

* Molecular Volume :-

Molecular volume of a substance is the volume in cm³ occupied by 1 gram molecule of the substance.

Thus,

$$\text{Molecular volume} = \frac{\text{Molecular weight}}{\text{density}}$$

* Kopp's Law :-

H. Kopp's studied the molecular volume of a large number of organic compounds at their boiling points and observed certain regularities in the results as follows -

- 1). Isomers belongs to the same homologous series had nearly equal molecular volume.
- 2). Any two successive members of the same homologous series of organic compounds differ in their molecular volume by about the same amount.

Kopp's deduced the values for the contribution of various elements to the molecular volume of substances and enunciated the following law known as Kopp's law.

A/c to this law :-

"Molecular volume of a liquid is the sum of the atomic volumes of the atoms constituting its molecules".

Let us take an example liquid Paraffin. (C_nH_{2n+2}).

The molecular volume of $-CH_2 = 22.0 \text{ cm}^3$.

H = 5.5 cm^3 .

$$\begin{aligned} \therefore \text{Molecular volume of } C_nH_{2n+2} &= n \times V_{CH_2} + 2V_H \text{ atoms} \\ &= n \times 22.0 + 2 \times 5.5 \end{aligned}$$

From the values of molecular volumes of a number of liquid paraffins, Kopp's found that the mean value of H-atoms is 5.5 cm^3 .

Hence, In $-CH_2$ groups, the molecular volume of C-atom is —

$$CH_2 = C \times 1 + 2 \times 5.5 \text{ cm}^3.$$

$$22.0 \text{ cm}^3 = C + 11.0 \text{ cm}^3$$

$$C = (22.0 - 11.0) \text{ cm}^3$$

$$C = 11.0 \text{ cm}^3.$$

With these known values, it is a simple matter to determine the values for other elements.

From,
Dr. A.K. Gupta,
chemistry (U.S. College)

* PARACHOR :-

Macleod showed an interesting relationship between the surface tension (γ) and density (ρ) for normal liquid by the following equation :-

$$\gamma = C(\rho - \rho')^4 \quad \text{--- (1)}$$

where ρ' is the density of the liquid.

ρ' is the density of the saturated vapour of the liquid at the same temperature.

'C' is a constant which holds good over a wide range of temperature.

Eqⁿ (1) may also be written as -

$$\gamma^{1/4} = C^{1/4} (\rho - \rho')$$

$$\therefore C^{1/4} = \frac{\gamma^{1/4}}{(\rho - \rho')} \quad \text{--- (2)}$$

on multiplied both side of eqs - (2) with M (mol. weight)

$$\left. \begin{aligned} M C^{1/4} &= \frac{M \gamma^{1/4}}{(\rho - \rho')} \\ &= [P] \end{aligned} \right\} \quad \text{--- (3)}$$

The resulting constant [P] is called Parachor.

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At ordinary temperature the density of vapour (ρ') will be very smaller in comparison with liquid.

$\therefore \rho'$ is dropped from eqs. — (3)

$$[P] = \frac{M \rho'^{1/4}}{\rho} \quad \text{--- (4)}$$

$$\approx [P] = V_m \rho'^{1/4} \quad \text{--- (5)}$$

If the temperature is such that ρ' is unity, then,

$$[P] = V_m \quad \text{--- (6)}$$

$$\text{density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\rho = \frac{M}{V_m}$$

$$V_m = \frac{M}{\rho}$$

Thus, Parachore may be defined as the molecular volume of a liquid at a temperature at which the surface tension is unity.

* Application :-

1) A number of structures were suggested for benzene. out of these Kekule's structure may be possible structure by Parachor measurement.

a) 6 Carbon = $6 \times 8.6 = 51.6$

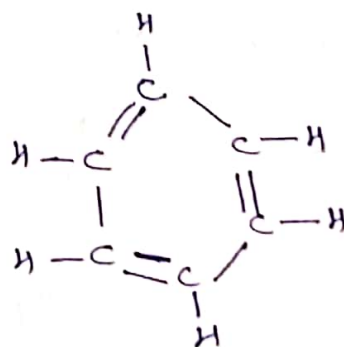
b) 6 Hydrogen = $6 \times 15.7 = 94.2$

c) 3 double bond = $3 \times 19.9 = 59.7$

d) One six membered ring = $1 \times 1.4 = 1.4$

Total $\Rightarrow 206.9$

observed Parachor $\Rightarrow 206.2$



From
Dr. A.K. Gupta
chemist
(L.S. collage)