

## 5.3

### Bond enthalpies

#### Understandings:

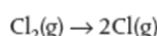
- Bond forming releases energy and bond breaking requires energy.
- Average bond enthalpy is the energy needed to break one mole of a bond in a gaseous molecule averaged over similar compounds.

#### Applications and skills:

- Calculation of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values.

## Breaking bonds is an endothermic process

The energy change, for example, during the formation of two moles of chlorine atoms from one mole of chlorine molecules can be represented as:



$$\Delta H^\ominus = +242 \text{ kJ mol}^{-1}$$

The situation is complicated in molecules which contain more than two atoms.

Breaking the first O–H bond in a water molecule requires more heat energy than breaking the second bond:

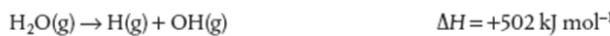


$$\Delta H^\ominus = +502 \text{ kJ mol}^{-1}$$



$$\Delta H^\ominus = +427 \text{ kJ mol}^{-1}$$

Similarly the energy needed to break the O–H in other molecules such as ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is different. In order to compare bond enthalpies which exist in different environments, **average bond enthalpies** are tabulated.



$$\begin{aligned} \text{Average bond enthalpy } E(\text{O–H}) &= \frac{+502 + 427}{2} \text{ kJ mol}^{-1} \\ &= \frac{929}{2} \\ &= 464.5 \text{ kJ mol}^{-1} \end{aligned}$$

#### 11. Bond enthalpies and average bond enthalpies at 298 K

##### Single bonds ( $\text{kJ mol}^{-1}$ )

	Br	C	Cl	F	H	I	N	O	P	S	Si
Br	193	285	219	249	366	178		201	264	218	330
C	285	346	324	492	414	228	286	358	264	289	307
Cl	219	324	242	255	431	211	192	206	322	271	400
F	249	492	255	159	567	280	278	191	490	327	597
H	366	414	431	567	436	298	391	463	322	364	323
I	178	228	211	280	298	151		201	184		234
N		286	192	278	391		158	214			
O	201	358	206	191	463	201	214	144	363		466
P	264	264	322	490	322	184		363	198		
S	218	289	271	327	364				266	293	
Si	330	307	400	597	323	234		466		293	226

##### Multiple bonds ( $\text{kJ mol}^{-1}$ )

C=C 614	C≡N 890	N≡N 945
C≡C 839	C=O 804	N=O 587
C=C (in benzene) 507	C=S 536	O=O 498
C=N 615	N=N 470	S=S 429

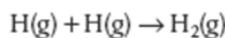


The average bond enthalpy is the energy needed to break one mole of bonds in gaseous molecules under standard conditions averaged over similar compounds.

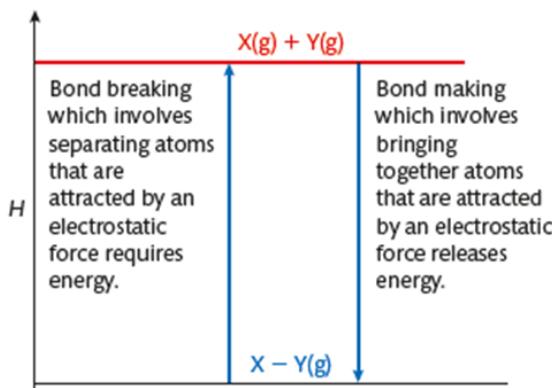


## Making bonds is an exothermic process

The same amount of energy is absorbed when a bond is broken as is given out when a bond is made (Figure 5.16). For example:



$$\Delta H^\ominus = -436 \text{ kJ mol}^{-1}$$



### Exercises

**29** Which of the following processes are endothermic?

- I  $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(g)}$
- II  $\text{CO}_2\text{(g)} \rightarrow \text{CO}_2\text{(s)}$
- III  $\text{O}_2\text{(g)} \rightarrow 2\text{O(g)}$

- A** I and II only      **B** I and III only      **C** II and III only      **D** I, II, and III

**30** Identify the equation which represents the bond enthalpy for the H-Cl bond.

- A  $\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl(g)}$
- B  $\text{HCl(g)} \rightarrow \frac{1}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{Cl}_2\text{(g)}$
- C  $\text{HCl(g)} \rightarrow \text{H}^+(\text{g}) + \text{Cl}^-(\text{g})$
- D  $\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

**31** Which of the following processes are endothermic?

- I  $\text{CO}_2\text{(g)} \rightarrow \text{CO}_2\text{(s)}$
- II  $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(g)}$
- III  $\text{O}_2\text{(g)} \rightarrow 2\text{O(g)}$

- A** I and II only      **B** I and III only      **C** II and III only      **D** I, II, and III

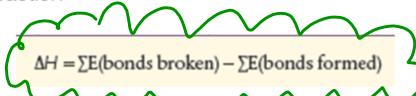
**32** Identify the bonds which are broken in the following process.



29 B      30 A      31 C

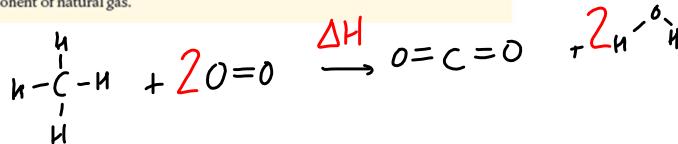
32  $1 \times \text{C-C} + 6 \times \text{C-H}$

Using bond enthalpies to calculate the enthalpy changes of reaction



**Worked example**

Use bond enthalpies to calculate the heat of combustion of methane, the principal component of natural gas.



Bonds broken	$\Delta H / \text{kJ mol}^{-1}$ (endothermic)	Bonds formed	$\Delta H / \text{kJ mol}^{-1}$ (exothermic)
4 C-H	4 (+414)	2 C=O	2 (-804)
2 O=O	2 (+498)	4 O-H	4 (-463)
Total	= +2652		= +3460

$$\Delta H = \sum E(\text{bonds broken}) - \sum E(\text{bonds formed})$$

$$\Delta H^\circ = +2652 + (-3460) \text{ kJ mol}^{-1} = -808 \text{ kJ mol}^{-1}$$

The value calculated from the bond enthalpies should be compared with the experimental value of  $-891 \text{ kJ mol}^{-1}$  measured under standard conditions given in section 13 of the IB data booklet. The values are different because the standard state of water is liquid and the bond enthalpy calculation assumes that the reaction occurs in the gaseous state. The use of average bond enthalpies is an additional approximation.

**Exercises**

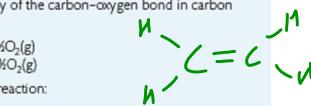
33 Which of the following is equivalent to the bond enthalpy of the carbon-oxygen bond in carbon monoxide?

- A  $\text{CO(g)} \rightarrow \text{C(s)} + \text{O(g)}$       C  $\text{CO(g)} \rightarrow \text{C(s)} + \text{CO}_2\text{(g)}$   
 B  $\text{CO(g)} \rightarrow \text{C(g)} + \text{O(g)}$       D  $\text{CO(g)} \rightarrow \text{C(g)} + \text{CO}_2\text{(g)}$

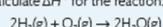
34 Use the bond enthalpies below to calculate  $\Delta H^\circ$  for the reaction:



Bond	Bond enthalpy / $\text{kJ mol}^{-1}$
C-C	+347
C=C	+612
H-H	+436
C-H	+413



35 Use the bond enthalpies below to calculate  $\Delta H^\circ$  for the reaction:

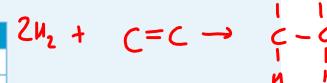


Bond	Bond enthalpy / $\text{kJ mol}^{-1}$
O=O	+498
H-H	+436
O-H	+464

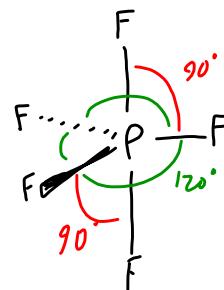
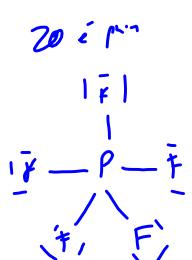


36 The hydrogenation of the alkene double bond in unsaturated oils is an important reaction in margarine production. Calculate the enthalpy change when one mole of C=C bonds is hydrogenated from the bond energy data shown.

Bond	Bond enthalpy / $\text{kJ mol}^{-1}$
H-H	436
C-C	347
C-H	412
C=C	612

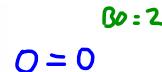


- A  $-224 \text{ kJ mol}^{-1}$       B  $-123 \text{ kJ mol}^{-1}$       C  $+123 \text{ kJ mol}^{-1}$       D  $+224 \text{ kJ mol}^{-1}$



**The bonds in oxygen and ozone are broken by UV of different wavelengths**

The bonds in oxygen and ozone are both broken when they absorb UV radiation of sufficient energy. The double bond in O<sub>2</sub> is stronger than the 1.5 bond in ozone and so is broken by radiation of higher energy and shorter wavelengths.



$$BO = 1\frac{1}{2}$$

We can use bond enthalpy information to calculate the wavelength of light needed to break that bond. To do this we must consider:

- That one photon is required to break one bond so 1 mole of photons will be required to break one mole of bonds.
- We can relate  $E = h\nu$  and  $c = \nu\lambda$   $\nu = \frac{c}{\lambda} \Rightarrow E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$

**Worked example**

The bond energy in ozone is 363 kJ mol<sup>-1</sup>. Calculate the wavelength of UV radiation needed to break the bond.

**Solution**

One mole of photons are needed to break one mole of bonds. The energy of a mole of photons is the energy of one photon multiplied by Avogadro's number (L) (page 15).

$$N_A$$

$$L \times E_{\text{photon}} = 363 \text{ kJ} = 363000 \text{ J}$$

$$E_{\text{photon}} = \frac{363000}{6.02 \times 10^{23}} \text{ J}$$

$$\begin{aligned} \lambda &= \frac{hc}{E_{\text{photon}}} \\ &= 6.63 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ ms}^{-1} \times \frac{6.02 \times 10^{23}}{363000} \text{ J}^{-1} \\ &= 3.30 \times 10^{-7} \text{ m} \\ &= 330 \text{ nm} \end{aligned}$$

Any radiation in the UV region with a wavelength smaller than 330 nm breaks the bond in ozone.

Do the same for the wavelength of light required to break a O=O. Data - Bond enthalpy 498 kJ/mol

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ Js} \\ c &= 3.00 \times 10^8 \text{ ms}^{-1} \end{aligned}$$

$$\begin{aligned} 40 \quad L \times E_{\text{photon}} &= 498 \text{ kJ} = 498000 \text{ J} \\ E_{\text{photon}} &= \frac{498000}{6.02 \times 10^{23}} \text{ J} (= 8.272 \times 10^{-19} \text{ J}) \\ \lambda &= hc/E_{\text{photon}} \\ &= 6.63 \times 10^{-34} \times 3.00 \times 10^8 \times \frac{6.02 \times 10^{23}}{498000} \\ &= 2.41 \times 10^{-7} \text{ m} \\ &= 241 \text{ nm} \end{aligned}$$

Any radiation in the UV region with a wavelength shorter than 241 nm breaks the O=O bond in oxygen.

**Exercises**

39 The concentration of ozone in the upper atmosphere is maintained by the following reactions.

- O<sub>2</sub> → 2O<sup>•</sup>
- O<sub>2</sub> + O<sup>•</sup> → O<sub>3</sub>
- O<sub>3</sub> → O<sub>2</sub> + O<sup>•</sup>

The presence of chlorofluorocarbons (CFCs) in the upper atmosphere has led to a reduction in ozone concentration.

- Identify the step which is exothermic.
- Identify with reference to the bonding in O<sub>2</sub> and O<sub>3</sub>, the most endothermic step.

40 Use section 11 of the IB data booklet to calculate the minimum wavelength of radiation needed to break the O=O double bond in O<sub>2</sub>.

41 Explain why ozone can be decomposed by light with a longer wavelength than that required to decompose oxygen.

137    35.5    1    16

9. Una muestra de 7,33 gramos de  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  se disuelve en agua, y se le añade una disolución de ácido sulfúrico con una riqueza del 60 % en peso y una densidad de 1,5 g/mL. Si la reacción que tiene lugar es:



Calcular: a) la molaridad de la disolución de ácido sulfúrico, y b) el volumen, en mL, de la disolución de ácido sulfúrico que es necesario añadir para que reaccione todo el bario contenido en la muestra.

(Extremadura, 2008)

$$\text{Molaridad} = \frac{\text{mol}}{\text{L}}$$

a.  $1.5 \frac{\cancel{g}}{\cancel{\text{mL}}} \cdot \frac{60}{100} \cdot \frac{1000 \cancel{\text{mL}}}{1 \text{ L}} \cdot \frac{1 \text{ mol}}{98 \cancel{g}} = 9.18 \frac{\text{mol}}{\text{L}}$

b.  $M_{\text{BaCl}_2 \cdot 2\text{H}_2\text{O}} = 244 \frac{\text{g}}{\text{mol}}$       Moles =  $\frac{7.33 \text{ g}}{244 \text{ g/mol}} = 0.030$   
 ↓ moles  
 Same no. of  $\text{H}_2\text{SO}_4$

$$\text{Conc} = \frac{\text{mol}}{\text{Vol}} \quad \text{Vol} = \frac{\text{mol}}{\text{Conc}} = \frac{0.030}{9.18} = 0.00326 \frac{\text{L}}{\text{L}} = 3.26 \text{ mL}$$

10.

En el lanzamiento de naves espaciales se emplea como combustible hidracina,  $\text{N}_2\text{H}_4$ , y como comburente peróxido de hidrógeno,  $\text{H}_2\text{O}_2$ . Estos dos reactivos arden por simple contacto según:



$$\begin{array}{l} \text{N} - 14 \\ \text{H} - 1 \\ \text{O} - 16 \end{array}$$

Los tanques de una nave llevan 15 000 kg de  $\text{N}_2\text{H}_4$  y 20 000 kg de  $\text{H}_2\text{O}_2$ .

a) ¿Sobrará algún reactivo? Y si sobra, ¿en qué cantidad?

b) ¿Qué volumen de nitrógeno se obtendrá en c.n.?  $P: 1 \text{ atm}$   $T = 298 \text{ K}$   
(Andalucía. 2007)

$$R = 0.082$$

$$\text{Moles } \text{N}_2\text{H}_4 = 15000 \text{ kg} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol}}{32 \text{ g}} = \frac{468750 \text{ mol}}{1} = " "$$

$$\text{Moles } \text{H}_2\text{O}_2 = 20000 \text{ kg} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol}}{34 \text{ g}} = \frac{588235 \text{ mol}}{2} = 294117.5 \text{ mol}$$

(Limiting)



1	:	2
$x$	:	588235

$$x = 294117.5$$

$$468750 - 294117.5 = 174632.5 \text{ mol}$$