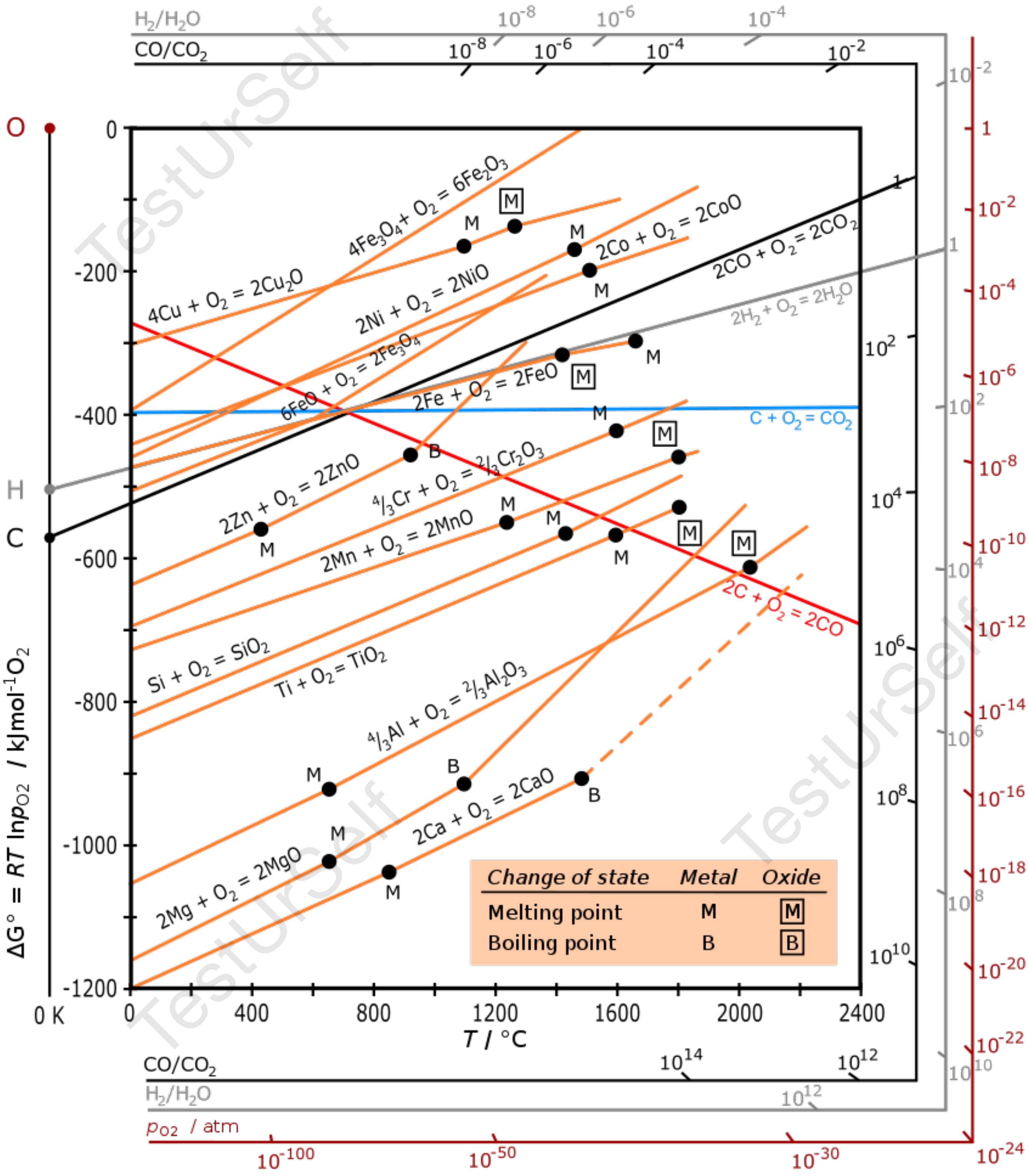
Notes on

Ellingham Diagram:



Definitions:

Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes a reaction occur. A negative value for ΔG indicates that a reaction can proceed spontaneously without external inputs, while a positive value indicates that it will not. The equation for Gibbs free energy is:

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the enthalpy, T is absolute temperature, and ΔS is entropy.

Enthalpy (ΔH) is a measure of the actual energy that is liberated when the reaction occurs (the "heat of reaction"). If it is negative, then the reaction gives off energy, while if it is positive the reaction requires energy.

Entropy (ΔS) is a measure of the change in the possibilities for disorder in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.

Construction of an Ellingham diagram:

The construction of an Ellingham diagram provides a visual representation of the thermodynamics involved in the formation of metal oxides from metals and oxygen. By plotting the change in Gibbs free energy (ΔG) against temperature for various reactions, the diagram serves as a valuable tool for understanding and predicting the conditions under which these reactions will occur spontaneously. Here's a detailed explanation of how these diagrams are constructed and interpreted, focusing on the reaction of metals with oxygen to form oxides.

Basics of the Ellingham Diagram

- Y-Axis (ΔG): The vertical axis of the diagram represents the Gibbs free energy change for the formation of oxides from metals and oxygen. By convention, $\Delta G = 0$ is positioned at the top, and the axis extends downward to show negative values of ΔG. This orientation emphasizes that negative ΔG values signify reactions that can occur spontaneously.

- **X-Axis (Temperature):** The horizontal axis indicates the temperature in degrees Celsius or Kelvin. The diagram thus illustrates how the spontaneity of reactions (as indicated by ΔG) changes with temperature.

Plotting the Reactions:

- **Straight Lines:** For a given reaction, the plot of ΔG versus temperature is approximated as a straight line under the assumption that ΔH (enthalpy change) and ΔS (entropy change) remain constant with temperature, in the absence of phase changes. This linearity simplifies the diagram and makes it easier to interpret.

- **Slope and Y-Intercept:** In the formula $\Delta G = \Delta H - T\Delta S$, ΔH and ΔS are constants for a given reaction, making the relationship between ΔG and T linear. The **slope** of each line is determined by $-\Delta S$ (since entropy change influences the temperature dependence of ΔG), and the y-intercept corresponds to ΔH.

- **Phase Changes:** When a metal or oxide undergoes a phase change (melting or vaporization), the slope of the line changes. This is due to the significant change in ΔS associated with phase transitions.

Specific Features on an Ellingham Diagram:

- **Metal Oxides:** For most metal oxides, the free energy of formation (ΔG) is negative under standard conditions. Thus, the reactions are plotted with negative ΔG values, indicating their spontaneity.

- **Temperature Markers:** Important temperatures, such as those where the metal or oxide changes phase (melts or vaporizes), are marked on the diagram. These markers are crucial for understanding the temperature ranges within which the metals or oxides maintain their phases and how these transitions affect reaction spontaneity.

- **Oxidation of Carbon:** The oxidation reactions of carbon to carbon dioxide ($C + O_2 \rightarrow CO_2$) and carbon monoxide ($2C + O_2 \rightarrow 2CO$) highlight different entropy effects. The formation of CO_2 shows little change in entropy, resulting in a nearly horizontal line, as it involves a solid reacting with a gas to form another gas. In contrast, the formation of CO involves a solid reacting with a gas to produce two moles of gas, leading to a significant increase in entropy and a line that slopes sharply downward.

Applications and Interpretation:

- **Predicting Reaction Spontaneity:** By examining the positions and slopes of the lines at different temperatures, one can predict whether a particular metal will oxidize under given conditions.

- **Comparing Reactivities:** The diagram allows for the comparison of different metals' tendencies to oxidize by comparing their ΔG values across the temperature range.

- **Thermodynamic Insights:** The Ellingham diagram reveals the thermodynamic feasibility of reducing metal oxides to metals, which is fundamental in metallurgical processes.

There are three main uses of the Ellingham diagram:

1. Determine the relative ease of reducing a given metallic oxide to metal;

2. Determine the partial pressure of oxygen that is in equilibrium with a metal oxide at a given temperature; and

3. Determine the ratio of carbon monoxide to carbon dioxide that will be able to reduce the oxide to metal at a given temperature.

Ease of Reduction:

The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature. Reactions closer to the top of the diagram are the most "noble" metals (for example, gold and platinum), and their oxides are unstable and easily reduced. As we move down toward the bottom of the diagram, the metals become progressively more reactive and their oxides become harder to reduce.

A given metal can reduce the oxides of all other metals whose lines lie above theirs on the diagram. For example, the $2Mg + O_2 => 2MgO$ line lies below the $Ti + O_2 => TiO_2$ line, and so magnesium can reduce titanium oxide to metallic titanium.

Since the $2C + O_2 => 2CO$ line is downward-sloping, it cuts across the lines for many of the other metals. This makes carbon unusually useful as a reducing agent, because as soon as the carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to metal. So, for example, solid carbon can reduce chromium oxide once the temperature exceeds approximately 1225°C, and can even reduce highly-stable compounds like silicon dioxide and titanium dioxide at temperatures above about 1620°C and 1650°C, respectively. For less stable oxides, carbon monoxide is often an adequate reducing agent.

Equilibrium Partial Pressure of Oxygen

The scale on the right side of the diagram labelled "Po_2" is used to determine what partial pressure of oxygen will be in equilibrium with the metal and metal oxide at a given temperature. The significance of this is that, if the oxygen partial pressure is higher than the equilibrium value, the metal will be oxidized, and if it is lower than the equilibrium value then the oxide will be reduced.

To use this scale, you will need a straightedge. First, find the temperature you are interested in, and find the point where the oxidation line of interest crosses that temperature. Then, line up the straightedge with both that point, and with the point labelled " 0 " that is marked with short radiating lines (upper left corner of the diagram). Now, with the straightedge running through these two points, read off the oxygen partial pressure (in atmospheres) where the straightedge crosses the "PO_2" scale, and this is the equilibrium partial pressure.

It is possible to reach the equilibrium oxygen partial pressure by use of a hard vacuum, purging with an inert gas to displace the oxygen, or using a scavenger chemical to consume the oxygen.

Ratio of $\frac{CO}{CO_2}$ Needed for Reduction

When using carbon as a reducing agent, there will be a minimum ratio of CO to CO_2 that will be able to reduce a given oxide. The harder the oxide is to reduce, the greater the proportion of CO needed in the gases.

To determine the $\frac{CO}{CO_2}$ ratio to reduce a metal oxide at a particular temperature, use the same procedure as for determining the equilibrium pressure of oxygen, except line up the straightedge with the point marked "C" (center of the left side of the diagram), and read the ratio off of the scale marked "CO/CO_2".

Here are some multiple-choice questions (MCQs) on the topic of Ellingham diagrams:

1. Which of the following best describes an Ellingham diagram?

A) A plot of entropy change (ΔS) versus temperature
B) A plot of enthalpy change (ΔH) versus temperature
C) A plot of Gibbs free energy change (ΔG) versus temperature
D) A plot of heat capacity change (ΔC_p) versus temperature

Ans: C

An Ellingham diagram is a graph showing how the Gibbs free energy change (ΔG) of metal oxidation reactions varies with temperature. It plots ΔG against temperature and helps predict reaction spontaneity and stability of metal oxides at different temperatures. Each reaction is represented by a straight line, with slope indicating entropy change (ΔS) and y-intercept representing enthalpy change (ΔH). Phase changes affect the lines, and the diagram aids in selecting reducing agents and understanding high-temperature reactions in metallurgy and materials science.

2. In an Ellingham diagram, what does the y-intercept of a reaction line represent?

A) Enthalpy change (ΔH)
B) Entropy change (ΔS)
C) Gibbs free energy change (ΔG)
D) Activation energy

Ans: A

In an Ellingham diagram, the y-intercept of a reaction line represents the enthalpy change (ΔH) of the corresponding chemical reaction. This value reflects the heat absorbed or released during the reaction at zero Kelvin, influencing the spontaneity of the reaction. Exothermic reactions have negative y-intercepts, indicating energy release, while endothermic reactions have positive y-intercepts, indicating energy absorption. Enthalpy change is a critical factor alongside entropy change and temperature in determining reaction spontaneity.

3. Which of the following statements about the slope of a reaction line on an Ellingham diagram is correct?

A) The slope represents the activation energy of the reaction.
B) The slope represents the change in entropy ($-\Delta S$) of the reaction.
C) The slope represents the change in Gibbs free energy (ΔG) of the reaction.
D) The slope represents the change in enthalpy (ΔH) of the reaction.

Ans: B

In an Ellingham diagram, the slope of a reaction line represents the change in entropy ($-\Delta S$) of the reaction. A steeper slope indicates a larger entropy change, while a shallower slope suggests a smaller entropy change. This relationship reflects how the disorder of the system changes as the reaction progresses. Entropy change influences the temperature dependence of the Gibbs free energy change (ΔG) according to the equation $\Delta G = \Delta H - T\Delta S$, making the slope crucial in understanding the thermodynamics of reactions. It doesn't directly represent activation energy (E_a), Gibbs free energy change (ΔG), or enthalpy change (ΔH).

4. Which statement is correct in reference to the Ellingham diagram?

A) For temperatures at which the C/CO line lies above the metal oxide line, C can be used to reduce the metal oxide. The C is oxidized to CO.
B) For temperatures at which the C/CO line lies below the metal oxide line, C can be used to reduce the metal oxide. The C is oxidized to CO.
C) For temperatures at which the CO/CO_2 line lies below the metal oxide line, C can be used to reduce the metal oxide. The C is oxidized to CO.
D) None of these

Ans: B

The correct statement in reference to the Ellingham diagram is:

(B) For temperatures at which the C/CO line lies below the metal oxide line, C can be used to reduce the metal oxide. The C is oxidized to CO.

Explanation in Detail:

The Ellingham diagram provides a graphical representation of the temperature dependence of the Gibbs free energy (ΔG) for various reactions. For the purpose of understanding metal reduction processes, particularly those involving carbon (in the forms of C, CO, and CO_2), this diagram is an invaluable tool.

Understanding the C/CO Line:

- Position Relative to Metal Oxides: The line representing the reaction of carbon (as a reducing agent) to carbon monoxide (C to CO) serves as a benchmark for determining whether a given metal oxide can be reduced by carbon.

- Below the Metal Oxide Line: When the C/CO line is below the line for a metal oxide in the Ellingham diagram, this indicates that the reaction of carbon with oxygen (to form CO) has a lower Gibbs free energy (ΔG) than the decomposition of the metal oxide at that specific temperature. In simpler terms, carbon can thermodynamically reduce the metal oxide to metal because it is energetically more favorable for carbon to react with the oxygen from the metal oxide, reducing it to metal, while the carbon itself is oxidized to carbon monoxide.

The Thermodynamics Behind the Reduction:

- **Gibbs Free Energy:** The driving force behind chemical reactions is the change in Gibbs free energy (ΔG). A reaction can occur spontaneously at a given temperature if ΔG is negative.

- **ΔG of Reactions:** For a metal oxide to be reduced by carbon, the ΔG for the reduction reaction (metal oxide to metal) must be more positive than the ΔG for the oxidation of carbon to CO. This is the case when the C/CO line is below the metal oxide line on the diagram.

- **Practical Implications:** In industrial processes, this principle is applied in the reduction of metal oxides (like those of iron in the blast furnace process) where carbon (in the form of coke) is used as a reducing agent. The position of the C/CO line relative to various metal oxide lines guides the choice of reducing agents and the operational temperatures for efficient reduction of metal oxides.

Statement (B) correctly explains the use of carbon to reduce metal oxides based on the positions of the respective lines on the Ellingham diagram. When the C/CO line is below a metal oxide line, it implies that carbon has a sufficient thermodynamic potential to reduce that oxide, thereby releasing the metal and forming CO in the process.