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NATIONAL TESTING AGENCY

Chemistry

Physical Chemistry - 1

SIERRA INNOVATIONS

INDEX

Physical Chemistry - 1

Basic Concepts of Chemistry

The International System of Units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	Metre	m
Mass	m	Kilogram	kg
Time	t	Second	s
Electric current	I	Ampere	A
Thermodynamic temperature	T	Kelvin	k
Amount of substance	n	Mole	mol
Luminous intensity	I_v	Candela	cd

Significant Figures

A. What is a "significant figure"?

The number of significant figures in a result is simply the number of figures that are known with some degree of reliability. The number 13.2 is said to have 3 significant figures. The number 13.20 is said to have 4 significant figures.

B. Rules for deciding the number of significant figures in a measured quantity:

(1) All nonzero digits are significant

1.234 g has 4 significant figures,

1.2 g has 2 significant figures.

(2) Zeroes between nonzero digits are significant:

1002 kg has 4 significant figures,

3.07 mL has 3 significant figures.

(3) Zeroes to the left of the first nonzero digits are not significant; such zeroes merely indicate the position of the decimal point:

0.001° C has only 1 significant figure,

0.012 g has 2 significant figures.

(4) Zeroes to the right of a decimal point in a number are significant:

0.023 mL has 2 significant figures,

0.200 g has 3 significant figures.

(5) When a number ends in zeroes that are not to the right of a decimal point, the zeroes are not necessarily significant:

190 miles may be 2 or 3 significant figures, 50, 600 calories may be 3, 4, or 5 significant figures. The potential ambiguity in the last rule can be avoided by the use of standard exponential, or "scientific," notation. For example, depending on whether 3, 4, or 5 significant figures is correct, we could write 50, 6000 calories as:

5.06×10^4 calories (3 significant figures)

5.060×10^4 calories (4 significant figures), or

5.0600×10^4 calories (5 significant figures).

C. What is a "exact number"?

Some numbers are exact because they are known with complete certainty.

Most exact numbers are integers : exactly 12 inches are in a foot, there might be exactly 23 students in a class. Exact numbers are often found as conversion factors or as counts of objects.

Exact numbers can be considered to have an infinite number of significant figures. Thus, number of apparent significant figures in any exact number can be ignored as a limiting factor in determining the number of significant figures in the result of a calculation.

D. Rules for mathematical operations

In carrying out calculations, the general rule is that the accuracy of a calculated result is limited by the least accurate measurement involved in the calculation.

(1) In addition and subtraction, the result is rounded off to the last common digit occurring furthest to the right in all components. For example, 100 (assume 3 significant figures) + 23.643 (5 significant figures) = 123.643, which should be rounded to 124 (3 significant figures).

(2) In multiplication and division, the result should be rounded off so as to have the same number of significant figures as in the component with the least number of significant figures. For example, 3.0 (2 significant figures) 12.60 (4 significant figures) = 37.8000 which should be rounded off to 38 (2 significant figures).

E. Rules for rounding off numbers

(1) If the digit to be dropped is greater than 5, the last retained digit is increased by one. For example, 12.6 is rounded to 13.

(2) If the digit to be dropped is less than 5, the last remaining digit is left as if is. For example, 12.4 is rounded to 12.

(3) If the digit to be dropped is 5, and if any digit following it is not zero, the last remaining digit is increased by one. For example,

12.51 is rounded to 13.

(4) If the digit to be dropped is 5 and is followed only by zeroes, the last remaining digit is increased by one if it is odd, but left as it is if even. For example,

11.5 is rounded to 12,

12.5 is rounded to 12.

This rule means that is the digit to be dropped is 5 followed only by zeroes, the result is always rounded to the even digit. The rationale is to avoid bias in rounding: half of the time we round up, half the time we rounded down.

1. Non-zero digits = SF.

2. Zero → between non-zero digits = SF

→ between decimal and non-zero digit = not SF

⟶ After the non-zero digit

(with/after decimal) → SF: 0.2400, SF = 4

(without decimal) → Non SF: 8400, SF = 2 $= \underline{8.4} \times 10^3$

→ Shows accuracy.

3. With unit → SF (shows measurement)

$$8400 \text{ cm} \rightarrow SF = 4 \Rightarrow S \leq 4$$

8.4×10^3 cm $\rightarrow$ SF $= 2$

8.4×10^3 cm $\rightarrow$ SF $= 3$

8.400×10^3 cm $\rightarrow$ SF $= 4$

		SF
E.g.,	123	3
	12.3	3
	12.34	4
	1.203	4
	1.203	4
	1.002	4
	1.0024	5
	0.024	2 $[= 2.4 \times 10^{-3}]$
	0.0024	2

Rounding off :

$\Rightarrow$ Removing last (uncertain) digit

E.g.,

27.326	$\rightarrow$ 27.33
27.33	$\rightarrow$ 27.3
27.535	$\rightarrow$ 27.54
27.545	$\rightarrow$ 27.54

Calculation of Digits

1. Addition/subtraction $\rightarrow$ Least number of decimal digits in answer.

2. Multiple/Division $\rightarrow$ Least number of significant figures in answer.

Q. 60 mL of a mixture of nitrous oxide and nitric oxide was exploded with excess of H_2. If 38 mL of N_2 is formed, then calculate volume composition of the mixture.

Sol. $$N_2O + NO + H_2O \longrightarrow N_2 + H_2O$$

a $(60a)$ 38 mL

$$N_2O \longrightarrow N_2 \qquad NO \longrightarrow \frac{1}{2}N_2$$

$$a \qquad a \qquad 60a \qquad \frac{60a}{2}$$

$$a + \frac{60-a}{2} = 38$$

$$2a + 60 - a = 76 \quad \Rightarrow a = 16$$

$N_2O \rightarrow$ 16 mL, NO $\rightarrow$ 44 mL

Laws of Chemical Combination

A. Law of conservation of Mass :

Given by Lavoisier (1776).

According to this law, during a physical or chemical change, total mass of the substance is conserved.

or

weight of product formed is always equal to weight of reactants reacted.

1. Physical Change

$$\text{Ice (s)} \xrightarrow{\text{Melting}} \text{Water } (l)$$

Total wt. of water = wt. of Ice

2. Chemical Change

$$R \longrightarrow P$$

wt. of P formed = wt. of R reacted

3. Exception : Nuclear Reactions

where, $\varepsilon = MC^2$

M = decay in mass

C = light velocity

If m = 1 amu $= 1.67 \times 10^{-24}$ g $= 1.67 \times 10^{-27}$ kg

$$\varepsilon = 931 \text{ MeV}$$

E.g.,

$$Mg + \frac{1}{2}O_2 \longrightarrow mgO$$

Initial Q.	30g	30g		60g
Reacted Q.	30g	20g		50g
Remained Q.	0g	10g	50g	60g

B. Law of constant Proportion : [Law of definite proportions]

Given by Proust.

According to this law, all pure samples of a compound contain same elements in definite proportions of their mass.

E.g., CO_2

$$CaCO_3 \xrightarrow{\Delta} CaO + \boxed{CO_2}$$

$$C + O_2 \longrightarrow \boxed{CO_2}$$

$$CH_4 + O_2 \longrightarrow H_2O + \boxed{CO_2}$$

$\boxed{C : O}$

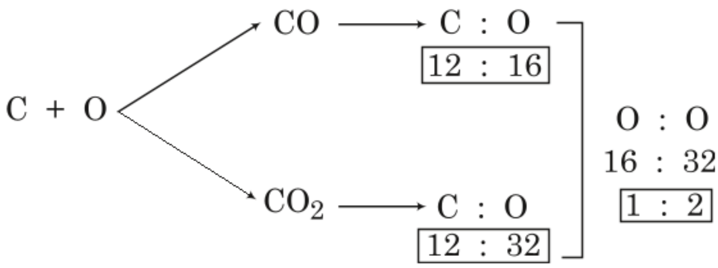
12 : 32

$\boxed{3 : 8}$

C. Law of Multiple Proportion :

Given by Dalton

E.g.,



According to this law, when 2 elements combine together and form more than 1 type of molecules, the different masses of 1 element which combine with the same mass of other element are in simple ratio.

E.g.,

$S + O$ → SO_2 → S : O = 32 : 32
$S + O$ → SO_3 → S : O = 32 : 48

O : O
32 : 48
2 : 3

$P + Cl$ → PCl_2 → P : Cl = 31 : 35.5×3
$P + Cl$ → PCl_5 → P : Cl = 31 : 35.5×5

Cl : Cl
3 : 5

$H + O$ → H_2O → H : O = 2 : 16
$H + O$ → H_2O_2 → H : O = 2 : 32

O : O
1 : 2

N + O →

	N	O	Ratio of O
N_2O	28	16	1
$(NO)_2$	14×2 28	16×2 32	2
N_2O_3	28	48	3
N_2O_4	28	64	4
N_2O_5	28	80	5

D. Law of Reciprocal Proportion :

Given by Richter.

According to this law when 2 elements A and B separately combine with a fixed mass of 3rd element C, then the combining ratio of A and B can be achieved if they combined directly.

$$C + O_2 \longrightarrow CO_2$$

$$C + H \longrightarrow CH_4$$

C : O
12 : 32

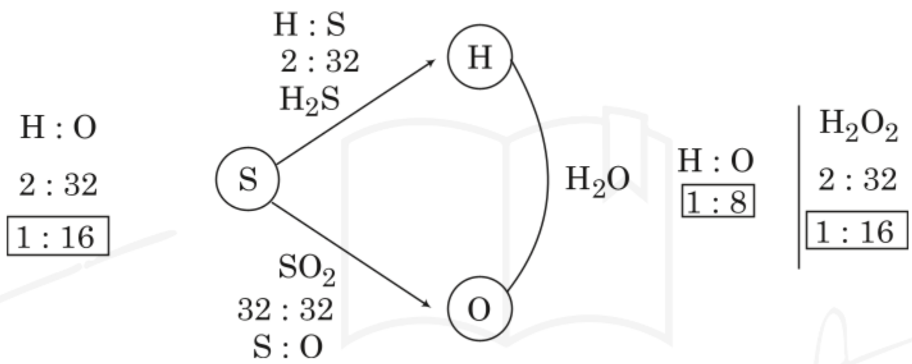
C : H
12 : 4

H : O
4 : 32
1 : 8

$$H + O \longrightarrow H_2O$$

H : O
2 : 16
1 : 8

H_2O_2
2 : 32
1 : 16



Q. In which of the following set of molecular L of RP is applicable?

1. H_2S, SO_2 and SO_3.

2. NaCl, KCl and HCl.

3. PH_3, P_2O_3 and P_2O_5.

4. PH_3, P_2O_3 and H_2O.

Ans. Option (4) i.e., PH_3, P_2O_3 and H_2O.

E. Law of Gaseous Volumes :

Given by Gay Lussac.

According to this law, under similar conditions of temperature and pressure in a reaction, volume ratio of gaseous components is always simple ratio.

E.g., 1.

$$\underset{(g)}{H_2} + \underset{(g)}{Cl_2} \longrightarrow 2HCl(g)$$

V V 2V

$$1 : 1 : 2$$

2. $N_2 + 3H_2 \longrightarrow 2NH_3$

V 3V 2V

$1:3:2$

Q. What Vol, of O_2 is required for complete combustion of 20 ml CH_4 gas CHO

Ans. 1 2

$CH_4 + 2O_2 \quad CO_2 + 2H_2O$

20 ml

$$\frac{V_{CHv}}{V_{O_2}} = \frac{n_1}{n_2}$$

$$V_{O_2} = 2 \times V_{CH_4}$$

$$= 2 \times 20 = 40 \text{ ml}$$

F. Berzelius Hypothesis

Under the similar conditions of temperature and pressure, equal volumes of all gases contain the same number of atoms.

E.g., 1. $H_2 + Cl_2 \longrightarrow 2HCl$

H_2	Cl_2	$2HCl$
n atoms	n atoms	$2n$ compound atoms
V	V	2V
1 atom	1 atom	2 compound atoms
$\frac{1}{2}$ atom	$\frac{1}{2}$ atom	1 comp. atom

But this is against Dalton's law.

2. $N_2 + 3H_2 \longrightarrow NH_3$

N_2	$3H_2$	NH_3
n atoms	$3n$ atoms	$2n$ compound atoms
$\frac{1}{2}$ atom	3 atoms	2 compound atoms

$\frac{1}{2}$ atoms $\quad$ $\frac{3}{2}$ atoms $\quad$ 1 compound atoms

Again, this is against the Dalton Law.

G. Avogadro Hypothesis

Avogadro introduced a new intermediate particle, "molecule".

Under similar conditions of temperature and pressure, equal volumes of all gases contains the same no. of molecules.

Gas $\longrightarrow$ Molecule $\longrightarrow$ Atom

E.g., $H_2 + Cl_2 \longrightarrow 2HCl$

V	V	2V
n molecules	n molecules	$2n$ molecules
1 molecule	1 molecule	2 molecules
$\frac{1}{2}$ molecule	$\frac{1}{2}$ molecule	1 molecule

If H_2 and Cl_2 is diatomic

1 atom	1 atom	1 atoms
[H]	[Cl]	$[H_1Cl_1]$

E.g., $N_2 + 3H_2 \longrightarrow 2NH_3$

1 molecule	+	3 molecules	$\rightarrow$	2 molecules
$\frac{1}{2}$ molecule	+	$\frac{3}{2}$ molecule	$\rightarrow$	1 molecule
1 atom		3 atom	$\rightarrow$	1 atom
[N]		[3H]	$\rightarrow$	$[N_1H_3]$

Q. 2.16 g metallic Cu forms 2.7 g CuO on heating in oxygen. In another experiment, 1.15 g CuO on reduction forms 0.92 g Cu. Show that these observations are according to law of definite proportions.

Sol. $Cu + O \longrightarrow CuO$

2.16 2.7

$CuO \rightarrow Cu + O$

1.159 0.92

$$\frac{2.7}{2.16} = \frac{270}{216} = \frac{135}{108} = \frac{45}{36} = \frac{5}{4}$$

$\Rightarrow$ $Cu + O$ = CuO $\qquad \frac{Cu}{O} = \frac{2.16}{0.54} = \frac{216}{54}$

2.16 g

2.7 g → Cu, O

Cu 2.16, O 0.54 g

$$= \frac{24}{6} = \frac{4}{1}$$

$CuO \longrightarrow Cu + O \qquad \frac{Cu}{O} = \frac{92}{23} = \frac{4}{1}$

1.15 0.92 0.23

Q. One metal forms 2 oxides, which contains 50% and 60% oxygen. If formula of first oxide in MO, then formula of 2nd oxide will be :

1. M_2O 2. MO_2 3. M_2O_3 4. None of these

$M + O$ → $M + O$, $M + O$

$\Rightarrow$ MO

50	50	40	60	$M \rightarrow 1:1$	M_xO_y
1	1	1	$\frac{60}{40}$	$O \rightarrow 1:\frac{3}{2}$	$M_1O_{3/2}$
1 : 1		1 : $\frac{3}{2}$			M_2O_3

$1:1$ $\quad$ $2:3$ $\quad$ $M_2O_{3\times 3/2}$

$\Rightarrow$ M_2O_3 $\quad$ M_4O_9

$\Rightarrow$ M_2O $\quad$ $M_2O_{3/2} \Rightarrow M_4O_3$

Q. One metal forms 2 oxides. Higher oxide contains 80% of metal, 0.72 g of lower oxide on oxidation forms 0.8 g of higher oxide, show that these observations are according to law of multiple proportions.

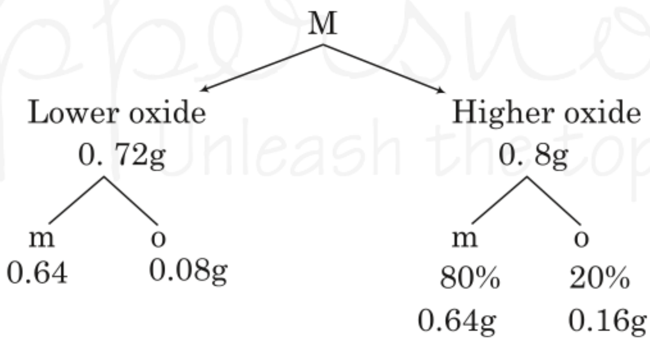
$$M + O \longrightarrow MO$$

$$MO + O \longrightarrow MO$$

0.72 $\quad$ 0.08 $\quad$ 0.8

$\downarrow$

80% metal

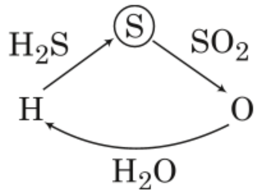


$$\frac{80}{100} \times \frac{0.8}{10} = 0.64 \text{ gM}$$

$$\frac{0.08}{0.16} = \frac{1}{2}$$

$\Rightarrow$ Law of multiple proportions Proved.

Q. H_2S contains 94.11% of S, SO_2 contains 50% of O and H_2O contains 11.11% of H. Show that these observations are according to law of reciprocal proportions.



$$H_2S \qquad\qquad SO_2$$

$$1 : \frac{5.89}{94.11} \qquad\qquad 1:1$$

$$1 : \frac{1}{16} \qquad\qquad 1:1$$

$$11.11\%\ H + 88.89\%\ O$$

$$H : O = \frac{1}{16} : 1 \quad \Rightarrow \quad 1:16$$

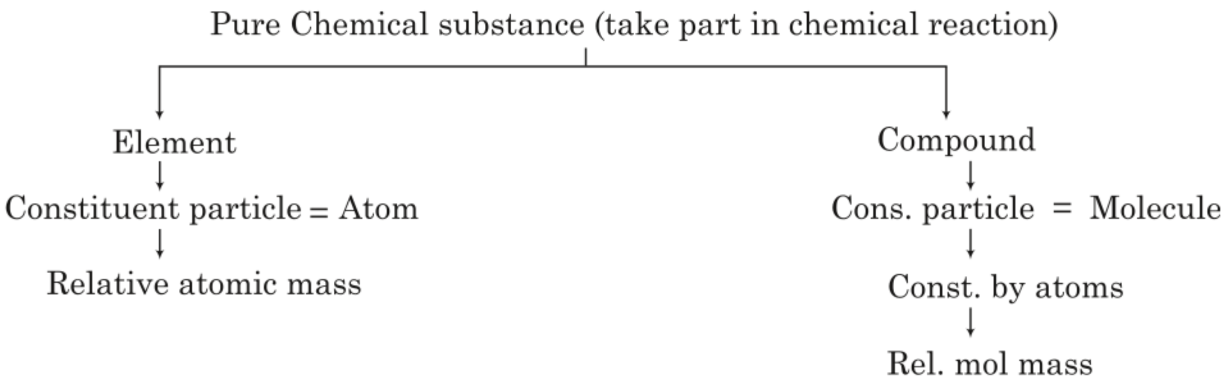
H : O

$$H : O \Rightarrow 11.11 : 88.89 \Rightarrow 1 : \frac{88.89}{11.11} = 1:8$$

$$\therefore \qquad \frac{1:16}{1:8} = \frac{2}{1} = 2:1$$

Mole

* It is a measuring unit of quantity of chemical substances. It is an SI unit. Symbol is mol.



A. Relative Atomic Mass

* It (of an element) is a number which represents 1 atom of the element is how many times heavier than $\frac{1}{12}$th wt. of 1 atom of C-12.

$$\text{Relation at mass} = \frac{\text{wt. of 1 atom of element}}{\frac{1}{12} \times \text{wt. of 1 atom of } C^{12}}$$

wt. of $1P = 1.0072$ amu

wt. of $1n = 1.0078$ amu

Am > Decay in mass

$\Downarrow$

Energy = Binding

amu = atomic mass unit

1 amu $= 1.67 \times 10^{-24}$ g

C^{12} < 6P, 6n $= 12.000$ amu

* unitless quantity.

B. Calculation of Atomic Mass

Proton number + Neutron number $= A$

E.g.,

Fe < 26P, 30N] 56

Zn < 30P, 35n] 65

S < 16P, 16N] 32

* For isotopes – Average atomic mass

i.e.,
$$\text{Average atomic mass} = \frac{M_1X_1 + M_2X_2 \ldots}{X_1 + X_2 \ldots}$$

M_1, M_2 = Atomic mass of different isotopes.

X_1, X_2 = Relative occurrence in nature.

E.g., $_{17}Cl^{35}$ $_{17}Cl^{37}$

75% 25%

3 1

$$\text{Average mass} = \frac{35 \times 75 + 37 \times 25}{(75 + 25)} = 35.5$$

or

$$\text{Average mass} = \frac{35 \times 3 + 37 \times 1}{(3 + 1)} = 35.5$$

Q. Calculate % of $B^{10} \times B^{11}$ in nature when average atomic mass of B is 10.8.

Ans. Let relative occurrence of B^{10} and B^{11} in nature are $x\%$ and $y\%$ respectively, then $x + y = 100$ or $y = 100 - x$

$$10.8 = \frac{10 \times x + 11 \times y}{x + y}$$

$$10x + 11y = 10.8x + 10.8y$$

$$0.2y = 0.8x$$

$$\frac{x}{y} = \frac{1}{4}$$

$$\% \text{ of } B^{10} = x = \frac{1}{5} \times 100\% = 20\%$$

or

$$\% \text{ of } B^{11} = 80\%$$

$$\frac{10x + 11(100 - x)}{100} = 10.8$$

$$10x + 1100 - 11x = 1080$$

$$x = 20$$

* Br^{79} Br^{81} Average mass = 80

50% 50%

$_1H^1$ $_1H^2$ $_1H^3$ Average mass = 1

↓ ↓ ↓

99.98% 0.016% $10^{-15}\%$