Anderson Serangoon Junior College H2 Chemistry CHEMICAL ENERGETICS II (THERMODYNAMICS)

Contents/Outline

- 1 Introducing spontaneous process
- 2 Defining entropy and explaining the factors affecting entropy of a chemical system
- 3 Predicting the spontaneity of a reaction using Gibbs Free Energy Change
- 4 Determining the effect of temperature on the spontaneity of a reaction

Learning Outcomes

Students should be able to:

- (a) explain and use the term entropy.
- (b) discuss the effects on the entropy of a chemical system by the following:
 - (i) change in temperature
 - (ii) change in phase
 - (iii) change in the number of particles (especially for gaseous systems)
 - (iv) mixing of particles
 - [quantitative treatment is not required]
- (c) predict whether the entropy change for a given process or reaction is positive or negative
- (d) define standard Gibbs free energy change of reaction by means of the equation $\Delta G^{\ominus} = \Delta H^{\ominus} T\Delta S^{\ominus}$
- (e) calculate ΔG[⊕] for a reaction using the equation ΔG[⊕] = ΔH[⊕] − TΔS[⊕]
 [the calculation of standard entropy change, ΔS[⊕], for a reaction using standard entropies, S[⊕], is not required]
- (f) state whether a reaction or process will be spontaneous by using the sign of ΔG^{\ominus}
- (g) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

References

- 1. Chemistry for Advanced Level, Cann and Hughes, Murray
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1 SPONTANEOUS PROCESS

- What is a spontaneous process?
- Can an endothermic reaction be spontaneous?

The main objective of studying chemical thermodynamics is to be able to predict whether a reaction is spontaneous.

A spontaneous process is one that takes place without any outside interference i.e. takes place by itself without an ongoing input of energy from outside the system. It occurs in a definite direction. Spontaneous reactions can be fast or slow. Slow spontaneous reactions can include ripening, rusting and aging.

A spontaneous change is **irreversible** as it cannot be brought back to its original state unless some outside influence is introduced.

Some examples of spontaneous reactions:

- A lump of sugar dissolves spontaneously in a cup of coffee but dissolved sugar does not spontaneously reappear in the original form.
- Iron exposed to water and oxygen forms rust but rust does not spontaneously change back to iron.
- The expansion of a gas in an evacuated bulb is a spontaneous process. The reverse, i.e. the gathering of all the gas molecules into one bulb, is not.

Generally, when enthalpy $\Delta H < 0$, the tendency of a spontaneous reaction is higher. However, the signs of ΔH alone cannot be used to predict the spontaneity of a reaction.

There are other factors that affect the spontaneity of a reaction. Some examples of spontaneous reactions that are endothermic:

• The melting of ice $H_2O(s) \longrightarrow H_2O(l)$ $\Delta H^{\ominus} = +6.01 \text{ kJ mol}^{-1}$

Ice melts spontaneously above 0 °C even though the process is endothermic.

• The dissolving of ammonium nitrate in water $NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H^{\ominus} = +25 \text{ kJ mol}^{-1}$

The temperature of water decreases as ammonium nitrate dissolves in water. Hence, the dissolution is spontaneous even though it is endothermic.

Hence, it is possible for endothermic reactions to be spontaneous and possible for exothermic reactions to be non-spontaneous. Thus, consideration of energy changes (ΔH) is not enough to predict the spontaneity of a process.

In this part of the Chemical Energetics, the concept of **entropy** and **free energy** will be introduced to provide an explanation why some reactions are spontaneous while others are not spontaneous.

2 ENTROPY, S

What is entropy?

• What are some factors that affect the entropy of a chemical system?

2.1 Definition

Entropy (S) measures the degree of disorder/ randomness of matter.

It gives a measure of the extent to which particles (atoms, molecules or ions) and their energies (vibrational, translational and rotational) are distributed in a system.

The **greater** the number of ways to distribute particles and their energies within a system, the **greater** the degree of disorder in the system and hence the **larger** the entropy of the system. Hence the more spontaneous the reaction will be.

It has the unit of **J mol⁻¹ K⁻¹**.

Entropy, like enthalpy, is a **state** function because its value depends solely on external conditions of temperature, pressure and concentration/ amount/ composition.

At absolute zero (i.e. 0 K or -273 °C), all matter is in a crystalline solid state. In such a state, all particles attain a perfectly ordered arrangement with no lattice vibration. In this state, the matter is considered to possess *zero entropy (S)*. Entropy starts to increase when temperature increases from 0 K.

Thus, the change in entropy of the system (ΔS_{sys}) depends only on the difference between its final and initial values, and is independent of how the change is brought about:



(Recall Hess' Law: ΔH is independent of reaction pathway used)

Example 2.1.1

At temperatures below 13 °C, shiny, ductile metallic tin, known as 'white tin', changes slowly into a grey powder which is brittle. Data for each form of tin are given in the table.

	S [⊖] / J K ⁻¹ mol ⁻¹
white	51.4
grey	44.1

What is the value of ΔS^{\ominus} for the formation of grey tin from white tin at 12 °C?

Solution:

white tin → grey tin ∆*S*[⊖] = 44.1 - 51.4 = -7.3 J K⁻¹ mol⁻¹

2.2 Factors affecting the Entropy of a Chemical System

(a) <u>Temperature</u>



Maxwell–Boltzmann distributions of kinetic energy of an ideal gas at 2 different temperatures

- Based on the diagram, the energy distribution curve broadened at a higher temperature.
- When temperature increases, the average kinetic energy of the particles increases.
- Particles move more randomly and vigorously.
- The kinetic energies will be **distributed** over a wider range at a higher temperature.
- There are **more ways** to distribute the particles and their energies in the system, resulting in **greater disorder** in the system.
- Hence, entropy of the system increases when temperature increases.

(b) <u>Change in phase</u>



Element	S° 298	Compound	S° 298
H ₂ (g)	131	H ₂ O(l)	70
O ₂ (g)	205	$H_2O(g)$	189
N ₂ (g)	193	$H_2O_2(g)$	110
Cl ₂ (g)	223	$N_2O_4(g)$	304
He <i>(g)</i>	126	$NH_3(g)$	192
Ne(g)	146	NaCl(s)	72
C(s, diamond)	2.4	NaCl(aq)	116
C(s, graphite)	5.7	$CH_4(g)$	186
S <i>(s)</i>	32	$CO_2(g)$	213

Above table shows the absolute entropy (S) of substances at T = 298 Kand 101325 kPa.

- For a fixed amount (in moles) of a substance in a system, entropy increases as it changes from a solid to a liquid to a gas (S_{solid} < S_{liquid} << S_{gas}).
- From solid to liquid (melting)
 - When a solid melts, the order in the solid is destroyed but the volume change is negligible.
 - Particles in liquid can now move about more freely and there are more ways to distribute the particles and their energies, hence resulting in greater disorder in the system.
 - > There is an **increase** in entropy ($\Delta S_{fus}^{\ominus} > 0$).
- From liquid to gas (boiling)
 - When a liquid boils, the gas particles can now move with great disorder in a larger volume of space as compared to particles in the liquid.
 - There are even more ways to distribute the particles and their energies hence resulting in the greatest disorder in the system among the three states.
 - > There is an **even greater increase** in entropy $(\Delta S_{vap}^{\ominus} > \Delta S_{fus}^{\ominus})$.

Is the entropy of graphite greater/smaller than that of diamond?

The carbon atoms in diamond are arranged rigidly in an extensive tetrahedral network.

Whereas, graphite consists of extensive layers of planar hexagonal rings o carbon atoms and the layers readily slide over on another.

Hence there is a greater degree of disorder in graphite than in diamond.



- (c) Change in the number of gaseous particles
 - The arrangement of particles in a gas is the **most disordered** among the three states of matter as they move randomly in all directions.
 - When the products of a reaction contain more gas particles than the reactants,
 - there are more ways to distribute the particles and their energies since there are more gas particles moving randomly.
 - > The greater disorder in the system results in an increase in entropy of the system.

$$\Delta n_{gas} = n$$
 (gaseous products) – n (gaseous reactants)

Example 2.2.1

Complete the table below.

Reaction	Δn_{gas}	Entropy of system	ΔS_{sys}
$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$	+3	Increases	> 0
$N_2O(g) \longrightarrow N_2(g) + \frac{1}{2}O_2(g)$			
NaHCO ₃ (s) + HC l (aq) \longrightarrow NaC l (aq) + H ₂ O(l) + CO ₂ (g)			
$2NO_2(g) \longrightarrow N_2O_4(g)$			

(d) <u>Mixing of particles</u>

(i) Mixing of gases





Diagram showing how the particles mix when the partition is removed

- When mixing gases, each gas expands to occupy the whole container.
- There are **more ways** to distribute the particles and their energies, resulting in a **greater disorder** in the system.
- Hence entropy increases $(\Delta S^{\ominus} > 0)$.
- (ii) Mixing of liquids
 - When mixing liquids of similar polarities (e.g. benzene and hexane), the molecules have greater volume of space to move about.
 - There are **more ways** to distribute the particles and their energies, resulting in a **greater disorder** in the system.
 - Hence entropy increases $(\Delta S^{\ominus} > 0)$.

(iii) Dissolving an ionic solid

The nature of solute and solvent and the dissolving process affect the overall entropy change.

- Two entropy terms operate when an ionic solid is dissolved in water:
 - Entropy increases because the giant ionic lattice breaks down and the ions become free to move.
 - Entropy decreases because the water molecules form ion-dipole attractions with the ions, resulting in the water molecules becoming more restricted in their movement.



• The overall entropy change depends on which of the above two factors is more significant.

Example

	NaC/	A/Cl ₃
S [⊖] (s)	72.1	167
S [⇔] (aq)	115.1	-148
∆S⇔	+43	-315

- NaCl(s) \longrightarrow Na⁺(aq) + Cl⁻(aq) $\Delta S^{\ominus} > 0$
 - Breaking down of the giant ionic lattice increases disorder, since Na⁺ and Cl⁻ which were previously rigidly held in the solid are now free to move about in the solution.
 - The hydration process however decreases disorder about Na⁺ and Cl⁻ since it puts the hydrating water molecules into an orderly arrangement about the Na⁺ and Cl⁻ ions.
 - Since the disordering process is more dominant, the overall dissolution process results in a **net increase** in entropy.
- $AlCl_3(s) \longrightarrow Al^{3+}(aq) + 3Cl^{-}(aq) \qquad \Delta S^{\Theta} < 0$
 - For salts such as AlCl₃ which contain more highly charged ions, the hydrating water molecules are more highly ordered about the ions.
 - Since the ordering process is more dominant, the overall dissolution process results in a net decrease in entropy.

Example 2.2.2

For each of the following processes, identify the factor which determines whether the change in entropy of the system is positive or negative. Assume that the temperature is 298 K and the pressure is 1 atm unless otherwise stated.

Process	ΔS_{system}	Factor affecting entropy
$H_2O(s)$ at 273 K \longrightarrow $H_2O(l)$ at 273 K		
$H_2O(l)$ at 298 K \longrightarrow $H_2O(l)$ at 308 K		
$Cl_2(g) \longrightarrow 2Cl(g)$		
$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$		

3. GIBBS FREE ENERGY CHANGE OF A REACTION, ΔG

How do we use △G to predict if a process is spontaneous?
How does the temperature affect the spontaneity of a reaction?

3.1 Definition

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- The spontaneity of a reaction involves two thermodynamic concepts: **enthalpy** and **entropy**.
- To use ΔH and ΔS to predict whether a given reaction will be spontaneous, a new state function, the Gibbs free energy, *G*, can be defined.
- The free energy change of a reaction, ΔG , is a measure of the spontaneity of the reaction and of the useful energy available from it. It is defined by the following equation:

$$\Delta \boldsymbol{G}_{\rm sys} = \Delta \boldsymbol{H}_{\rm sys} - \mathsf{T} \Delta \boldsymbol{S}_{\rm sys}$$

Units of $\triangle G$ and $\triangle H$: kJ mol⁻¹Units of $\triangle S$: kJ mol⁻¹ K⁻¹Units of T: K

3.2 Predicting spontaneity of reaction using the sign of ΔG^{e}

- The sign of ΔG depends on the signs and magnitudes of both ΔH and ΔS as well as the temperature of the reaction.
- At constant temperature and pressure, a reaction is considered spontaneous if there is a decrease in the free energy of the system (ΔG < 0):

$\Delta G < 0$	\Rightarrow forward reaction is spontaneous
$\Delta G > 0$	⇒ forward reaction is not spontaneous ⇒ backward reaction is spontaneous
$\Delta G = 0$	 ⇒ reaction is at equilibrium ⇒ phase changes (e.g. melting and boiling) are processes at equilibrium

- ΔG only indicates the <u>thermodynamic spontaneity</u> of a reaction.
- ΔG gives **NO** information about the **kinetic feasibility** (whether the reaction proceeds at an observable rate). The kinetic feasibility of a reaction depends on the **activation energy**.
- Thus, a reaction with $\Delta G < 0$ may not occur if the rate of reaction is extremely slow.
 - > For example, the reaction between $CH_4(g)$ and $O_2(g) / H_2(g)$ and $O_2(g)$, at room temperature is highly spontaneous (ΔG has a large negative value). However, in the absence of a catalyst or a flame, the reaction does not occur to a measurable extent because its rate is so slow.

(Why is the rate so slow? This will be covered in the topic "Reaction Kinetics".)

Example 3.2.1

Potassium chlorate, a common oxidising agent in fireworks, undergoes a solid state disproportionation reaction when heated.

$$4KClO_3(s) \longrightarrow 3KClO_4(s) + KCl(s)$$

ΔS_r^{\ominus}	$\Delta H_{\rm f}^{\ominus}$ of KC l O ₃	∆ <i>H</i> f [⊖] of KC <i>l</i> O₄	ΔH_{f}^{\ominus} of KC l
–36.8 J mol ⁻¹ K ⁻¹	+ 143.1 kJ mol ⁻¹	+ 151.0 kJ mol ⁻¹	+ 82.6 kJ mol ⁻¹

(i) Calculate the $\Delta H_{\rm r}^{\ominus}$.

(ii) Hence calculate the ΔG^{\ominus} for this reaction and predict whether the reaction is spontaneous.

Solution:

(i)
$$\Delta H_{\rm f}^{\ominus} = \Sigma \Delta H_{\rm f}^{\ominus} (\text{products}) - \Sigma H_{\rm f}^{\ominus} (\text{reactants})$$

= [3 × $\Delta H_{\rm f}^{\ominus} (\text{KC}/\text{O}_4) + 1 × \Delta H_{\rm f}^{\ominus} (\text{KC}/)] - [4 × \Delta H_{\rm f}^{\ominus} (\text{KC}/\text{O}_3)]$
= [(3 × 151.0) + (1 × 82.6)] - [4 × 143.1]
= -36.8 kJ mol⁻¹

(ii) $\Delta S_r^{\oplus} = -36.8 \text{ J mol}^{-1} \text{ K}^{-1} = -0.0368 \text{ kJ mol}^{-1} \text{ K}^{-1}$

At 298 K: $\Delta G_r^{\ominus} = \Delta H_r^{\ominus} - T \Delta S_r^{\ominus}$

Since ΔG_r^{\ominus} \Rightarrow reaction is _____.

3.3 The Effect of Temperature on Spontaneity of a Reaction

- The sign of ΔG depends on the signs and magnitudes of ΔH and ΔS , as well as temperature.
- Using $\Delta G = \Delta H T \Delta S$, we can predict the sign of ΔG when temperature is varied. However, a very crucial assumption must be be made to apply this equation.

Assumption:

The values of ΔH and ΔS are relatively constant over a small temperature range. Note: the above assumption is not valid if there is a change in phase of one of the reactants or products as the temperature is varied.

- (i) Spontaneous at all T when $\Delta H < 0$ and $\Delta S > 0$
 - \blacktriangleright –T Δ S is **negative**
 - > Since $\Delta G = \Delta H T\Delta S \Rightarrow \Delta G$ is **negative**
 - $\Rightarrow \Delta G$ will always be negative and the reaction is spontaneous at all temperatures.

E.g. $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$ $\Delta H = -196 \text{ kJ mol}^{-1} \text{ and } \Delta S = +125 \text{ J mol}^{-1} \text{ K}^{-1}$

(ii) Not spontaneous at all T when $\Delta H > 0$ and $\Delta S < 0$

 \blacktriangleright -T Δ S is **positive**

- > Since $\Delta G = \Delta H T\Delta S \Rightarrow \Delta G$ is **positive**
 - $\Rightarrow \Delta G$ will always be positive and the reaction is not spontaneous at all temperatures.
- E.g. $3O_2(g) \longrightarrow 2O_3(g)$ $\Delta H = +286 \text{ kJ mol}^{-1} \text{ and } \Delta S = -137 \text{ J mol}^{-1} \text{ K}^{-1}$

- When △*H* and –T△S have opposite signs, the sign of △*G* will depend on the magnitudes of these two terms. In these instances, temperature is an important consideration.
- Generally, ΔH and ΔS change very little with temperature. However, the value of T directly affects the magnitude of $-T\Delta S$.
- As the temperature increases, the magnitude of the term $-T\Delta S$ increases and it will become relatively more important in determining the sign and magnitude of ΔG .
- (iii) Spontaneous at high T when $\Delta H > 0$ and $\Delta S > 0$
 - \blacktriangleright –T Δ S is **negative**
 - Since $\Delta G = \Delta H T\Delta S \Rightarrow \Delta G$ becomes **negative** when $|T\Delta S| > |\Delta H|$. This happens at **higher** temperatures.
 - > ΔG will be **negative** and the reaction will be **spontaneous** at **higher temperatures**.

E.g. $2N_2O(g) + O_2(g) \longrightarrow 4NO(g) \Delta H = +197.1 \text{ kJmol}^{-1} \text{ and } \Delta S = +198.2 \text{ Jmol}^{-1}\text{K}^{-1}$

The oxidation of N_2O occurs spontaneously at **T > 994 K**.

- (iv) Spontaneous at low T when $\Delta H < 0$ and $\Delta S < 0$
 - \blacktriangleright –T Δ S is **positive**
 - Since $\Delta G = \Delta H T\Delta S \Rightarrow \Delta G$ becomes **negative** when $|\Delta H| > |T\Delta S|$. This happens at **lower** temperatures.
 - > ΔG will be **negative** and the reaction will be **spontaneous** at **lower temperatures**.

E.g.4Fe(s)+ $3O_2(g) \longrightarrow 2Fe_2O_3(s)$ $\Delta H = -1651 \text{ kJmol}^{-1} \text{ and } \Delta S = -549.4 \text{ Jmol}^{-1} \text{ K}^{-1}$

The production of iron(III) oxide occurs spontaneously at any T < 3004 K.

Summary	of Effect of	Temperature on S	Spontaneity	of Reactions

ΔH	∆S	-T∆S	$\Delta G = \Delta H - T \Delta S$	Spontaneity of reaction	
-	+	-	_	Spontaneous at all T	
+	-	+	+	Not spontaneous at all T	
+	+	_	+ or –	Spontaneous at high T; Not spontaneous at low T	
-	-	+	+ or –	Spontaneous at low T; Not spontaneous at high T	

Example 3.3.1

A key step in the production of sulfuric acid is the oxidation of $SO_2(g)$ to $SO_3(g)$:

 $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

At 298 K, $\Delta G^{\ominus} = -141.6 \text{ kJ mol}^{-1}$; $\Delta H^{\ominus} = -198.4 \text{ kJ mol}^{-1}$; $\Delta S^{\ominus} = -187.9 \text{ J mol}^{-1} \text{ K}^{-1}$

- (i) Use the data to decide if the reaction is spontaneous at 25 °C, and predict how ΔG will change with increasing T.
- (ii) Predict whether the reaction is spontaneous at 900°C. State any assumptions used.

Solution:

(i) ΔG^{\ominus} _____ 0, so the oxidation of SO₂ to SO₃ is ______ at 25 °C.

Using $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, since $\Delta S^{\ominus} _ 0$ and $\Delta H^{\ominus} _ 0$, as temperature increases, $(-T\Delta S^{\ominus})$ will become $_$.

Hence ΔG^{\ominus} will become ______ and this ______ the spontaneity of the reaction as temperature increases.

Note that if ΔS^{\ominus} is not given, you can still predict using observation,

From observation, Δn of gaseous molecules = (2) – (2+1) = -1. Since the reaction results in **a decrease in the no. of moles of gaseous molecules**, $\Delta S^{\circ} < 0$.

(ii) At 900 °C, T = 273 + 900 = 1173 K

 $\Delta G_{1173 \text{ K}} = \Delta H_{1173 \text{ K}} - T\Delta S_{1173 \text{ K}}$ $\approx \Delta H^{\ominus} - T\Delta S^{\ominus}$ =

Since ΔG_{1173K} _____, the reaction is ______at 1173 K.

Assumption: Values of ΔH and ΔS ______.

The assumption that ΔH and ΔS remain relatively constant is <u>not valid</u> if there is a <u>change in</u> <u>phase</u> of one of the reactants or products as the temperature is changed. Under these conditions, both ΔH and ΔS change significantly.

e.g. The reaction between hydrogen and iodine at 298K and 500K

	т/к	∆ <i>H</i> / kJ mol ^{−1}	∆S / J mol ⁻¹ K ⁻¹	∆G / kJ mol ⁻¹
$H_2(g) + \mathrm{I}_2(\boldsymbol{s}) \to 2HI(g)$	298	+53.0	+166.0	+3.5
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	500	-11.0	+18.0	-20.0

As a result of the phase change in I₂ (from solid to gas), ΔG changes from being slightly positive at 298K to being negative at 500K.

This means the synthesis of HI is not spontaneous at 298K but becomes spontaneous if the temperature is raised above the boiling point of I_2 .

Example 3.3.2

For the synthesis of ammonia at 300 K,

 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

 $\Delta H = -92$ kJ mol⁻¹ and $\Delta G = -33$ kJ mol⁻¹.

Calculate ΔG at 750 K and predict whether the reaction is spontaneous. State any assumptions used in the calculations.

Solution:

Since $\Delta G = \Delta H - T\Delta S \implies -T\Delta S = \Delta G - \Delta H$

At 300 K:
$$-T\Delta S = (-33) - (-92) = +59 \text{ kJ mol}^{-1}$$

 $\Delta S = -(59 / 300)$
 $= -0.1966 \text{ kJ mol}^{-1} \text{ K}^{-1}$

At 750 K: $\Delta G_{750K} = \Delta H - T\Delta S$ = (-92) - (750)(-0.1966) = +55.5 kJ mol⁻¹

Since $\Delta G_{750K} > 0 \implies$ reaction is **not spontaneous** at 750 K.

Assumption: ΔH and ΔS do not change with temperature.

3.4 <u>Temperature at which a reaction becomes spontaneous</u>

This is the temperature at which a positive ΔG changes to a negative ΔG because of the changing magnitude of the term $-T\Delta S$.

We can find this particular temperature by setting $\Delta G < 0$ and solving for T:

$$\Delta H - T\Delta S < 0$$

$$\Rightarrow T\Delta S > \Delta H$$

$$\Rightarrow T > \frac{\Delta H}{\Delta S}$$

$$\Rightarrow T > \frac{\Delta H}{\Delta S}$$

Example 3.4.1

Calculate the temperature for the following reaction to become spontaneous:

 $Cu_2O(s) + C(s) \longrightarrow 2Cu(s) + CO(g)$ $\Delta H = +58.1 \text{ kJ mol}^{-1} \text{ and } \Delta S = +165 \text{ J mol}^{-1} \text{ K}^{-1}$

Solution:

For reaction to become spontaneous, $\Delta H - T\Delta S < 0$

$$\Rightarrow T > \frac{\Delta H}{\Delta S}$$
$$\Rightarrow T > \frac{58.1}{165 \times 10^{-3}}$$

> 352.1 K ≈ 352 K

The reaction becomes spontaneous at temperature above 352 K.

Note: State a specific value for temperature instead of giving it as a range or an inequality.

-END -