_____ Dec. 11 2002:   Lecture 33: _____

Equilibrium Conditions for Solid Solutions

<u>Last Time</u>

Non-Ideal Solution Models
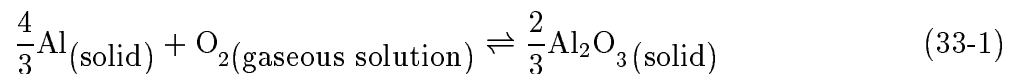
Regular Solutions
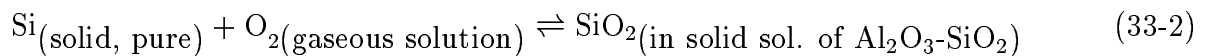
Spinodal Decomposition

_____ Equilibria for Reactive Solids and Vapors (Oxidation) _____

Consider a reaction where a solid is reacting with a gaseous component to produce a solid phase, such as the oxidation of aluminum metal to aluminum oxide:

$$\frac{4}{3}\text{Al}_{(\text{solid})} + \text{O}_{2(\text{gaseous solution})} \rightleftharpoons \frac{2}{3}\text{Al}_2\text{O}_{3}\,(\text{solid}) \tag{33-1}$$

or, for the case of pure silicon embedded to silica dissolved in alumina:

$$\text{Si}_{(\text{solid, pure})} + \text{O}_{2(\text{gaseous solution})} \rightleftharpoons \text{SiO}_2(\text{in solid sol. of Al}_2\text{O}_3\text{-SiO}_2) \tag{33-2}$$
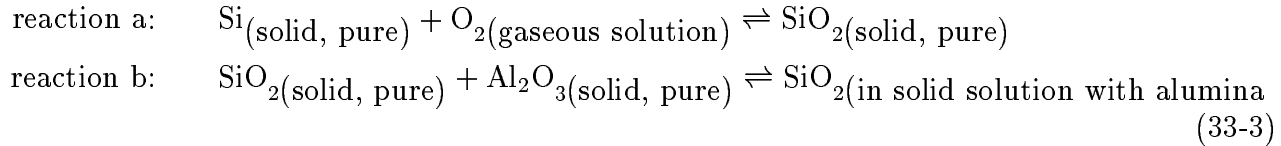
In the most simple cases (e.g., Eq. 33-1), it is assumed that the reactions and products are pure (i.e., the solubility of oxygen is neglected in the solid phases.).

In more realistic cases (e.g., Eq. 33-2), it should be clear that, as well as the free energies of formation, considerations the free energy charges for forming a solution—such as those that have been considered in previous lectures—must also be applied.

In any case, it simplifies to divide a complex reaction into simpler steps.

For example Eq. 33-2, can be broken into two independent reactions:

reaction a: $\mathrm{Si}_{(\text{solid, pure})} + \mathrm{O}_2(\text{gaseous solution}) \rightleftharpoons \mathrm{SiO}_2(\text{solid, pure})$

reaction b: $\mathrm{SiO}_2(\text{solid, pure}) + \mathrm{Al}_2\mathrm{O}_3(\text{solid, pure}) \rightleftharpoons \mathrm{SiO}_2(\text{in solid solution with alumina}$

$$\text{(33-3)}$$

In this way, free energy changes can be calculated (with respect to some standard state, usually taken as a pure component at a particular temperature).

Reaction (a) in Eq. 33-3 will involve the molar free energies of formation with respect to the pure components. These are usually tabulated in data books (e.g. the JANAF tables, the book by O. Kubaschewski and C.B. Alcock)

Reaction (b) in Eq. 33-3 will involve the free energies of mixing were considered in the construction of phase diagrams. Data is available for many practical systems and ThermoCalc (software) is a method for extrapolating such data from known values and phase diagrams.

The Standard Approximation

Consider the general case:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \tag{33-4}$$

Assuming the system is closed, the condition for equilibrium is just:

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D \tag{33-5}$$

which becomes, if reference is made to the pure states

$$\begin{aligned} a(\mu_{A_\circ}(T,P) + RT\log a_A) &+ b(\mu_{B_\circ}(T,P) + RT\log a_B) \\ &= c(\mu_{C_\circ}(T,P) + RT\log a_C) + d(\mu_{D_\circ}(T,P) + RT\log a_D) \end{aligned} \tag{33-6}$$

so the condition for equilibrium becomes

$$\frac{a_C^c a_D^d}{a_A^a a_B^b} = e^{-\frac{\Delta \overline{G_{Rx\circ}}}{RT}} \tag{33-7}$$

where the activity of a component is $a_A = \gamma_A X_A$ which is to be determined empirically.

However, there are *standard approximations* in which the solid phases in the reaction can be considered to be pure. In this approximation, and through use the additional thermodynamic approximations for material behavior:

> Standard Approximation for Solid Phase Reactions
>
> 1. Each component is in equilibrium with its vapor.
>
> 2. The vapor is treated as an ideal gas.
>
> 3. The molar free energy of the solid phase is relatively insensitive to pressure changes.

Approximate equilibrium conditions can be obtained by practical means.
Consider the oxidation (or, the reverse, the reduction) of a pure metal:

$$M_{(solid, pure)} + \frac{1}{2}O_{2(gaseous\ solution)} \rightleftharpoons MO_{(solid, pure)} \tag{33-8}$$
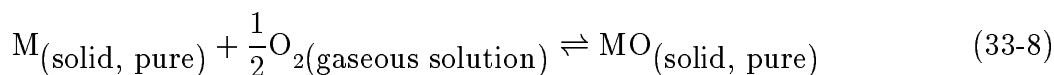
The chemical potentials of each each component in each solid phase is in equilibrium with the gaseous phase.

$$\mu_{M\ (solid)} = \mu_{M\ (gas)} \quad \text{and} \quad \mu_{MO\ (solid)} = \mu_{MO\ (gas)} \tag{33-9}$$

Therefore, it is appropriate to consider equilibrium in the gas phase.
Considering an ideal gas mixture

$$\overline{\Delta G_{Rx}} =$$
$$= \overline{G}_{MO\ (gas\ sol)}(P=1,T) - \frac{1}{2}\overline{G}_{iO_2\ (gas\ sol)}(P=1,T) - \overline{G}_{M\ (gas\ sol)}(P=1,T)$$
$$= RT\log\frac{P_M P_{O_2}^{\frac{1}{2}}}{P_{MO}}$$
$$\tag{33-10}$$

What is remarkable about Equation 33-10 is that it is true!

P_M for typical metals is 10^{-8}–10^{-12}atm. P_{MO} for typical oxides is 10^{-18}–10^{-24}atm. Such tiny numbers which would be very, very difficult to measure.

Also $\overline{G}_{M(gas)}(P=1,T)$ and $\overline{G}_{MO(gas)}(P=1,T)$ represent molar free energies that are highly unstable with respect to forming a solid or a liquid at sub-solar temperatures.

Expressions for $\overline{G}_{M(gas)}$ and $\overline{G}_{MO(gas)}$ can be obtained by integrating the pressures for the gas phase and the condensed phase:

$$\overline{G}_{M\ (gas\ sol)}(P=1,T) + RT\log P_M = \overline{G}_{M\ (solid)}(P=1,T) + \int_{P=1}^{P=P_M} V_{M\ (solid)} dP$$
$$\tag{33-11}$$

For almost every condensed phase the last term in Equation 33-11 is always very small compared to the others, so to very good approximation:

$$\overline{G}_{M\ (gas\ sol)}(P=1,T) + RT\log P_M \cong \overline{G}_{M\ (solid)}(P=1,T) \tag{33-12}$$

Putting this into Equation 33-10, the following approximation is obtained:

$$RT \log P_{O_2}^{\frac{1}{2}} =$$

$$= \overline{G}_{MO\ (solid)}(P=1,T) - \frac{1}{2}\overline{G}_{O_2\ (gas\ sol)}(P=1,T) - \overline{G}_{M\ (solid)}(P=1,T)$$
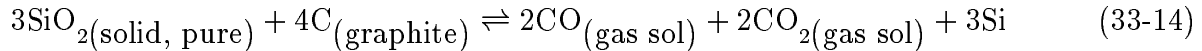
$$(33\text{-}13)$$

In other words,

> **To good approximation, the activities of the pure solid reactants or products can be replaced with unity ($a = 1$) and the partial pressures of the gaseous phases can be determined by the equilibrium expression.**

_____ An Example of a Gaseous Reaction with Pure Condensed Phase

Consider the reduction of SiO_2 to Si by heating it at $P = 1$ atm. At what temperature will the reduction take place and what will be the pressure of CO (gas) if the reaction takes place at 740°C?

The pertinent reaction is

$$3SiO_{2(solid,\ pure)} + 4C_{(graphite)} \rightleftharpoons 2CO_{(gas\ sol)} + 2CO_{2(gas\ sol)} + 3Si \qquad (33\text{-}14)$$

The following reactions are tabulated:

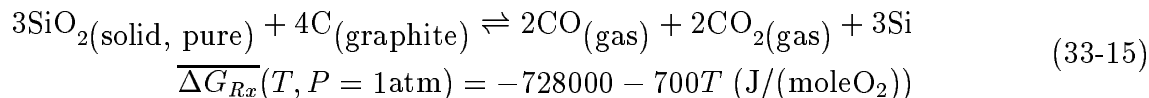| Reaction	$\Delta \overline{G}_{rx}(T, P = 1\text{atm})(\text{J}/(\text{mole } O_2))$
$Si_{(solid)} + O_{2(gas\ sol)} \rightleftharpoons SiO_{2(solid,\ pure)}$	$-94556 + 174T(700 - 1700°K)$
$2C_{(graphite)} + O_{2(gas\ sol)} \rightleftharpoons 2CO_{(gas\ sol)}$	$-223400 - 175.3T(298 - 2500°K)$
$C_{(solid)} + O_{2(gas\ sol)} \rightleftharpoons CO_{2(gas\ sol)}$	$-394100 - 0.84T(298 - 2000°K)$

Notice that:

1. The expressions for the molar free energies of reactions take the form: $\Delta \overline{G} = \Delta \overline{H} - T\Delta \overline{S}$ where $\Delta \overline{H}$ and $\Delta \overline{S}$ are treated as independent of T (This is approximately true if the molar heat capacities are nearly the same.).

2. The appearance of one mole of gas is associated with an entropy production of about $175 \frac{J}{°K}$.

The reaction of interest can be written as:

$$-3 \times (\text{First Reaction}) + (\text{Second Reaction}) + 2 \times (\text{Third Reaction})$$

or

$$3SiO_2(\text{solid, pure}) + 4C_{(\text{graphite})} \rightleftharpoons 2CO_{(\text{gas})} + 2CO_{2(\text{gas})} + 3Si$$
$$\overline{\Delta G_{Rx}}(T, P = 1\text{atm}) = -728000 - 700T \ (\text{J}/(\text{mole} O_2)) \tag{33-15}$$

so that

$$P^2_{CO_2} P^2_{CO} = e^{\frac{-\Delta \overline{G_{Rx}}}{RT}} \tag{33-16}$$

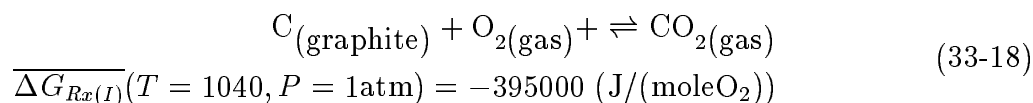Since $\overline{\Delta G_{Rx}} < 0$ at all T, the reaction will favor the products.
The total pressure is given by

$$P_{CO} + P_{CO_2} + P_{O_2} = 1 \tag{33-17}$$

Question: Why is P_{O_2} included? Because one can't balance a reaction between carbon monoxide and carbon dioxide without it.
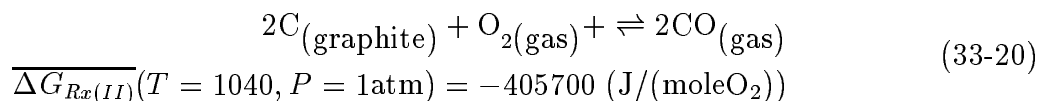For

$$C_{(\text{graphite})} + O_{2(\text{gas})} + \rightleftharpoons CO_{2(\text{gas})}$$
$$\overline{\Delta G_{Rx(I)}}(T = 1040, P = 1\text{atm}) = -395000 \ (\text{J}/(\text{mole} O_2)) \tag{33-18}$$

So

$$\frac{P_{O_2(\text{gas})}}{P_{CO_2(\text{gas})}} = e^{-\frac{395000}{(8.3)(1040)}} = \text{small number} \tag{33-19}$$

for

$$2C_{(\text{graphite})} + O_{2(\text{gas})} + \rightleftharpoons 2CO_{(\text{gas})}$$
$$\overline{\Delta G_{Rx(II)}}(T = 1040, P = 1\text{atm}) = -405700 \ (\text{J}/(\text{mole} O_2)) \tag{33-20}$$

$$\frac{P_{O_2(\text{gas})}}{P^2_{CO(\text{gas})}} = e^{-\frac{405700}{(8.3)(1040)}} = \text{small number} \tag{33-21}$$

We conclude that P_{O_2} is small compared to P_{CO} and P_{CO_2}

$$P_{CO} + P_{CO_2} \approx 1 \tag{33-22}$$

Therefore:

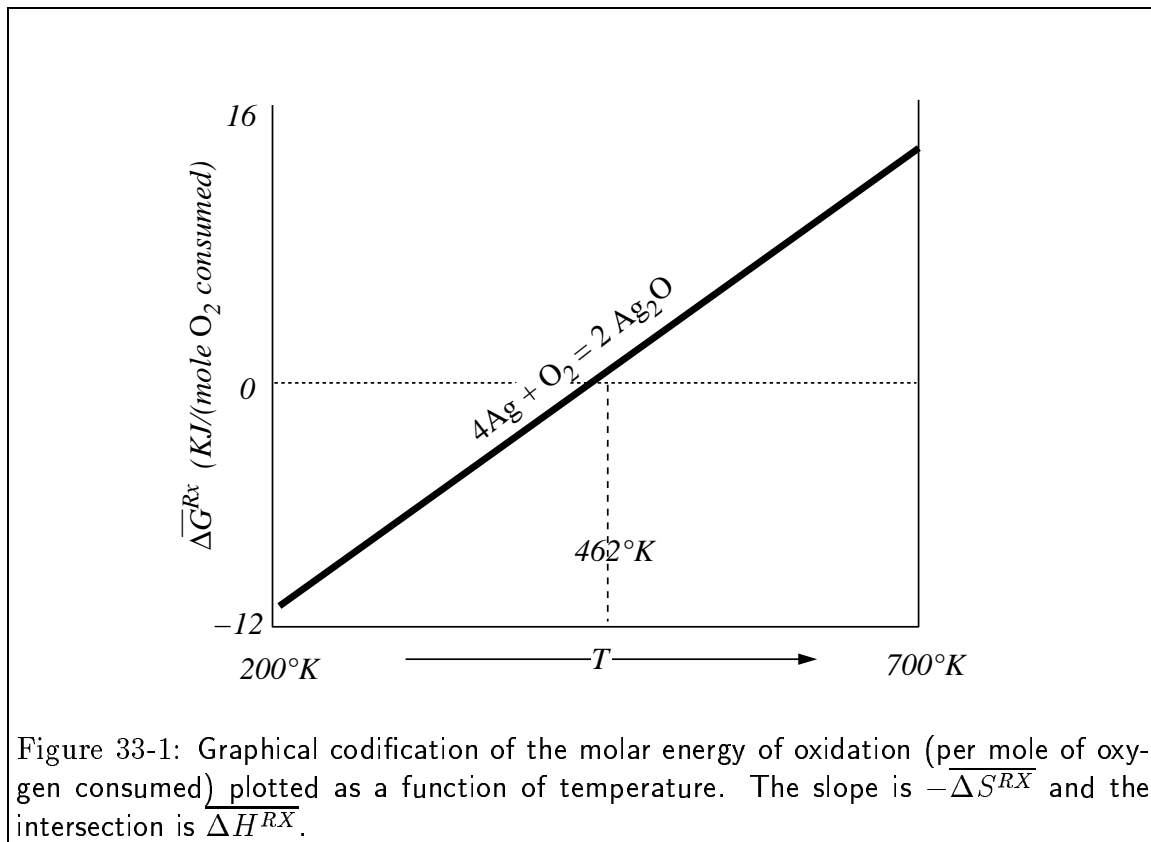$$\frac{P_{CO_2}}{P_{CO}^2} = e^{-\frac{\overline{\Delta G_{Rx(I)}} - \overline{\Delta G_{Rx(II)}}}{RT}} = 3.45 \tag{33-23}$$

$$\frac{1 - P_{CO}}{P_{CO}^2} = 3.45 \implies P_{CO} = 0.41 \tag{33-24}$$

Question: Will the fraction of CO go up or down with temperature?

Ellingham Diagrams

Thermodynamic data for the oxidation of a number of common metals can be usefully and graphically codified in an *Ellingham Diagram* (Gaskell, page 272).

For example:

Figure 33-1: Graphical codification of the molar energy of oxidation (per mole of oxygen consumed) plotted as a function of temperature. The slope is $-\overline{\Delta S^{RX}}$ and the intersection is $\overline{\Delta H^{RX}}$.
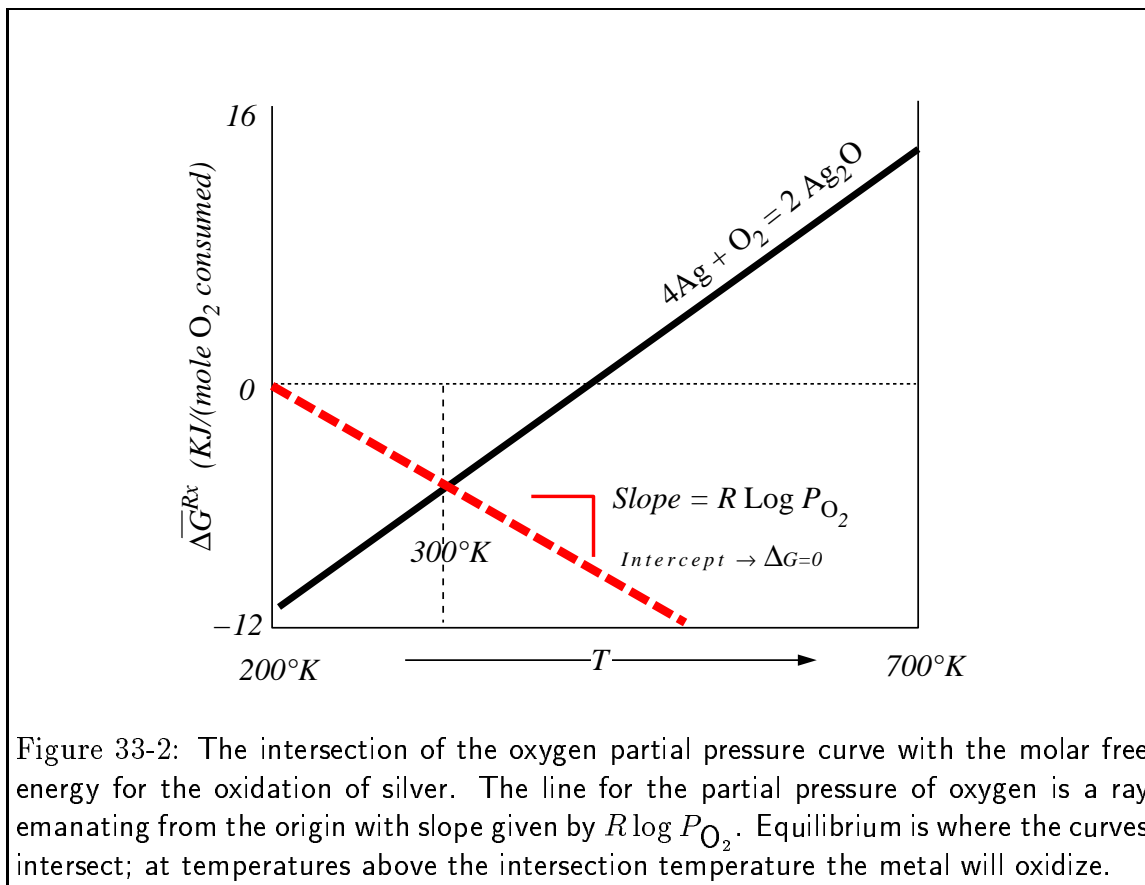
It can be observed at a glance that reaction tends to favor the products below 462K; however, the partial pressure of oxygen must also be considered.

Consider the the equilibrium of this reaction as a function of oxygen partial pressure.

$$\frac{1}{P_{O_2}} = e^{\frac{-\overline{\Delta G_{Rx}}}{RT}}$$

$$\overline{\Delta G_{Rx}}(T) = RT \log P_{O_2} \tag{33-25}$$

This represents the intersection of two lines: one is $\Delta\overline{G}(T)$ that is plotted and the other is a straight line that emanates from $\Delta\overline{G}(T=0)=0$ with slope given by $R\log P_{O_2}$. To determine what P_{O_2} will Ag *not* oxidize at room temperature.

Figure 33-2: The intersection of the oxygen partial pressure curve with the molar free energy for the oxidation of silver. The line for the partial pressure of oxygen is a ray emanating from the origin with slope given by $R\log P_{O_2}$. Equilibrium is where the curves intersect; at temperatures above the intersection temperature the metal will oxidize.

For the case of Silver, the reaction is very close to equilibrium at standard temperature and pressure. This explains, in part, why silver develops a slight tarnish.

Richardson and Jeffes had the clever idea of adding a handy scales on the outside of the diagram so that the equilibrium partial pressures for hydrogen/water vapor and the equilibrium partial pressures of carbon monoxide and carbon dioxide can be read analogously to the partial pressure of oxygen. The result is a useful graphical compendium of thermodynamic data for many condensed metal/vapor reactions.
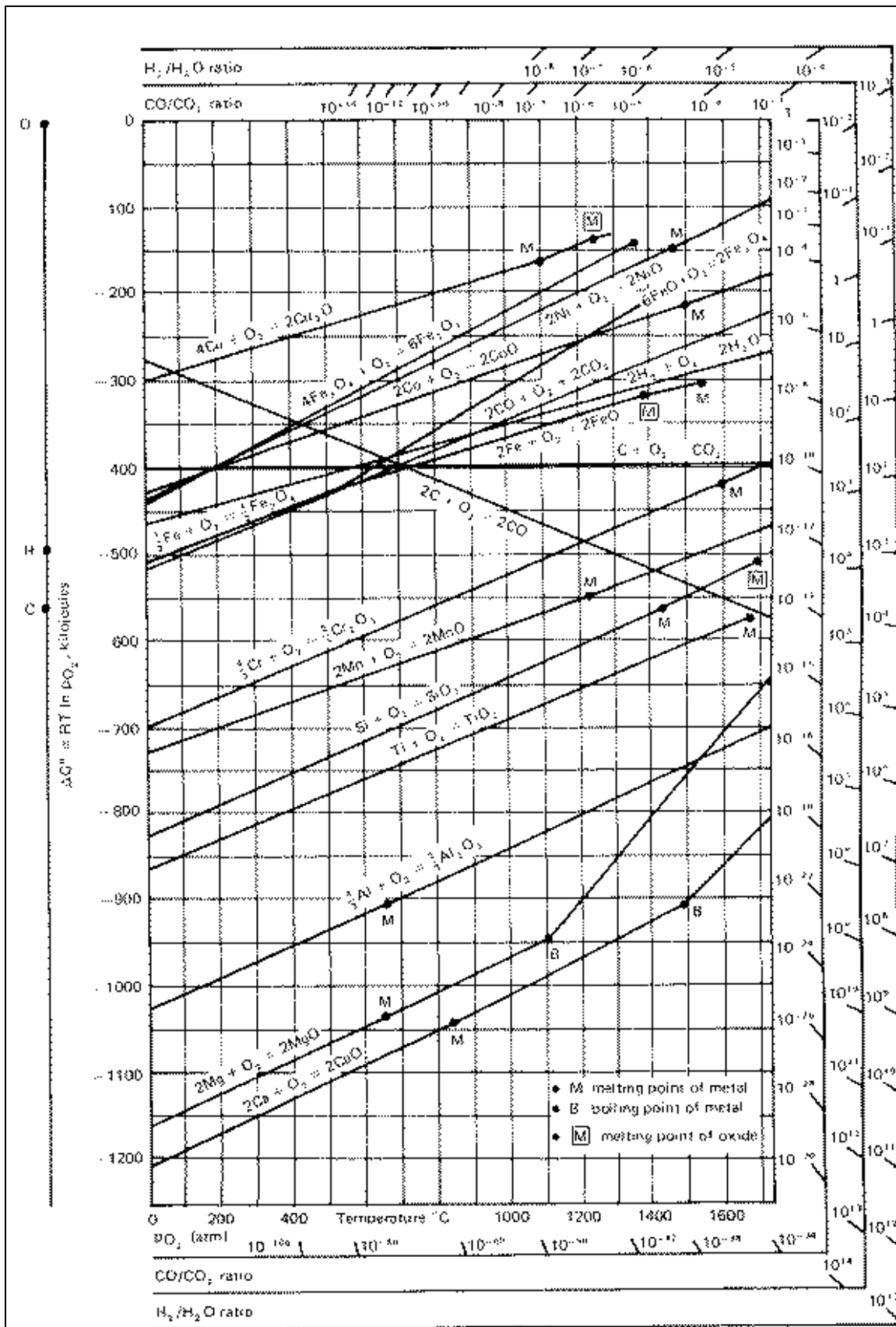
Figure 33-3: A scan of the Ellingham Diagram with the Richardson and Jeffes scale as it appears in Gaskell, page 287.