

## 7.7 Energy and Equilibrium: Laws of Thermodynamics

Thermodynamics provides the explanation as to whether or not a given change (physical or chemical) is possible, and if it is possible, to what extent it will occur— without the need to study the particular reaction in question.

We can predict the value of the equilibrium constant of a reaction solely from information about the products and reactants themselves.

Some chemical behaviours and reactions are spontaneous (only occur in one direction) and once they are allowed to commence, they will proceed to the finish without any outside intervention

Throwing cards in the air

Hot objects cooling cold objects warming when they mix

Gases expanding

Books falling

Many “classical reactions”

### **The First Law of Thermodynamics:**

The total amount of energy in the universe is constant.

The direction of reactions is not governed by the energy changes of the system. Many spontaneous reactions can be exo- or endothermic.

Although the total energy of the system and the surroundings (and thus, of the world) is unchanged, there is something about the world that has changed, and this is its degree of disorder.

### **Second Law of Thermodynamics**

The entropy (or the tendency toward randomness) of the universe always increases and never decreases.

Although some reactions look to form products with less entropy the work involved in doing so increases the entropy of the universe. Eventually all “order” will dissipate into energy.

## Entropy is a description of the disorder of the system

Entropy  $\rightarrow$  disorder (randomness)  $\rightarrow S$

(You will be given  $S$  values– actual values not relative all values  $> 0$ )

**Third Law of Thermodynamics:** The entropy of a perfectly ordered pure crystalline substance is zero at absolute zero.

- What causes an increase in entropy? (Page 497)
- Examples for chemistry:
  1. A reaction when a gas is formed from a solid.
  2. A reaction when is gas is evolved from a solution.
  3. A reaction where the number of gaseous product is greater than the number of moles of gaseous reactant.
  4. A reaction where crystals dissolve in water.

Read the first part of Chapter 7.7 – summary and question 1 page 498

---

The chief use of the value of entropy of the system is to determine the potential energy (Gibbs free energy –  $G$ ) of the chemical system

Although most natural processes in the large scale always go in the direction of higher entropy. In the chemical world we also have to take into account if the reaction is exothermic or endothermic

- Hess's Law can determine the enthalpy of the reaction
- Comparing the amount of energy required to break bonds and the amount of energy released when bonds are broken can also determine the enthalpy of the reaction
- Enthalpy  $\rightarrow$  heat  $\rightarrow H$  (*relative values to elements in standard state*)

## Spontaneity of a Reaction

- Enthalpy and entropy can be used to predict the spontaneity of a reaction.
- Most spontaneous reactions are reactions where there is a decrease in enthalpy ( $-\Delta H$ ) and an increase in entropy ( $+\Delta S$ ).

$$\begin{array}{l} \Delta H^\circ = \sum nH^\circ_f \text{ products} - \sum nH^\circ_f \text{ reactants} \\ \Delta S^\circ = \sum nS^\circ \text{ products} - \sum nS^\circ \text{ reactants} \end{array} \left. \vphantom{\begin{array}{l} \Delta H^\circ \\ \Delta S^\circ \end{array}} \right\} \text{Units are different}$$

- The calculation of free energy ( $G$ ) can be used to predict the probable spontaneity of a reaction.
- This can also explain why some endothermic reactions are spontaneous
- Can be calculated using Gibbs-Helmholtz equation (make sure units are the same)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (T \text{ is in Kelvin normally } 298\text{K})$$

**Note: All values are at standard conditions (SATP)**

$\Delta H < 0$  exothermic

$\Delta H > 0$  endothermic

$\Delta S < 0$  decrease in disorder

$\Delta S > 0$  increase in disorder

$\Delta G < 0$  reaction is spontaneous in the forward direction

$\Delta G > 0$  reaction is not spontaneous in the forward direction **BUT** is spontaneous in the reverse direction

AND

If  $\Delta G = 0$  the system is at equilibrium

## Temperature and Equilibrium

So if  $\Delta G = 0$  at equilibrium then we can use the Gibbs-Helmholtz equation to **estimate** the temperature of changes of state since they are points of equilibrium between two different states.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$\frac{\Delta H^\circ}{\Delta S^\circ} = T \quad (T = \text{approximate temp in Kelvin})$$

## Homework

- Practice 1,2,3
- Questions on page 512