

Lecture 5. Principles of Metal Extraction.

The tendency of an element to pass from one combined state to another can be predicted by applying thermodynamic principles. Hence, thermodynamics can indicate the feasibility of various chemical reactions associated with possible extraction processes.

Many of the well-known extraction processes have been evolved over a period of time by empirical methods.

The task of the extraction metallurgist is becoming more and more difficult because he is being called upon to produce metals from increasingly leaner ores and refine them to a much higher degree of purity than stipulated hitherto. Fortunately, much thermodynamic data have accumulated over the years, and these enable us to calculate the equilibrium of various chemical reactions.

The concepts of energy and entropy, which provide the framework for thermodynamics, are derived from the first and second laws of thermodynamics, respectively.

Thermodynamic principles help us determine the direction in which a given reaction will proceed, but they cannot give any useful information on the rate at which a reaction will take place. Many common base metals and their alloys are thermodynamically unstable in air even at the room temperature, since their final equilibrium state is the oxide. The use of these metals depends on the extremely slow kinetics that governs their oxidation. In metal extraction, it is important to know the kinetics of a reaction precisely, because a slow reaction can make a process unsuitable even if the thermodynamic factors are highly favourable. Kinetics also helps us understand the factors that govern the rates of constituent reactions, thus making it possible to increase the efficiency of the entire process.

Important laws and equations:

The Laws of Thermodynamics:

Zeroth Law

If two thermodynamic systems are each in thermal equilibrium with a third, then all three are in thermal equilibrium with each other.

First Law of Thermodynamics

- ***The total energy of the universe is a constant.***
- ***Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.***

Spontaneous Processes: oxidation of Fe

Non- Spontaneous Processes: reduction of Fe_2O_3

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

Entropy

- Entropy can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.

Like total energy, E, and enthalpy, H, entropy is a state function. Therefore,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Entropy increases with the freedom of motion of molecules.

Therefore, $S(\text{g}) > S(\text{l}) > S(\text{s})$

Second Law of Thermodynamics

The entropy of the universe does not change for reversible processes and increases for spontaneous processes.

Reversible (ideal): $\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$

Irreversible (real, spontaneous): $\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero is 0.

Practical uses: surroundings & system

...Gibbs Free Energy

$-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG .

For spontaneous processes: $\Delta S_{\text{universe}} > 0$

And therefore: $\Delta G < 0$.

Gibbs Free Energy

1. If ΔG is negative, the forward reaction is spontaneous.
2. If ΔG is 0, the system is at equilibrium.

If ΔG is positive, the reaction is spontaneous in the reverse direction.

Very key equation:

$$\Delta G = \Delta H_{sys}^{\circ} - T\Delta S_{system}$$

This equation shows how ΔG° changes with temperature.

(We assume S° & ΔH° are independent of T.)

KINETICS

Kinetics - studies the rate at which a chemical process occurs.

- Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly *how* the reaction occurs).

Factors That Affect Reaction Rates

- Concentration of Reactants
 - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.
- Temperature
 - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.
- Catalysts
 - Speed reaction by changing mechanism.

Temperature and Rate

Generally, as temperature increases, so does the reaction rate. This is because k is temperature dependent.

Activation Energy

In other words, there is a minimum amount of energy required for reaction: the activation energy, E_a . Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a : $k = Ae^{-\frac{E_a}{RT}}$

where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.

Words and Word-Combinations to Be Memorized

combined state	сложное состояние
thermodynamic principles	термодинамические принципы
feasibility	целесообразность, возможность
evolve	развиваться
increasingly leaner ores	все более истощающие руды
stipulate	предусматривают
thermodynamic data	термодинамические данные
enable	включить
equilibrium	равновесие
the equilibrium of various chemical reactions	равновесие различной химических реакций
provide the framework for thermodynamics	обеспечивает основу для термодинамики
derive	получить
first and second laws of thermodynamics	первый и второй законы термодинамики
determine the direction	определить направление
the rate of reaction	скорость реакции
the factors that govern the rates of constituent reactions	факторы, которые регулируют скорость составных реакций
favourable	благоприятный для повышения
to increase the efficiency of the entire process	для повышения эффективности всего процесса
the total energy of the universe	общая или суммарная энергия вселенной
converted from one form to another	переходит из одной формы в другую
surrounding	окружение, среда
spontaneous processes	самопроизвольные (спонтанные) процессы
non- spontaneous processes	несамопроизвольные (неспонтанные) процессы
oxidation	окисление
reduction	восстановление, снижение
the reverse direction	обратное направление
a measure of the randomness of a system	мера произвольности системы
the various modes of motion in molecules	различные режимы движения в молекулах
a state function	функция состояния
reversible processes	обратимые процессы
irreversible (real, spontaneous):	необратимые (реальный, спонтанное)
the forward reaction is spontaneous	прямая реакция происходит спонтанно
sheds light on the reaction mechanism (exactly how the reaction occurs).	проливает свет на механизм реакции (как именно происходит реакция)
as the concentration of reactants increases, so does the likelihood that reactant molecules will collide	Как концентрация реагентов увеличивается, так же вероятность того, что молекулы реагента будут сталкиваться
collide more often and with greater energy	сталкиваются чаще и с большей энергией
a multistep process	многоступенчатый процесс

