

# Unit 7 reduction of metal oxide



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- aluminothermic [əljʊːmaɪnə'θɜ:mɪk] 铝热法的
- carbon monoxide 一氧化碳
- contamination [kənˌtæmə'neɪʃən] 污染, 污染物
- dissociation [dɪˌsəʊsi'eɪʃn] 分解, 分离
- enthalpy [en'θælpɪ] 焓, 热焓
- ferrotitanium [ferəʊtaɪ'teɪniəm] 钛铁
- ferroniobium [fe'rɒni:əʊbjəm] 铌铁
- ferrovanadium [ferəvə'neɪdiəm] 钒铁
- ferrochromium [ˌferəʊ'kroʊmiəm] 铬铁
- metallothermic reduction reactions [mɪtælə'θɜ:mɪk] 金属热还原法
- monoxide 一氧化物
- reducing agent 还原剂
- reversing reaction 逆向反应
- standard thermodynamic condition 标准热力学条件

## ➤ Stylistic features of EST (科技英语的文体特点)

### □ Non-Finite Verb (非谓语动词)



可对所修饰的词进行严格的说明和限定，同时保证行文简练、结构紧凑。

## ➤ What can we learn?

- 1、 What is reduction principle?
- 2、 What are the reducing agents in common use?
- 3、 The principle of “reduction with C, CO, H<sub>2</sub>, metal”.
- 4、 What is the difference between C, CO and H<sub>2</sub>?

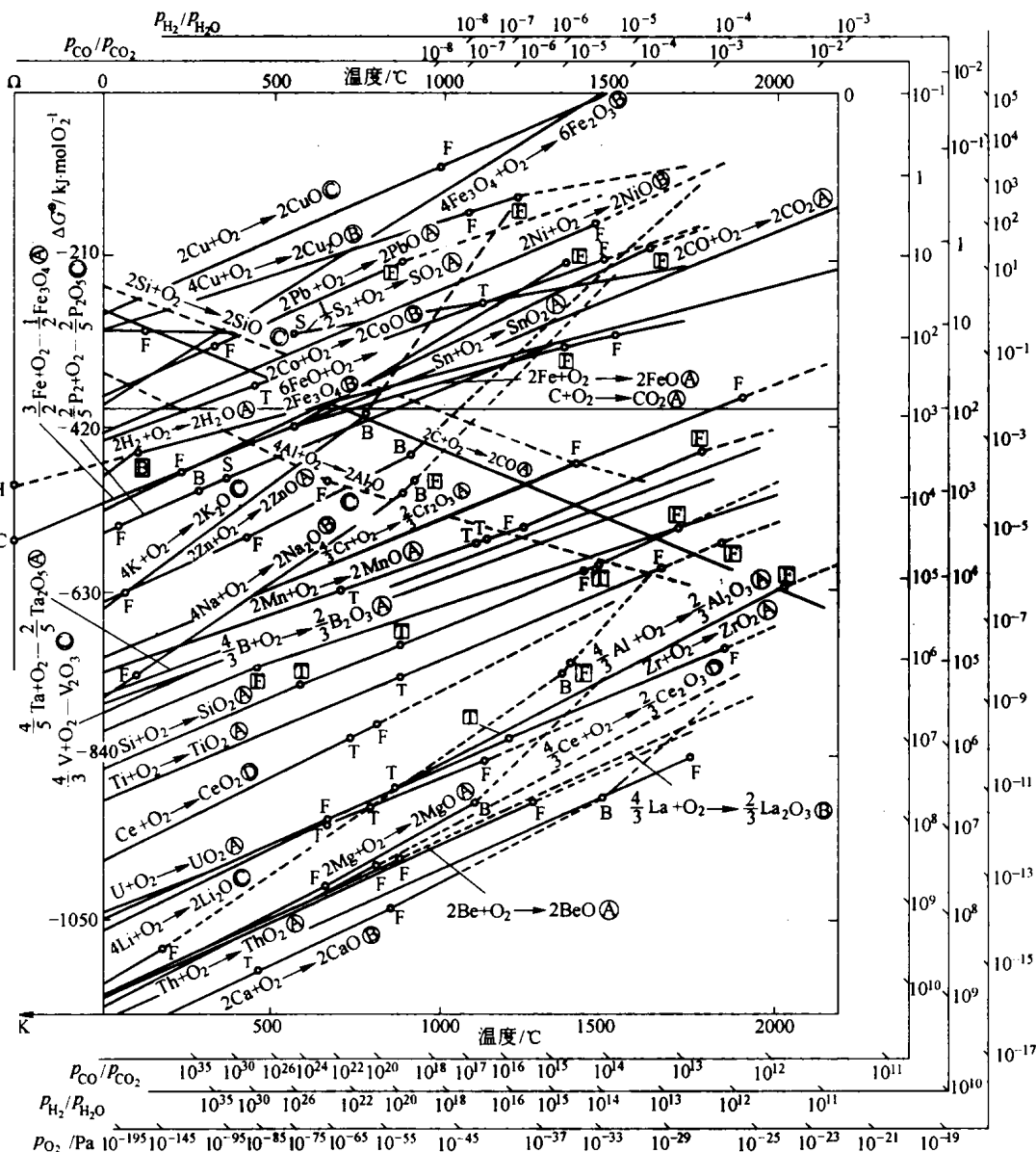
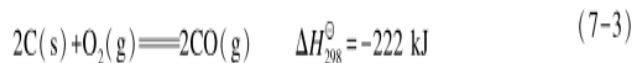
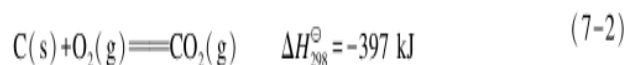
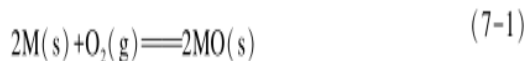
# ➤ $\Delta G - T$ diagram

- Metal oxide

reduction

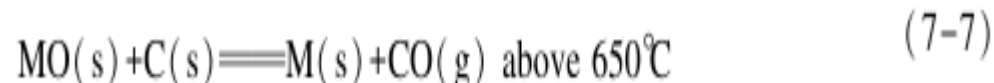
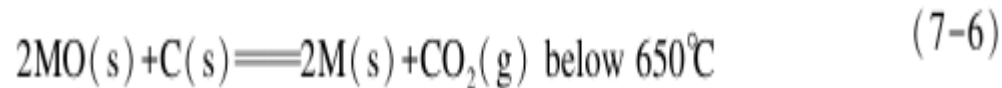
metal

H<sub>2</sub>  
CO  
C  
Metal



- Metal oxides may be reduced to the metal by carbon, carbon monoxide, hydrogen or other metals which form more stable oxides ( more negative  $\Delta G$  for oxide formation) than the metal oxide to be reduced.
- If the oxides and reduced phases are assumed to be pure solids and MO is the hypothetical metal oxide required to be reduced, the reaction lines on the  $\Delta G - T$  diagram can be used to assess the various reducing agents.

- It can be seen that if a sufficiently high temperature is achieved any metal oxide may be reduced with carbon according to the reaction:



- As the minimum reduction temperature rises above  $1800^\circ\text{C}$ , the cost of reduction with carbon increases substantially. This is due to the problem of providing refractory materials that can cope with these high temperatures and the increased reactivity of the metal with its environment **resulting in increased contamination**. For these reasons, iron, manganese, chromium, tin, lead, and zinc are the main metal oxides reduced with carbon.

- Under standard thermodynamic conditions CO gas will reduce all the oxides above the  $6\text{FeO} + \text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_4$  reaction line and, as stated above, is normally achieved with an evolution of heat for the less stable oxides, e. g. Fe. Thus, reduction of most metal oxides with carbon is endothermic due to the smaller exothermic nature of reaction (7-3) compared with reaction (7-4) while reduction of FeO and less stable oxides with CO is exothermic; the enthalpy values become more positive in each case with increasing stability of the oxide.
- Changing the partial pressures of CO, CO<sub>2</sub> and O<sub>2</sub> will alter the position of the reaction lines on the diagram. If the CO / CO<sub>2</sub> ratio is increased the  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  reaction line will be lowered ( more negative  $\Delta G$ ) **allowing other metal oxides**, e. g. ZnO, to be reduced with CO.

后置定语



- Reduction of metal oxides with CO is the most favorable reaction at the lower temperatures ( below  $700^{\circ}\text{C}$  ) in the blast furnace while above this temperature reduction with C is thermodynamically favorable. However, due to the high CO /  $\text{CO}_2$  ratios, the  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  reaction line is lowered and the improved reaction kinetics associated with the gas-solid reaction( 7 – 8) compared with the solid-solid reaction( 7 – 7), reduction of metal oxides with CO takes place at higher temperatures than  $700^{\circ}\text{C}$  in the blast furnace.
- At the onset of slag formation, the surface of the metal oxide will be covered with a layer of liquid slag which will prevent contact with carbon monoxide ( CO is insoluble in liquid slags). The only method available for reduction at this stage is for the solid coke to penetrate the slag layer and provide a solid coke–solid metal oxide reaction according to reaction (7-7). Thus, although predominantly indirect reduction of metal oxides with coke takes place in the blast furnace there is also some direct reduction.

Compared with 与。。。比较  
associated with: 与。。。相关联

- Reduction of metal oxides with hydrogen is of less importance industrially than C or CO. The lower enthalpy value for the reaction  $2\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$  results in less exothermic reduction of metal oxides with hydrogen than with carbon monoxide; most metal oxides being reduced endothermically. Examination of reaction(7-2), reaction (7-3), reaction (7-5) indicates that  $\text{H}_2$  is a better reducing agent of metal oxides than carbon at the lower temperature( below  $650^\circ\text{C}$  ). From the same thermodynamic reasoning, CO should be a better reducing agent than  $\text{H}_2$  below  $800^\circ\text{C}$  and  $\text{H}_2$  better than CO above  $800^\circ\text{C}$ . However, due to its increasing diffusivity, hydrogen is often superior to CO below  $800^\circ\text{C}$  in the reduction of metal oxides while, due to improved reduction kinetics, CO is a more effective reducing agent above  $800^\circ\text{C}$ . In certain cases, CO and  $\text{H}_2$  are added as joint reducing agents.

|               | Comparing $\text{H}_2$ and C |                       | Comparing $\text{H}_2$ and CO |                       |
|---------------|------------------------------|-----------------------|-------------------------------|-----------------------|
|               | $\text{H}_2$                 | C                     | CO                            | $\text{H}_2$          |
| thermodynamic | < $650^\circ\text{C}$        | > $650^\circ\text{C}$ | < $800^\circ\text{C}$         | > $800^\circ\text{C}$ |
| kinetics      |                              |                       | > $800^\circ\text{C}$         | < $800^\circ\text{C}$ |

$MO + 2C \rightarrow MC + CO$  Which needs another reducing agent other than carbon, CO

- a metal oxide is reduced with another metal which forms a more stable oxide. These are called metallothermic reduction reactions and are normally used when the metal to be extracted forms stable carbides ( Ti, Cr, Nb) on reduction with carbon.
- These reactions never go to completion, leaving some residual unreacted reducing agent in the final metal product together with some unreduced metal oxide in the oxide or slag phase.
- Metallothermic reductions are normally exothermic, the stronger the reducing agent the more exothermic the reaction.

$3MO + 2Al \rightarrow 3M + Al_2O_3$  Exothermic, Al and M are present in the product

$2MO + Si \rightarrow 2M + SiO_2$  exothermic

| Reducing agent | T      | Metal oxide            |
|----------------|--------|------------------------|
| C              | >650   | Fe, Mn, Cr, Sn, Pb, Zn |
| CO             | >800   | Cu, Pb                 |
| H <sub>2</sub> | <800   | Fe, Cu, Pb             |
| metal          | High T | Stable oxide           |

### ➤ Homework

Choose and describe a typical .....



# End



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