

Entropy and Gibbs energy

14.1 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

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

 For practice questions on these topics, see questions 1 and 2 at the end of this chapter (p.692).

14.2 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 molar entropy of a substance with temperature is given by the equation

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

 For practice questions on these topics, see questions 3, 4, 6, and 12 at the end of this chapter (p.692).

14.3 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.
- The standard entropy of a substance at temperatures other than 298 K can be found using

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

assuming the substance remains in the same phase between 298 K and T .



For practice questions on these topics, see questions 7, 8, and 9 at the end of this chapter (p.692).

14.4 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

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

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

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

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

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



For practice questions on these topics, see questions 5, 10, 11, and 13 at the end of this chapter (p.692).

14.5 Gibbs energy

- The Gibbs energy, G , is a state function.

- The change in Gibbs energy, ΔG , 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;
- $\Delta G > 0$, 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 mol 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

$$\Delta_r G_{298}^\ominus = \sum \nu_i \Delta_f G_{298}^\ominus (\text{products}) - \sum \nu_j \Delta_f G_{298}^\ominus (\text{reactants})$$

- 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 be made to 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.



For practice questions on these topics, see questions 14 and 16–21 at the end of this chapter (pp.692–693).

14.6 Variation of Gibbs energy with conditions

- Thermodynamic activity, a , is defined as the ratio of the concentration or pressure to a standard value:

- for ideal gases, $a = \frac{p}{p^\ominus}$, where $p^\ominus = 1 \text{ bar}$ and p is the partial pressure in bar;

- for ideal solutions, $a = \frac{[A]}{[A]^\ominus}$, where $[A]^\ominus = 1 \text{ mol dm}^{-3}$ and $[A]$ is the concentration in mol dm^{-3} ;

- for pure solids and pure liquids, $a = 1$.

- The thermodynamic activity is used to describe how the Gibbs energy depends on the composition of a mixture.

- The variation of Gibbs energy with composition is given by

$$G = G^\ominus + RT \ln a.$$

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

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

- The variation of the Gibbs energy change with temperature for a reaction is given by

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

- Ellingham diagrams provide a useful way of deciding whether the reduction of a metal oxide will be a spontaneous reaction.



For practice questions on these topics, see questions 15, 22, and 23 at the end of this chapter (pp.692–693).



Concept review

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 temperature, pressure, and concentration.
- Define the thermodynamic activity of a substance.



Key equations

Entropy and number of ways of organizing a system	$S = k_B \ln W$	(14.2)
Total entropy change: the Second Law of thermodynamics	$\Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$	(14.3)
Entropy change in the system	$\Delta S(\text{system}) = \frac{q_{\text{rev}}}{T}$	(14.4)
Change of entropy with temperature	$\Delta S_T = S_T + C_p \ln \frac{T_f}{T_i}$	(14.7)
Entropy change of reaction	$\Delta_r S_{298}^\ominus = \underbrace{\sum \nu_i S_{298}^\ominus(\text{products})}_{\substack{\text{The sum of} \\ \text{the standard} \\ \text{entropies of all} \\ \text{of the products}}} - \underbrace{\sum \nu_i S_{298}^\ominus(\text{reactants})}_{\substack{\text{The sum of} \\ \text{the standard} \\ \text{entropies of all} \\ \text{of the reactants}}}$	(14.11)
Standard entropy change at temperature T	$\Delta_r S_T^\ominus = \Delta_r S_{298}^\ominus + \Delta C_p \ln \frac{T}{298 \text{ K}}$ where $\Delta C_p = \sum \nu_i C_p(\text{products}) - \sum \nu_i C_p(\text{reactants})$	(14.12)
Entropy change in the surroundings	$\Delta_r S(\text{surroundings}) = \frac{-\Delta_r H}{T}$	(14.14)
Gibbs energy change	$\Delta G = \Delta H - T\Delta S$	(14.16)
Gibbs energy and spontaneity	For a spontaneous change $(\Delta G)_{p,T} < 0$	(14.17)
Gibbs energy change of reaction	$\Delta_r G_{298}^\ominus = \sum \nu_i \Delta_f G_{298}^\ominus(\text{products}) - \sum \nu_i \Delta_f G_{298}^\ominus(\text{reactants})$	(14.18)
Thermodynamic activity	Ideal gases: $a = \frac{p}{p^\ominus}$ $p^\ominus = 1 \text{ bar}$	(14.19a)
	Ideal solutions: $a = \frac{[A]}{[A]^\ominus}$ $[A]^\ominus = 1 \text{ mol dm}^{-3}$	(14.19b)
	Pure liquid or solid: $a(\text{pure solid}) = a(\text{pure liquid}) = 1$	(14.19c)
Variation of G with activity	$G = G^\ominus + RT \ln a$	(14.20)
Variation of G with temperature	$\left(\frac{dG_m}{dT}\right)_p = -S_m$	(14.25)