

Lecture 29

Thermodynamics of Reactive Systems

The Ellingham Diagram



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Topics to Discuss

- The Ellingham Diagrams
 - Salient features and limitations

Patterns of Behaviour in the Reactive Systems

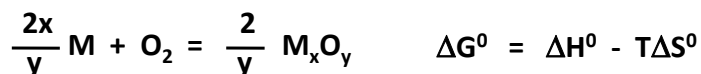
- We have seen that, evaluation of the equilibrium constant for a reaction is the key to the solution of practical problems in reacting systems.
- The equilibrium constant is, in turn, most frequently computed from information about the standard free energy change for the reaction through equation

$$\Delta G^0 = -RT \ln K_a$$

- Values of the standard free energy change for chemical reactions and other thermodynamic functions are presented in the literature, usually as **graphs** or **tables**.
- The diagrams of most practical importance are those for oxides, sulphides, halides, carbides and nitrides. Among those, the most frequently used diagram is the **Ellingham diagram**.

The Ellingham Diagrams

- Ellingham plotted the experimentally determined standard free energy of formation, ΔG^0 , of various oxides (and sulphides) using one mole of oxygen with temperature.

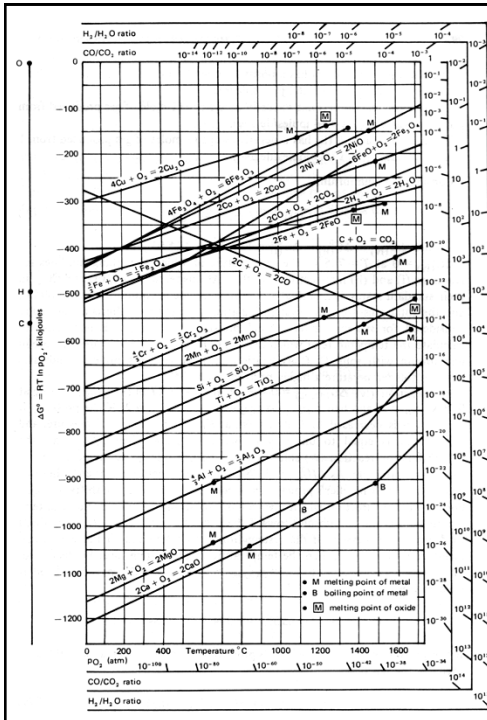


- Ellingham pointed out that, the standard enthalpy and entropy of formation of a compound do not change significantly with the temperature as long as there is no change of state of product or reactant.

$$\Delta G^0_T \approx \Delta H^0_{298} - T\Delta S^0_{298}$$

- Thus, the general forms of ΔG^0 -T relationships could be approximated to straight lines over temperature ranges

$$\Delta G^0_T = A + BT \quad A = \Delta H^0_{298} \quad \text{and} \quad B = -\Delta S^0_{298}$$



$$\Delta G^0_T \approx \Delta H^0_{298} - T\Delta S^0_{298}$$

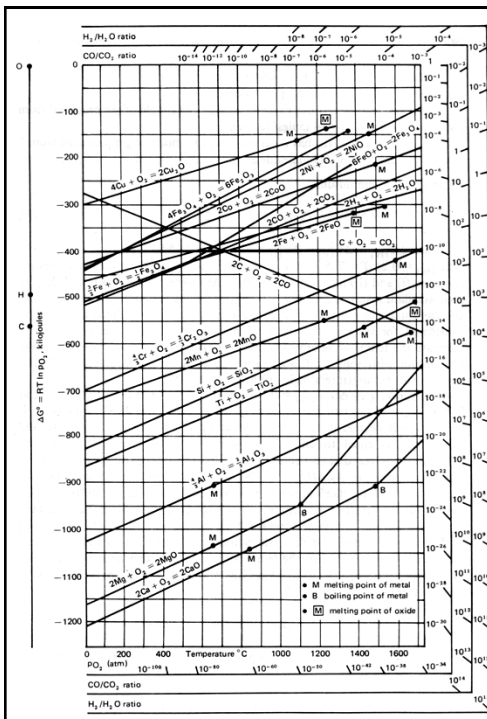
$$\Delta G^0_T = A + BT$$

$$A = \Delta H^0_{298}$$

$$B = -\Delta S^0_{298}$$

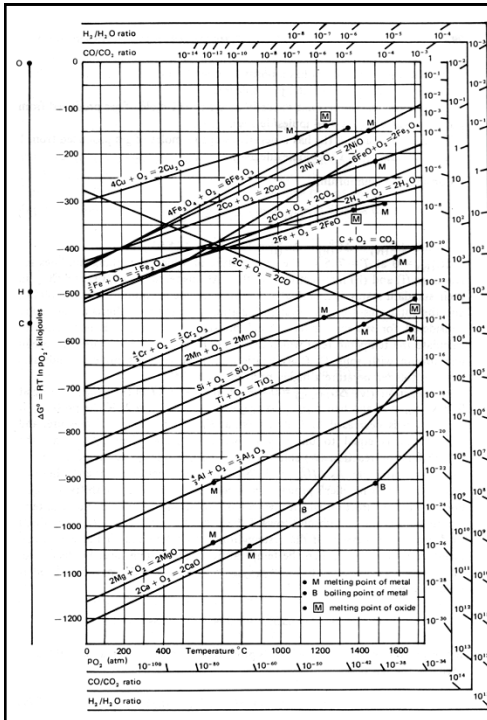
FIGURE 8.2

The Ellingham diagram showing variation of the standard free energy of formation with temperature of some selected oxides.



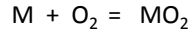
The Salient Features of the Ellingham diagram for oxides

1. The straight lines represented by the function $\Delta G^0(T)$ in the diagram represent the **relative stability of oxides**.
2. It is possible to visualise directly the **affinities of metals for oxygen** in their standard conditions by observing the relative positions of the lines in the diagram.
3. It is possible to identify that there are **easily reducible oxides** of Au, Ag, Hg; there are others **oxides of greater stability** such as FeO, Cr_2O_3 , MnO, etc; and **refractory oxides**, which are very difficult to reduce, such as ZrO_2 , Al_2O_3 , MgO, CaO, etc.



5. The slope of the curve is $-\Delta S^0$ is a function of entropy of the products and the reactants.

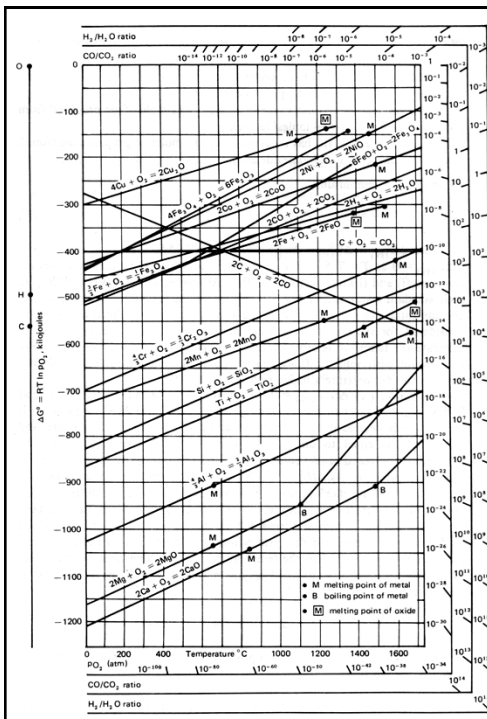
$$\Delta S^0 = \sum S^0 (\text{products}) - \sum S^0 (\text{reactants})$$



$$\Delta S^0 = S^0 (\text{solid } MO_2) - S^0 (\text{solid } M) - S^0 (O_2 \text{ gas}) \approx -S^0 (O_2 \text{ gas})$$

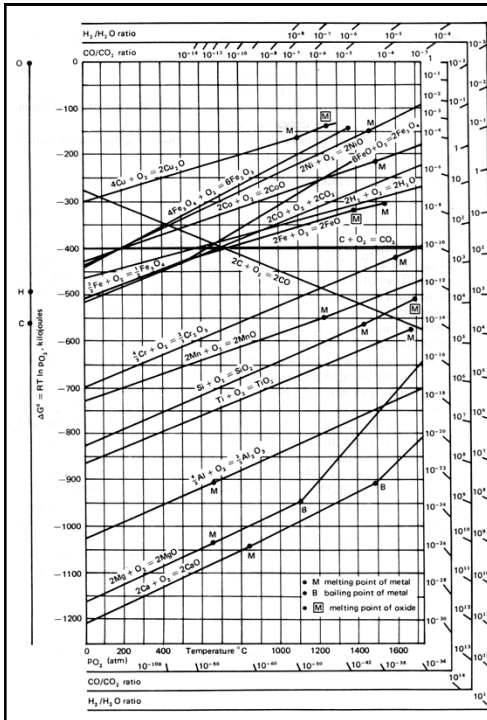
Thus slope of most of the curves ($-\Delta S^0$) becomes **positive**.

Since the reactions of formation of oxides from elements are written for the same number of moles of reactant gas, **the lines are practically parallel** for a given state.



The change of entropy depends on the states of the reactants and products.

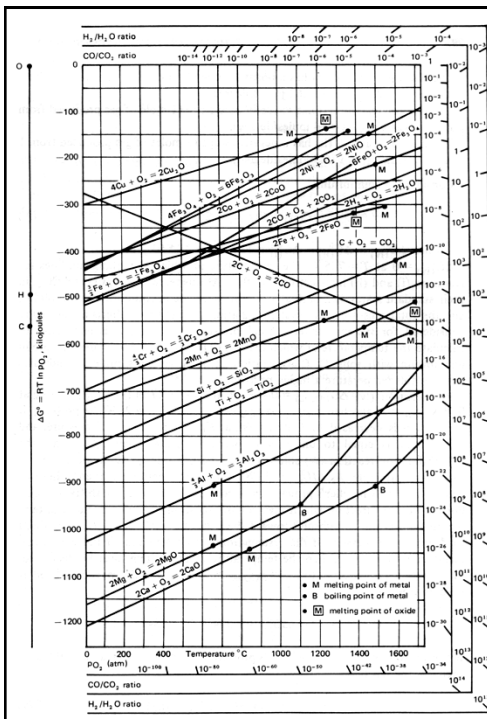
As long as the reactants and products stay in the same physical state, the variation of ΔS^0 will be small and the curves will not change their slopes appreciably.



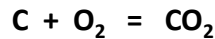
6. There is a change in entropy during fusion or vaporisation and, as a result, the slope of the curve also changes during fusion or vaporisation.

The slope increases if the reactants change their state with a rise in temperature, and decreases when the products change the state.

Since a larger change in entropy is occurred during vaporisation, the change of slope is larger as compared to that during fusion.

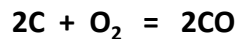


7. Behaviour of CO₂ and CO lines



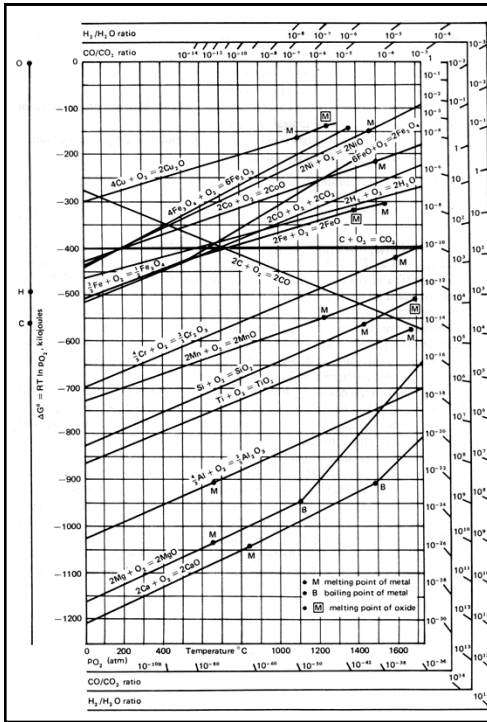
$$\Delta S^0 = S^0 (1 \text{ mol } CO_2 \text{ gas}) - S^0 (1 \text{ mol solid C}) - S^0 (1 \text{ mol } O_2 \text{ gas}) \approx 0$$

Thus the line becomes horizontal.



$$\Delta S^0 = S^0 (2 \text{ mol CO gas}) - S^0 (2 \text{ mol solid C}) - S^0 (1 \text{ mol } O_2 \text{ gas}) \approx \text{positive}$$

Thus the slope of the line (-ΔS⁰) becomes negative.



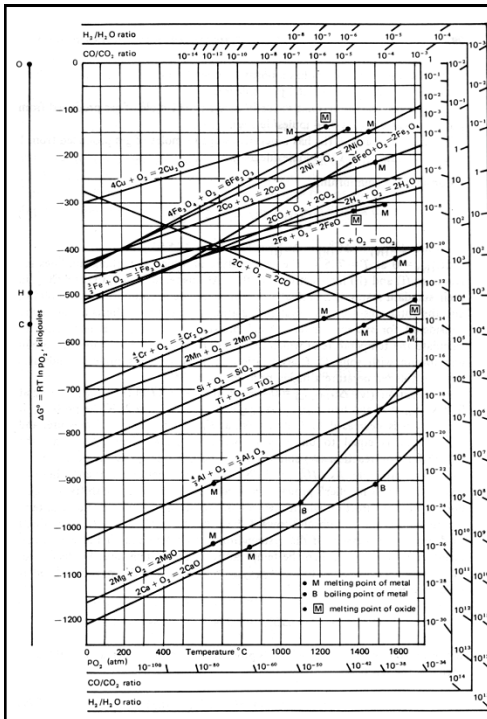
The line for CO intersects the lines of most of the metals.

This explains why carbon is considered as an **energetic reducing agent** at high temperature.

The lines of ΔG^0 for CO and CO_2 crosses at about 700 C. Hence C is more stable than CO_2 at temperatures higher than 700 C.

The reduction of Cu_2O and FeO by carbon is feasible above 100 and 720 C respectively.

However, reduction of so-called refractory oxides (TiO_2 , Al_2O_3 , MgO , etc.) by C is difficult because of high temperature involved.

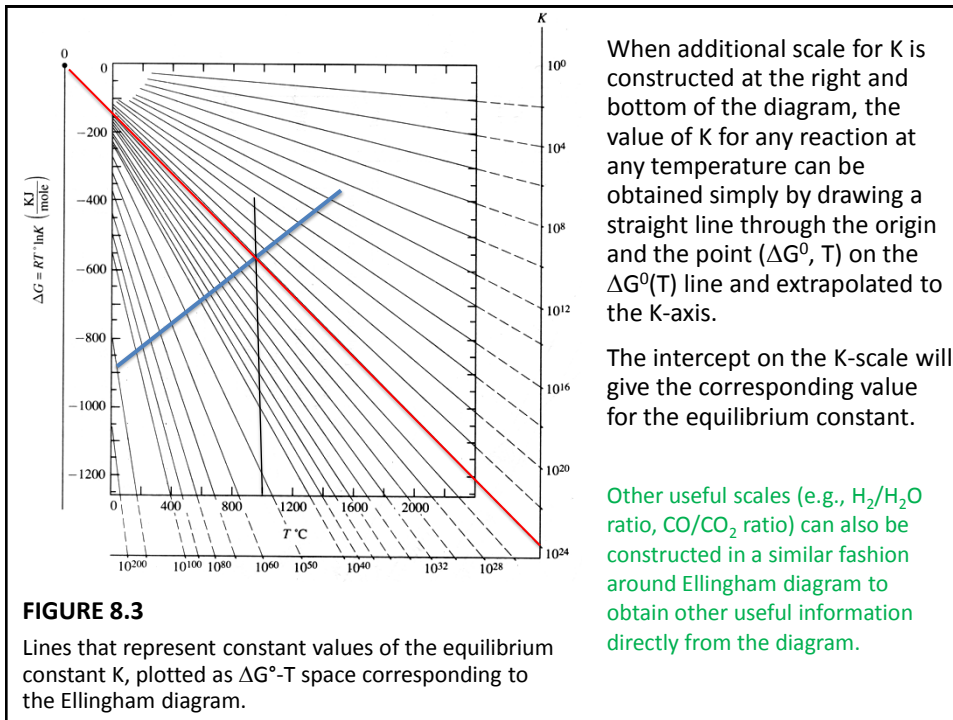


Additional scales on the Ellingham diagram

$$\Delta G^0 = -RT \ln K = (-R \ln K) \cdot T$$

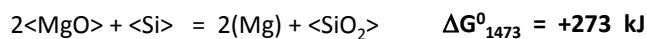
Any combination of values (ΔG^0 , T) on the diagram also represents a particular value of K.

The locus of points in (ΔG^0 , T) space that all share the same value of K is a straight line through the origin with a slope equal to $(-R \ln K)$.



Limitations of the Ellingham diagram

1. ΔG^0 is the standard free energy change of the reaction and does not take into account the activities of reactants or products which will significantly be different from unity.



$$\Delta G_{1473} = \Delta G^0_{1473} + RT \ln \frac{(p_{Mg})^2 \cdot (a_{SiO_2})}{(a_{MgO})^2 \cdot (a_{Si})}$$

If p_{Mg} and a_{SiO_2} can be lowered sufficiently, ΔG can be made negative even though ΔG^0 is positive.

In the Pidgeon process for the commercial production of magnesium, p_{Mg} is lowered by applying a vacuum of about 10^{-4} atm and a_{SiO_2} is reduced by adding CaO in the charge.

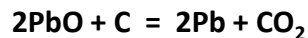
CaO reacts with SiO_2 to form $2\text{CaO} \cdot \text{SiO}_2$ slag and lowers the activity of silica in the product. A basic slag reduces the activity of SiO_2 down to 0.001 and the strong attraction of CaO for SiO_2 reduces the possibility of loss of MgO as magnesium silicate.

The magnesium is evolved as a gas, which is condensed in massive form without reoxidation.

- Thus, when the activities of reactants or products differ significantly from unity, **the van't Hoff isotherm gives a better indication** of the thermodynamic possibilities of the reaction than ΔG^0 and the Ellingham diagram.

2. No account of the kinetics of the reaction is taken during the measurements of thermodynamic variables.

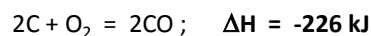
From a thermodynamic aspect, the reaction



will take place at 100 C, because ΔG^0 is negative.

But a blast furnace charge of solid lead oxide, coke and limestone will remain **virtually unaltered at 100 C** because the rate of chemical reaction would be too slow.

But if preheated air is introduced via the tuyeres of the furnace the coke will burn in the tuyere zone and the following overall reaction occurs



The reaction is exothermic so, once started, the reaction continues and soon the temperature of the furnace rises to about 1200 C and the reduction of PbO takes place.

3. The accuracy of data and the difficulty in reading the distance between two closely spaced curves do not permit to obtain a definite conclusion when the lines are much less than 20–40 kJ apart.

Next Class

Lecture 30

Thermodynamics of Reactive Systems

Tutorial - Problem Solving