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# Entropy and Gibbs energy

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## 15.1 What are spontaneous processes?

- Spontaneous reactions, once started, will continue towards equilibrium without any outside intervention.
- Entropy is a measure of the randomness or disorder in a system.
- Entropy is related to the number of arrangements that a system can adopt by the Boltzmann formula

$$S = k_B \ln W \quad k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

## 15.2 Entropy and the Second Law of thermodynamics

- The Second Law of thermodynamics: spontaneous processes increase the total entropy of the Universe

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- The entropy change of a system is related to the heat transferred and the temperature by

$$\Delta S(\text{system}) = \frac{q_{\text{rev}}}{T}$$

- A change of state at  $T_b$  or  $T_m$  is a reversible process at 1 bar since it occurs at equilibrium

$$\Delta_{\text{vap}} S^\ominus = \frac{\Delta_{\text{vap}} H^\ominus}{T_b} \quad \text{and} \quad \Delta_{\text{fus}} S^\ominus = \frac{\Delta_{\text{fus}} H^\ominus}{T_m}$$

- The variation of the entropy of substance with temperature is given by the equation

$$S_{T_f} = S_{T_i} + C_p \ln \frac{T_f}{T_i}$$

### 15.3 The Third Law and absolute entropies

- The Third Law of thermodynamics: the entropy of a perfect crystal at zero kelvin is zero.
- The standard entropy,  $S_{298}^{\ominus}$ , of a substance is the entropy of 1 mol at 298 K and 1 bar pressure. This refers to a reference state where  $S^{\ominus} = 0$  at 0 K.
- Values of  $S_{298}^{\ominus}$  are determined by adding the entropy changes involved in heating 1 mol of the substance from 0 K to 298 K, taking into account any phase changes that occur (see Box 15.2).

### 15.4 Entropy changes in chemical reactions

- The standard entropy change for a reaction at 298 K is given by
- $$\Delta_r S_{298}^{\ominus}(\text{reaction}) = \sum \nu_i S_{298}^{\ominus}(\text{products}) - \sum \nu_i S_{298}^{\ominus}(\text{reactants})$$
- The standard entropy change for a reaction at another temperature,  $T$ , is given by

$$\Delta_r S_T^{\ominus} = \Delta_r S_{298}^{\ominus} + \Delta C_p \ln \frac{T}{298 \text{ K}}$$

$$\text{where } \Delta C_p = \sum \nu_i C_p(\text{products}) - \sum \nu_i C_p(\text{reactants})$$

- For a chemical change to be spontaneous, the total entropy change of the Universe must have a positive value.

$$\Delta_r S(\text{total}) = \Delta_r S(\text{system}) + \Delta_r S(\text{surroundings})$$

$$\Delta_r S(\text{surroundings}) = \frac{-\Delta_r H}{T} \quad (\text{at constant pressure})$$

### 15.5 Gibbs energy

- The Gibbs energy,  $G$ , is a state function.
  - The change in *Gibbs energy*,  $\Delta G$ , is defined by
- $$\Delta G = \Delta H - T \Delta S$$
- The requirement for a change to be spontaneous is
- $$(\Delta G)_{p,T} < 0$$
- The Gibbs energy change for a reaction,  $\Delta_r G$ , is given by

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

- The Gibbs energy change for a reaction can be used to predict whether or not a reaction is spontaneous under a given set of conditions:
  - if  $\Delta G < 0$ , the reaction or process is spontaneous;
  - if  $\Delta G > 0$ , the reaction or process is non-spontaneous;
  - if  $\Delta G = 0$ , the reaction or process is at equilibrium.
- The standard Gibbs energy change of formation at 298 K,  $\Delta_f G_{298}^\ominus$  is the change in Gibbs energy when 1 mole of a compound is formed at 1 bar and 298 K from its elements in their standard states.
- Gibbs energy changes of formation can be used to calculate the change in Gibbs energy during a reaction using
 
$$\Delta_r G_{298}^\ominus = \sum \nu_i \Delta_f G_{298}^\ominus (\text{products}) - \sum \nu_i \Delta_f G_{298}^\ominus (\text{reactants})$$
- The value of  $\Delta_r G^\ominus$  is negative for a spontaneous reaction at 1 bar pressure.
- A reaction may be spontaneous but may occur so slowly that it does not appear to take place.
- A non-spontaneous reaction may take place if it is coupled to a reaction that has a larger, negative value of  $\Delta_r G$ .
- The value of the Gibbs energy change of reaction is equivalent to the maximum non-expansion work that can be obtained from a system.

## 15.6 Variation of Gibbs energy with conditions

- The thermodynamic activity,  $a$ , is used to describe how the Gibbs energy depends on the composition of a mixture.
- Thermodynamic activity is defined as the ratio of the concentration or pressure to a standard value:
  - for ideal gases,  $a = \frac{P}{p^\ominus}$        $p^\ominus = 1 \text{ bar}$ ;
  - for solutions,  $a = \frac{[A]}{[A]^\ominus}$        $[A]^\ominus = 1 \text{ mol dm}^{-3}$ ;
  - For pure solids and pure liquids,  $a = 1$ .
- The variation of Gibbs energy with composition is given by
 
$$G = G^\ominus + RT \ln a.$$

- The molar entropy of a substance is given by the variation of the molar Gibbs energy with temperature

$$\left(\frac{dG_m}{dT}\right)_p = -S_m$$

- The variation of the Gibbs energy change with temperature for a reaction gives the entropy change

$$\left(\frac{d\Delta_r G}{dT}\right)_p = -\Delta_r S$$

## Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe, and give examples of, spontaneous changes.
- Use changes in entropy and Gibbs energy to assess the spontaneity of processes or reactions.
- Calculate the temperature dependence of entropy using heat capacities.
- Account for the sign of entropy changes in terms of the disorder of a system.
- Calculate absolute entropies of compounds and describe the origin of residual entropies.
- Calculate entropy changes of reaction from absolute entropies.
- Calculate Gibbs energy changes from enthalpy and entropy changes.
- Describe how coupling of reactions allows non-spontaneous reactions to take place.
- Describe how Gibbs energy changes with conditions.
- Define the thermodynamic activity of a substance.