

# 2106NSC

# Physical & Analytical Chemistry

# Thermodynamics 3

## Fundamentals of Thermodynamics: Entropy

# Entropy

Entropy is related to the disorderly dispersal of energy.

The change in entropy is related to how much energy is reversibly transferred as heat.

Units:  $[S] = \text{J K}^{-1}$

# Entropy

The change in entropy of the surroundings:

$$d S_{surr} = \frac{d Q_{surr, rev}}{T_{surr}}$$

The temperature of the surroundings is constant so there is a defined heat flow  $\Delta Q$ :

$$\Delta S_{surr} = \frac{\Delta Q_{surr, rev}}{T_{surr}}$$

For a reaction at constant pressure, the enthalpy change in the system  $\Delta H_{sys}$  can be used to determine the entropy change of the surroundings.  $\Delta H = \Delta Q$ , because  $\Delta W = 0$ , therefore:

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}}$$

If the system is adiabatic (no heat transfer allowed, i.e.  $\Delta Q = \Delta H = 0$ ):

$$\Delta S_{surr} = 0$$

# Entropy

Consider reversible processes:

$$dS = \frac{dQ_{rev}}{T}$$

Reversible processes refer to processes that occur while the system remains at equilibrium at all times. They are generally hypothetical, unless no overall change is occurring in the system.

Equilibrium can be considered as the point where there is a cross-over from the forward reaction to the reverse reaction which would both occur naturally.

An important equilibrium process is a substance boiling at its boiling point:

$$\Delta S = \frac{\Delta H_{vapourisation}}{T_{bp}} \quad ; p = \text{const.}$$

or freezing at its freezing point:

$$\Delta S = \frac{\Delta H_{fusion}}{T_{mp}} \quad ; p = \text{const.}$$

# The 2<sup>nd</sup> Law of Thermodynamics

**The entropy of the universe increases in the course of every natural change.**

In light of the dwindling energy resources, a critical appraisal shows that the 1<sup>st</sup> Law of Thermodynamics eliminates the conventional worries: energy cannot be destroyed, so there is no worry that it would be used up.

However, it is the way in which energy is being dispersed that is cause for concern. By consuming energy, we increase the entropy (disperse the energy) and thus destroy its availability. In this sense, there is an entropy crisis rather than an energy crisis.

# The 2<sup>nd</sup> Law of Thermodynamics

Observation tells us that there is a direction associated with all processes. The 2<sup>nd</sup> Law of Thermodynamics predicts what direction a process or reaction will go in.

It answers questions such as:

- will a solution freeze or melt?
- will a compound dissolve?
- will an ion diffuse across a cell membrane?
- will the drug react with calcium?
- will a ball fall to the ground when dropped?
- etc

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. Energy is always dissipated.

Interesting implications: direction of a macroscopic process is always the same  
hot coffee cools if let to stand - never gets hotter  
bread becomes toast - toast doesn't become bread

# The 3<sup>rd</sup> Law of Thermodynamics

Nernst heat theorem:  $\lim_{T \rightarrow 0} S = 0$

**If the entropy of every element in any crystalline state at  $T = 0$  is set to zero ( $S_0 = 0$ ), then all substances have a positive entropy. At  $T = 0$ , the entropy of substances in their ideal crystalline states is zero.**

At absolute zero, the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimum energy state.

If the system does not have a well-defined order (e.g. if its order is glassy), then a finite entropy will remain as the system is brought to very low temperatures since the system becomes locked into a configuration with non-minimal energy. This constant value is called the residual entropy of the system.





# Revision of terms

Adiabatic change	no heat transfer: $\Delta Q = 0$
Isothermal change	temperature constant
State function	a property that only depends on the current state of the system (e.g. $E$ , $U$ , $H$ , ...)
Path function	a function that depends on how the process occurs (e.g. $Q$ , $W$ )
Intensive property	a property that doesn't change when you change the amount of substance (e.g. $T$ , $p$ , molar heat capacity)
Extensive property	a property that depends on the amount of material (e.g. mass, $V$ , $U$ )

# Revision of the laws of thermodynamics

## 0<sup>th</sup> Law of Thermodynamics

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

## 1<sup>st</sup> Law of Thermodynamics

The internal energy of an isolated system is constant.

$$\Delta U = \Delta Q + \Delta W$$

## 2<sup>nd</sup> Law of Thermodynamics

The entropy of a system must increase until the system reaches equilibrium.

$$\Delta S_{\text{universe}} > 0$$

## 3<sup>rd</sup> Law of Thermodynamics

The entropy of perfect crystalline substances is zero at  $T = 0$ .

# Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2<sup>nd</sup> Edition, Structural Chemistry Program, Griffith University.  
Sections II.1.10-II.2.1

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9<sup>th</sup> Edition, Oxford University Press.  
Sections 3.1 – 3.4, I3.2 (pp. 94-112)