* Bond energies and Resonance :—

Agreement between the calculated value of enthalpy of formation obtained by using the bond-enthalpy concept and any other method is usually good. But for compounds involving alternate single and double bonds, however, large deviations are observed. Eg,

$$C_6H_6\,(g) \longrightarrow 6\,C\,(g) + 6\,H(g)$$

$$\Delta H^\circ = 5368.5\ KJ$$

on the basis bond enthalpy (energy), it is found that,

$$3\epsilon_{C-C} + 3\epsilon_{C=C} + 6\epsilon_{C-H}$$

$$= (3 \times 347.7\ KJ) + (3 \times 615.1\ KJ) + (6 \times 413.4\ KJ)$$

$$= 5368.5\ KJ$$

of course, the experimental result shows the value is, 5535.1 KJ.

This amounts to the fact that

benzene is more stable by 166'6 KJ/mole
This is due to Resonance. That is in benzene there is no localisation of single and double bonds but the molecule is resonating from one extreme to another.

* Calculation of Bond-energy :—

The Knowledge of heats of formation of a substance and the heat of atomisation of the Constituent's enables us to evaluate the bond energy

(I) C–H bond energy — From the following thermochemical data find out the C–H bond energy. given,

(a) $C(s) + 2H_2(g) = CH_4$; $\Delta H_f = -17'9$ KCal

(b) $C(s) = C(g)$; $\Delta H = 170'9$ KCal

(c) $2H_2(g) = 4H(g)$; $\Delta H = 4 \times 52'1$ KCal

Rearranging eqn. (a) ⇒

(d) $CH_4 = C(s) + 2H_2(g)$; $\Delta H = 17'9$ K.Cal

Adding equ^n. (b), (c) & (d) $\Rightarrow$

$$\cancel{C(s)} = C(g) \;;\; \Delta H = 170.9 \text{ K.Cal}$$

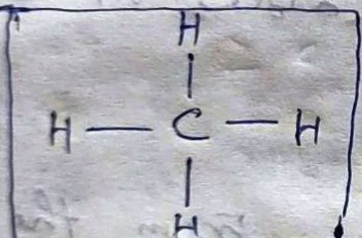
$$\cancel{2H_2(g)} = 4H(g) \;;\; \Delta H = 208.4 \text{ K.Cal}$$

$$CH_4 = \cancel{C(s)} + \cancel{2H_2(g)} \;;\; \Delta H = 17.9 \text{ K.Cal}$$

$$CH_4 = C(g) + 4H(g) \;;\; \Delta H = 397.2 \text{ K.Cal}$$

$\therefore$ the energy required for breaking up four C–H bonds = 397.2 K.Cal

ie. C–H bond energy $= \frac{1}{4} \times 397.2$ K.Cal



= 99 K.Cal.

(II) C–C bond energy :– From the following thermo-chemical data find out the C–C bond energy, given,

(a) $2C(s) + 3H_2(g) = C_2H_6(g) \;;\; \Delta H_f = -20.3$ K.Cal

(b) $2C(s) = 2C(g) \;;\; \Delta H = 2 \times 170.9$ K.Cal.

(c) $3H_2(g) = 6H(g) \;;\; \Delta H = 6 \times 52.1$ K.Cal

Rearranging equ^n. (a) $\rightarrow$

(d) $C_2H_6(g) = 2C(s) + 3H_2(g) \;;\; \Delta H = 20.3$ K.Cal

Adding eqn. (b), (c) & (d) ⇒

$2C(s) = 2C(g)$; $\Delta H = 341.8$ K. Cal.

$3H_2(g) = 6H(g)$; $\Delta H = 312.6$ K. Cal.

$C_2H_6(g) = 2C(s) + 3H_2(g)$; $\Delta H = 20.3$ K. Cal

$C_2H_6(g) = 2C(g) + 6H(g)$; $\Delta H = 674.7$ K. Cal

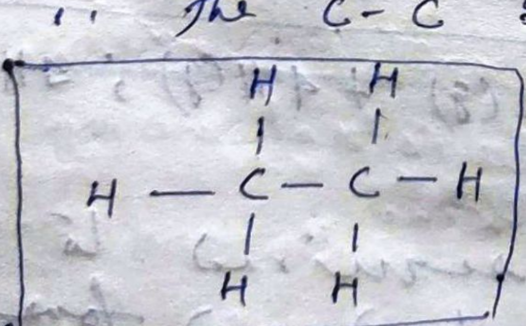
∴ the energy required for breaking up one C − C and six C − H bonds = 674.7 K. Cal.

We have, the bond energy of six C − H bonds

= 6 × 99 K. Cal.

= 594 K. Cal.

∴ The C − C bond energy = (674.7 − 594) K. Cal.



= 81 K. Cal. #

(III) C = C bond energy :— From the following thermo-chemical data, find out the C = C bond energy, given

(a) $2C(s) + 2H_2(g) = C_2H_4(g)$; $\Delta H_f = 12.5$ K.Cal

(b) $2C(s) = 2C(g)$; $\Delta H = 2 \times 170.9$ K.Cal

(c) $2H_2(g) = 4H(g)$; $\Delta H = 4 \times 52.1$ K.Cal

Rearranging the eqn. (a) ⇒

(d) $C_2H_4(g) = 2C(s) + 2H_2(g)$; $\Delta H = -12.5$ K.Cal

Adding, eqn. (b), (c) & (d) ⇒

$\cancel{2C(s)} = 2C(g)$; $\Delta H = 341.8$ K.Cal

$\cancel{2H_2(g)} = 4H(g)$; $\Delta H = 208.4$ K.Cal

$C_2H_4(g) = \cancel{2C(s)} + \cancel{2H_2(g)}$; $\Delta H = -12.5$ K.Cal

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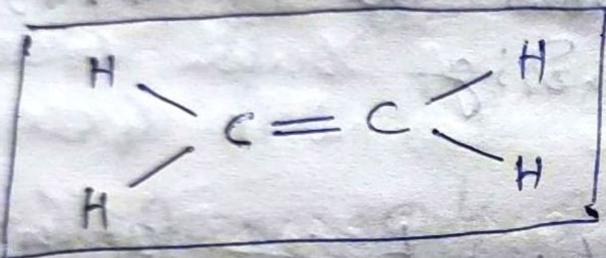
$C_2H_4(g) = 2C(g) + 4H(g)$; $\Delta H = 537.7$ K.Cal

∴ The energy required to breaking up one C = C bond and four C—H bonds = 537.7 K. Cal.

We have the bond energy of four C - H bond $= 4 \times 99$ K. Cal.

$= 396$ K. Cal.

∴ The C = C bond energy $= (537.7 - 396.0)$ K. Cal.



$= 141.7$ K. Cal.

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Note:

The bond energy (ϵ) of triple or double bonds is larger than that of the single bond. The bond energy ratio is,

$$\epsilon_{C-C} : \epsilon_{C=C} : \epsilon_{C \equiv C} = 1 : 1.77 : 2.48$$

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