

19. H, S, C, and G Diagrams Module

The diagram module presents the basic thermochemical data for the given species in graphical format. Eight different diagram types can be drawn as a function of temperature:

- H Enthalpy (total)
- H Enthalpy (latent)
- S Entropy
- Cp Heat Capacity
- G Gibbs Energy
- DH
- DS
- DG (Ellingham diagrams)

The basic steps for drawing a diagram for all types are quite similar, except for a small difference with the DG diagrams. These steps are described in more detail below, see the example in **Fig. 1**:

1. Type the **species** formulae in the first column of the **X-data** sheet. There is no need to open the other sheets, because these are in internal use only.
2. Select the diagram type from the **Diagram Type** list, in this example H Enthalpy (latent) has been selected, see **Fig. 1**.
3. **DG diagrams only**: Select an element from the list (for example: O for oxides, S for sulfides, Cl for chlorides, etc.) and press **Balance Element Amount**.
4. Press **Diagram** to draw diagram 1. This will search for data from the database for the given ranges. You can force HSC to use its own or main database by selecting 1 or 2 in the Database No column. Without this setting, the diagram module looks for the data first from the own database and then from the main database. You can also modify all the default settings such as x- and y-axis ranges and units.

An example of a diagram is shown in **Fig. 1**, **Fig. 2** and **Fig. 4**. The scales, lines, and labels can be edited in the same manner as in the other graphics routines.

The DG (Ellingham) diagrams show the relative stability of various oxides, sulfates, chlorides etc. These diagrams must contain only the same type of substances, such as oxides, sulfides, chlorides, etc. The species amounts must be balanced to contain exactly the same amount of the main element, such as oxygen in oxides and sulfur in sulfides.

An example of Ellingham diagram settings is given in **Fig. 2 - Fig. 6**. The results in **Fig. 4** show, for example, that iron oxides can be reduced with carbon at higher temperatures than 700 °C, i.e. $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}(\text{g})$. Metals whose oxide DG is smaller at a selected temperature, **Fig. 4**, can be used to reduce these oxides where the DG is higher. The most stable oxides (Cr_2O_3 , MgO) are located at the bottom of the diagram.

In this example, an Ellingham diagram is calculated and illustrated using the HSC8 Thermodynamic Data Diagrams module (Dia). The idea of Ellingham diagrams is to see and compare which of the metal oxides is the most stable. In order to make comparisons, the $\text{O}_2(\text{g})$ amount needs to be balanced. This is illustrated with FeO and Fe_2O_3 oxides here:



In HSC, the user needs to give only metal oxides and after that the balance O amount with 2 atoms ($O_2(g)$) using the **Balance Element Amount** button. After that selecting the **Diagram** button draws the figure.

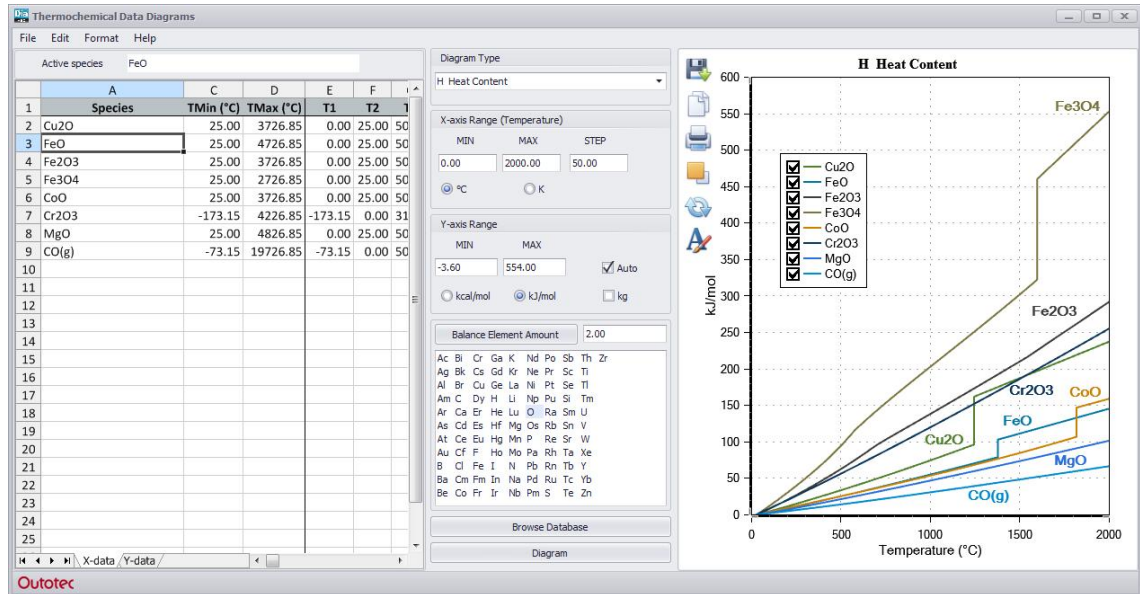


Fig. 1. Diagram menu. Enthalpy (latent) diagram type selected.

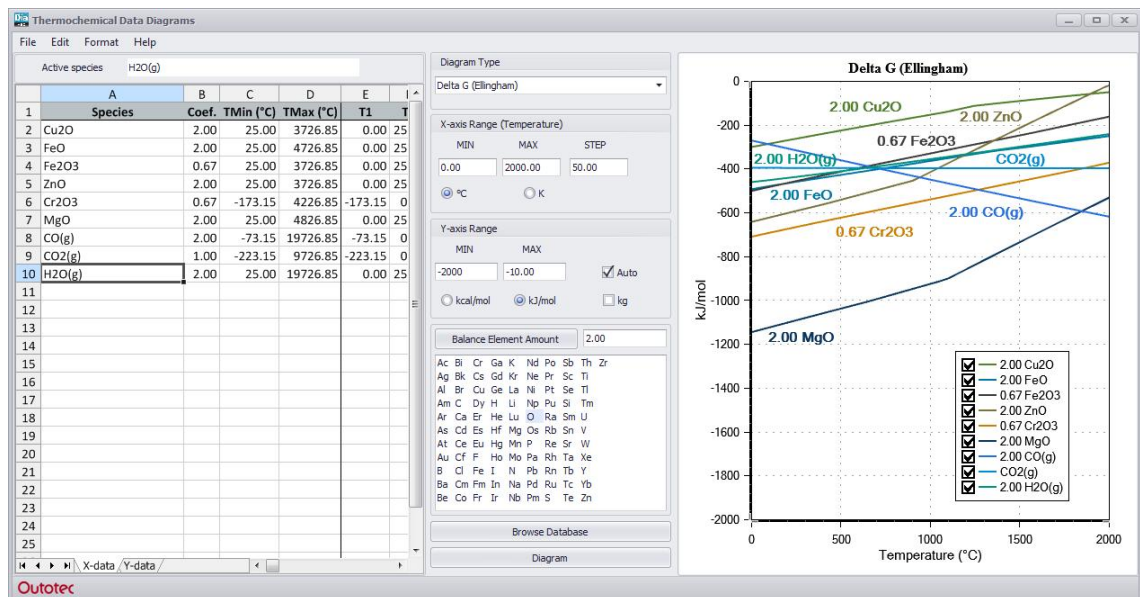


Fig. 2. Ellingham diagram.

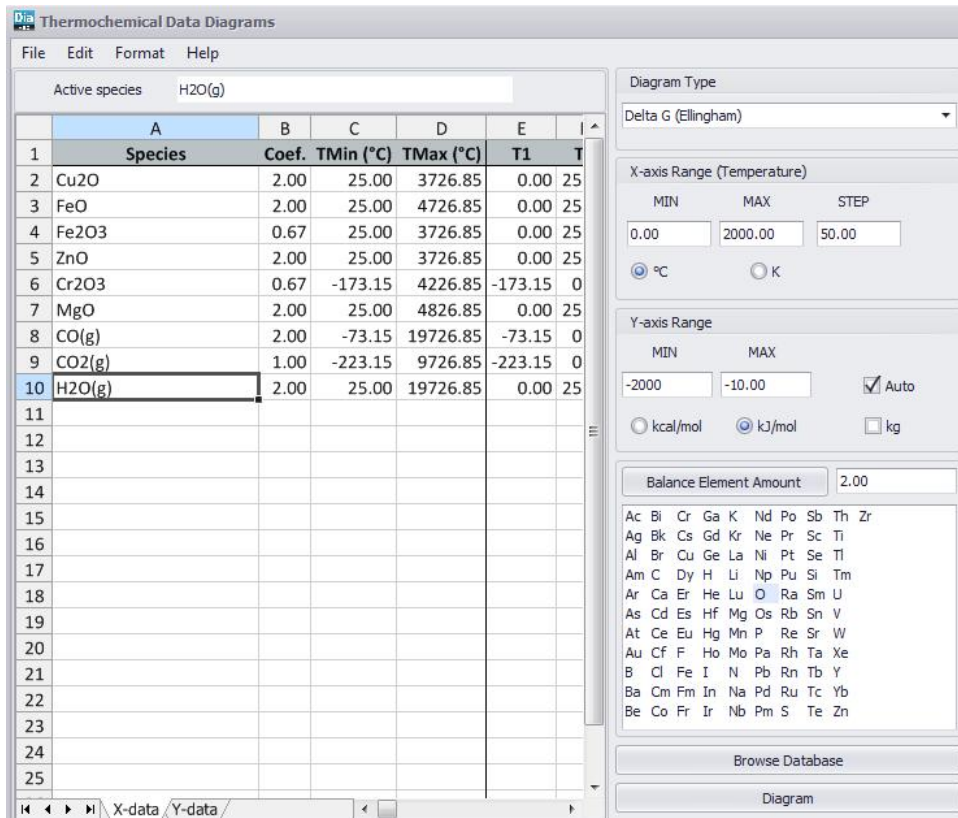


Fig. 3. Initial values needed for Ellingham diagram calculation. Note that the amount of oxygen must be balanced (in this example 2 oxygen atoms have been chosen since $O_2(g)$ is a stable molecule) before drawing the diagram.

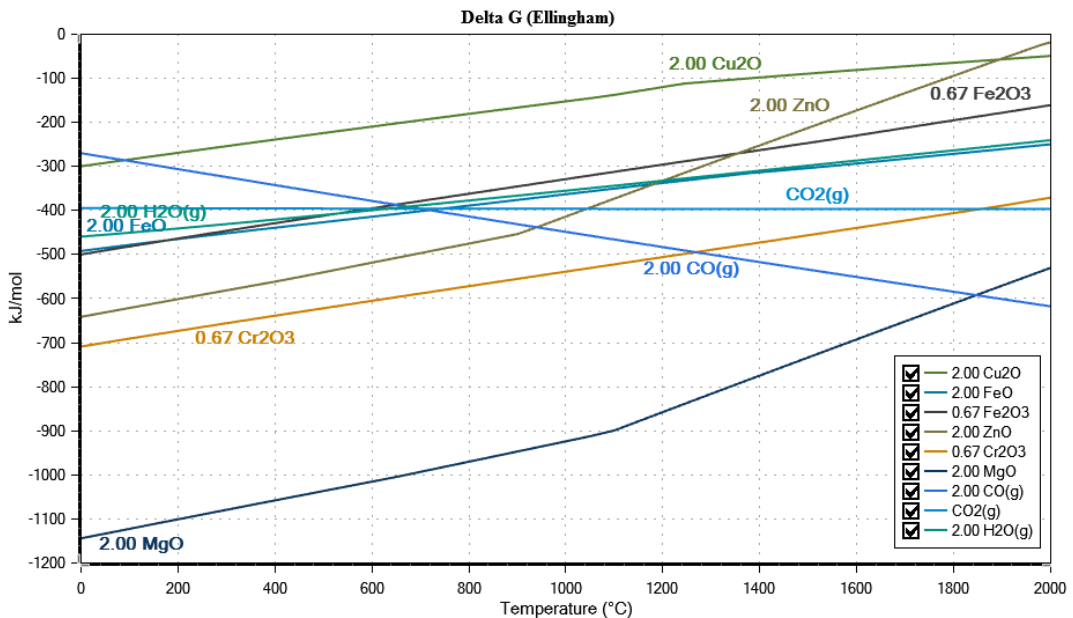


Fig. 4. Ellingham diagram of metal oxides. Also shown are $CO(g)$, $CO_2(g)$, and $H_2O(g)$ lines that are important in metallurgical processes.

MgO is the most stable of the oxides in **Fig. 4**, i.e. the most stable oxides are located at the bottom of the diagram (most negative Gibbs energy value). It also shows that the stability of ZnO will change more with temperature compared to iron and copper oxides. At lower temperatures, ZnO is the most stable, while as the temperature increases other oxides become more stable in the following order: FeO , Fe_2O_3 and Cu_2O . The Ellingham diagram

also shows that the metals whose oxides are at the bottom of the diagram can be used to reduce oxides higher in the diagram to metals, see Equation (3):

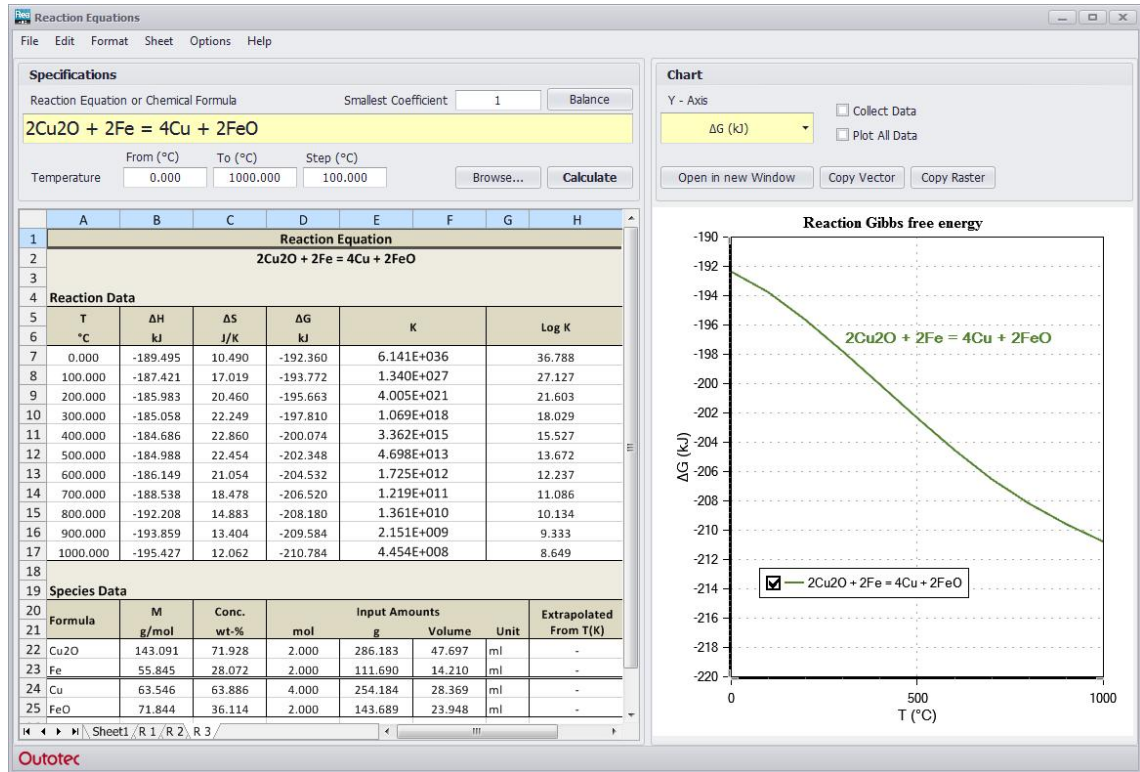
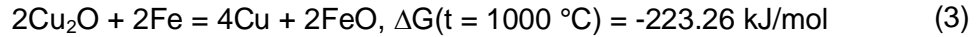


Fig. 5. Gibbs energy of reaction using Reaction Equations module.

There is one more important property often added to an Ellingham diagram, which is the partial pressure of oxygen. In HSC you can also calculate oxygen pressure easily using the Reaction Equations module. It is important to write equations so that O₂(g) is the product, see Fig. 5. This is because the equilibrium constant is then equal to the partial pressure of oxygen. Some metals vaporize at low temperatures. Such metals are Mg and Zn in this example. This also affects the Ellingham diagram, as can be seen in the changing slope of the curves of these metals (Zn and Mg boil at 907 and 1088 °C, respectively). The boiling point of the metal must be taken into account when calculating the partial pressure of oxygen using the Reaction Equations module, see Fig. 6.

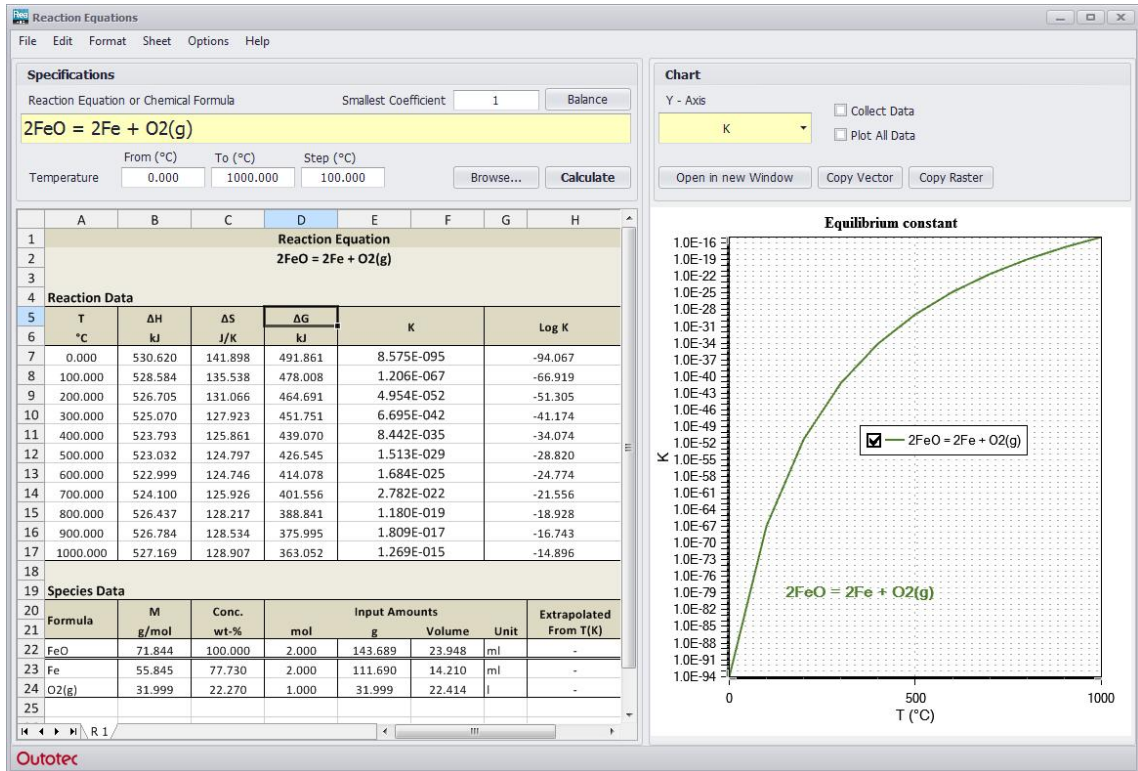


Fig. 6. Partial pressure of oxygen for FeO. Note that $K = p(\text{O}_2(\text{g}))$.

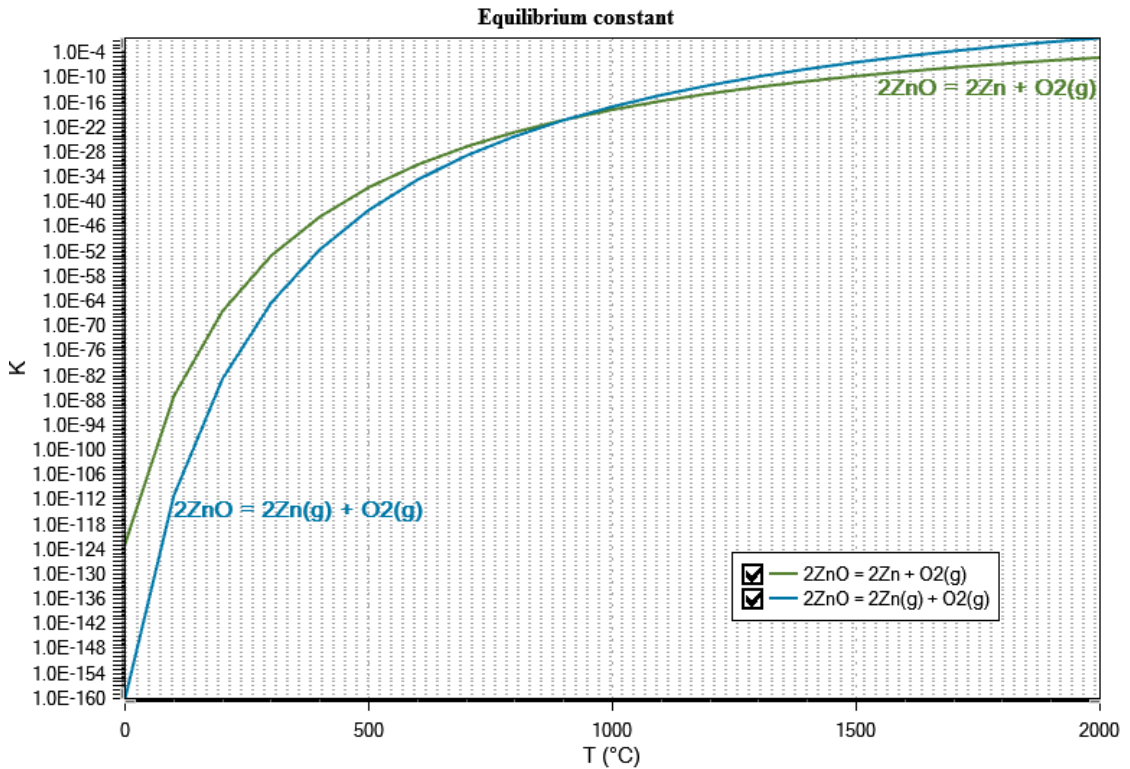


Fig. 7. Partial pressure of oxygen for ZnO. Boiling point of Zn must be taken into account, i.e. the Zn value is correct up to 907 °C and Zn(g) at higher temperatures. Note that $K = p(\text{O}_2(\text{g}))$.

Appendix 1. Ellingham diagram theory

pO_2 scale

For example, the Ellingham diagram for oxides includes species for which the formation reaction can be presented as:



In this reaction, the oxygen **element** balance is equal to 1 (the default option in HSC diagrams), which gives the 1/2 coefficient for $O_2(g)$.

The equilibrium constant, K, for this reaction can be presented as:

$$K = \frac{(a_{Me_A O_B})^{\frac{1}{B}}}{(a_{Me})^{\frac{A}{B}} \cdot (p_{O_2(g)})^{0.5}} \quad (5)$$

If the oxide and the metal can be approximated as pure substances, then their activities are equal to 1 and the equilibrium constant can be expressed in terms of the oxygen partial pressure:

$$K = \frac{1}{(p_{O_2(g)})^{0.5}} \quad (6)$$

Taking the natural logarithm on both sides yields:

$$\ln K = \ln \frac{1}{(p_{O_2(g)})^{0.5}} = \ln (p_{O_2(g)})^{-0.5} \quad (7)$$

This equation can now be connected to the Gibbs free energy:

$$\Delta G = \Delta G^0 + RT \ln K \quad (8)$$

In equilibrium the $\Delta G=0$:

$$\Delta G^0 = -RT \ln K \quad (9)$$

Substituting $\ln K$:

$$\Delta G^0 = -RT \ln (p_{O_2(g)})^{-0.5} = 0.5RT \ln (p_{O_2(g)}) \quad (10)$$

For constant values of oxygen partial pressures, the above equation is that of a line with a Y-intercept at absolute zero, $\Delta G^0 = 0$.

The partial pressure can also be expressed with the base 10 logarithm:

$$\Delta G^0 = 0.5RT \ln (p_{O_2(g)}) = 0.5RT \ln(10) \cdot \log(p_{O_2(g)}) \quad (11)$$

CO/CO₂ - and H₂/H₂O-ratio -scales

Scales using CO/CO₂ or H₂/H₂O ratios can also be constructed. The reaction for carbon monoxide oxidation is:



The equilibrium constant of the reaction is:

$$K_{\frac{\text{CO}}{\text{CO}_2}} = \frac{(p_{\text{CO}_2(g)})}{(p_{\text{CO}(g)}) \cdot (p_{\text{O}_2(g)})^{0.5}} \quad (13)$$

Taking the natural logarithm on both sides:

$$\ln K_{\frac{\text{CO}}{\text{CO}_2}} = \ln \frac{(p_{\text{CO}_2(g)})}{(p_{\text{CO}(g)})} + \ln (p_{\text{O}_2(g)})^{-0.5} \quad (14)$$

Solving $\ln ((p_{\text{O}_2})^{-0.5})$:

$$\ln (p_{\text{O}_2(g)})^{-0.5} = \ln K_{\frac{\text{CO}}{\text{CO}_2}} - \ln \frac{(p_{\text{CO}_2(g)})}{(p_{\text{CO}(g)})} = \ln K_{\frac{\text{CO}}{\text{CO}_2}} + \ln \frac{(p_{\text{CO}(g)})}{(p_{\text{CO}_2(g)})} \quad (15)$$

For oxidation of metals, the equation for the equilibrium constant is:

$$\ln K_{\frac{\text{Me}}{\text{MeO}}} = \ln (p_{\text{O}_2(g)})^{-0.5} \quad (16)$$

Now we can combine the two equations above:

$$\ln K_{\frac{\text{Me}}{\text{MeO}}} = \ln K_{\frac{\text{CO}}{\text{CO}_2}} + \ln \frac{(p_{\text{CO}(g)})}{(p_{\text{CO}_2(g)})} \quad (17)$$

Linking the Equilibrium constants to Gibbs energy:

$$-\frac{\Delta G_{\frac{\text{Me}}{\text{MeO}}}^0}{RT} = -\frac{\Delta G_{\frac{\text{CO}}{\text{CO}_2}}^0}{RT} + \ln \frac{(p_{\text{CO}(g)})}{(p_{\text{CO}_2(g)})} \quad \text{or} \quad (18)$$

$$\Delta G_{\frac{\text{Me}}{\text{MeO}}}^0 = \Delta G_{\frac{\text{CO}}{\text{CO}_2}}^0 - RT \ln \frac{(p_{\text{CO}(g)})}{(p_{\text{CO}_2(g)})} \quad (19)$$

This equation can now be used to form the nomographic CO/CO₂ ratio scale.

Using a similar approach, the O₂ partial pressure can also be expressed in terms of the H₂/H₂O ratio. In that case the reaction equation is:



and the final equation:

$$\Delta G_{\frac{Me}{MeO}}^0(T) = \Delta G_{\frac{H_2}{H_2O}}^0(T) - RT \ln \frac{(p_{H_2(g)})}{(p_{H_2O(g)})} \quad (21)$$

Please note: these equations presume that the elemental oxygen balance is 1 for the oxide species and also that the coefficient of oxygen in CO/CO₂ and H₂/H₂O reactions is 1/2.

If the nomographic scales can be implemented easily, then adding scales could also be considered e.g. for sulfides (H₂/H₂S), halides (F₂(g), Cl₂(g), Br₂(g), I₂(g)), and phosphides (P₂(g)).