1.6. Entropy

Entropy is the overall distribution of positions and energies within a system… basically a measure of the disorder in the system

A system's entropy is affected by a variety of factors including Temperature, states of matter, quantity of molecules, pressure etc…

1.6.1. Second Law of Thermodynamics

In any spontaneous process there is always an increase in the total entropy of the universe

This can be defined by the following equation:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounds}$$

Where $\Delta S = S_{final} \quad S_{initial}$ which is a **state function**

1.6.2. Rules of Entropy Changes

1. S^{θ} for elements is **not** equal to zero

2. Reactions that consume or create gases can have predictable entropy changes

3. In terms of entropy content: $solids < liquids < gas$

4. The more complex the molecule, the higher the entropy

5. Forming a solution from a molecular solid yields an increase in entropy

6. Forming a solution from a salt may increase **or** decrease the entropy

7. Pressure and temperature both affect the entropy

1.6.3. Entropy and spontaneity

A system's entropy is also a means of gauging the spontaneity of a reaction

- A reaction may be spontaneous but the reaction rate may be very slow

- A spontaneous reaction is one in which the reaction can occur without outside intervention

In the above equation, the following scenario's apply:

1. If $\Delta S_{univ} > 0$ than the process is spontaneous

2. If $\Delta S_{univ} > 0$ than the process is spontaneous in the opposite direction

3. If $\Delta S_{univ} = 0$ than the process is at equilibrium

1.6.4. Third Law of Thermodynamics

At absolute zero ($0K$) the entropy of a perfectly ordered pure crystalline substance is zero. i.e. $S = 0$

This is evidenced by the increase in disorder that appears when the crystal is warmed, leading to an increase in entropy.

S^{θ} is the symbol used for *absolute entropy*.

1.7. Gibbs Energy

- Denoted by the symbol G and is in units of Joules (J)
- The spontaneity of a chemical process held at constant temperature and pressure can be predicted by the sign of Gibbs energy change for the process
- General formula is

$$G = H - T S$$

Where H is enthalpy $[J]$, S is the entropy $\left[\frac{J}{K}\right]$ and T is the temperature $[K]$.

- However, the absolute values of H and S are virtually impossible to determine and as a result we tend to use the 'difference' in these values…
- At constant temperature the change in Gibbs Energy equation is:

$$\Delta_r G^\theta = \Delta_r H^\theta - T \Delta_r S^\theta$$

1.7.1. Gibbs energy and spontaneity

The following scenarios apply for Gibbs energy and Spontaneity:

1. If $\Delta_r G < 0$, the reaction is spontaneous
2. If $\Delta_r G > 0$, the reaction is non-spontaneous
3. If $\Delta_r G = 0$, the reaction is at equilibrium

1.7.2. Determining Gibbs Energy Change

As with enthalpy, the Gibbs energy change can be calculated as the difference between products and reactants:

$$\Delta_r G = \sum (n_i \cdot G_i)_{products} - \sum (n_i \cdot G_i)_{reactants}$$

Additionally, the following equation holds true:

$$\Delta_r G = \Delta_r H - T \Delta_r S = {}^- T \Delta S_{universe}$$

Putting it back to standards (which is what we usually deal with…)

For the reaction: $aA + bB \rightarrow cC + dD$ the following is the method of determining the net reaction Gibbs Energy:

$$\Delta_r G^\theta = \left(c\Delta_f G^\theta(C) + d\Delta_f G^\theta(D) \right) - \left(a\Delta_f G^\theta(A) + b\Delta_f G^\theta(B) \right)$$

As with enthalpy and entropy, for an element in its standard state, the $\Delta_f G^\theta = 0$