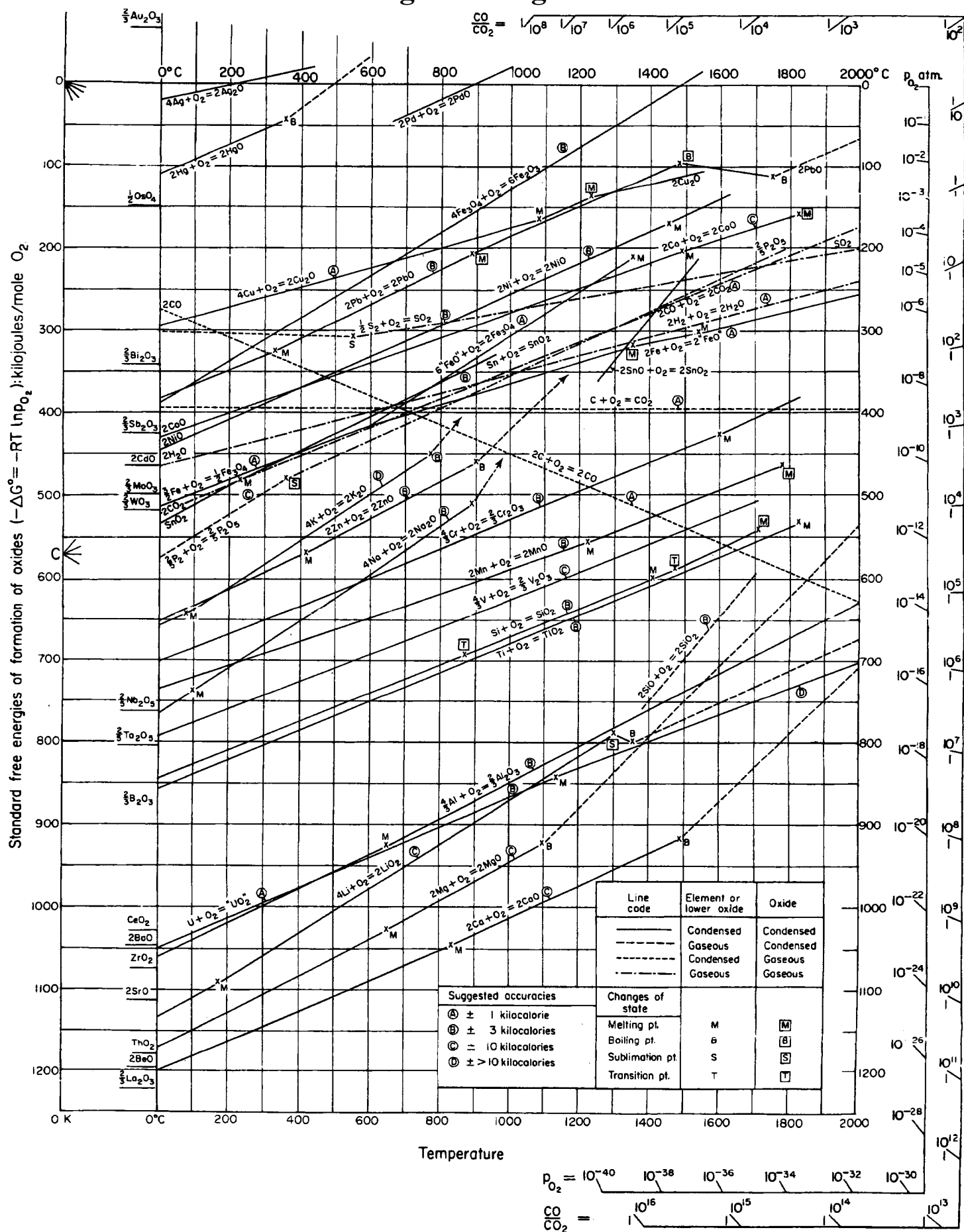


Ellingham Diagrams



Definitions

The 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.

The 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.

The 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.

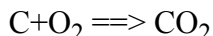
Construction of an Ellingham Diagram

An Ellingham diagram is a plot of ΔG versus temperature. Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept. The slope of the line changes when any of the materials involved melt or vaporize.

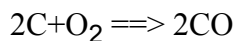
Free energy of formation is negative for most metal oxides, and so the diagram is drawn with $\Delta G=0$ at the top of the diagram, and the values of ΔG shown are all negative numbers. Temperatures where either the metal or oxide melt or vaporize are marked on the diagram.

The Ellingham diagram shown is for metals reacting to form oxides (similar diagrams can also be drawn for metals reacting with sulfur, chlorine, etc., but the oxide form of the diagram is most common). The oxygen partial pressure is taken as 1 atmosphere, and all of the reactions are normalized to consume one mole of O_2 .

The majority of the lines slope upwards, because both the metal and the oxide are present as condensed phases (solid or liquid). The reactions are therefore reacting a gas with a condensed phase to make another condensed phase, which reduces the entropy. A notable exception to this is the oxidation of solid carbon. The line for the reaction



is a solid reacting with a mole of gas to produce a mole of gas, and so there is little change in entropy and the line is nearly horizontal. For the reaction



we have a solid reacting with a gas to produce two moles of gas, and so there is a substantial increase in entropy and the line slopes rather sharply downward. Similar behavior can be seen in parts of the lines for lead and lithium, both of which have oxides that boil at slightly lower temperatures than the metal does.

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 $2\text{Mg} + \text{O}_2 \implies 2\text{MgO}$ line lies below the $\text{Ti} + \text{O}_2 \implies \text{TiO}_2$ line, and so magnesium can reduce titanium oxide to metallic titanium.

Since the $2\text{C} + \text{O}_2 \implies 2\text{CO}$ 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 CO/CO₂ Needed for Reduction

When using carbon as a reducing agent, there will be a minimum ratio of CO to CO₂ 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 CO/CO₂ 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/CO₂”.