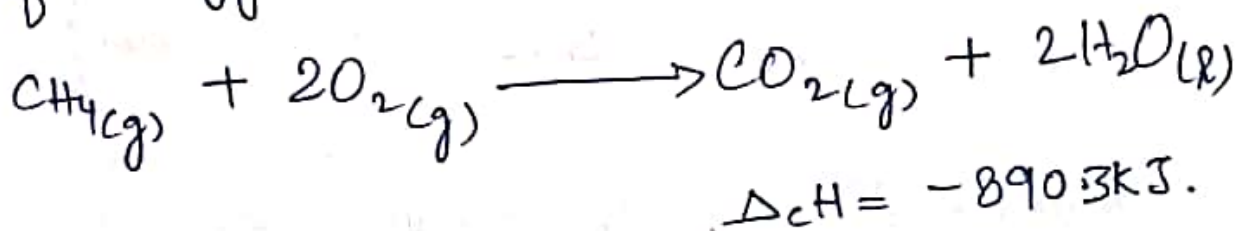


Calorific value of foods and fuels: The amount of <sup>(43)</sup>

heat produced in Calories (or joules) when one gram of a substance (food or fuel) is completely burnt. The calorific value is usually expressed in K.Cal per gram or Kilojoules per gram ( $1 \text{ kcal} = 4.184 \text{ kJ}$ )

For example, when methane burns,  $890.3 \text{ kJ mol}^{-1}$  of energy is liberated as.



Therefore, calorific value of methane is:

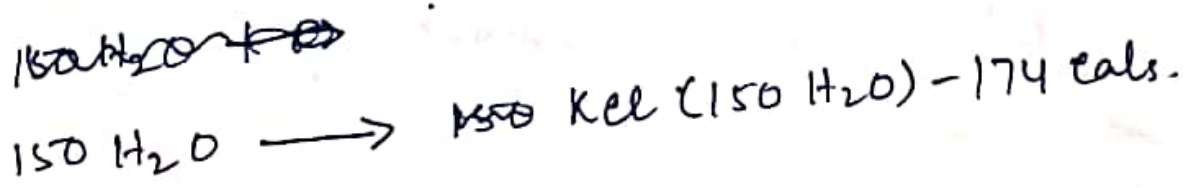
$$\text{Heat produced per gram} = \frac{890.3}{16} = 55.6 \text{ kJ}$$

(Molar Mass of  $\text{CH}_4 = 16$ )

Calorific values of some common fuels and foods

S.No.	Substance	Ca'	Calorific value (kJ/g)
1.	Hydrogen (fuel)		150
2.	Methane (fuel)		55
3.	Butane (LPG) (fuel)		55
4.	Butter (food)		30.4
5.	Rice (food)		14.5
6.	Meat		12.0

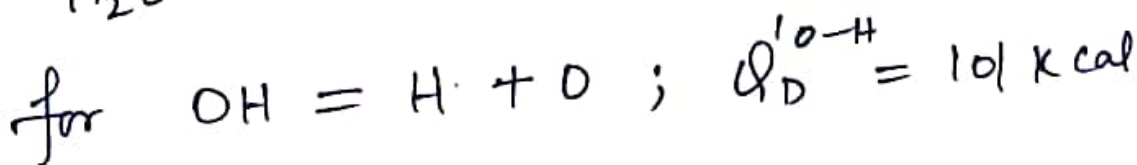
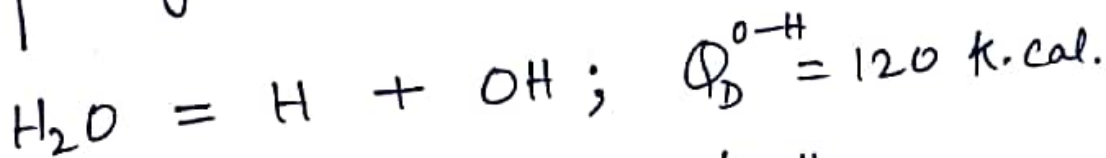
By subtraction,  ~~$KCl(s) + 150 H_2O \rightarrow 150 KCl(150 H_2O) - 174$~~  of eq ① from ~~150 H<sub>2</sub>O~~  
 we get for KCl



ie. KCl (50 H<sub>2</sub>O) to  $\frac{1}{4}$ th its conc., ie. -174 cal of heat would be absorbed.

Bond Energy <sup>and</sup> Bond dissociation energy: It is defined as the average amount of energy required to dissociate bonds of that type present in one molecule of the compound.

for ex. in H<sub>2</sub>O, dissociation energy of separating a H-atom is 120 k.cal, ie.



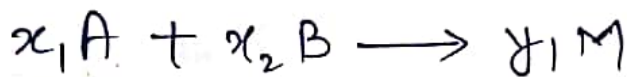
$$Q_D + Q_D = \frac{120 + 101}{2} = 110.5 \text{ k.cal}$$

This average of dissociating energies are is equal to the bond ~~dis~~ energy (AHD)

Variation of Enthalpy of reaction with temperature  
 i.e., Kirchoff's equation: Enthalpy of reaction, in

general, varies with temperature and its variation with temperature can be deduced as follows:

Let  $x_1$  moles of substance A react with  $x_2$  moles of B to form  $y_1$  moles of M, at a constant temperature, each substance being in a certain specific state. Thus,



The enthalpy of the reactants ( $H_1$ ) is given by,

$$H_1 = x_1 H_A + x_2 H_B$$

The enthalpy of the products ( $H_2$ ) is given by,

$$H_2 = y_1 H_M$$

The increase in enthalpy ( $\Delta H$ ) for the change at constant pressure is,

$$\Delta H = H_2 - H_1 = y_1 \boxed{H_M} - x_1 \boxed{H_A} - x_2 \boxed{H_B} \quad \text{--- ①}$$

Similarly, the increase in internal energy ( $\Delta E$ ) at constant volume is,

$$\Delta E = E_2 - E_1 = y_1 E_M - x_1 E_A - x_2 E_B \quad \text{--- ②}$$



where 'E' terms represent the respective internal energy.

Differentiating eq. (1) with respect to temperature at constant pressure and eq. differentiating eq. (2)

w.r.t temperature at constant volume, we get,

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = y_1 \left( \frac{\partial H_M}{\partial T} \right)_P - x_1 \left( \frac{\partial H_A}{\partial T} \right)_P - x_2 \left( \frac{\partial H_B}{\partial T} \right)_P \quad (3)$$

$$\left[ \frac{\partial(\Delta E)}{\partial T} \right]_V = y_1 \left( \frac{\partial E_M}{\partial T} \right)_V - x_1 \left( \frac{\partial E_A}{\partial T} \right)_V - x_2 \left( \frac{\partial E_B}{\partial T} \right)_V \quad (4)$$

We know that,

$$C_p = \left( \frac{\partial H}{\partial T} \right)_P \quad \& \quad C_v = \left( \frac{\partial E}{\partial T} \right)_V$$

$\therefore$  eq. (3) & eq. (4) reduces to

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = y_1 (C_p)_M - x_1 (C_p)_A - x_2 (C_p)_B = \Delta C_p \quad (5)$$

$$\left[ \frac{\partial(\Delta E)}{\partial T} \right]_V = y_1 (C_v)_M - x_1 (C_v)_A - x_2 (C_v)_B = \Delta C_v \quad (6)$$

where,  $\Delta C_p$  and  $\Delta C_v$  refer to overall changes in heat capacities in the reaction,

i.e., refer to their algebraic sum. Expressions

(5) & (6) are mathematical forms of Kirchoff's

and represents that variations of heat content and internal energy of the reactants & products with temperature.

Integrating eq. (5) & (6) between proper limits, we have,

$$\int_{H_1}^{H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

Assuming  $\Delta C_p$  to be independent of temperature, we get. ~~eqn (7)~~  $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$  — (7)

Where  $\Delta H_2$  and  $\Delta H_1$  are the enthalpies of reaction at constant pressure at temperature  $T_2$  &  $T_1$ , respectively.

Integrating equation (6) between proper limits, we get.

$$\int_{E_1}^{E_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_v \cdot dT$$

$$\Delta E = \Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \cdot dT$$

Assuming  $\Delta C_v$  to be independent of temperature, we get  $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$  — (8)

where  $\Delta E_2$  and  $\Delta E_1$  are the enthalpies of reaction at constant volume, at temperature  $T_2$  and  $T_1$ , respectively.

Kirchoff's law is valid for physical and chemical changes and is independent of nature of and complexity of the systems.