Lecture 28

Thermodynamics of Reactive Systems

Applications of the Equilibrium Constant

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Today's Topics

- Applications of the Equilibrium Constant
  ① Stability of compounds
  ② Controlled atmosphere
  ③ Deoxidation in steelmaking process

1. The Stability of Compound

- The equilibrium constant of a reaction can be used to predict the relative stability of a compound.

$4Cu + O_2 = 2Cu_2O$; $$K = \frac{(a_{Cu2O})^2}{(a_{Cu})^2 \cdot p_{O2}} = 10^3$$

$4/3Al + O_2 = 2/3Al_2O_3$; $$K = \frac{(a_{Al2O3})^{2/3}}{(a_{Al})^{4/3} \cdot p_{O2}} = 10^{20}$$

$8Fe + N_2 = 2Fe_4N$; $$K = \frac{(a_{Fe4N})^2}{(a_{Fe})^8 \cdot p_{N2}} = 10^{-5}$$

- Assuming that we have pure metals and pure oxides and nitrides, we can calculate the equilibrium partial pressure of oxygen and nitrogen for these reactions.

Compound Formed	Equilibrium Pressure at 1600 C
Cu_2O	$p_{O2} = 10^{-3}$
Al_2O_3	$p_{O2} = 10^{-20}$
Fe_4N	$p_{O2} = 10^5$

- **These values of equilibrium pressures are pressures below which the compounds will dissociate**, above which they will not dissociate.

  For this reasons these pressures (p_{O2}) and (p_{N2}) are called the **dissociation pressures** of relevant oxides and nitrides.

- In the above case, since the partial pressure of N_2 is above the atmospheric pressure, Fe_4N will decompose.

  On the other hand, in order to decompose Al_2O_3, the partial pressure of O_2 will have to be lowered below 10^{-20} atm pressure, which is impracticable.

- Hence we see that the values of dissociation pressure, based on the equilibrium constant of the dissociation reaction, are the **measure of the relative stability of compounds**.

  The higher the equilibrium constant of a reaction, the more stable the compound will be.

- So the basis of causing dissociation of a compound is to lower the partial pressure of gaseous component of reactant in the atmosphere in contact with the compound below the equilibrium pressure.

  This can be achieved either by placing a vacuum pump or, by passing an inert gas containing very small or no amount of relevant gas.

2. Controlled Atmosphere

- Most of the commonly used metals oxidise readily and, since the normal atmosphere contains oxygen, heating of metals without oxidation is difficult.
- One way of controlling oxidation is the reduction of oxygen partial pressure, also known as **the oxygen potential**, by reducing the total pressure of the system by using vacuum.
  - **Since the best vacuum attainable in the laboratory is about 10^{-10} atm, which is well above most dissociation pressures, this approach to controlling oxidation is both inflexible and very limited.**

- The most convenient means for controlling the oxygen potential of an atmosphere is through control of the chemical composition of the gas phase.
- The simplest atmospheres that provide this control are the mixtures of CO/CO_2, H_2/H_2O, or both.

Oxidation behaviour of the mixture CO/CO_2

$$2CO + O_2 = 2CO_2$$

If the total pressure is 1 atm, then

$$K_p = \frac{(p_{CO2})^2}{(p_{CO})^2 \cdot (pO_2)}$$

and the oxygen potential

$$p_{O2} = \left(\frac{p_{CO2}}{p_{CO}}\right)^2 \cdot \frac{1}{K_p}$$

To decrease the oxygen potential of an atmosphere, increase the relative concentration of the reducing gas, CO.

Example

In a steel annealing furnace, a gaseous atmosphere of CO and CO_2 gases could be maintained to prevent the oxidation of iron during heat treatment.

$$(CO_2) + <Fe> = <FeO> + (CO) \qquad K = \frac{a_{FeO} \cdot p_{CO}}{p_{CO2} \cdot a_{Fe}} \approx \frac{p_{CO}}{p_{CO2}}$$

Temperature	500 C	700 C	1000 C
Equilibrium constant	0.83	1.43	2.50

Consider a gas mixture containing **30% CO** and **20% CO_2** and 50% N_2.

The activity quotient of the atmosphere, **Q** = (pCO/pCO_2) = 0.30/0.20 = **1.50.**

- If we use this mixture at 700 C, then **(Q/K) > 1**, and the reaction would not occur. We would have an excess amount of CO than the equilibrium amount.
- If the temperature of the system is increased to 1000 C, then **(Q/K) <1**, and the reaction would occur.

3. Deoxidation in Steelmaking Processes

- In the steel making process, liquid pig iron containing impurities is refined by adding oxygen into the liquid steel bath at about 1600 C.
  During the process, a loss of iron is occurred by forming FeO slag.
- To recover iron from slag and reduce the harmful oxygen concentration in the bath, **deoxidation** is carried out.

$$\{\underline{FeO}\} + \langle \underline{C} \rangle = \{\underline{Fe}\} + (CO) \qquad K = \frac{a_{Fe} \cdot p_{CO}}{a_{C} \cdot a_{FeO}} \approx \frac{p_{CO}}{a_{C} \cdot a_{FeO}}$$

- If the amount of C dissolved in iron is very small, p_{CO} would be very high.
- So dissolving C in molten iron is a very efficient method of removing oxygen from the molten iron. **This is the basis of all steel making techniques.**
- The use of **primary raw materials** (pig iron containing higher carbon), thus, always produce a better quality steel than those produced using **the secondary raw materials** (steel scraps, containing lower carbon).

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Lecture 29

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The Ellingham Diagram