Survey of Brazing,"³ published in June 1952.

Both diagrams were obtained utilizing thermochemical equilibrium calculations. Authors of both diagrams used the well known monograph entitled *Metallurgical Thermochemistry* as compiled by Kubaschewski and Evans⁴ as the basis for their calculations. Dr. Chang used the 1955 Edition for his calculations, while Armour Research Foundation workers used the older, 1951 edition of *Metallurgical Thermochemistry*. The 1967 edition of *Metallurgical Thermochemistry* has been used for the calculations of the present diagram.

In the last fifteen years considerable amounts of research work have been done on investigation of the thermochemical properties of the "high stress to weight-ratio metals"—titanium, zirconium and beryllium, and also on the columbium, and tungsten. Also, the basic concepts concerning the number of oxides of almost each of these metals, the composition of the oxides, and their thermochemical properties have undergone considerable changes.

These changes show as a shift in the position of the metal-metal oxide equilibrium curves in the pertinent equilibrium diagram. For instance, in the 1956 diagram the equilibrium curve for titanium metal defines the equilibrium conditions between pure titanium and titanium dioxide (TiO_2). According

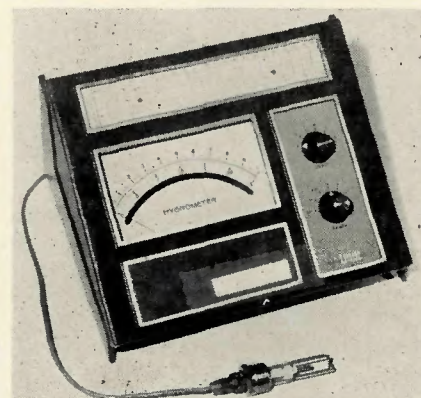


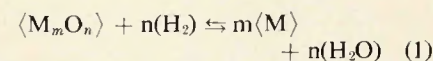
Fig. 2—An instrument of a type used for measuring dew point of hydrogen

to the most recent thermodynamic data, the most stable Ti oxide in all temperature ranges from 0° C up to 1700° C is TiO . Since the free energy of formation of TiO is not the same as of TiO_2 in the new diagram, the equilibrium curve had to be determined for the Ti-TiO equilibrium, and not for the Ti- TiO_2 equilibrium, as it was in the old diagram.

These considerations plus the need for curves on many additional metals indicated that time has come to prepare a revised version of the metal-metal oxide equilibrium diagram on the basis of the newest thermochemical data, and including in the diagram as many practically used metals as possible. The equivalent partial pressure of water vapor has also been added on the right ordinate. The new, revised equilibrium diagram is presented in Fig. 1.

Thermochemical Calculations

The equilibrium curves in the new diagram essentially have been determined utilizing the same thermodynamic calculations which were used for establishing the original diagram. For the sake of a better surveillance, the basic equilibrium reaction taking place between hydrogen and the given metallic oxide on one side, and the oxide free metal and water vapor on the opposite side, has to be written in the same form as in Dr. Chang's presentation:



where M designates the given metal, and M_mO_n the given metal oxide, m is the number of metal atoms in the oxide, and n is the number of oxygen atoms in the given oxide. Angular brackets denote the solid state, and round brackets the gaseous state. A five-step calculation process was applied for each selected equilibrium temperature for determining each metal-metal oxide equilibrium curve. The five consecutive steps comprised the following calculations:

1st Step

The first step comprised calculating the free energy $\Delta G_{M_mO_n}$ for the oxide dissociation reaction $\langle M_mO_n \rangle \rightarrow m\langle M \rangle + \frac{n}{2}(O_2)$. In the 1967 edition of *Metallurgical Thermochemistry*, Table E, ("Standard Free Energies of Reaction," pages 421-429) the three basic parameters— A , B and C —required for calculating the free energies, are given for a large number of various metallic oxides. According to Kubaschewski and Evans, the free energies are calculated with the help of a simplified formula:

$$\Delta G_T = A + BT \cdot \log T + CT \quad (2)$$

2nd Step

The second step comprises the calculation of the free energy ΔG_{H_2O} for the hydrogen combustion reaction $(H_2) + \frac{1}{2}(O_2) = (H_2O)$. According to Kubaschewski and Evans, the free energy of this reaction can be determined for every selected temperature in the entire temperature range from 298 to 2500° K. This free energy can be calculated with the help of the simplified formula:

$$\Delta G_T = A + BT \log T + CT \quad (4)$$

where $A = -58,900$, $B = 0$, and $C = +13.1$.

3rd Step

The third step comprises the calculation of the free energy change ΔF for the metallic oxide reducing reaction presented in eq (1). The metal oxide reducing reaction essentially consists of two reactions:

1. Of the metallic oxide dissociation reaction which results in the increase of the free energy of the given system ($\Delta G_{H_mO_n}$).
2. Of the hydrogen oxidation (combustion) reaction which results in the decrease of the free energy of the given system (ΔG_{H_2O}).

Accordingly, the total change of the free energy of the metallic oxide reducing reaction can be obtained by subtracting the two free energies from each other:

$$\Delta F = -\Delta G_{M_mO_n} + \Delta G_{H_2O}$$

4th Step

The fourth step involves determining the P_{H_2O}/P_{H_2} ratios from the change of the free energy ΔF for every given equilibrium temperature. In order to do this, the equilibrium constant K_p for the chemical reaction described by eq (1) has to be determined first. This equilibrium constant can be written in the exact form, correlating it to the P_{H_2O}/P_{H_2} ratio; as

$$K_p = \left(\frac{P_{H_2O}}{P_{H_2}} \right)^n$$

For the chemical reaction presented by eq (1), the total change for free energy ΔF is related to the equilibrium constant K_p by thermodynamic function, which is derived from Van't Hoff's equilibrium box experiment:

$$\begin{aligned} \Delta F &= -RT \cdot \ln K_p \\ &= -RT \cdot \ln (P_{H_2O}/P_{H_2})^n \\ &= -4.576 \cdot n \cdot T \cdot \log P_{H_2O}/P_{H_2} \quad (4) \end{aligned}$$

Using eq (4), the ratio P_{H_2O}/P_{H_2} can be determined for every equilibrium temperature T for which the change of the free energy F has been calculated:

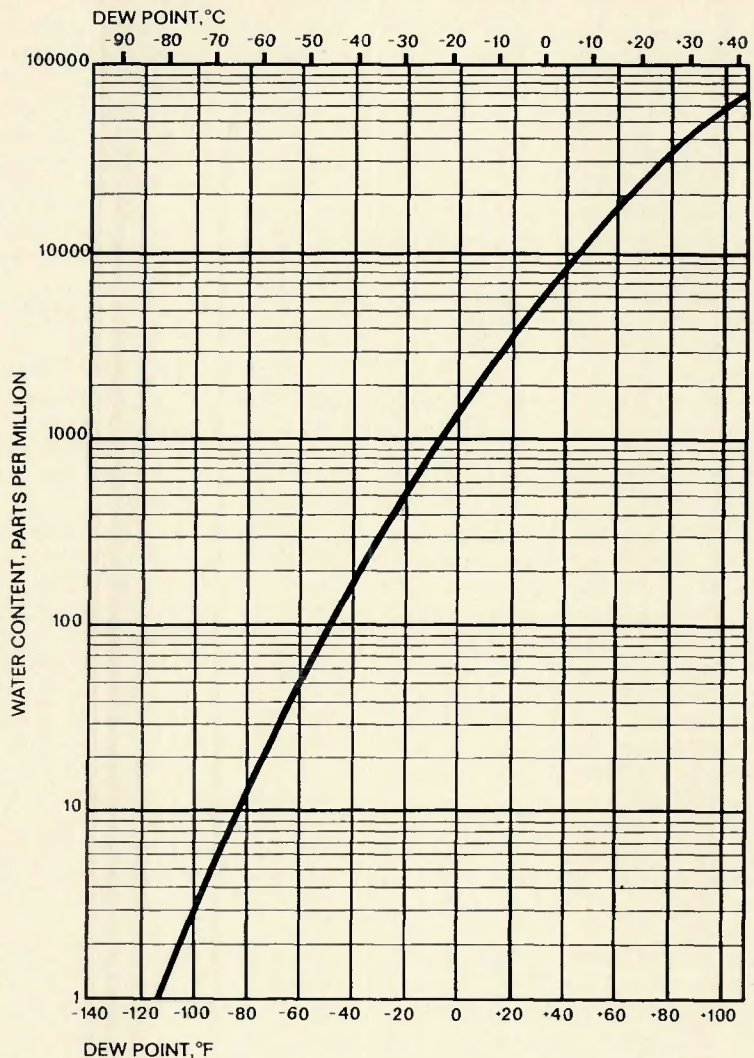


Fig. 3—Dew point vs. ppm water content

$$\log \frac{P_{H_2O}}{P_{H_2}} = -\frac{\Delta F}{4.576 \cdot n \cdot T} \quad (5)$$

identical, indicating that there are no discrepancies between the two curves.

5th Step

The fifth step comprises determination of the dew points for the thermodynamically determined P_{H_2O}/P_{H_2} ratios. For the conversion of the given P_{H_2O}/P_{H_2} ratios to the corresponding dew points, a special dew point vs. P_{H_2O}/P_{H_2} conversion curve was plotted. Figure 3 shows the relationship between parts per million water vapor vs. equivalent dew point.

A similar chart relating P_{H_2O}/P_{H_2} to dew point was used for the conversion to dew point. The table entitled "Relation Between Dew Point and Moisture Content of Gases" in the monograph, *Protective Atmospheres*,⁵ (in the temperature range from +100 to -100° F) was used with the dew point versus water content curve obtained from Perry's *Chemical Engineering Handbook*, 3rd Edition (comprising the temperature range from 0 to -140° F). The overlapping parts of the two curves between 0 and -100° F were almost

Example Showing the Details of an Equilibrium Point Calculation

In order to illustrate the application of the five-step calculation process used for determination of the dew point vs. equilibrium temperature curves, the following example of a detailed calculation for the equilibrium of the reaction $(MoO_2) + 2(H_2) \rightarrow (Mo) + 2(H_2O)$ at 500° K (227° C = 441.6° F) is presented step by step:

1st Step

Calculation of the change of the free energy, ΔG_{MoO_2} for the dissociation reaction of molybdenum dioxide:

According to Table E of *Metalurgical Thermochemistry*, the change of the free energy can be determined by substituting $A = 140,500$, $B = 4.6$, and $C = -55.8$ into the simplified formula $\Delta G = A + BT \cdot \log T + CT$ (equation (2)) accordingly for the equilibrium at 500° K: $\Delta G_{MoO_2} = 140,500 + 4.6 \cdot T$

$$\begin{aligned} \cdot \log T - 55.8 \cdot T &= 140,500 + 4.6 \\ \times 500 \times \log \cdot 500 - 55.8 \times 500 \\ &= 140,500 + 4.6 \times 500 \times 2.69897 \\ -55.8 \times 500 &= 140,500 + 6,208 \\ -27,900 &= 118,808 \text{ calories, i.e.,} \end{aligned}$$

$$\Delta G_{\text{MoO}_2} = 118,808 \text{ calories}$$

2nd Step

Calculation of the change of the free energy, $\Delta G_{\text{H}_2\text{O}}$ for the reaction $(\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O})$:

According to Table E of *Metalurgical Thermochemistry* for this reaction, $A = -58,900$, $B = 0$, and $C = +13.1$:

Consequently, for the equilibrium at 500°K : $\Delta G_{\text{H}_2\text{O}} = -58,900 + 13.1 \times 500 = -52,350$ calories, for formation of two molecules of water vapor: $n = 2$, and the change of free energy will comprise $2\Delta G_{\text{H}_2\text{O}} = -104,700$ calories.

3rd Step

Calculation of the change of the free energy for the reducing reaction $(\text{MoO}_2) + 2(\text{H}_2) = (\text{Mo}) + 2(\text{H}_2\text{O})$

$$\begin{aligned} \Delta F &= \Delta G_{\text{MoO}_2} - \Delta G_{\text{H}_2\text{O}} = 118,808 \\ &\quad - 104,700 = 14,108 \text{ calories} \end{aligned}$$

4th Step

Calculation of the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio for the MoO_2 reducing reaction at 500°K (441°F):

$$\Delta F = 14,108 = -4.576 \times T \times n \times \log P_{\text{H}_2\text{O}}/P_{\text{H}_2}$$

$$\begin{aligned} \log P_{\text{H}_2\text{O}}/P_{\text{H}_2} &= \frac{-14,108}{4.576 \times 2 \times 500} \\ &= -3.0833 = +0.9167 - 4 \end{aligned}$$

$$\text{Accordingly, } \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = 0.000825 \text{ or } 0.08 \text{ vol } \% \text{ H}_2\text{O}$$

5th Step

The dew point vs. water content diagram (Fig. 3) shows that 0.08 vol % H_2O corresponds to a dew point of -12°F .

Calculating the Equilibrium Curves

In calculating the equilibrium curves, the equilibrium points for each metal

were determined at intervals of 50°K , or 100°K . The pertinent equilibrium curves have been obtained by connecting the individual equilibrium points with curved lines. Many of the curves were extrapolated beyond the range of the thermochemical data. The extrapolated regions are shown as broken lines. These may be in error since they represent extrapolation beyond known data; however, they are presented since it is believed the relative position of these curves are correct.

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"Control of Distortion and Shrinkage in Welding"

By Koichi Masubuchi

This paper, prepared for the Interpretive Reports Committee of the Welding Research Council, covers the development of analytical means for predicting and controlling weld distortion. The report presents basic background information and pertinent data upon which an analytical system can be developed for studying weld distortion.

A discussion is presented in a general manner: (1) what parameters need to be included for analyzing weld distortion in actual structures; (2) what steps of analysis are involved; and (3) how much is known about these steps. It is pointed that such a system has not yet been completed, but it is suggested how it could be completed. Discussions are then made of mathematical analyses that have been developed and empirical and analytical studies that relate to this system. Finally, areas for future approaches to the problem of weld distortion are suggested.

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