MME 231: Lecture 08

The Laws of Thermodynamics

The Third law of thermodynamics

A. K. M. B. Rashid
Professor, Department of MME
BUET, Dhaka

Today's Topics

- The concept of temperature
  - The zeroth law of thermodynamics
- The third law of thermodynamics
  - The development
  - Experimental validation

Introduction

- The first and the second laws deal with only the **changes** in energy and entropy, respectively.
- The zero levels for both energy and entropy are arbitrary.
- **Does there exist any particular choice for the zero level of energy or entropy?**

The Concept of Temperature

- Temperature is a property of matter that provides a universal measure of the tendency of system to exchange heat.
- Attempts to quantify this aspect of behaviour of matter lead to the development of the **Zeroth Law of Thermodynamics**:

  If two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other

- Experiments studying cryogenic behaviour of matter established that
  - the energy and entropy of a body are decreased with falling temperature
  - there is a lower limit to temperature, known as the absolute zero.

- If the energy of each element at absolute zero is assigned a zero value, the energy of a compound at absolute zero is, however, found to be not zero

  because the energy change accompanying chemical reactions is not zero at absolute zero

- The choice of the absolute zero for the zero entropy is fruitful and leads to the development of the third law of thermodynamics.

Development of the Third Law of Thermodynamics

Work of T.W. Richards (1902):

For many reactions, the changes in entropy and heat capacity approach zero at low temperature.

Work of Nernst (1906): Nernst heat theorem

- Generalisation of Richard's finding:

For all reactions involving substances in the condensed state, the change in entropy is zero at the absolute zero.

- For reaction A + B = AB, the change in entropy at 0K,

$$\Delta S = S_{AB} - (S_A + S_B) = 0$$

- if the entropies of elements S_A and S_B are assigned zero values at the absolute zero, then the entropy of the compound S_{AB} is also zero
- constitutes one statement of the third law of thermodynamics

Work of Planck:

Entropy of any homogeneous substance, which is in complete internal equilibrium, may be taken as zero at 0 K.

- Entropy of substance having non-equilibrium structure will not be zero at 0 K.

The Third Law:

There exists a lower limit to the temperature that can be attained by matter, called the absolute zero of temperature, and the entropy of all homogeneous substances which are in complete internal equilibrium is the same at that temperature and may be taken as zero.

Validation of Third Law

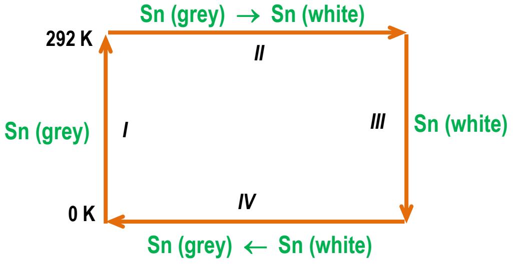
A direct validation of the Third Law is difficult.

1. The temperature 0 K could not be attained.
   even if attained by extrapolation, the kinetics of reaction at these low temperatures is very sluggish.

2. A direct measure of entropy change, $\Delta S = Q_{rev}/T$, is possible only for reversible reactions.
   reactions at 0 K is hardly reversible.

Indirect Validation of the Third Law:

- Consider the cyclic process:



I. Heat one mole of grey tin from 0 K to 292 K

II. Let the grey tin transforms into white tin at 292 K:

III. Cool the white tin from 292 K to 0 K

IV. The white tin transforms into grey tin at 0 K (by an imaginary process)

- The net entropy change in this cyclic process

$$\Delta S_{cyc} = \Delta S_I + \Delta S_{II} + \Delta S_{III} + \Delta S_{IV} = 0$$

$$\Delta S = \int_0^T \frac{\Delta C_P}{T} dT$$

Debye's formula :

for the atomic heat capacity of a crystalline substance at temperatures approaching 0 K

$$C_V = \frac{12\pi^4 R}{5}\left(\frac{T}{\theta}\right)^3 = 464.6\left(\frac{T}{\theta}\right)^3 \text{ cal/deg.mol} \quad [\,0 < T < \theta/10\,]$$

θ = Debye characteristic temperature of the substance

Experimental data:

ΔS_I = 9.11 cal/mol-K
ΔS_{II} = 1.85
ΔS_{III} = -11.04
ΔS_{IV} = - 0.08

$\Delta S_{IV} = 0$

$\Delta S_I + \Delta S_{II} + \Delta S_{III} \cong 0$

$\Delta S_{II} = -(\Delta S_I + \Delta S_{III})$

- This is a **pervasive** observation!!
  and, therefore, confirms the third law.
- **The entropy of all substances is the same at 0 K.**
  by convention, this is considered to be as ZERO !

Next Class

Lecture 09
Problem Solving
Rashid/ Ch#3