

CHAPTER 6: Chemical Energetics

6.1 Enthalpy Changes

6.2 Standard Enthalpy Changes

6.3 Hess' Law

6.4 Bond Energy

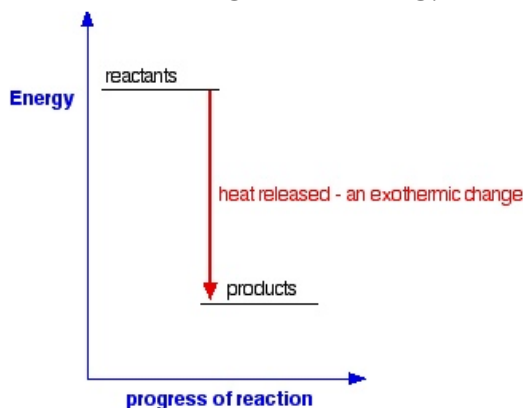
Learning outcomes:

- (a) explain that some chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH , negative) or endothermic.
- (b) explain and use the terms:
 - (i) enthalpy change of reaction and standard conditions, with particular reference to: formation, combustion, hydration, solution, neutralisation, atomisation.
 - (ii) bond energy (ΔH positive, i.e. bond breaking).
- (c) calculate enthalpy changes from appropriate experimental results, including the use of the relationship enthalpy change, $\Delta H = -mc\Delta T$.
- (d) apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:
 - (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion.
 - (ii) average bond energies.
- (e) construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy.

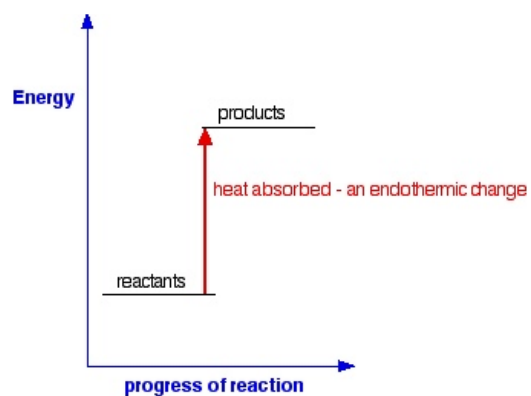
6.1 Enthalpy Changes

Exothermic and endothermic reactions

- 1) Most chemical reactions are accompanied by energy changes. Some absorb energy while some release it.
- 2) An *exothermic reaction* is a reaction that **releases energy** to the surroundings. Therefore the product contains **less** energy with respect to the reactants. The energy is released as heat energy, so the surroundings **warm up**.
- 3) An *endothermic reaction* is a reaction that **absorbs energy** from the surroundings. Therefore the products contain **more** energy with respect to the reactants. The energy is absorbed as heat energy, so the surroundings **cool down**.
- 4) An energy level diagram shows the relative energies of the products and reactants. The higher its energy, the higher its position.



An exothermic reaction



An endothermic reaction

- 5) i. Examples of exothermic reactions are neutralisation, combustion, dissolving anhydrous salts and the reaction between acids and metal carbonates.
ii. Examples of endothermic reactions are atomisation, photosynthesis, dissolving crystalline salts and thermal decomposition.

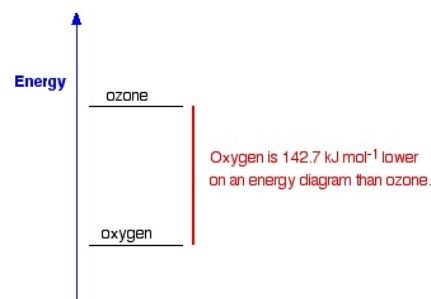
Enthalpy changes

- 1) *Enthalpy*, H is an indication of the total energy of a substance and it cannot be measured directly. However, enthalpy change, ΔH is measurable.

- 2) *Enthalpy change of a reaction*, ΔH is the heat change (heat is absorbed or evolved) when a chemical reaction takes place.
- 3) i. In exothermic reactions, the enthalpy change is **always negative**. ($\Delta H < 0$)
 ii. In endothermic reactions, the enthalpy change is **always positive**. ($\Delta H > 0$)

Energetic stability of a system

- 1) Exothermic reactions are more energetically favourable than endothermic ones because a system with lower energy content is more stable.
- 2) Thus, the more negative the ΔH value, the more stable the system is.
- 3) For example, oxygen, O_2 is energetically more stable than ozone, O_3 . Their relative positions on the energy level diagram are as follow:



- 4) But ozone does not convert to oxygen immediately in atmosphere, this is because ozone is **kinetically stable** although it is energetically unstable with respect to the products. The activation energy is not sufficient for the reaction to take place.

Measuring enthalpy changes

- 1) Enthalpy changes can be measured experimentally by measuring the temperature change as a reaction proceeds. Two common examples are measuring the enthalpy change of neutralisation and combustion.
- 2) The formulae:

Heat energy absorbed or released	$= mc\Delta T$
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where m = mass of substance (or solution) / g
 c = specific heat capacity of solution / $J\ g^{-1}\ ^\circ C^{-1}$
 (c is normally assumed to be $4.18\ J\ g^{-1}\ ^\circ C^{-1}$)
 ΔT = change in temperature / $^\circ C$

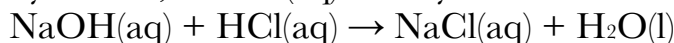
$\Delta H = \frac{\text{heat energy absorbed or released}}{\text{no. of moles of the limiting reagent}}$

Unit = $kJ\ mol^{-1}$

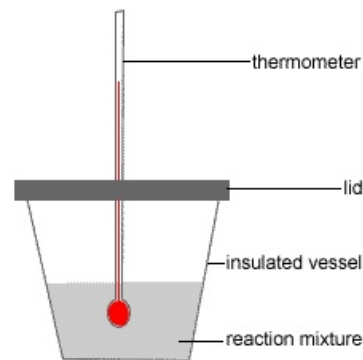
3) Assumptions made in this calculation:

- The density of all aqueous solution is 1 g cm^{-3} . Thus, numerically, $1 \text{ cm}^3 = 1 \text{ g}$.
- The solution has the same specific heat capacity as water ($4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$).

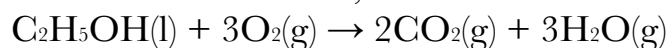
4) An example - to calculate the enthalpy change of the reaction between sodium hydroxide, NaOH(aq) and hydrochloric acid, HCl(aq) .



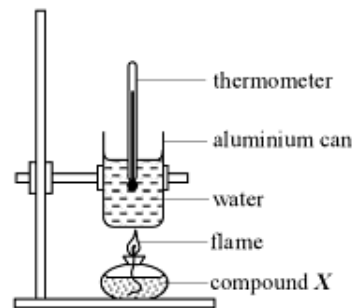
- Pour 25 cm^3 of NaOH into 25 cm^3 of HCl in a polystyrene cup (polystyrene cup is used because it is a good heat insulator). Both solutions have concentrations of 1.0 mol dm^{-3} .
- Measure the initial and maximum temperature reached.
- For example, the mean initial temperature of both solutions is $18.1 \text{ }^\circ\text{C}$ and the maximum temperature reached is $24.8 \text{ }^\circ\text{C}$. Then, $\Delta T = 6.7 \text{ }^\circ\text{C}$.
- Mass of both solutions is $(25+25) \times 1 = 50 \text{ g}$ since density = mass/volume.
- Therefore heat released = $50 \times 4.18 \times 6.7 = 1400 \text{ J} = 1.4 \text{ kJ}$
- Number of moles of water = 0.025 mol
- Therefore $\Delta H = -(1.4/0.025) = -56 \text{ kJ mol}^{-1}$



5) Another example - to calculate the enthalpy change of the reaction of combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}$.



- In this experiment, a spirit burner is used to combust the flammable liquid ethanol. The heat evolved is used to heat up the water, the maximum temperature reached is then measured.
- Mass of water = 250 g
Initial temperature of water = $19.5 \text{ }^\circ\text{C}$
Maximum temperature of water = $23.7 \text{ }^\circ\text{C}$
Initial mass of ethanol = 41.36 g
Final mass of ethanol = 41.18 g
- Therefore, $\Delta T = 4.2 \text{ }^\circ\text{C}$ and $m = 250 \text{ g}$.
- Heat released = $250 \times 4.18 \times 4.2 = 4389 \text{ J} = 4.389 \text{ kJ}$
- Number of moles of ethanol burned = $0.18/46 = 0.0039 \text{ mol}$
- Therefore $\Delta H = -(4.389/0.0039) = -1100 \text{ kJ mol}^{-1}$ (2 s.f)



6.2 Standard Enthalpy Changes

The standard condition

- 1) To make comparison of enthalpy changes a fair comparison, same conditions must be used. These are called the **standard conditions**:
 - A pressure of **100 kPa**(approximately atmospheric pressure).
 - A temperature of **298 K or 25 °C**.
 - Where solutions are involved, a concentration of **1.0 mol dm⁻³**.
 - Every substance involved must be in its **normal physical state** at 100 kPa and 298 K. For example, water is in liquid, not ice or steam.
 - If allotropes are involved, the allotrope which is more energetically stable is used. For example, for carbon, graphite is chosen over diamond because graphite is energetically more stable than diamond.
- 2) Standard enthalpy changes can be represented by the symbol ΔH° . This refers that the reaction is carried out under standard conditions. For example:

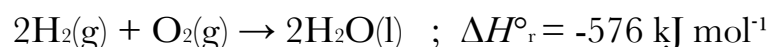


Various enthalpy changes

- 1) Enthalpy changes are described according to the type of reaction. Examples:
 - standard enthalpy change of reaction, ΔH°_r (in general)
 - standard enthalpy change of formation, ΔH°_f
 - standard enthalpy change of combustion, ΔH°_c
 - standard enthalpy change of neutralisation, ΔH°_n
 - standard enthalpy change of atomisation, $\Delta H^\circ_{\text{at}}$
 - standard enthalpy change of solution, $\Delta H^\circ_{\text{sol}}$
 - standard enthalpy change of hydration, $\Delta H^\circ_{\text{hyd}}$

Standard enthalpy change of reaction, ΔH°_r

- 1) *Standard enthalpy change of reaction*, ΔH°_r is the enthalpy change when the amount of reactants shown in the equation react to give products under standard condition. The reactants and products must be in their standard states.



- 2) The equation shows that 576 kJ of energy is released when two moles of hydrogen react with one mole of oxygen to give two moles of water.
- 3) This is a theoretical reaction, it does not happen in practice. The enthalpy change can be found by applying Hess' law.

Standard enthalpy change of formation, ΔH°_f

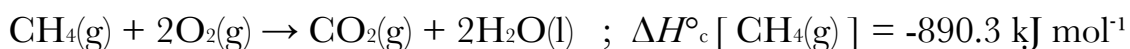
- 1) *Standard enthalpy change of formation, ΔH°_f* is the enthalpy change when one mole of a compound is formed from its elements under standard condition. The reactants and products must be in their standard states.



- 2) By definition, the standard enthalpy change of formation of an element is zero.
- 3) The standard enthalpy change of formation can be exothermic or endothermic.

Standard enthalpy change of combustion, ΔH°_c

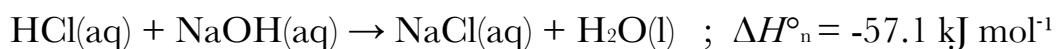
- 1) *Standard enthalpy change of combustion, ΔH°_c* is the enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions. The reactants and products must be in their standard states.



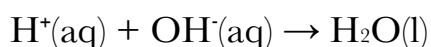
- 2) The standard enthalpy change of combustion is always exothermic.

Standard enthalpy change of neutralisation, ΔH°_n

- 1) *Standard enthalpy change of neutralisation, ΔH°_n* is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions.



- 2) For any acid-alkali reaction, the ionic equation is:



- 3) The enthalpy change of neutralisation between **strong acids and strong bases** is a constant(-57.1 kJ mol⁻¹). This is because all strong acids and strong bases dissociate completely in water to form aqueous ions.
- 4) So, neutralisation between strong acids and strong bases involves the same reaction, that is, H⁺ reacts with OH⁻ to form H₂O. The other ions present are just simply spectator ions. They do not take part in the reaction. Hence, the heat released is the same.
- 5) However, the enthalpy change of neutralisation between sulfuric acid and sodium hydroxide is more exothermic(-66.8 kJ mol⁻¹) than expected. This is because the enthalpy change of dilution of sulfuric acid is significant. When sulfuric acid is added to sodium hydroxide, the acid is diluted in the process and heat is released.
- 6) The enthalpy change of neutralisation involving **weak acids or weak bases** is less than 57.1 kJ mol⁻¹. For example:

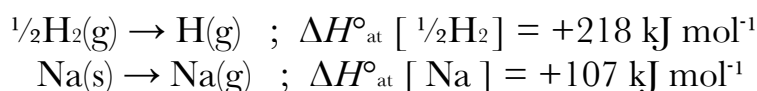
$$\text{CH}_3\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{COONa}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \quad ; \quad \Delta H^\circ_{\text{n}} = -56.1 \text{ kJ mol}^{-1}$$

$$\text{NaOH}(\text{aq}) + \text{HCN}(\text{aq}) \rightarrow \text{NaCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \quad ; \quad \Delta H^\circ_{\text{n}} = -11.7 \text{ kJ mol}^{-1}$$
- 7) This is because weak acids and weak bases only partially dissociated in water. For example:

$$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq}) \quad ; \quad \Delta H^\circ = \text{positive}$$
- 8) On addition of strong base such as NaOH, the OH⁻ ions react with H⁺ from the dissociation of CH₃COOH. The removal of H⁺ ions causes the position of equilibrium to shift to the right and more CH₃COOH molecules dissociate. However the dissociation of CH₃COOH is an endothermic process, hence, some energy is absorbed and the enthalpy change overall is less negative.
- 9) The standard enthalpy change of neutralisation is always exothermic.

Standard enthalpy change of atomisation, $\Delta H^\circ_{\text{at}}$

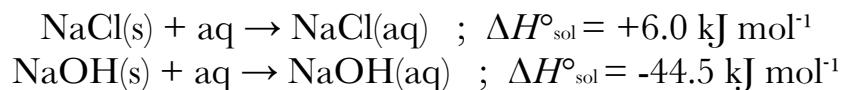
- 1) *Standard enthalpy change of atomisation, $\Delta H^\circ_{\text{at}}$* is the enthalpy change when one mole of gases atoms is formed from its element under standard conditions.



- 2) By definition, the standard enthalpy change of atomisation of the noble gases is zero because all of them exist as monoatomic gases at standard conditions.
- 3) The standard enthalpy change of atomisation of diatomic gases (example: O₂, Cl₂, N₂ and F₂) is equal to half the value of their bond energies.
- 4) The standard enthalpy change of atomisation is always endothermic.

Standard enthalpy change of solution, $\Delta H^\circ_{\text{sol}}$

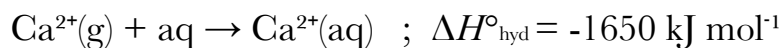
- 1) *Standard enthalpy change of solution*, $\Delta H^\circ_{\text{sol}}$ is the enthalpy change when one mole of solute is dissolved in a solvent to form an infinitely dilute solution under standard conditions.



- 2) An infinitely dilute solution is one which does not produce any further enthalpy change when more solvent is added.
- 3) The standard enthalpy change of solution can be exothermic or endothermic.

Standard enthalpy change of hydration, $\Delta H^\circ_{\text{hyd}}$

- 1) *Standard enthalpy change of hydration*, $\Delta H^\circ_{\text{hyd}}$ is the enthalpy change when one mole of gases ions dissolves in water to form hydrated ions of infinite dilution under standard conditions.



- 2) Water is a polar molecule, this means that it has a negative end and a positive end. The negative end of the water molecule will be attracted to the cations while the positive end of the water molecule will be attracted to the anions.
- 3) The attraction set up is called the ion-dipole forces.
- 4) The standard enthalpy change of hydration is always exothermic.

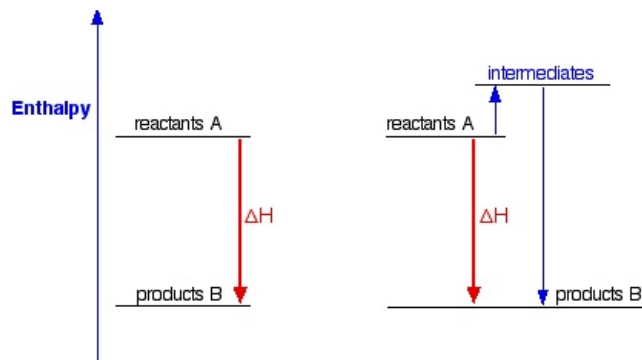
6.3 Hess' Law

Hess' law and Hess' cycle

- 1) *Hess' law* states that the total enthalpy change in a chemical reaction is independent of the route which the reaction takes place as long as the initial and final conditions are the same.
- 2) For example, the enthalpy change of reaction from **A** to **C** is the same whether the reaction takes place in one stage(**A** to **C**) or two stages(**A** to **B** then to **C**).



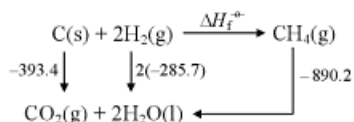
- 3) This is because the enthalpy change of a chemical reaction depends only on the difference between enthalpy of the products and the reactants. It does not depend on how the reaction took place.



- 4) Hess' law is useful to calculate enthalpy changes that cannot be measured directly from experiments(theoretical reactions that will not occur under standard conditions).
- 5) Steps to construct a Hess' cycle:
 - i. Write down the equation for the enthalpy change that you are asked to find and write ΔH on top of the arrow.
 - ii. Use the information that you have been given to complete a cycle.
 - iii. Find the direct route and indirect route. The routes should not go against any arrows. (Equations may be reversed when necessary, but do not forget to reverse the sign as well.)
 - iv. Apply Hess' law and form an equation to solve for ΔH .

6) Examples:

- 1: To calculate the standard enthalpy change of formation of CH_4 given that the standard enthalpies change of combustion of methane, graphite and hydrogen are $-890.2 \text{ kJ mol}^{-1}$, $-393.4 \text{ kJ mol}^{-1}$ and $-285.7 \text{ kJ mol}^{-1}$ respectively.



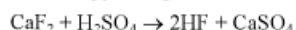
Alternatively,

$$\begin{aligned}
 \Delta H &= \Sigma \Delta H_c(\text{reactants}) - \Sigma \Delta H_c(\text{products}) \\
 &= -393.4 + 2(-285.7) - (-890.2) \\
 &= -74.6 \text{ kJ mol}^{-1}
 \end{aligned}$$

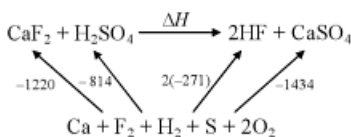
By Hess' Law,

$$\begin{aligned}
 \Delta H_f^\circ &= -393.4 + 2(-285.7) - (-890.2) \\
 &= -74.6 \text{ kJ mol}^{-1}
 \end{aligned}$$

- 2: To calculate the enthalpy change for the reaction:



given that the enthalpies change of formation of CaF_2 , H_2SO_4 , HF and CaSO_4 are $-1220 \text{ kJ mol}^{-1}$, -814 kJ mol^{-1} , -271 kJ mol^{-1} and $-1434 \text{ kJ mol}^{-1}$ respectively.



Alternatively,

$$\begin{aligned}
 \Delta H &= \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants}) \\
 &= 2(-271) + (-1434) - (-1220) - (-814) \\
 &= +58 \text{ kJ mol}^{-1}
 \end{aligned}$$

By Hess' Law,

$$\begin{aligned}
 \Delta H &= 2(-271) + (-1434) - (-1220) - (-814) \\
 &= +58 \text{ kJ mol}^{-1}
 \end{aligned}$$

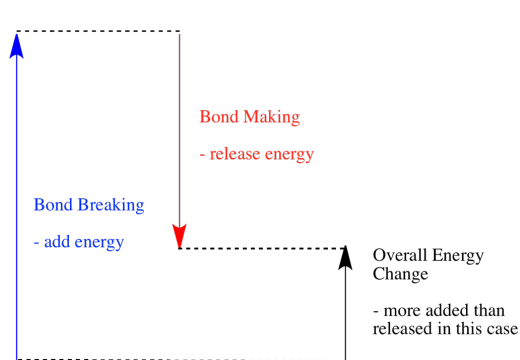
6.4 Bond Energy

Bond breaking and bond forming

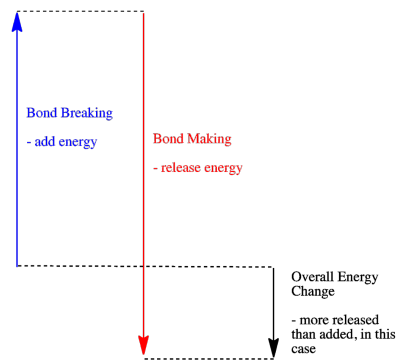
- 1) i. Breaking bonds needs energy, energy is absorbed from the surroundings. Therefore, bond breaking is an endothermic process.
 - ii. Forming bonds releases energy to the surroundings. Therefore, bond forming is an exothermic process.

- 2) i. If the energy needed to break bonds is **less than** the energy released when new bonds are formed, then the reaction will be exothermic
 - ii. If the energy needed to break bonds is **more than** the energy released when new bonds are formed, then the reaction will be endothermic.

- 3) In most chemical reactions, bonds have to be broken first and then reformed into a new compound.



An endothermic reaction



An exothermic reaction

Bond energy

- 1) *Bond energy*, E is the energy needed to break one mole of covalent bonds between two atoms in the gaseous state.



- 2) Bond energy is often called bond enthalpy or bond dissociation energy.

Average bond energy

- 1) Bond energy is often affected by the presence of other atoms in the molecule. For example, the O-H bond in water has a different bond energy value than the O-H bond in ethanol. Even in the same molecule, for example, CH_4 , the energy needed to break all the C-H bonds are not identical.
- 2) Therefore, bond energies are taken from a number of bonds of the same type from different environment and average out to get the **average bond energy**. The values are not always accurate.

Bond	Energy / kJ mol^{-1}
H—H	436
D—D	442
N=N	944
O=O	496
P=P	485
S=S	425
F—F	158
Cl—Cl	242
Br—Br	193
I—I	151

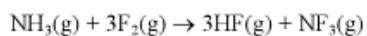
Bond	Energy / kJ mol^{-1}
C—H	410
C—Cl	340
C—Br	280
C—I	240
C—N	305
C=N	610
C≡N	890
C—O	360
C=O	740
C=O in CO_2	805

Hess' law involving average bond energy

1) Average bond energies can also be used to estimate enthalpy changes of reactions involving covalent molecules

2) Example:

e.g. Ammonia and fluorine reacts as follows:



Given average bond energies / kJ mol^{-1} :

$$\text{N-H} = 390; \text{F-F} = 158; \text{H-F} = 562; \text{N-F} = 272$$

By considering the bonds broken and the bonds formed, the value of ΔH^\ominus for this reaction could be calculated as follows:

<u>bonds broken</u>	(endothermic)	<u>bonds formed</u>	(exothermic)
3 N-H	3(+390)	3 H-F	3(-562)
3 F-F	3(+158)	3 N-F	3(-272)

$$\begin{aligned}\therefore \Delta H^\ominus &= 3(+390) + 3(+158) + 3(-562) + 3(-272) \\ &= -858 \text{ kJ mol}^{-1}\end{aligned}$$

3) If the given reactants or products are not in the gaseous state, **enthalpy change of vaporisation** or **enthalpy change of fusion** must be considered because the non-gaseous compounds needed to be converted to the gaseous state. Changing from other states to the gaseous state needs to absorb extra energy.