Physical Properties and Chemical Constitution

Physical properties of a substances depends on the intermolecular forces which originate in the internal structure or the constitution of the molecule. Thus, the determination of properties such as surface tension, viscosity, refractive index etc. can give valuable information about the structure of molecule.

Physical property

Additive property

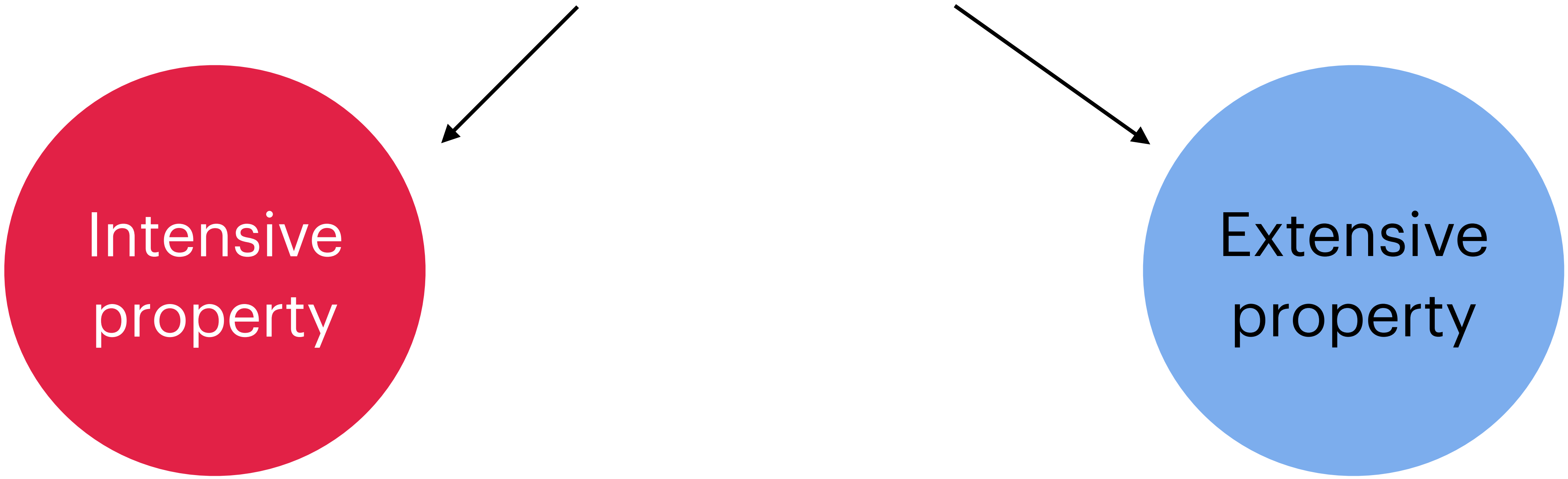
When a property of a substance is equal to the sum of the corresponding properties of the constituent atoms, it is called an additive property. Molar mass

Constitutive property

A property that depends on the arrangement of atoms and bond structure, in a molecule, is referred to as a constitutive property. **Surface tension, Viscosity, optical activity.**

An additive property which also depends on the intramolecular structure, is called additive and constitutive property. Surface tension, Viscosity, Parachor.

Macroscopic property



A property which does not depends on the quantity. concentration.

A property that does depend on the quantity of matter present on the system.

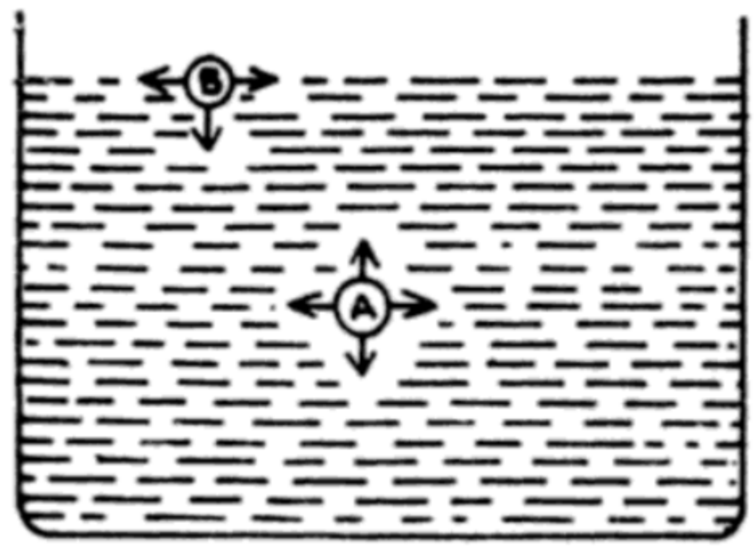
TABLE 7.1. COMMON PROPERTIES OF A SYSTEM.

Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

Surface tension

Molecule ‘A’ is surrounded by other molecules

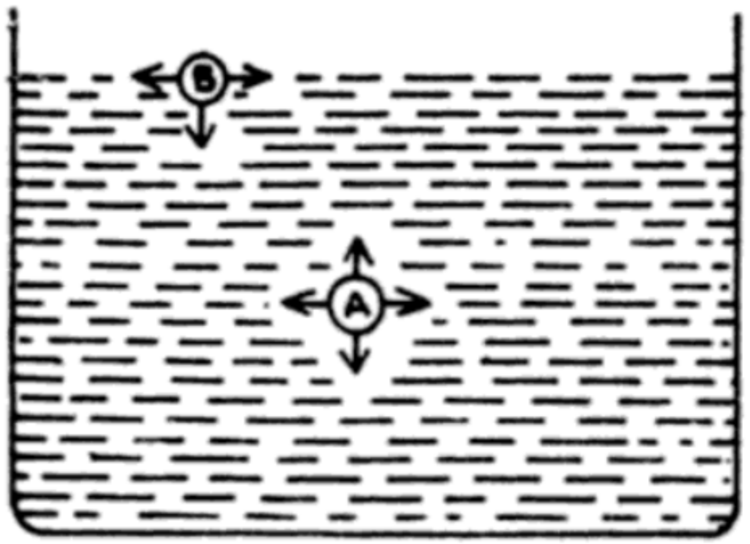
It is attracted equally in all directions by other molecules.



Molecule ‘A’ is partially surrounded by other molecules

It is experienced only downward force of attraction.

Surface tension



This unbalanced attractive force tends to draw the surface molecules inward, and the surface of a liquid tends to contract to the smallest possible area. As a result of the tendency to contract, a liquid surface behaves as if it were in a state of tension. This effect is called the **surface tension.**

Definition: The force in dynes (newton) acting alright angles along the surface of liquidate cm (1 m) in length. It is represented by γ

Unit: Dynes cm^{-1} or Nm-1

What are Parachors?

MacLeod in 1923 proposed an empirical relationship between the surface tension and density of a liquid in the form

$$\gamma = C\,(D-d)^4 \quad (3.14)$$

where D is the density of the liquid, d is the density of the vapour and C is a constant and is independent of temperature over a wide range for non associated liquids. For associated liquids, C is found to increase with increasing temperature.

$$C^{1/4} = \frac{\gamma^{1/4}}{D-d} \quad (3.15)$$

Multiplying both sides by the molar mass M, we get

$$MC^{1/4} = \frac{M\,\gamma^{1/4}}{D-d} \quad (3.16)$$

At temperatures, far below the critical temperature, density of the liquid is much greater than that of its vapour, i.e., $D \gg d$. Hence equation (3.16) reduces to

Parachor is a quantity that is defined by the following relationship between surface tension and density:

$$MC^{1/4} = \frac{M\,\gamma^{1/4}}{D}$$

$$= [P] \quad (3.17)$$

What are Parachors?

$$MC^{1/4} = \frac{M\gamma^{1/4}}{D} = [P] \quad (3.17)$$

Parachor is defined as the product of the molar volume and the surface tension to the power of 1/4.

$\left(\frac{M}{D}\right)$ is the molar volume of the liquid at the same temperature at which surface tension is measured. The quantity $MC^{1/4}$ is a constant characteristic of the liquid and is called *the parachor*. It is denoted by $[P]$. If $\gamma = 1$ then

$$MC^{1/4} = \frac{M}{D} = V_m = [P] \quad (3.18)$$

Hence parachor may be defined as *the molar volume of the liquid at a temperature where its surface tension is unity*. From equation (3.18), it is clear that a comparison of parachor values of two liquids in effect means a comparison of their molar volumes under conditions such that their surface tensions are equal. Thus,

$$\frac{[P_1]}{[P_2]} = \frac{V_{m_1}}{V_{m_2}}$$

Table 3.4 Parachor Values of Some Liquids at 298 K

Isomer	*Parachor*	*Homologous Series* — *Hydrocarbon*			*Ester*		
			Parachor	*Difference*		*Parachor*	*Difference*
Ethyl butyrate	293.6	Ethane	110.5	—	Methyl formate	138.1	—
Isoamyl formate	293.6	Propane	150.8	40.3	Methyl acetate	117.3	39.2
Butyl acetate	295.0	Butane	190.2	39.4	Methyl propionate	216.1	38.8
n-Propyl propionate	295.0	Hexane	270.1	40.2			
		Heptane	309.3	39.2			
o-Xylene	283.3						
m-Xylene	283.3						
p-Xylene	283.3						

What we see!

(a) Isomeric compounds of the same family such as esters, alcohols, xylenes, etc., have been found to have almost the same parachor values

(b) The difference in the parachor values of successive members of a homologous series is nearly the same irrespective of the series as shown in

The parachors of ethane and propane are 110.5 and 150.8 respectively. What values of parachor do you expect for hexane?

$$[P]\, C_2H_6 = 110.5$$
$$[P]\, C_3H_8 = 150.8$$
$$[P]\, CH_2 = [P]\, C_3H_8 - [P]\, C_2H_6$$
$$= 150.8 - 110.5 = 40.3$$
$$[P]\, C_6H_{14} = [P]\, C_3H_8 + 3[P]\, CH_2$$
$$= 150.8 + 3 \times 40.3 = 271.7$$

Use of parachor in elucidating structure

The atomic and structural parameters can be calculated from the experimental values of parachors of components. The contribution of a $>CH_2$ group to the parachor in a homologous series is about 39. The molar parachor would be the sum of the atomic parachors. On this basis the parachor value of hydrogen atom would be

$$P_{C_n H_{2n+2}} = nP_{CH_2} + 2P_H \tag{3.19}$$

For

$$C_4H_{10},\ P_{C_4 H_{10}} = 190.2 \text{ and } P_{CH_2} = 39$$

Substituting these values in equation (3.19), we get

$$190.2 = 39 \times 4 + 2\,P_H$$

or

$$P_H = \frac{190.2 - 156}{2} = 17.1$$

So, the atomic parachor of carbon $= P_{CH_2} - 2P_H$

$$= 39 - (17.1 \times 2)$$

$$= 4.8$$

Use of parachor in elucidating structure

So, the atomic parachor of carbon $= P_{CH_2} - 2P_H$

$$= 39 - (17.1 \times 2)$$
$$= 4.8$$

The parachor values for compounds containing double bonds, six membered ring, etc., can be calculated in the same manner. For example, the parachor value of $CH_2 = CH_2$ (99.5) may be used to calculate the parachor value for a double bond, i.e.,

Parachor value for a double bond $= P_{CH_2 = CH_2} - 2P_{CH_2}$

$$= 99.5 - (2 \times 39) = 21.5$$

From the study of the different unsaturated compounds, the average parachor value of the double bond has been found to be 23.2. Similarly, the contribution of a triple bond towards parachor value is 46.6. Table 3.5 shows some of the common atomic and structural parachor values.

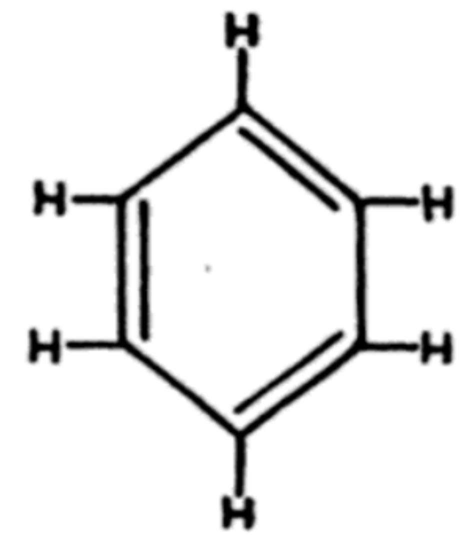
TABLE 13.1. SOME ATOMIC AND STRUCTURAL PARACHORS

Atom	Parachor Sugden	Parachor Vogel	Bond or Ring	Parachor Sugden	Parachor Vogel
C	4.8	8.6	Single bond	0	0
H	17.1	15.7	Double bond	23.2	19.9
O	20.0	19.8	Coordinate bond	–1.6	0
N	12.5	—	3- membered ring	17.0	12.3
Cl	54.3	55.2	6- membered ring	6.1	1.4

Use of parachor in elucidating structure

(i) ***Structure of benzene***: **The parachor value of benzene on the basis of Kekule structure may be calculated as**

6 C atoms	$= 6 \times 4.8$	=	28.8
6 H atoms	$= 6 \times 17.1$	=	102.6
3 double bonds	$= 3 \times 23.2$	=	69.6
1 six membered ring	$= 1 \times 6.1$	=	6.1
Total			207.1



Experimental value may be calculated as

$$[P] = \frac{M\,\gamma^{1/4}}{D}$$

Molar mass of benzene (M) = 78.10 g mole^{-1}
Density at 293 K = 0.878 g cm^{-3}
Surface tension of benzene at 293 K = 29.3 dyne cm^{-1}

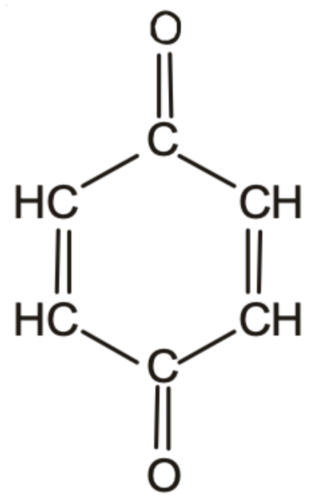
$$\therefore \quad [P] = \frac{(78.10).(29.3)^{1/4}}{0.878} = 206.4$$

The two values almost agree, thus supporting the Kekule structure.

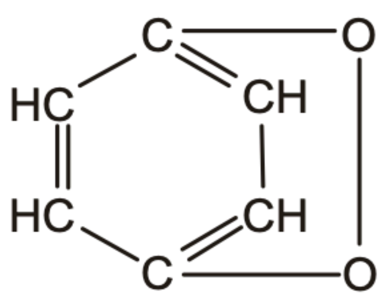
Establish the structure of quinone based upon parachor values.

(2) Structure of Quinone (Sugden)

The two possible structural formulas proposed for quinone are :



A



B

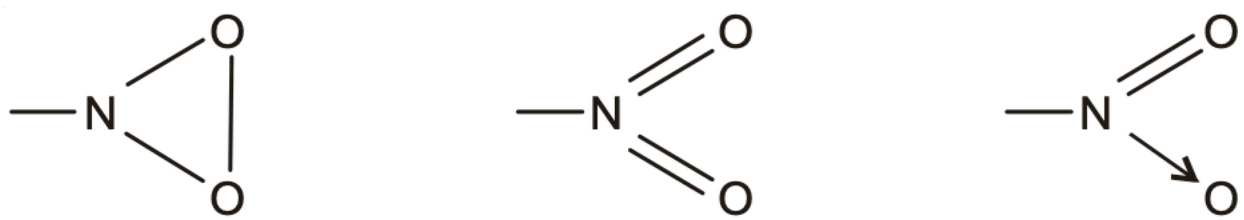
The parachors calculated for the two structures are :

Structure A		Structure B	
6 C	$6 \times 4.8 = 28.8$	6 C	$6 \times 4.8 = 28.8$
4 H	$4 \times 17.1 = 68.4$	4 H	$4 \times 17.1 = 68.4$
2 O	$2 \times 20.0 = 40.0$	2 O	$2 \times 20.0 = 40.0$
4 (=)	$4 \times 23.2 = 92.8$	3 (=)	$3 \times 23.2 = 69.6$
1 six-membered ring	$1 \times 6.1 = 6.1$	2 six-membered rings	$2 \times 6.1 = 12.2$
	Total = 236.1		**Total = 219.0**

The experimental value of parachor for quinone is 236.8. This corresponds to the parachor calculated from structure *A*. Therefore, the structure *A* represents quinone correctly.

(3) Structure of Nitro group (Sugden)

The parachor has also been found useful in providing information regarding the nature of bonds present in certain groups. The nitro group ($-NO_2$), for example, may be represented in three ways :



I II III

The calculated parachors are :

	Structure I		Structure II		Structure III
1 N	1 × 12.5 = 12.5	1 N	1 × 12.5 = 12.5	1 N	1 × 12.5 = 12.5
2 O	2 × 20.0 = 40.0	2 O	2 × 20.0 = 40.0	2 O	2 × 20.0 = 40.0
3-membered ring	1 × 17.0 = 17.0	2 (=)	2 × 23.2 = 46.4	1 (=)	1 × 23.2 = 23.2
				1 (→)	1 × (– 1.6) = – 1.6
	Total = 69.5		**Total = 98.9**		**Total = 74.1**

The experimental value of parachor for $-NO_2$ group has been found to be 73.0. This approximates to the calculated parachor for structure III which is, therefore, the appropriate structure of $-NO_2$ group.

Problem: The density of acetone at 20°C is 0.7910 g/ml. Calculate the surface tension of acetone, given that the parachor values of C, H, O and double bond are 7.2, 16.2, 20.0 and 23.2 respectively

$$\therefore \text{Parachor for acetone } (CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3) = 3\,[P]_C + 6\,[P]_H + [P]_O + [P]_{\text{double bond}}$$

$$= (3\times 7.2) + (6\times 16.2) + 20.0 + 23.2$$

$$= 162$$

Molecular weight of acetone *(M)* = 58
Surface tension is related to parachor according to the formula

$$\frac{M\gamma^{1/4}}{D} = [P]$$

$$\therefore \quad \gamma^{1/4} = \frac{[P]D}{M}$$

$$\text{or} \quad \gamma = \left[\frac{[P]D}{M}\right]^4$$

Substituting the value for *[P]*, *D* and *M*,

$$\gamma = \left[\frac{162\times 0.791}{58}\right]^4$$

$$= \mathbf{23.83\ dynes/cm}$$