SYSTEMATIC CHEMICAL CALCULATIONS

IN

VARIOUS BRANCHES OF CHEMISTRY

(Third Edition)

Part. I

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PREFACE

The present work has originated in connection with courses of lectures in various branches of chemistry including general, physical, analytical, inorganic and organic chemistry. The collected problems are intended to be of use to all students studying chemistry as their basic or supplementary course, e.g. students of pure chemistry, chemical engineering, pharmaceutical, agricultural and medical sciences.

This work is divided into two parts, part I covers various branches of general and physical chemistry to a level suitable for students sitting for examinations in preparatory and first year university courses. Part II includes problems in the same branches at higher level anp also covers the rest of the branches cited above.

Enough problems have been put as solved examples so as to cover and or supplement the greater part of each course. In some cases alternative methods of calculation have been inserted and, where definitions are considered to be advantageous, they have been included.

The book, for object of integrity, has been supplemented with an appendix containing tables of necessary data.

For the benefit of the beginners in university education an Arabic translation of the headings of the solved problems has been also added.

Any suggestions to improve the exposition or for better covering of different subjects will be appreciated.

THE AUTHORS

PART I

CONTENTS

CHAPTER I.

ATOMIC, EQUIVALENT AND MOLECULAR WEIGHTS

1. Lead chloride is found by chemical analysis to contain 74 5 percent lead and 25.5 percent chlorine. The atomic weight of chlorine is 35.45. The specific heat of lead is approximately 0.0309 cal g^{-1}. Using this information, decide among possible formulae such as Pb_2Cl, $PbCl$, $PbCl_2$, $PbCl_3$ and Pb_2Cl_4. Calculate the atomic weight of lead.

SOLUTION

According to the law of Dulong and Petit, at room temperature the product of the specific heat and the atomic weight of the solid elements is a constant, approximately 6.4 cal g^{-1}

$$\therefore \text{ Atomic weight of lead} = \frac{6.4}{0.0309} = 207.1$$

	lead		chlorine
Weight ratio	74.5	:	25.5
Ratio of number of atoms	$\frac{74.5}{207.1}$	:	$\frac{25.5}{35.45}$
or	0.36	:	0.72
or	1	:	2

∴ Possible fromulae of lead chloride are :

$$PbCl_2 \quad \text{and} \quad Pb_2Cl_4$$

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2 The specific heat of a metallic element M was found to be 0.0304, and when 2.694 g of its anhydrous bromide was heated in hydrogen 1.254 g of the metal was left. Calculate the valency and atomic weight of M.

b. The specific heats of a gaseous element G were found to be 0.0385 at constant pressure and 0.0231 at constant volume, and 300 ml of the gas at 16°C and 750 mm pressure weighed 1.624 g. Calculate the atomicity and molecular weight of gas G.

SOLUTION

a) According to Dulong and Petit's law the approximate atomic weight of the metal M = 6.4 ÷ 0.0304
= 210.52

Assuming the formula of the bromide to be $M\,Br_y$, then

$$M\,Br_y = M + y\,Br$$

$$2.694 = 1.254 + y\,Br$$

$$\therefore \quad y\,Br = 2.694 - 1.254 = 1.440$$

Since 1.440 g bromine combine with 1.254 g of M

80 g » » » $\dfrac{1.254 \times 80}{1.440}$

= 69.66 g of M

∴ Equivalent weight of M = 69.66

∴ Valency of M = $\dfrac{210.52}{69.66} = \underline{3}$

∴ True atomic weight of M = 69.7 × 3 = $\underline{209.1}$

Answer (a)

b) Ratio of specific heats of the gas = $\dfrac{0.0385}{0.0231} = 1.66$

∴ The gas is monatomic.

Answer (b)

Applying the ideal gas law ;

$$pv = nRT \quad \text{or} \quad pv = \frac{w}{M} RT$$

$$\left(\frac{750}{760}\right)\left(\frac{300}{1000}\right) = \frac{1.624}{M} \times 0.082 \times 289$$

$\therefore$ The molecular weight of the gas $= \dfrac{1.624 \times 0.082 \times 289 \times 760}{750 \times 0.300}$

$= \underline{130}$

Answer (b)

3. 2.120 g of barium chloride was treated with sulphuric acid and completely converted to barium sulphate. The weight of barium sulphate obtained was 2.378 g. Calculate the equivalent weight of barium. What is meant by the equivalent weight of an element, of a radical and of a compound ?

SOLUTION

The equivalent weight of an element (or a radical) is a number which represents the number of parts by weight of the element (or the radical) which combine with, or replace, one part by weight of hydrogen or 8 parts by weight of oxygen or the equivalent weight of another element.

The equivalent weight of a compound is the sum of the equivalent weights of the elements or radicals of which it is composed.

Sulphuric acid reacts with barium chloride as follows :

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ HCl$$

Let x = equivalent weight of barium (which is bivalent.)

The equivalent weight of Cl^- (which is monovalent) = 35.5

The equivalent weight of SO_4^{--} (which is bivalent)

$= \dfrac{32 + (4 \times 16)}{2}$

$= 48$

Hence $\frac{\text{wt. of } BaCl_2}{\text{corresponding wt. of } BaSO_4} = \frac{\text{Eq. wt. of } BaCl_2}{\text{Eq. wt. of } BaSO_4}$

$$= \frac{x + 35.5}{x + 48}$$

$$\therefore \frac{2.120}{2.378} = \frac{x + 35.5}{x + 48}$$

$$\therefore 2.12\,(x+48) = 2.378\,(x + 35.5)$$

$$\therefore x = \underline{\underline{67.5}}$$

Answer

4. The gaseous product of combustion from 0.3660 g of a metal sulphide was passed into bromine water. This solution after boiling and adding barium chloride gave 0.8754 g of barium sulphate. Calculate the equivalent weight of the metal in the sulphide.

SOLUTION

The reactions are as follows :

Metal sulphides yield SO_2 on combustion.

$$SO_2 + Br_2 + 2\,H_2O = H_2SO_4 + 2\,HBr$$

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2\,HCl$$

Hence $S \equiv SO_2 \equiv BaSO_4$

Since one mole of $BaSO_4$ contains one g atom of S,

∴ The weight of sulphur in original sulphide

$$= \frac{S}{BaSO_4} \times \text{weight of } BaSO_4$$

$$= \frac{32}{137 + 32 + 4 \times 16} \times 0.8754$$

$$= 0.1201 \text{ g}$$

The weight of metal in the original sulphide

$$= 0.3660 - 0.1201$$

$$= 0.2459 \text{ g}$$

Sulphur is divalent in metallic sulphides, hence its equivalent weight is 16.

The weight of metal which combines with 16 g sulphur

$$= 16 \times \frac{0.2450}{0.1201}$$

$= \underline{32.8} =$ equivalent weight of metal

answer

5. Explain what do you understand by isomorphism.

0.7160 g of hydrated metallic sulphate precipitated 0.7002 g of barium sulphate. On mixing with potassium sulphate and crystallizing, the metallic sulphate yielded an alum isomorphous with potash alum. Calculate the atomic weight of the metal.

SOLUTION

Mitscherlich's law of isomorphism states that elements which possess similar chemical characteristics are able to replace one another in crystalline compounds with little or no change in crystalline shape.

The formula of potash alum is :

$K_2SO_4.Al_2(SO_4)_3.24\ H_2O$ and of aluminium sulpate is

$Al_2(SO_4)_3.18\ H_2O$

and since the metal M and alumiuium are isomorphous, the formulae of metallic alum and metallic sulphate are :

$K_2SO_4.\ M_2(SO_4)_3.\ 24\ H_2O$ and $M_2(SO_4)_3\ .\ 18\ H_2O$ respectively where the metal is trivalent.

Since $M_2\ (SO_4)_3\ .\ 18\ H_2O \equiv 3\ BaSO_4$

$\therefore$ One mole of the metal sulphate $\equiv 3 \times 233$ g $BaSO_4$

aud since 0.716 g of the sulphate $\equiv$ 0.7002 g $BaSO_4$

$\therefore$ The molecular weight of the sulphate =

$$\frac{3 \times 233 \times 0.716}{0.7002} = 715$$

The atomic weight of the metal

$$= \frac{715 - [3(32+4\times16) + 18(2+16)]}{2}$$

$= \underline{51.5}$
Answer

6. 0.2 g of the hydride of the element X occupied 318.5 cc at 100°C and 730 mm pressure. Calculate the vapour density of the hydride at 100°C. A calcium salt $Ca_n X_2$ was obtained by the replacement of hydrogen in the hydride by calcium. On evaporation with excess of concentrated sulphuric acid, 1.343 g of this salt yielded 2.342 g of calcium sulphate. Calculate the equivalent weight of X. Hence deduce the valency and atomic weight of X.

SOLUTION

The volume of the hydride of element X reduced to N.T.P.

$$= 318.5 \times \frac{273}{373} \times \frac{730}{760} = a \text{ ml}$$

Since one mole of hydrogen occupies 22.4 litres at N.T.P.

$\therefore$ Weight of the same volume of hydrogen $= a \times \frac{2}{22400}$

$$= 318.5 \times \frac{273}{373} \times \frac{730}{760} \times \frac{2}{22400} = b \text{ g}$$

The vapour density of the hydride

$$= \frac{\text{weight of a volume of the hydride}}{\text{weight of the same volume of hyrogen}}$$

(under the same conditions of temperature and pressure)

$$= \frac{0.2}{b} = \underline{10.03}$$

Answer (1)

$$\underset{1.343\ g}{Ca_n X_2} + H_2SO_4 \longrightarrow \underset{2.342\ g}{n\ CaSO_4} + \ldots\ldots$$

2,342 g $CaSO_4$ contain $2{,}342 \times \frac{40}{136} = 0.6895$ g Ca.

This is the weight of Ca in 1,343 g of the salt $Ca_n X_2$

The weight of element X in the salt $= 1.343 - 0.6895$
$= 0\ 6535$ g

The equivalent weight of element X is the weight which combines with 20 g of Ca $= 20 \times \frac{0.6535}{0.6895} = \underline{\underline{19.0}}$

Answer (2)

The molecular weight of the hydride = Vapour density $\times$ 2
$= 10.03 \times 2 = 20.06$

Since the formula of the compound is $Ca_n X_2$ while Ca is divalent, then the valency of X is $\frac{n \times 2}{2} = n$.

∴ The formula of the hydride is $H_n X$ and its molecular weight = 20.06

It follows that $(n \times 1) + (n \times 19) = 20.06$

and hence n = 1

The valency of the element X = $\underline{\underline{1}}$

Answer (3)

and its atomic weight $= 19.0 \times 1 = \underline{\underline{19.0}}$

Answer (4)

7. 1.00 g of the anhydrous sulphate of a metal, when heated, gives a residue of the oxide weighing 0.298 g. The specific heat of this metal is 0.21. Calculate the atomic weight of the element.

SOLUTION

Let the equivalent weight of the metal be x.

The equivalent weight of the sulphate group (SO_4^{--})

$$= \frac{96}{2} = 48$$

The equivalent weight of oxygen = 8

$$\therefore \quad \frac{\text{The equivalent weight of the metal sulphate}}{\text{The equivalent weight of the oxide}}$$

$$= \frac{x + 48}{x + 8} = \frac{1.00}{0.298}$$

$\therefore \quad x = 8.97$

From Dulong and Petit's law, the apparent atomic weight of the element

$$= \frac{\text{the atomic heat}}{\text{the specific heat of the element}}$$

$$= \frac{6.4}{0.21} = 30.48$$

$\therefore$ The valency of the element $= \dfrac{30.48}{8.97} = 3.05$

$= 3$

$\therefore$ The exact atomic weight $= 8.97 \times 3 = \underline{26.91}$

Answer

8. The atomic weight of oxygen is 16 and that of silver, taking oxygen as standard, is 107.88.

1) It is required to calculate the atomic weights of chlorine and potassium from the following results.

3.6708 g of potassium chlorate $KClO_3$ were heated to give potassium chloride KCl of constant weight equal to 2.2368 g.

This residue was dissolved in water and the solution treated with silver nitrate, a precipitate of silver chloride was formed which weighed 4.3002 g when dry.

2) What will be the atomic weights calculated if part of the material is lost, and KCl after calcination of $KClO_3$ weighed 2.2350 g ? What will be the relative errors in the atomic weights with respect to the values calculated in (1) ?

SOLUTION

$$KClO_3 = KCl + \frac{3}{2} O_2$$

$$KCl + AgNO_3 = AgCl + KNO_3$$

One mole of $KClO_3$ gives one mole of KCl which precipitates one mole of AgCl. Let the weights be m, m_1 and m_2 g respectively.

Let the atomic weights of chlorine and potassium be x and y.

$$\frac{m}{x+y+48} = \frac{m_1}{x+y} = \frac{m_2}{x+107.88}$$

then $\frac{x+y+48}{x+y} = \frac{m}{m_1}$ and $\frac{48}{x+y} = \frac{m-m_1}{m_1}$

$$x + y = 48 \left(\frac{m_1}{m - m_1}\right)$$

Also $\frac{x+107.88}{x+y} = \frac{m_2}{m_1}$

then $\frac{107.88 - y}{x+y} = \frac{m_2 - m_1}{m_1}$

$$107.88 - y = 48 \left(\frac{m_2 - m_1}{m - m_1}\right)$$

$$\text{then} \quad y = 107.88 - 48 \left(\frac{m_2 - m_1}{m - m_1} \right)$$

$$\text{and} \quad x = 48 \left(\frac{m_2}{m - m_1} \right) - 107.88$$

Substituting for m, m_1 and m_2

$$x = 48 \left(\frac{4.3002}{3.6768 - 2.2368} \right) - 107.88 = 143.34 - 107.88$$

$$= 35.46$$

$$y = 107.88 - 48 \left(\frac{4.3002 - 2.2368}{3.6768 - 2.2368} \right)$$

$$= 39.10$$

∴ The atomic weight of chlorine is 35.46

and the atomic weight of potassium is 39.10

Answer (1)

If the weight of KCl $m_1 = 2.2350$ g

then $\Delta m_1 = m_1' - m_1 = 2.2350 - 2.2368 = -0.0018$ g

The relative error

$$\frac{\Delta m_1}{m_1} = -\frac{0.0018}{2.2368} \backsimeq -\frac{8}{10000}$$

The masses of KCl and AgCl, m_1 and m_2 are proportional to their molecular weights M_1 and M_2

$$\frac{m_2}{m_1} = \frac{M_2}{M_1}$$

$$\text{or} \quad \frac{m_2}{M_2} = \frac{m_1}{M_1}$$

$$\text{then} \quad \frac{\Delta m_2}{M_2} = \frac{\Delta m_1}{M_1} = -\frac{8}{1.C000}$$

The absolute error in the weight of Ag Cl $\Delta m_2 = -\frac{8}{10000} m_2$

$$= -\frac{8}{10000} \times 4.3002 = -0.0035 \text{ g}$$

Weight of Ag Cl precipitate = 4.3002 − 0.0035 = 4.2967 g

Then the new atomic weight of chlorine x′

$$= 48 \left(\frac{m_2'}{m - m_1'} \right) - 107.88$$

$$= 48 \left(\frac{4.2967}{3.6768 - 22350} \right) - 107.88$$

$$= 35.16$$

The relative error in the atomic weight of chlorine :

$$\frac{\Delta x}{x} = \frac{35.16 - 35.46}{35.46} \backsimeq \underline{\frac{9}{1000}}$$

Answer (2)

The new atomic weight of potasium :

$$y' = 107{\cdot}88 - 48 \left(\frac{m_2' - m_1'}{m - m_1'} \right)$$

$$= 170.88 - 48 \left(\frac{4.2967 - 2.2350}{3.6768 - 2.2350} \right)$$

$$= \underline{39.24}$$

The relative error in the atomic weight of potassium.

$$\frac{\Delta y}{y} = \frac{39.24 - 39.10}{39.10} \backsimeq \underline{\frac{4}{1000}}$$

Answer (2)

PROBLEMS FOR PRACTICE

1. A certain element X forms a compound which contains

only oxygen and potassium, in addition to the element. The compound contains 43.81 % of the element. This compound is isomorphous with potassium perchlorate ($KClO_4$). What is the atomic weight of the element ? (80.2)

2. 2.00g of barium carbonate was treated with dilute sulphuric acid and completely converted to barium sulphate. The weight of barium sulphate obtained was 2.37g. Calculate the equivalent weight of barium. (67.3)

3. 2.1g of the carbonate of a metal were heated and gave 668 cc of carbon dioxide measured over mercury at a pressure of 700mm and at a temperature of 27°C. What is the equivalent weight of the metal ? (12)

4. One gram of the carbonate of a metal, on conversion into the sulphate, gave 1.36 g. Find the equivalent weight of the metal. (20)

5. One gram of a dibasic acid combines with 0.8889 g of caustic soda. Find the molecular weight of the acid. (90.02)

6. The chloride of a metal was found to contain 47.2 % of the metal. The specific heat of the metal is 0.094. Find the exact atomic weight of the metal and its valency. (63.48) (2)

7. When 0.152g of an element is treated by a dilute acid, 106.6 cc of hydrogen, collected over water at 17°C and 755 mm mercury, are liberated. The sulphate of this element forms with potassium sulphate an alum which gives mixed crystals with potash alum [$(K_2SO_4.Al_2(SO_4)_3$. 24 $H_2O)$]. What is the atomic weight of the element ? The saturated water vapour pressure at 17°C is 14.4mm and one litre of hydrogen at N.T.P. weighs 0.0898g. (52)

CHAPTER II

GASES

9. Estimate the number of metric tons of carbon dioxide over a square mile of the earth's surface if the atmospheric pressure is 760 mm and the air contains 0.045 per cent of carbon dioxide by volume.

SOLUTION

Weight of air per cm^2 of earth's surface $= 76 \times 13.6$ g

,, ,, CO_2 ,, ,, ,, ,, $= \frac{76 \times 13.6 \times 0.046}{100}$

Weight of CO_2 per km^2 $= \frac{76 \times 13.6 \times 0.046}{100} \times 10^{10}$

$= 0.475 \times 10^{10}$ g

,, ,, per $mile^2$ $= 0.475 \times 10^{10} \times$

$\left(\frac{1760 \times 32}{1000 \times 35}\right)^2$

$= 0.475 \times 10^{10} \; (1.61)^2$

$= 1.23 \times 10^{10}$ g

$= \frac{1.23 \times 10^{10} \text{ g}}{10^6 \text{ g ton}^{-1}}$

$= \underline{1.23 \times 10^{4} \text{ tons}}$

Answer

10. (a) How many grams of air are there in the atmospehere surroundiug the earth, if it is assumed that the earth is a sphere with a diameter of 12 million metres and that atmospheric pressure is 760 mm every where on the surface ?

(b) How many moles of air are there in the total atmosphere if it is assumed that the average molecular weight of air is 28.8 ?

(c) How many molecules of oxygen are there in the earth's atmosphere if one-fifth of the air by volume is oxygen ?

SOLUTION

a) Pressure = weight of a column of air on 1 cm^2 of earth's surface

$= 76 \times 13.6$ gram force per cm^2.

Surface area of eath $= 4 \pi r^2$

$= 4 \pi (6 \times 10^6 \times 100)^2$

$= 144 \pi \times 10^{16}$ cm^2

Grams of air surrounding the earth $= (144 \pi \times 10^{16}) (76 \times 13.6)$

$= 4.68 \times 10^{21}$ g

Answer (a)

b) Number of moles of air $= \frac{w}{M} = \frac{4.68 \times 10^{21}}{28.8}$

$= 1.62 \times 10^{20}$ moles

Answer (b)

c) Since the moles of oxygen in air are one-fifth of the air, then molecules of oxygen = moles of O_2 × Avogadro's number

$= \left(\frac{1.62 \times 10^{20}}{5} \right) \times 6.023 \times 10^{23}$

$= 1.95 \times 10^{43}$

Answer (c)

11. An organic compound of empirical formula $C_3 H_6 O$ weighing 0.716 g gave 242.6 cm^3 of vapour at 200°C and 750 mm pressure. What is the molecular formula of the compound ?

SOLUTION

$$p\,v = \frac{w}{M}\,RT \qquad \therefore \quad M = \frac{w\,R\,T}{pv}$$

$$M = \frac{0.716 \times 0.082 \times 473}{\frac{750}{760} \times 0.2426} = 116$$

the empirical molecular weight = 12 × 3 + 6 + 16 = 58

The empirical formula should be multiplied by $\frac{116}{58} = 2$

to give the molecular fromula $C_6H_{12}O_2$
Answer

12. What is the number of molecules in a one litre flask containing air at 20°C and evacuated to 0.001 mm pressure ?

SOLUTION

$$pv = n\,RT$$

$$n = \frac{pv}{RT}$$

$$= \frac{0.001 \times 1}{760 \times 0.082 \times 293}$$

$$= 5.489 \times 10^{-8} \text{ moles}$$

The number of molecules in the vessel

$$= 5.489 \times 10^{-8} \times 6.023 \times 10^{23}$$

$$= 3.31 \times 10^{16} \text{ molecules}$$

Answer

13. Find the vapour density and the molecular weight of a substance from the following data : (Dumas method)

Weight of the bulb in air	23.449 g
Weight of bulb full of vapour at 15.5°C	23.720 g
Temperature of bath on sealing of bulb	110°C

Barometric pressure during the experiment	759 mm
Weight of bulb full of water + the tip	201.449 g
One litre of air at N.T.P. weighs	1 293 g

SOLUTION

Weight of water in the bulb = 201.449 − 23.449 = 178.000 g

Volume of the bulb = 178 cc

Weight of air in the bulb = $\frac{178}{1000} \times 1.293 = 0.2301$ g

Weight of glass of the bulb = 23.449 − 0.2301 = 23.2189 g

Weight of the vapour = 23.720 − 23.2189 = 0.5011 g

Volume of vapour at N.T.P. = $178 \times \frac{273}{383} \times \frac{759}{760} = 126.7$ cc

Weight of the same volume of H_2 = $\frac{126.7}{1000} \times \frac{2}{22.4} = 0.0114$ g

Vapour density of the substance = $\frac{0.5011}{0.0114} = \underline{43.95}$

Molecular weight of the substance = 43.59 × 2 = $\underline{87.90}$

Answer

14. A glass bulb fitted with a stopcock was evacuated and found to weigh 46.8542 g without correcting for buoyancy of the air. When the stopcock was opened and dry air was allowed to fill the bulb, the weight increased to 47.0465 g. The barometric pressure was 745 mm, and the temperature was 27°C.

(a) Calculate the total volume of the bulb from the known average molecular weight of air 28.8.

(b) Calculate the weight if the bulb was filled with dry hydrogen at this temperature and pressure.

SOLUTION

Weight of dry air = 47.0465 — 46.8542 = 0.1923 g

a) Moles of air $= \frac{0.1923}{28.8}$

$\because \quad pv = nRT$

$$\therefore \quad v = \frac{\left(\frac{0.1923}{28.8}\right) \times 0.0821 \times 300}{\left(\frac{745}{760}\right)}$$

$= 168 \times 10^{-3}$ litre

$= \underline{168}$ ml

Answer (a)

b) Since volume, pressure and temperature are the same, then $n_{H_2} = n_{air} = \frac{0.1923}{28.8}$

Weight of $H_2 = \frac{0.1923}{28.8} \times 2 = 0.0134$ g

Weight of bulb + H_2 = $\underline{46.8676}$ g

Answer (b)

15. What volume of hydrogen gas is necessary to react with 200 cc of nitrogen gas to give ammonia gas, if the hydrogen gas is measured at 15°C and under 800 mm pressure and the nitrogen gas measured at 31°C and under 600 mm prersure ? What is the volume of ammonia gas produced at N.T.P. ?

SOLUTION

$$N_2 + 3\ H_2 = 2\ NH_3$$

One volume of nitrogen gas reacts with three volumes of hydrogen gas to give two volumes of ammonia gas, under the same conditions of temperature and pressure.

At 31°C and 600 mm pressure 200 cc of nitrogen gas require 600 cc of hydrogen gas to produce 400 cc of ammonia gas.

∴ The volume of hydrogen gas at 15°C and 800 mm pressure

$$= 600 \times \frac{273+15}{273+31} \times \frac{600}{800} = \underline{426 \text{ cc}}$$

Answer

and the volume of ammonia gas at N.T.P.

$$= 400 \times \frac{273}{273+31} \times \frac{600}{760} = \underline{284 \text{ cc}}$$

Answer

16. Assuming that air behaves as an ideal gas, calculate exactly the weight of 1 cc of air at 25°C and 1 atm if the relative humidity of the air is 70 % and the vapur pressure of water at 25°C is 23.7 mm. The composition of dry air is 80% N_2 aud 20% O_2 by volume.

SOLUTION

Choosing 1 litre of air as a basis for the calculation.

∴ number of moles of air per litre $= \frac{pv}{RT}$

$$= \frac{1 \times 1}{0.0821 \times 298}$$

$$= 0.041 \text{ mole}$$

$$\text{Relative humidity} = \frac{\text{partial pressure of water vapour}}{\text{vapour pressure of water}}$$

$$0.70 = \frac{p_w}{23.7}$$

The partial pressure of water vapour $P_w = 0.7 \times 23.7 = 16.59$ mm

But from Dalton's law ; $\frac{p_w}{p_{total}} = \frac{n_w}{n_{total}}$

$$\text{or } \frac{16.59}{760} = \frac{n_w}{0.041}$$

$$n_w = \frac{16.59 \times 0.041}{760} = 0.00089 \text{ mole/litre air}$$

$$n_{dry\ air} = 0.041 - 0.00089 = 0.04011 \text{ mole/l}$$

$$n_{N_2} = 0.04011 \times 0.8 = 0.03209 \text{ mole/l}$$

$$n_{O_2} = 0.04011 \times 0.2 = 0.00802 \text{ mole/l}$$

Total weight of 1 litre of air $= 0.00089 \times 18$ $+ 0.03209 \times 28 + 0.00802 \times 32 = 1.1717$ g

Weight of 1 cc of air $= \underline{1.1717 \times 10^{-3}}$ g

Answer

17. The density of helium is 0.1782 g per litre at N.T.P., what is its density at 25°C and under 740 mm pressure ?

SOLUTION

$$pv = nRT = \frac{w}{M} RT$$

$$\frac{p}{T} = \frac{w}{v} \times \frac{R}{M} \text{ and since } d = \frac{w}{v} = \text{density}$$

$$\frac{p}{d \times T} = \frac{R}{M} = \text{constant}$$

$$\frac{p}{d \times T} = \frac{p'}{d' \times T'}$$

$$\frac{760}{0.1782 \times 273} = \frac{740}{d' \times 298}$$

$$\therefore\ d' = \underline{0.1588} \text{ g/l}$$

Answer

18. What is the density of a mixture of methane and ethane in each of the following cases :

a) if the two gases are in a mass ratio of their molecular weights at 100°C and 700 mm Hg ?

b) if the two gases are in a volume ratio of their molecular weights at 100°C and 700 mm Hg ?

SOLUTION

a) Since the mixture of the two gases is in the mass ratio of their molecular weights, it must consist of equal volumes of the two gases (The same number of moles of different gases occupy equal volumes under the same conditions of temperature and pressure).

The partial pressure of each gas $= \frac{700}{2} = 350$ mm

The weight of methane (CH_4) per litre of the mixture may be calculated as follows ;

$$p\,v = \frac{w}{M} RT$$

$$w_{CH_4} = \frac{pv\,M}{RT} = \frac{\frac{350}{760} \times 1 \times 16}{0.082 \times 373} = 0.241 \text{ g/l}$$

Similarly for ethane (C_2H_6)

$$w_{C_2H_6} = \frac{\frac{350}{760} \times 1 \times 30}{0.082 \times 373} = 0.452 \text{ g/l}$$

∴ The density of the mixture = grams of methane per litre + grams of ethane per litre

$= 0.241 + 0.452 = \underline{0.693}$ g/l

Answer

b) Since the mixture of the two gases is in the volume ratio of their molecular weights,

∴ the partial pressure of CH_4 $= \frac{700 \times 16}{16 + 30}$

$= 244$ mm Hg

The weight of methane (CH_4) per litre of mixture may be calculated from

$$pv = \frac{w}{M} RT$$

$$\frac{244}{760} \times 1 = \frac{w}{16} \times 0.082 \times 373$$

$$w_{CH_4} = \frac{16 \times 244}{760 \times 0.082 \times 373} = 0.168 \text{ g/l}$$

Similarly

$$w_{C_2H_6} = \frac{30 \times (700 - 244)}{760 \times 0.082 \times 373} = 0.590 \text{ g/l}$$

Density of the mixture $= 0.168 + 0.590$

$= \underline{0.758}$ g/l

Answer (b)

19. The weight of a certain evacuated vessel is found to increase 0.2500, 0.5535 aud 0.5268 g when oxygen, chlorine, and a compound of oxygen and chlorine, respectively, are separately admitted into the vessel under the same conditions of temperature and pressure. Calculate form these data alone the molecular weights of chlorine and the oxide of chlorine. What can you say from these data regarding the number of atoms in the chlorine molecule ? What is the formula of the chlorine oxide ?

SOLUTION

Applying the ideal gas equation for the 3 gases :

$$pv = nRT$$

Since p, v and T are the same in the 3 cases, then n is the same for the 3 gases.

i.e $\quad n_{O_2} = n_{Cl_2} = n_{\text{oxide of chlorine}}$

$$\text{or} \qquad \frac{w_{O_2}}{M_{O_2}} = \frac{w_{Cl_2}}{M_{Cl_2}} = \frac{w_{oxide}}{M_{oxide}}$$

$$\text{or} \qquad \frac{0.2500}{32} = \frac{0.5535}{M_{Cl_2}} = \frac{0.5268}{M_{oxide}}$$

The molecular weight of chlorine $M_{Cl_2} = \frac{32 \times 0.5535}{0.2500} = \underline{70.87}$

Answer

The molecular weight of the oxide $M_{oxide} = \frac{32 \times 0.5268}{0.2500}$

$= \underline{67.45}$ g/mole

Since atomic weight of Cl $= 35.45$

The number of atoms of Cl in a chlorine molecule $= \frac{70.87}{35.45}$

$= \underline{2}$

Answer

Since the molecular weight of the chlorine oxide is 67.45, it cannot, therefore, contain more than one Cl – atom and the rest is oxygen.

Number of O – atoms in the compound $= \frac{67.45 - 35.45}{16}$

$= \frac{32}{16} = 2$

Formula of oxide is $\underline{ClO_2}$

Answer

20. One gram of a mixture of two metals, both of which give hydrogen with dilute acids is treated with dilute hydrochloric acid, and 650 cc of hydrogen are evolved at 12°C and 770 mm. Calculate the percentage composition of the mixture if the equivalent weights of the metals are 12 and 20 respectively.

Volume of hydrogen evolved at N.T.P. $= 650 \times \frac{770}{760} \times \frac{273}{285}$

$= 631$ cc

1 g of metal A (eq. wt. 12) yields $\frac{11200}{12}$ cc hydrogen at N.T.P.

1 g of metal B (eq. wt. 20) yields $\frac{11200}{20}$ cc hydrogen at N.T.P.

If 1 g of the mixture contains x g of A and (1 - x) g of B,

then hydrogen evolved due to metal A $= \frac{11200}{12} \cdot x$ cc at N.T.P.

and hydrogen evolved due to metal B $= \frac{11200}{20} (1 - x)$ cc at N.T.P.

$$\frac{11200}{12} . x + \frac{11200}{20} (1 - x) = 631$$

$\therefore x = 0.1902$ g

$\therefore$ The percentage composition is 19.02% of metal A and 80.98% of metal B.

Answer

21. A mixture of 0.1 g of hydrogen and 0.2 g of nitrogen is to be stored at 760 mm pressure and 26°C.

a) What must the volume of the container be, if it is assumed that there is no interaction between nitrogen and hydrogen ?

b) Calculate the mole fraction of hydrogen.

c) What is the partial pressure of hydrogen ?

SOLUTION

a) Moles of $H_2 = \frac{0.1}{2.016} = 0.04961$ mole

,, ,, $N_2 = \frac{0.2}{28.016} = 0.00714$ mole

Total moles = 0.04961 + 0.00714 = 0.05675 mole

$$V = \frac{n R T}{P} = \frac{0.05675 \times 0.082 \times 299}{1}$$

$$= \underline{1.389} \text{ litres}$$

Answer (a)

b) Mole fraction of $H_2 = \frac{0.04961}{0.05675} = \underline{0.874}$

Answer (b)

c) Partial pressure of H_2 = Total pressure × mole fraction of H_2

$= 1 \times 0.874 = \underline{0.874}$ atm

Answer (c)

22. Four volumes of a gas diffuse in the same time as three volumes of oxygen. Find the molecular weight of the gas.

SOLUTION

According to Graham's law of diffusion :

$$\frac{R_1}{R_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where R_1 and R_2 are the rates of diffusion of gases 1 and 2; M_1 and M_1 are their respective molecular weights.

$$\frac{4}{3} = \sqrt{\frac{32}{M_1}}$$

$$\frac{16}{9} = \frac{32}{M_1}$$

$$M_1 = \frac{32 \times 9}{16} = \underline{18}$$

Answer

23. Calculate the molecular weight of air saturated with water vapour at 25°C and 1 atm. The vapour pressure of water at 2·°C is 23.7 mm and dry air contains 80% nitrogen and 20% oxygen by volume.

SOLUTION

Since the vapour pressure of water at 25°C = 23.7 mm

∴ The partial pressure of dry air at 25°C = 760 − 23.7 = 736.3 mm

Since dry air contains N_2 and O_2 in the volumetric ratio of 80 ; 20,

∴ The partial pressure of N_2 = 736.3 × 0.8 = 589.04 mm

» » » » O_2 = 736.3 × 0.2 = 147.26 mm

$$\therefore \quad n_{H_2O\ vap} : n_{N_2} : n_{O_2} = P_{H_2O} : P_{N_2} : P_{O_2} = 23.7 : 589.04 : 147.26$$

∴ 1 g mole of air saturated with water vapour at 25°C and 1 atm contains :

a) $\frac{23.7}{760}$ mole of water vapour $= \frac{23.7}{760} \times 18 = 0.56$ g

b) $\frac{589.04}{760}$ mole of N_2 $= \frac{589.04}{760} \times 28 = 21.70$ g

c) $\frac{147.26}{760}$ mole of O_2 $= \frac{147.26}{760} \times 32 = 6.20$ g

$\therefore$ The molecular weight of saturated air = 0.56 + 21.70 + 6.20 = 28.46

Answer

24. When 5 g of ammonium carbamate $NH_4.CO_2.NH_2$ were vaporized at 200°C, their volume was 7.66 litres at 740 mm pressure. Calculate the degree of dissociation according to the following equation :

$$NH_4\,CO_2\,NH_2 = 2NH_3 + CO_2$$

SOLUTION

Let the weight of ammonium carbamate be w grams and its molecular weight be M.

$$\frac{w}{M} \text{ is the number of moles.}$$

If a is the degree of dissociation, and since one molecule of the carbamate, on dissociation, gives 2 a molecules of NH_3, a molecules of CO_2 and (1 − a) molecules of the carbamate remaining undissociated at equilibrium,

then the total number of molecules at equilibrium

$$= 1 - a + 3a = 1 + 2a \text{ molecules.}$$

From $\frac{w}{M}$ moles of carbamate, there will be $\frac{w}{M}$ (1 + 2 a) moles at equilibrium.

The equation pv = n R T becomes,

$$pv = \frac{w}{M}(1 + 2a)RT$$

$M = 78$, $P = \frac{740}{760}$ atm, $w = 5$ g, $T = 273 + 200 = 473°K$

$R = 0.082$ litre atm.

$$\therefore \frac{740}{760} \times 7.66 = \frac{5}{78}(1 + 2a) \times 0.082 \times 473$$

$$\therefore \quad a \simeq 1$$

Answer

The compound is almost completely dissociated.

PROBLEMS FOR PRACTICE

1. 45 cc of oxygen gas and 25 cc of hydrogen gas measured at N.T.P. were mixed together and allowed to expand to the total volume 120 cc at 0°C. Find the total pressure of the mixture and the partial pressures of the constituents. (443.2) (284.9) (158.3)

2. If atmospheric air consists of 21% and 79% by volume of oxygen and nitrogen respectively, calculate the partial pressures of the two gases in air at 760 mm total pressure. (159.6) (600.4)

3. What are the weights of hydrogen, oxygen and nitrogen in a 10 litre vessel at 27°C and under 750 mm pressure, if the composition of the mixture is 10% hydrogen, 15% oxygen and 75% nitrogen by volume? (0.08) (1.98) (8.43)

4. If a certain weight of a gas occupies 240 ml at 1.25 atmospheres, what is its volume at 0.75 atmosphere? What is the volume at the latter pressure if the weight is doubled? (400) (800)

5. If the composition of air is 23% oxygen and 77% nitrogen by weight, what are the partial pressures of the two gases in a one litre vessel containing 2 g of air at 15°C? (0.3401) (1.2989)

6. 1.531 g of a gas occupy 612 cc at 10°C and under 2 atmospheres, at what pressure (cm Hg) 0.218 g of the same gas occupy 150 cc at 25°C? (92.983)

7. Find the volume occupied by 85 g ammonia gas at 100°C and 410 mm pressure assuming ideal behaviour (283.48)

8. A mixture of 0.355 g of gas A (mol. wt. 71) and 0.90 g of gas B (mol. wt. 90) has a total pressure of 0.1 atmosphere. Calculate the partial pressures for A and B. (0.033) (0.067)

9. 125 cc of gas A at 0.6 atmosphere and 150 cc of gas B at 0.8 atmosphere are mixed together in a 500 cc vessel. Find the total pressure of the mixture if the temperature is constant. (0.39)

10. How much does a litre of octane gas weigh at 150°C and 1 atm pressure ? (3.29)

11. 150 cc of a gas are collected over water at 25°C. The total pressure during the experiment is 740 mm mercury. If the saturated water vapour pressure at 24°C is 24 mm mercury, find the volume of the dry gas at 25°C and 750 mm pressure. (181.3)

12. What is the volume of 10 g of helium at 25°C and 760 mm pressure ? (61.07)

13. Calculate the concentration of a gas in moles per litre at 500°C and under atmospheric pressure. Does the concentration depend on the nature of the gas ? (0.0158)

14. Calculate the weight of a gas which occupies 10 litres volume at 27°C and 780 mm pressure, if 2 g of the same gas occupy 3.9 litres at 23°C and 740 mm assuming ideal behaviour. (5.3)

15. The speeds of diffusion of carbon dioxide and ozone gases were found to be as 0.29 and 0.27 litres respectively. If the relative density of carbon dioxide is 22, find the relative density of ozone. (25.19)

16. A certain hydrocarbon is found to have a vapour density of 2.550 g per litre at 100°C and 760 mm. Chemical analysis shows that the substance contains 1 atom of carbon to 1 atom of hydrogen. What is its molecular formula ? (C_6H_6)

17. What is the volume occupied by 11 g of carbon dioxide at 10°C and under 500 mm pressure ? (8.816)

18. In Victor Meyer experiment, 0.2350 g of a liquid is vaporized, and the volume of displaced air measured over water in a gas burette is 40.2 cc at 23.0°C and 730 mm, what is the molecular weight of the vaporizod material ? (152.7)

19. If one litre of sulphur dioxide and of nitrous oxide measured at N.T.P. weighs 2.9265 and 1.9777 g respectively, calculate the value of the gas constant R for both cases if Boyle's law holds. (0.0801) (0.0815)

20. The volume of a certain quantity of gas is 250 cc at 21°C and under 1.4 atm. At what pressure does the volume change to 300 cc if the temperature is raised to 49°C ? (1.44)

21. 100 cc of oxygen gas measured at 15°C and under 760 mm pressure are mixed with 80 cc nitrogen gas measured at 0°C and under 700 mm pressure. The mixture is introduced in a 250 cc vessel, and the temperature of the vessel is raised to 40°C. What is the total pressure in the vessel ? What are the partial pressures of the gases ? (290.3) (33.4) (256.9)

22. An open vessel was hetaed till one third of the air originally in the vessel at 20°C was expelled. Find the temperature to which the vessel was heated. (166.5)

23. The volume of a certain weight of a gas is 360 cc at

15^0C at what temperature the volume becomes 480 cc at constant pressure ? (111)

24. What is the volume of one mole of an ideal gas at 25^0C and 755 mm pressure ? (24.6)

25. Ten grams of mercury were introduced into a glass vessel which was snbsequently completely evacuated and sealed, then heated to 600^0C Calculate the pressure in atmospheres assuming that the molecule of mercury vapour is monatomic and the volume of the vessel is 1200 cc. (0.993)

26. In a Victor Meyer's experiment 0.241 g of chloroform replaces 47.9 cc of air (over mercury) at 23^0C and under 764 mm pressure. Find the molecular weight of chloroform. (121.5)

27. If 2 litres of a gas at 23^0C and 740 mm pressure weigh 1.73 g. find the volnme of 10 g of the same gas at 73^0C and 1000 mm pressure. (10)

28. A gaseous mixture of 0 495 g gas A (mol. wt. 66) and 0.182 g gas B (mol. wt. 45.5) has a total pressure 762 mm, find the partial pressure of the two gases. (494.61) (267.39)

29. When a piece of metal weighing between 0.5 and 0.6 g is treated with excess dilute acid 181 cc of hxdrogen gas is liberated masured at N.T.P. The atomic weight of the metal is 63.5. Find the accurate weight of the piece of metal to the fourth decimal. (0.5131)

CHAPTER III

THERMOCHEMISTRY

25. The heat of dissociation of hydrogen peroxide by platinum black is – 23060 cal. If the heat of formation of liquid water is – 68360 cal, find the heat of formation of hydrogen peroxide.

SOLUTION

1. $H_2O_{2(l)} = H_2O_{(l)} + \frac{1}{2} O_{2(g)}$ $\Delta H = -23060$ cal

2. $H_{2(g)} + \frac{1}{2} O_{2(g)} = H_2O_{(l)}$ $\Delta H_f = -68360$ cal

3. $H_{2(g)} + O_{2(g)} = H_2O_{2(l)}$ $\Delta H_f = ?$

Subtracting equation 1 from equation 2 we get equation 3

$$H_{2(g)} + \frac{1}{2} O_{2(g)} - H_2O_{2(l)} = H_2O_{(l)} - H_2O_{(l)} - \frac{1}{2} O_{2(g)}$$

$$\therefore H_{2(g)} + O_{2(g)} = H_2O_{2(l)} \quad \text{and} \quad \Delta H_f = -68360 + 23060$$

$$= -\underline{45300} \text{ cal}$$

Answer

26. The heats of solution of anhydrous magnesium sulphate, magnesium suphate monohydrate and magnesium sulphate heptahydrate are – 20280, – 13300 and + 3800 cal respectively. Find the heat of hydration of the following :

a. anhydrous magnesium sulphate to the monohydrate.

b. anhydrous magnesium sulphate to the heptahydrate.

c. magnesium sulphate monohydrate to the heptahydrate.

SOLUTION

1. $MgSO_{4(s)}$ + water = $MgSO_{4(aq)}$ ΔH = – 20280 cal

2. $MgSO_4 . HO_{4(s)}$ + water = $MgSO_{4(aq)}$ ΔH = – 13300 cal

3. $MgSO_4 . 7HO_{4(s)}$ + water = $MgSO_{4(aq)}$ ΔH = + 3800 cal

Subtracting equation 2 from equation 1 :

$$MgSO_{4(s)} + H_2O_{(l)} - MgSO_4.H_2O_{(s)} = MgSO_{4(aq)} - MgSO_{4(aq)}$$

$$\Delta H = (-20280 + 13300)$$

(One mole of H_2O is taken from the excess water present)

$$MgSO_{4(s)} + H_2O_{(l)} = MgSO_4 . H_2O_{(s)} \quad \Delta H = - \underline{6980} \text{ cal}$$

Answer (a)

Similarly subtracting equation 3 from euation 1 :

$$MgSO_{4(s)} + 7H_2O_{(l)} = MgSO_4 . 7H_2O_{(s)} \quad \Delta H = - \underline{24080} \text{ cal}$$

Answer (b)

Also, subtracting equation 3 from equation 2 :

$$MgSO_4 . H_2O_{(s)} + 6H_2O_{(l)} = MgSO_4 . 7H_2O_{(s)} \quad \Delta H = - \underline{17100} \text{ cal}$$

Answer (c)

27. Write the thermochemical equation for the formation of nitrous acid solution and find its heat of formation from the following equations ;

1. $NH_4NO_{2(s)} = N_{2(g)} + 2H_2O_{(l)}$ $\quad \triangle H = -71770$ cal

2. $2H_{2(g)} + O_{2(g)} = 2H_2O_{(l)}$ $\quad \triangle H = -136730$ cal

3. $N_{2(g)} + 3H_{2(g)} + \text{water} = 2NH_{3(aq)}$ $\quad \triangle H = -40640$ cal

4. $NH_{3(aq)} + HNO_{2(aq)} = NH_4NO_{2(aq)}$ $\quad \triangle H = -9110$ cal

5. $NH_4NO_{2(s)} + \text{water} = NH_4NO_{2(aq)}$ $\quad \triangle H = +4750$ cal

SOLUTION

The heat of formation of nitrous acid solution can be obtained from the equation :

6. $\frac{1}{2} H_{2(g)} + \frac{1}{2} N_{2(g)} + O_{2(g)} + \text{water} = HNO_{2(aq)}$ $\quad \triangle \bar{H}_f = Q$

Starting by $H_{2(g)}$, $N_{2(g)}$, $O_{2(g)}$ and water we can form $NH_4NO_{2(aq)}$ by two ways :

Way I :

Multiplying equation 3 by $\frac{1}{2}$ and adding it to equations 4 and 6 we get :

$$2H_{2(g)} + N_{2(g)} + O_{2(g)} + \text{water} = NH_4NO_{2(aq)} \quad \triangle H = -29430 + Q \text{ cal}$$

Way II :

Adding equations 2 and 5 and subtracting equation 1 from the sum we get :

$$2H_{2(g)} + N_{2(g)} + O_{2(g)} + \text{water} = NH_4NO_{2(aq)} \quad \triangle H = -60210 \text{ cal}$$

It follows that :

$$-29430 + Q = -60210$$

$\therefore \; Q = -\underline{30780}$ cal

Answer

28. The action of ozone on a solution of potassium iodide evolves a certain quantity of heat. The action of hydrogen peroxide on potassium iodide solution gives a smaller quantity of heat. The difference referring to one mole of KI is 4 kcal. On the decomposition of one mole of H_2O_2 21.6 kcal are evolved. Calculate the heat of formation of ozone O_3.

SOLUTION

			$\triangle H$ kcal
1.	$O_3 + 2KI + H_2O$	$= 2KOH + O_2 + I_2$	x
2.	$H_2O_2 + 2KI$	$= 2KOH + I_2$	(x+8)
3.	H_2O_2	$= H_2O + \frac{1}{2}O_2$	– 21.6
4.	$O_2 + \frac{1}{2}O_2$	$= O_3$	$\triangle \overline{H}_f$

Adding equations 1 and 3 and subtracting equation 2 we get

$$O_3 = O_2 + \frac{1}{2}O_2 \qquad \triangle H = -29.6 \text{ kcal}$$

By rearrangement we get :

$$O_2 + \frac{1}{2}O_2 = O_3 \qquad \triangle \overline{H}_f = +29.6 \text{ kcal}$$

Answer

Since both reactions 1 and 2 are exothermic, $\triangle H$ in both cases has negative values. As a smaller quantity of heat is evolved in equation 2, the numerical value of $\triangle H$ is less by 4 for each mole of KI and the absolnte value is therefore higher by 8 kcal.

29. A certain volume of methane, on complete combustion in a bomb calorimeter, produces 2.0194 g of liquid water and 11.95 kcal are evolved. Calculate the heat of formation of methane.

Heat of formation of CO_2, $\triangle \overline{H}_f$ = – 94 kcal.

Heat of formation of liquid water, $\triangle \overline{H}_f$ = – 69 kcal.

SOLUTION

$$CH_{4(g)} + 2\,O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)}$$

In the above equation $2H_2O_{(l)}$ formed correspond to $2 \times 18 = 36$ g liquid water per mole (16 g) methane.

$\therefore$ 2.0194 g of liquid water formed were accompanied by 11.95 kcal.

$\therefore$ one mole of CH_4 when completely burnt liberates :

$$11.95 \times \frac{36}{2.0194} = 213.03 \text{ kcal}$$

If the heat of formation of methane $\Delta \overline{H}_f = x$

$\therefore C_{(s)} + 2H_{2(g)} = CH_{4(g)}$ $\qquad \Delta \overline{H}_f = x$ kcal

also $CH_{4(g)} + 2\,O_{2(g)} = 2H_2O_{(l)} + CO_{2(g)}$ $\Delta H = -213.03$kcal

By addition :

$$C_{(s)} + 2H_{2(g)} + 2\,O_{2(g)} = 2H_2O_{(l)} + CO_{2(g)}$$

$$\Delta H = x - 213{,}03 \text{ kcal} \quad (1)$$

Also $C_{(s)} + O_{2(g)} = CO_{2(g)}$ $\quad \Delta \overline{H}_f = -94$ kcal

$2H_{2(g)} + O_{2(g)} = 2H_2O_{(l)}$ $\quad \Delta H = -138$ kcal

By addition : $C_{(s)} + 2H_{2(g)} + 2\,O_{2(g)} = 2H_2O_{(l)} + CO_{2(g)}$

$$\Delta H = -232 \text{ kcal} \quad (2)$$

From equations 1 and 2 :

$x - 213.03 = -232$

$\therefore$ $x = -18.97$ kcal

$\therefore$ $\Delta \overline{H}_f$ for $CH_{4(g)} = -$ 18.97 kcal

Answer

30. If the heats of neutralization of NaOH and NH_4OH with hydrochloric acid are — 13680 and — 12270 cal respectively, calculate the heat of ionization of NH_4OH, assuming that it is practically not ionized.

SOLUTION

1. $HCl_{(aq)} + NaOH_{(aq)} = NaCl_{(aq)} + H_2O_{(l)}$

$\triangle H = -13680$ cal

2. $HCl_{(aq)} + NH_4OH_{(aq)} = NH_4Cl_{(aq)} - H_2O_{(l)}$

$\triangle H = -12270$ cal

Taking the ionization into consideration, the two equations may be rewritten as follows :

3. $H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} = Na^+_{(aq)}$
$+ Cl^-_{(aq)} + H_2O_{(l)}$ $\triangle H = -13680$ cal

4. $H^+_{(aq)} + Cl^-_{(aq)} + NH_4OH_{(aq)} = NH_4^+_{(aq)} + Cl^-_{(aq)}$
$+ H_2O_{(l)}$ $\triangle H = -12270$ cal

The ionization of NH_4OH could be represented by :

$NH_4OH_{(aq)} = NH_4^+_{(aq)} + OH^-_{(aq)}$ $\triangle H = x$ cal

Subtracting equation 3 from 4 we get :

$NH_4OH_{(aq)} - OH^-_{(aq)} = NH_4^+_{(aq)}$

$\triangle H = -12270 + 13680$ cal

$\therefore NH_4OH_{(aq)} = NH_4^+_{(aq)} + OH^-_{(aq)}$

$\triangle H = +1410$ cal

Answer

31. The heat of neutralization of hydrochloric acid by sodium hydroxide is 13780 cal and that for monochloroacetic acid ($CH_2Cl.\ COOH$) is 14280 cal. If one g equivalent of hydrochloric acid is added to one g equivalent of sodium monochloroacetate in a dilute solution, heat is absorbed equivalent to 455 cal. Calculate the amount of acetate decomposed according to the equation :

$$CH_2Cl.\ COONa_{(aq)} + HCl_{(aq)} = NaCl_{(aq)} + CH_2Cl\ .\ COOH_{(aq)}$$

<u>SOLUTION</u>

1. $HCl_{(aq)} + NaOH_{(aq)} = NaCl_{(aq)} + H_2O_{(l)}$

$$\triangle H = -\ 13780 \text{ cal}$$

2. $CH_2Cl\ .\ COOH_{(aq)} + NaOH_{(aq)} = CH_2Cl.COONa_{(aq)} + H_2O_{(l)}$

$$\triangle H = -\ 14280 \text{ cal}$$

Subtracting equation 2 from equation 1 we get equation 3 :

3. $CH_2Cl.COONa_{(aq)} + HCl_{(aq)} = CH_2Cl.COOH_{(aq)} + NaCl_{(aq)}$

$$\triangle H = +\ 500 \text{ cal}$$

Since the heat absorbed in the reaction is only 455 cal,

$\therefore$ the amount of the acetate decomposed $= \dfrac{455}{500} \times 1$

$= \underline{0.9099}$ g equivalent

Answer

32. Calculate the heat of formation of $CS_{2(l)}$ and $H_2S_{(g)}$ using the following information :

		$\triangle H$ kcal
1.	$2\ H_{2(g)} + O_{2(g)} = 2\ H_2O_{(l)}$	$-\ 136$
2.	$S_{(s)} + O_{2(g)} = SO_{2(g)}$	$-\ 71.08$

3. $2\,H_2S_{(g)} + 3O_{2(g)} = 2\,H_2O_{(l)} - 2\,SO_{2(g)}$ – 267

4. $CS_{2(l)} + 3O_{2(g)} = CO_{2(g)} + 2\,SO_{2(g)}$ – 253

5. $C_{(s)} + O_{2(g)} = CO_{2(g)}$ – 96

SOLUTION

Multiplying equation (2) by 2 and adding equation (5) to the resulting equation then subtracting equation (4). we get :

$$2\,S_{(s)} + C_{(s)} = CS_{2(l)} \qquad \triangle\bar{H}_f = 14.84 \text{ kcal}$$

Answer

Similarly dividing equation (1) by 2 and adding equation (2) to the resulting equation then subtracting equation (3) after dividing it by 2, we get :

$$H_{2(g)} + S_{(s)} = H_2S_{(g)} \qquad \triangle\bar{H}_f = -5.58 \text{ kcal}$$

Answer

33. Calculate the heat of hydration of one mole of anhydrous copper sulphate by 5 moles of water vapour at 25°C provided that the heat of evaporation of water is + 10.52 kcal per mole and the heats of solution of anhydrous copper sulphate and copper sulphate pentahydrate are – 28.97 and – 10.12 kcal respectively.

SOLUTION

1. $H_2O_{(l)} = H_2O_{(g)}$ $\triangle = +10.52$ kcal.

2. $CuSO_{4(s)} + 5H_2O_{(g)} = CuSO_4.5H_2O_{(s)}$ $\triangle H = Q$ kcal

3. $CuSO_4.5H_2O_{(s)}$ + water = $CuSO_{4(aq)}$ $\triangle H = -10.12$ kcal

4. $CuSO_{4(s)}$ + water = $CuSO_{4(aq)}$ $\triangle H = -28.97$ kcal

Multiplying equation (1) by 5 and adding the product to equation (2) and (3) gives :

$$5\ H_2O_{(l)} + CuSO_{4(s)} + 5\ H_2O_{(g)} + CuSO_4.5H_2O_{(s)}\ \text{water}$$

$$= 5\ H_2O_{(g)} + CuSO_4.5\ H_2O_{(s)} + CuSO_{4(aq)}$$

$$\triangle H = (10.52 \times 5 + Q - 10.12)$$

$$\therefore\ CuSO_{4(s)} + \text{water} = CuSO_{4(aq)} \quad \triangle H = 42.48 + Q\ \text{kcal}$$

which is the same as equation (4)

$$\therefore \quad 42.48 + Q = -\ 28.97$$

$$Q = -\ 71.45\ \text{kcal}$$

Answer (3)

34. The fusion of $Na_2SO_4.10H_2O$ at constant temperature gives a saturated solution containing x moles of water for each mole of Na_2SO_4 and anhydrous Na_2SO_4 is precipitated. During the fusion 16509 cal are absorbed per each mole of Na_2SO_4.$10H_2O$ changing to the saturated solution and the anhydrous sulphate. If x = 15.6, find :

i) The number of moles of sulphate in the saturated solution and the moles of anhydrous sulphate resulting from one mole of $Na_2SO_4.10H_2O$.

ii) The heat evolved on the formation of $Na_2SO_4.10H_2O$ from one mole of anhydrous Na_2SO_4 and a saturated solution of sodium sulphate.

SOLUTION

The composition of the saturated solution is one mole of is Na_2SO_4

per x moles of water.

For each mole of $Na_2SO_4 . 10H_2O$ on decomposition, $\frac{10}{x}$ mole of Na_2SO_4 is in solution.

Hence the reaction taking place on fusion could be represented by the equation :

$$Na_2SO_4 . 10\,H_2O = \underset{\text{sat. solution}}{\frac{10}{x}\,Na_2SO_4 . 10\,H_2O} + \underset{\text{precipitate}}{\left(1 - \frac{10}{x}\right) Na_2SO_4}$$

Since x = 15.6

$\therefore$ The sulphate in the saturated solution $= \frac{10}{15.6} = \underline{0.641}$ mole

and the precipitated sulphate $= 1 - \frac{10}{15.6} = \underline{0.359}$ mole

Answer (i)

Substituting for x in the above equation :

$$Na_2SO_4 . 10\,H_2O = \text{sat. sol.} + 0.359\ Na_2SO_4 \quad \triangle H = +16509\ \text{cal}$$

$$\therefore \text{sat. sol.} + 0.359\ Na_2SO_4 = Na_2SO_4 .\ 10H_2O \quad \triangle H = -16509\ \text{cal}$$

The heat evolved when one mole Na_2SO_4 reacts with the saturated solution of sulphate $= 16509 \times \frac{1}{0.359}$

$= \underline{46000}$ cal

Answer(ii)

35. 0 0874 g of iodine replaced 13.7 cc of air in a Victor Meyer's apparatus at 21.5°C and 728 mm pressure. Calculate the vapour density of the iodine and its degree of dissociation at the temperature of the experiment.

(Water vapour pressure at 21.5°C = 19.2 mm)

SOLUTION

Volume of air collected in the experiment at N.T.P =

volume of the vapour at N.T.P. $= 13.7 \times \frac{273}{294.5} \times \frac{(723 - 19.2)}{760}$ cc

which weigh 0.0874 g.

Since the molecular weight of a substance in grams (one g mole) occupies 22400 cc at N.T.P.,

$$\therefore \text{ Mol. wt.} = \frac{0.0874 \times 294.5 \times 760 \times 22.400}{13.7 \times 273 \times 703.8}$$

$$= 166.3 \text{ g}$$

This is the apparent mol. wt. of iodine under the conditions of the experiment.

The apparent vapour density of iodine $= \frac{166.3}{2} = \underline{83.15}$

Answer

The calculated vapour density of iodine

$$= \frac{\text{The actual mol. wt.}}{2}$$

$$= \frac{254}{2} = 127$$

$$I_2 \rightleftarrows 2\,I$$

$$(1-\alpha) \qquad 2\alpha$$

If α is the degree of dissociation at equilibrium and we start with one mole of undissociated iodine, then a fraction α will dissociate and $(1-\alpha)$ mole will remain undissociated. The α mole will dissociate to give 2α g atoms of iodine.

The total number of iodine g moles and g atoms at equilibrium is $(1 + \alpha)$.

According to Avogadro's hypothesis.

$$\frac{\text{Volume after dissociation}}{\text{Volume before dissociation}} = \frac{\text{number of moles after dissociation}}{\text{number of moles before dissociation}}$$

Since the density is inversily proportional to the volume

$$\therefore \frac{D_1}{D_2} = \frac{1+\alpha}{1}$$

where D_1 and D_2 are the vapour densities before and after dissociation respectively.

$$\therefore \quad \frac{127}{83.15} = \frac{1+\alpha}{1}$$

$$\therefore \alpha = \underline{0.5273}$$

Answer

α could also be obtained by substituting directly in the equation :

$$\alpha = \frac{D_1 - D_2}{D_2\ (n-1)}$$

where n is the number of units produced by the dissociation of one mole of the reactant.

36. In a series of five eaperiments with HI 0.96 g of the latter in each experiment is entirely converted into vapour at the given temperatures and constant pressure and then quickly cooled. The amount of iodine liberated in each experiment is determined by titration with 0.1N sodium thiosulphate and the volumes of the latter at the corresponding temperatures are as follows :

Temperature °C	250	290	330	360	420
Volumecc	13.25	12.4	12.0	14.6	15.7

Calculate the percentage of HI dissociated at each temperature and express your results in the form of a graph. What conclusions could you draw from the form of the curve?

SOLUTION

Number of equivalents of H I = $\frac{0.96}{128}$ = 0.0075.

The number of equivalents of I_2 formed could be obtained by multiplying the volume of thiosulphate used in cc by the normality 0.1, and dividing by 1000.

The percentage dissociation could be calculated by dividing the equivalents of iodine by 0.0075 and multiplying by 100.

Temperature°C	250	290	330	360	420
Volume of thiosulphate in cc	13.25	12.4	12.0	14.6	15.7
Equivalents of iodine $\times 10^4$	13.25	12.4	12.0	14.6	15.7
% dissociation	17.66	16.63	16.00	19.46	20.93

If the curve is drawn it will show a minimum at about 320°C. Below this temperature the dissociation decreases with rise of temperature, so the reaction is exothermic. Above the minimum the dissociation increases with rise of temperature, showing that the reaction becomes endothermic.

37. When carbon monoxide, hydrogen and methyl alcohol are burnt completely in closed vessels containing oxygen, the heats evolved are 67700, 68400 and 170600 cal per mole respectively. Using these data, find the heat change in the following reaction :

$$CO_{(g)} + 2\,H_{2(g)} = CH_3OH_{(l)}$$

If this reaction is carried out under atmospheric pressure at 300°C, what is the work done by the atmosphere on the system per mole of methyl alcohol formed? What is the effect produced on the heat of the reaction if it takes place under constant pressure or at constant volume?

SOLUTION

1. $CO_{(g)} + \frac{1}{2} O_{2(g)} = CO_{2(g)}$ $\triangle E = -67700$ cal

2. $H_{2(g)} + \frac{1}{2} O_{2(g)} = H_2O_{(l)}$ $\triangle E = -68400$ cal

3. $CH_3OH_{(l)} + 1\frac{1}{2} O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)}$

$\triangle E = -170600$ cal

4. $CO_{(g)} + 2H_{2(g)} = CH_3OH_{(l)}$ $\triangle E = Q_V$ cal

$\triangle E$ and Q_V are used since the process is carried out at constant volume.

If equation (2) is multiplied by 2 and added to equation (1), then equation (3) is subtracted from the sum, equation (4) is obtained.

$\therefore CO_{(g)} + 2H_{2(g)} = CH_3OH_{(l)}$ $\triangle E = -33900$ cal
Answer

The work done by the atmosphere on the system is $P \triangle V$.

where $\triangle V$ is the change in volume.

Assuming the gases to be ideal $\therefore P \triangle V = \triangle n RT$

where $\triangle n$ is the change in number of moles of gases.

$\therefore \triangle n$ = number of moles of gaseous resultants - number of moles of gaseous reactants

$= 0 - 3 = -3$

$\therefore$ The work done $= \triangle n\ RT$

$= -3 \times 1.987 \times 573 = -$ 3416 cal

Answer

The negative sign indicates work done on the system by the atmosphere.

The heat of the reaction at constant pressure Q_p (or $\triangle H$) differs therefore, from the heat of the reaction at constant volume Q_v by the value of the work done.

$$\triangle H = \triangle E + P\triangle V$$

$$\text{or} \quad Q_p = Q_v + P\triangle V$$

$$= Q_v + \triangle n\ RT$$

$$= -33900 - 3416 = -37316 \text{ cal}$$

Answer

38. The heats of formation of $NaOH_{(aq)}$, $NaNO_{3(aq)}$ and $OH^-_{(aq)}$ are $-$ 112.236, $-$ 106.651 and $-$ 54.957 kcal mole^{-1} respectively. From this data calculate the heat of formation of $NO_3^-{}_{(aq)}$.

SOLUTION

1. $Na_{(s)} + \frac{1}{2} H_{2(g)} + \frac{1}{2} O_{2(g)}$ + water = $Na\,OH_{(aq)}$

$= Na^+_{(aq)} + OH^-_{(aq)}$ (*) $\triangle \bar{H}_f = -112.236$ kcal.

(*) The heat of formation of an aqueous strong electrolyte is the sum of the heats of formation of aqueous ions into which the electrolyte ionizes.

2. $Na_{(s)} + \frac{1}{2} N_{2(g)} + \frac{3}{2} O_{2(g)}$ + water = $NaNO_{3(aq)}$

$= Na^+_{(aq)} + NO_3^-{}_{(aq)}$ $\Delta \bar{H}_f$ = - 106.651

3. $\frac{1}{2} O_{2(g)} + \frac{1}{2} H_{2(g)}$ + e + water = $OH^-_{(aq)}$

$\Delta \bar{H}_f$ = − 54.957

Adding equations (2) and (3) and subtracting (1) :

$$\frac{1}{2} N_{2(g)} + \frac{3}{2} O_{2(g)} + e + \text{water} = NO_3^-{}_{(aq)}$$

$\Delta \bar{H}_f$ = − 49.372 kcal

∴ Heat of formation of $NO_3^-{}_{(aq)}$ = − 49.372 kcal $mole^{-1}$
Answer

39. Calculate the integral heat of dilution for the addition of 195 moles of H_2O to 1 mole of HCl in 5 moles of H_2O. The integral heats of solution of HCl in 5 moles of water and 200 moles of water are − 15.31 and − 17.74 kcal respectively.

SOLUTION

The integral heat of solution is the enthalpy change for the solution of 1 mole of solute in n moles of solvent.

Integral heat of solution

1. $HCl_{(g)} + 200\ H_2O_{(l)}$ = HCl in 200 H_2O ΔH = − 17.74 kcal

2. $HCl_{(g)} + 5\ H_2O_{(l)}$ = HCl in 5 H_2O ΔH = − 15.31 kcal

The integral heat of dilution is the enthalpy change when a solution containing 1 mole of solute is diluted from one concentration to another.

By subtracting equation (2) from equation (1) :

195 H_2O = HCl in 200 H_2O — HCl in 5 H_2O

ΔH = − 2.43 kcal

or, by rearranging :

$$HCl \text{ in } 5\,H_2O + 195\,H_2O = HCl \text{ in } 200\,H_2O$$

The integral heat of dilution $\triangle H = -$ 2·43 kcal

Answer

40· From heats of formation data given in Table I (see appendix) calculate the enthalpy change at 25°C per kg of fuel and oxidizer for each of the following reactions :

a) $H_{2(g)} + \frac{1}{2}\ O_{2(g)} = H_2O_{(g)}$

b) $CH_3OH_{(l)} + {}^3/_2\ O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$

c) $H_{2(g)} + F_{2(g)} = 2HF_{(g)}$

SOLUTION

a) Since ΔH for a reaction = sum of heats of formation of products minus sum of heats of formation of reactants

For the reaction :

	$H_{2(g)}$	$+ \frac{1}{2}\ O_{2(g)}$	$= H_2O_{(g)}$
Heats of formation at 25°C	0	0	$-$ 57.8 kcal

$\therefore\ \Delta H = -$ 57.8 kcal

$\therefore$ Enthalpy change at 25°C per kg of fuel and oxidizer

$$= \frac{-57.8}{2 + \frac{1}{2} \times 32} \times 1000 = -\ 3210 \text{ kcal}$$

Answer (a)

b) $CH_3OH_{(l)} + {}^3/_2\, O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$

Heats of formation at 25°C: -57.02 0 -94.05 $2\,(-57.8)$ kcal

$$\therefore\ \Delta H = -94.05 + 2\,(-57.8) - (-57.02)$$
$$= -152.63 \text{ kcal}$$

∴ Enthalpy change at 25°C per kg of fuel and oxidizer

$$= -\frac{152.63}{32+48} \times 1000 = -\underline{1908} \text{ kcal}$$

Answer (b)

c) $H_{2(g)} + F_{2(g)} = 2HF_{(g)}$

Heats of formation at 25°C: 0 0 $2(-64.2)$ kcal

$$\therefore\ \Delta H = -2 \times 64.2 = -128.4 \text{ kcal}$$

∴ Enthalpy change at 25°C per kg of fuel and oxidizer

$$= \frac{-128.4}{2+2\times 19} \times 1000 = -\underline{3210} \text{ kcal}$$

Answer

41. In a bomb calorimeter, the combustion of 1 735 g of sucrose produces a temperature rise of 2.907°C. The heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) is 1349.6 kcal mole^{-1}

a) What is the total heat capacity of the water and the calorimeter ?

b) If the calorimeter contains 1850 grams of water (specific heat = 1.0 cal deg^{-1} g^{-1}), what is the effective heat capacity of the calorimeter ? In this problem, corrections for the oxidation of the wire and residual nitrogen may be neglected.

SOLUTION

$$\text{Heat of combustion of sucrose per g} = \frac{\text{heat of combustion per mole}}{\text{mol. wt. of sucrose}}$$

$$= \frac{1349.6}{342} \text{ kcal g}^{-1}$$

a) Heat capacity of water and calorimeter $\times \Delta t$ =
Heat liberated from combustion of 1.753 g sucrose
or heat capacity of water and calorimeter $\times$ 2.907

$$= \frac{1349.6}{342} \times 1.753$$

$$\therefore \text{Heat capacity of calorimeter and water} = \frac{1349.6 \times 1.753}{342 \times 2.907}$$

$$= \underline{2.375} \text{ kcal deg}^{-1}$$

Answer

b) 2.375×10^3 cal deg^{-1} = heat capacity of water + heat capacity of calorimeter

= 1850 × 1 + heat capacity of calorimeter

Heat capacity of calorimeter = 2375 − 1850 = $\underline{525}$ cal deg^{-1}

Answer (b)

42. Calculate the enthalpy change for the following reactions :

a) $HCl_{(aq)} + Na\,Br_{(aq)} = Na\,Cl_{(aq)} + HBr_{(aq)}$

b) $Ca\,Cl_{2(aq)} + Na_2CO_{3(aq)} = Ca\,CO_{3(s)} + 2NaCl_{(aq)}$

c) $Li_{(s)} + {}^1/_2\ Cl_{2(g)} + \text{water} = Li^+_{(aq)} + Cl^-_{(aq)}$

Note : data on enthalpies of formation of ions are obtained from text-books of physical chemistry.

SOLUTION

(a) $HCl_{(aq)} + NaBr_{(aq)} = NaCl_{(aq)} + HBr_{(aq)}$

No heat is evolved or absorbed in such reaction.

i.e. $\Delta H = \underline{0}$

Answer (a)

Reason : Strong electrolytes are completely dissociated and their heats of dilution are very small in dilute solutions and the above reaction can be represented by :

$$H^{+}_{(aq)} + Cl^{-}_{(aq)} + Na^{+}_{(aq)} + Br^{-}_{(aq)} = Na^{+}_{(aq)} + Cl^{-}_{(aq)} + H^{+}_{(aq)} + Br^{-}_{(aq)}$$

It is apparent that no heat effect would be expected.

b) $CaCl_{2\,(aq)} + Na_2CO_{3(aq)} = CaCO_{3(s)} + 2NaCl_{(aq)}$

This reaction can be written as follows :

$$Ca^{++}_{(aq)} + 2Cl^{-}_{(aq)} + 2Na^{+}_{(aq)} + CO_3^{--}{}_{(aq)}$$

$$= CaCO_{3(s)} + 2Na^{+}_{(aq)} + 2Cl^{-}_{(aq)}$$

or $Ca^{++}_{(aq)} + CO_3^{--}{}_{(aq)} = CaCO_{3(s)}$

Heats of formation	− 129.77	− 161.63	— 288.45 kcal

$$\Delta H = -288.45 - (-129.77 - 161.63)$$

$$= +\underline{2.95}\text{ kcal}$$

Answer (b)

c) $Li_{(s)} + \frac{1}{2} Cl_{2(g)} +$ water $= Li^{+}_{(aq)} + Cl^{-}_{(aq)}$

eats of formation 0 0 − 66.55 − 40.02 kcal

$\therefore \quad H\triangle = -\ 66.55 - 40.02 - 0$

$= -\ \underline{106.57}$ kcal

Answer (c)

PROBLEMS FOR PRACTICE

1. Calculate the heat of formation of lithium chloride in 12 moles of water, if the heat of formation of lithium chloride solid at 25°C is – 97 7 kcal and the integral heat of solution of lithium chloride in 12 moles of water is – 8.011 kcal. (– 105.711)

2. Calculate the heat of formation of hydrochloric acid in 200 moles of water, given that the heat of formation of hydrochloric acid is — 22.063 kcal and that the integral heat of solution of hydrochloric acid in 200 moles of water is — 17,740 kcal. (– 39.803)

3. The heat of combustion at constant pressure and 25°C of liquid carbon disulphide is 256.6 kcal per mole. Calculate its heat of formation Heats of formation data in appendix. (21.0)

4. The heat of combustion at constant pressure at 25°C of liquid toluene is 934.5 kcal per mole. Calculate the heat of formation of liquid toluene if the heats of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are – 94.052 and – 68.317 kcal mole^{-1} respectively. (2.868)

5. Calculate the heats of hydration of anhydrous calcium chloride to $CaCl_2.6H_2O$ from the following data :

$$Ca\ Cl_{2(s)} + \text{water} = Ca\ Cl_{2(aq)} \quad \triangle H = -\ 18.0\ \text{kcal}$$

$$Ca\ Cl_2.6H_2O_{(s)} + \text{water} = Ca\ Cl_{2(aq)} \quad \triangle H = +\ 4.5\ \text{kcal}$$

(– 22.5)

6. Using data on heats of formation in the appendix,

calculate the heats of combustion ($\Delta \bar{H}$) at 25°C of the following subtances to $H_2O_{(l)}$ and $CO_{2(g)}$:

a) n-butane b) methanol c) acetic acid.

(—687.9) (—173.63) (—208.2)

7. For acetone. ΔH^0_f is — 61.4 kcal mole^{-1} at 25°C

a) Calculate the heat of combustion at constant pressure.

b) Calculate the heat evolved when 2 g of acetone is burnt under pressure in a closed bomb at 25°C. (–425.65) (14.64)

8. The combustion of oxalic acid in a bomb calorimeter yields 673 cal g^{-1} at 25°C. Calculate $\Delta \bar{E}$ and $\Delta \bar{H}$ for the combustion of 1 mole of oxalic acid. (–60570) (–59683)

9. Calculate the heat evolved at 25°C in the reaction :

$$3\ Mg_{(s)} + Fe_2\ O_{3(s)} = 3\ Mg\ O_{(s)} + 5\ Fe_{(s)}$$

When Mg is oxidized to MgO, ΔH = – 145.7 kcal. The heat of formation of Fe_2O_3 is – 196.5 kcal mole^{-1} ? (240.6)

10. In determining the heat of combustion of naphthalene in a bomb calorimeter, it was found that ;

$$C_{10}H_{8(s)} + 12\ O_{2(g)} = 10\ CO_{2(g)} + 4H_2O_{(l)}$$

$$\Delta E = -\ 1234\ kcal$$

Find (a) the heat content change in the reaction and (b) the heat of formation of naphthalene from its elements at 25°C. Use data given in table I. (–1235.17) (21.38)

11. a) Calculate the heat evolved when 1 gram of ethylene is exploded at constant pressure at 25°C with an excess of air.

b) Calculate the heat evolved when 1 g of ethylene is exploded with an excess of pure oxygen at 20 atm pressure in a closed bomb. (– 12.02) (12.0)

12. Calculate the heat of formation of $PCl_{5(s)}$, given the heats of the following reactions at 25°C :

1) $2P_{(s)} + 3Cl_{2(g)} = 2\ PCl_{3(l)}$ $\Delta H = -151800$ cal

2) $PCl_{3(l)} + Cl_{2(g)} = PCl_{5(s)}$ $\Delta H = 32810$ cal

(– 108.7)

13. If the heat of solution of barium chloride is — 2070 cal and the heat of hydration to $BaCl_2.2H_2O$ is – 6970 cal, find the heat of solution of the hydride and write the necessary equations. (4900)

14. The vapour density of vaporized SO_3 at 630°C and atmospheric pressure is 9.27×10^{-4} g/cc. Calculate the degree of dissociation of the gas. (0.03528)

15. Phosphorous pentachloride, on evaporation at 127°C dissociates to the extent of 20%. Calculate the work done in calories, when 104.3 g of phosphorous pentachloride are evaporated at the same temperature. (480)

16. If the heats of combustion at 27°C for carbon monoxide and carbon to carbon dioxide are – 67950 and – 96950 cal respectively under constant pressure, find the heat of formation of carbon monoxide under constant pressure and under constant volume. (—29300) (– 29000)

17. When 10 g of sodium are dissolved in a big quantity of water 18800 cal of heat are evolved. When 20 g of sodium

oxide are dissolved under the same conditions 20400 cal are evolved. Find the heat of formation of sodium oxide if the heat of formation of liquid water from oxygen and hydrogen gases is – 68000 cal. (— 91240)

18. Given that :

1) $K_{(s)} + H_2O_{(l)} + aq = KOH_{(aq)} + \frac{1}{2}H_{2(g)}$ $\Delta H = -481$ kcal

2) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(l)}$ $\Delta \bar{H}_f = -68.4$ kcal

3) $KOH_{(s)} + aq = KOH_{(aq)}$ $\Delta H = -133$ kcal

Find the heat of formation of KOH from its elements. (— 1032)

19. Calculate the heat of the reaction :

$$2\ Al_{(s)} + Cr_2O_{3(s)} = Al_2O_{3(s)} + 2\ Cr_{(s)}$$

if the heats of formation of aluminium oxide and chromium oxide are — 380 and – 270 kcal respectively. (– 110)

20. If the heats of combustion of carbon, hydrogen and formic acid are – 97, – 68 and — 66 kcal respectively. find the heat of formation of formic acid. (- 99)

21. In an adiabatic calorimeter 0.4362 g of naphthalene caused a rise of 1.707°C in temperature. The heat capacity of the calorimeter and water was 2460 cal per deg. If corrections for the wire and residual nitrogen are neglected, what is $\Delta \bar{E}$ for the combustion of naphthalene per mole ? (– 1232)

22. Calculate the amount of work and heat produced, at constant volume at 327°C, for the following reaction :

$$CH_3OH_{(l)} + \frac{1}{2}O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$$

$\Delta H = -196400$ cal

(−199400)

23. How many litres of methane, measured at N.T.P. must be present to raise the temperature of 2 kg of water from 20°C to 30°C. The heat of combustion of methane is 213 kcal. (2.1)

24. If the heat of combustion of diamond and graphite are − 94.5 and − 94.05 kcal respectively, what is the heat of transformation of graphite to diamond ? (450)

25. If the heat of combustion of carbon, hydrogen and ethyl alcohol are − 94.05, − 68.32 and − 326.7 kcal respectively, find the heat formation of ethyl alcohol. (− 66.36)

26. If the heat of neutralization of sodium hydroxide with hydrochloric acid is − 13680 cal, with acetic acid is — 13400 cal and with butyric acid is − 13800 cal respectively, find the heat of ionization of the two latter acids. (280) (−120)

27. 0.702 g of benzoic acid (heat of combustion = 6234 cal/g) are burnt in oxygen under pressure in an adiabatic calorimeter. The temperature is raised by 1.263°C. When 0.621g of a fuel oil is burnt under the same conditions the temperature is raised by 1.682°C. What is the heat of combustion of the fuel oil ? (9385)

28. If the heats of formation of ferric oxide and aluminium oxide are −195.6 kcal and −381.0 respectively, find out the heat

of reduction of ferric oxide by aluminium. Is it an endothermic or exothermic reaction ? (— 185.4)

29. Gold hydroxide dissolves in hydrochloric acid according to :

$$Au(OH)_{3(s)} + 4HCl_{(aq)} = HAuCl_{4(aq)} + 3H_2O_{(l)} \quad \triangle H = -23000cal$$

and in hydrobromic acid according to :

$$Au(OH)_{3(s)} + 4HBr_{(aq)} = HAuBr_{4(aq)} + 3H_2O_{(l)} \quad \triangle H = -36800cal$$

If one mole $HAuBr_4$ is mixed with 4 moles of hydrochloric acid heat equivalent to 510 cal is absorbed. What percentage of bromo-auric acid changes to chloro – auric acid ? (3.7)

30. The heats of combustion of ethane, ethylene and hydrogen are — 370440, – 333350 and – 68400 cal respectively. Find the heat of reduction of ethylene to ethane according to the equation :

$$C_2H_{4(g)} + H_{2(g)} = C_2H_{6(g)} \quad (-31310)$$

31 $$HCl_{(aq)} + AgNO_{3(aq)} = AgCl_{(s)} + HNO_{3(aq)} \quad \triangle H = -15800cal$$

$$KCl_{(aq)} + AgNO_{3(aq)} = AgCl_{(s)} + KNO_{3(aq)} \quad \triangle H = -15800cal$$

$$\tfrac{1}{2}BaCl_{2(aq)} + AgNO_{3(aq)} = AgCl_{(s)} + \tfrac{1}{2}Ba(NO_3)_{2(aq)}$$

$$\triangle H = -15800cal$$

Give reasons for the constant enthalpy changes in the above reactions and find the enthalpy change for the following reaction :

$$CsCl_{(aq)} + CH_3COOAg_{(aq)} = AgCl_{(s)} + CH_3COOCs_{(aq)}$$

(—15800)

32. Find the heat of formation of carbon disulphide if the heats of formation of sulphur dioxide and carbon dioxide are −71 and −94.3 kcal respectively and the heat of combustion of carbon disulphide is −265.1 kcal. (28.8)

33. The heat of neutralization of nitric acid by sodium hydroxide is −13680 cal and that of chloroacetic aeid ($CHCl_2COOH$) by sodium hydroxide is −14830 cal. If one equivalent of sodium hydroxide is added to a dilute solution containing one equivalent of nitric acid and one equivalent of chloroacetic acid and −13960 cal are evolved, find the distribution ratio of the sodium hydroxide between the two acids. (3.1 : 1)

CHAPTER IV

SOLUTIONS

43. A solution of KNO_3 contains 192.6 grams of salt per litre of solution. The density of the solution is 1.1432 g ml^{-1}. Calculate the concentration in terms of :

(a) molality (b) molarity (c) mole fraction (d) weight per cent.

SOLUTION

Molecular weight of $KNO_3 = 39 + 14 + 48 = 101$

Weight of a litre of solution containing 192.6 g of KNO_3

$$= 1000 \times 1.1432 = 1143.2 \text{ g}$$

Weight of solvent in a litre of solution $= 1143.2 - 192.6$

$$= 950.6 \text{ g}$$

a) $$\text{Molality} = \frac{\text{moles solute}}{\text{1000 g solvent}} = \frac{\frac{192.6}{101}}{\frac{950.6}{1000}}$$

$$= \underline{2.005} \text{ molal}$$

Answer (a)

b) $$\text{Molarity} = \frac{\text{moles solute}}{\text{litres of solution}} = \frac{\frac{192.6}{101}}{1}$$

$$= \underline{1.905} \text{ molar}$$

Answer (b)

c) Mole fraction (of solute)

$$= \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}}$$

$$= \frac{\frac{192.6}{101}}{\frac{192.6}{101} + \frac{950.6}{18}} = \underline{0.0348}$$

Answer (c)

d) Weight per cent $= \frac{\text{grams of solute}}{\text{100 grams of solution}}$

$$= \frac{192.9 \times 100}{1143.2} = \underline{16.85}$$

Answer (d)

44. Solutions of hydrogen chloride in chlorobenzene obey Henry's law. In dilute solutions,

$$K = \frac{p}{m} = 0.438$$

where K is Henry's constant, p is given in atmospheres and m is the molality. What is the partial pressure of HCl in mm over a 1 per cent by weight solution of HCl in chlorobenzene ?

SOLUTION

Weight of HCl in 1000 g chlorobenzene $= \frac{1000 \times 1}{99} = 10.1$g

Molality of HCl $= \frac{10.1}{36.5} = 0.277$ mole per 1000 g solvent.

But $K = \frac{p}{m} = 0.438$

$\therefore \quad p = 0.438\, m = 0.438 \times 0.277$ atm

$= 0.438 \times 0.277 \times 760$

$= \underline{92.1}$ mm

Answer

45. A 10 litre tank of methane at 470 mm total pressure and 25°C contains 1 litre of water. How many grams of methane are dissolved in the water ?

Henry's law constant for methane at 25°C :

$$K_2 = \frac{P_2}{x_2} = \frac{\text{partial pressure of gas in mm}}{\text{mole fraction of gas in solution}} \quad (*)$$

$$= 31.4 \times 10^6$$

and the vapour pressure of water at 25°C is 23.76 mm.

SOLUTION

Substituting in Henry's law : $K_2 = \frac{P_2}{x_2}$

$$31.4 \times 10^6 = \frac{760 - 23.76}{x_2}$$

$x_2 = \frac{716.24}{31.4 \times 10^6} = 22.8 \times 10^{-6}$ = mole fraction of methane in aqueous solution.

(*) The Subscript 2 indicates solute ; a subscript 1 indicates solvent.

$$x_2 = \frac{n_2}{n_2 + n_1} \backsimeq \frac{n_2}{n_1}$$

n_2 is negligible compared to n_1 because the solution is very dilute.

$$n_2 = 22.8 \times 10^{-6} \times n_1$$

$$= 22.8 \times 10^{-6} \times \frac{1000}{18} = 1.27 \times 10^{-3} \text{ moles}$$

Grams of methane dissolved in water $= n_2 \times$ mol. wt. of CH_4

$= 1.27 \times 10^{-3} \times 16$

$= 0.0203$ g

Answer

46. Dry air is drawn in succession through a series of bulbs containing 4.257 g of a substance X dissolved in 52.68 g of ethyl alcohol (C_2H_5OH) and then through a similar series of bulbs containing pure alcohol. The indrawn air and the two sets of bulbs are at the same constant temperature. The loss of weight in the first series of bulbs is 1.292 g and in the second series 0.0313 g. Calculate the molecular weight of X.

SOLUTION

Raoult's law can be expressed as :

$$\frac{p^0 - p}{p^0} = \frac{n_2}{n_1 + n_2} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

Where p^0 is the vapour pressure of the pure solvent, p the vapour pressure of the solution, w_2 the weight of the solute, M_2 its molecular weight, w_1 the weight of the solvent and M_1 its molecular weight. The loss of weight of the first series of bulbs is proportional to the vapour pressure of the solution (p) and the loss of weight of the second series of bulbs is proportional to the lowering of vapour prrssure ($p^o - p$).

$$\frac{0.0313}{0.0313 + 1.292} = \frac{\frac{4.257}{M_2}}{\frac{52.68}{46} + \frac{4.257}{M_2}}$$

$\therefore \; M_2 = \underline{153.5}$

Answer

47 The vapour pressure of a solution containing 6.69 g of $Ca(NO_3)_2$ in 100 g of water is 746.9 mm at 100°C. What is the degree of dissociation of the salt ?

SOLUTION

$$\begin{matrix} Ca(NO_3)_2 & \rightleftarrows & Ca^{++} & + & 2NO_3^- \\ 1 - \alpha & & \alpha & & 2\alpha \end{matrix}$$

Mol. wt. of $Ca(NO_3)_2$ = 164.1

Moles of $Ca(NO_3)_2$ in 100 g water $= \frac{6.69}{164.1}$

Moles of H_2O in 100 g water $= \frac{100}{18}$

Raoult's law can be approximated since $n_2 << n_1$.

$$\frac{p^0 - p}{p^0} = \frac{n_1}{n_2}$$

If α is the degree of dissociation of $Ca(NO_3)_2$, then at equilibrium, the total number of units present in solution are $(1 + 2\alpha)$.

Since the initial number of moles of the solute is n_2, then, at equilibrium, it will be $n_2\ (1 + 2\ \alpha)$.

$$\therefore \quad \frac{760 - 746.9}{760} = \frac{\frac{6.69}{164.1}(1 + 2\alpha)}{\frac{100}{18}}$$

$$\therefore \quad \alpha = \underline{0.675}$$

Answer

48. A mixture of ethylene dibromide ($C_2H_4Br_2$) and water boils at 91°C. What is the percentage composition distilled over on steam-distilling the mixture ?

(saturated water vapour pressure at 91°C is 545 mm)

SOLUTION

The molecular weight of ethylene dibromide = 188.

From Raoult's law :

$$\frac{\text{The moles of the component A in the distillate } n_A}{\text{The moles of the component B in the distillate } n_B} = \frac{\text{The vapour pressure } p_A}{\text{The vapour pressure } p_B}$$

at the temperature of distillation.

$$\therefore \quad \frac{w_A / M_A}{w_B / M_B} = \frac{P_A}{P_B}$$

where w_A , w_B , M_A and M_B are weights in grams and molecular weights of the components A and B respectively.

$$\therefore \frac{w_A}{w_B} = \frac{P_A \ M_A}{P_A \ M_B}$$

The total vapour pressure over the mixture at its boiling point is equal to the atmospheric pressure 760 mm.

∴ The vapour pressure of the bromide at the same temperature = 760 – 545 = 215 mm.

$$\therefore \frac{w_{H_2O}}{w_{bromide}} = \frac{545 \times 18}{215 \times 188} = \frac{4.12}{1}$$

∴ The percent weight of bromide $= \frac{5.12 - 4.12}{4.12 + 1} \times 100 = 19.5$

Answer

49. An aqueous solution of a non – volatile solute freezes at — 0.200°C. What is its boiling point ? What is its vapour pressure at 100°C ? The molal boiling point constant for water is 0.51 and the molal freezing point constant is 1.86.

SOLUTION

The molal freezing point constant for water K_f is the lowering in the freezing point of an aqueous solution containing one mole of the non-volatile solute in 1000 g of water, and the molal boiling point constant K_n is the rise of the boiling point of the same solution.

$$\therefore \Delta t_f = K_f \frac{w_2}{M_2 w_1} \times 1000$$

also $\Delta t_b = K_b \dfrac{w_2}{M_2 w_1} \times 1000$

$$\therefore \frac{\Delta t_f}{\Delta t_b} = \frac{K_f}{K_B}$$

$$\therefore \Delta t_b = \frac{\Delta t_f \times K_b}{K_f}$$

But $\Delta t_f = 0.2$, $K_b = 0.51$ and $K_f = 1.86$

$$\therefore \Delta t_b = \frac{0.2 \times 0.51}{1.86} = 0.055$$

$\therefore$ The boiling point of the solution $= 100 + 0.055$

$= \underline{100.055°C}$

Answer

$\because \Delta t_b = K_b \times m$

where m is the molality of the solute in water.

$\therefore 0.055 = 0.51 \times m$

$m = \dfrac{0.055}{0.51} = 0.1078$ mole per 1000 g water.

$$0.1078 = \frac{w_2}{M_2 w_1} \times 1000$$

$$= \frac{n_2}{w_1} \times 1000$$

$$\therefore \frac{0.1078}{1000} = \frac{n_2}{w_1}$$

$$\therefore \quad \frac{n_2}{n_1} = \frac{n_2}{w_1/M_1} = \frac{0.1078}{1000} \times M_1$$

$$= \frac{0.1078 \times 18}{1000}$$

But from Raoult's law :

$$\frac{n_2}{n_1} = \frac{p^0 - p}{p^0}$$

$$\therefore \frac{0.1078 \times 18}{1000} = 1 - \frac{p}{p^0}$$

The vapour pressure of pure water $p^0 = 1$ atm at 100°C

$$\therefore \quad p = 1 - \frac{0.1078 \times 18}{1000}$$

$$= \underline{0.998} \text{ atm}$$

Answer

50. A hydrocarbon of the type $H(CH_2)_n H$ is dissolved in ethylene bromide, which freezes at 10.00°C. A solution which contains 0.81 gram of hydrocarbon per 190 grams of ethylene bromide freezes at 9.47°C. Calculate the value of n.

SOLUTION

$$\triangle t_f = 10 - 9.47 = 0.53^0$$

K_f (for ethylene bromide) = 12.5 deg mol l^{-1} (appendix table II),

$$\triangle t_f = K_f m = K_f \cdot \frac{w_2}{M_2} \cdot \frac{1000}{w_1}$$

$$0.53 = 12.5 \times \frac{0.81}{M_2} \times \frac{160}{1000}$$

$\therefore \quad M_2 = 100.5$

But the molecular weight of the hydrocarbon $H(CH_2)_n H$

$= 2 + 14n$

$\therefore 2 + 14n = 100.5$

$\therefore \quad n = 7$

Answer

51· Ten grams of benzene, 10 grams of toluene and 10 grams of naphthalene are added together to give a homogeneous solution. If it is assumed that the solution is ideal, how many grams of toluene will be vaporized by passing through 10 litres of air at 30°C if the vapour pressure of toluene at this temperature is 36.7 mm, that of benzene is 118.5 mm and that of naphthalene is negligible ?

SOLUTION

The mol. wts. of benzene C_6H_6, toluene $C_6H_5CH_3$ and naphthalene $C_{10}H_8$ are 78, 92 and 128 respectively.

Moles of benzene $= \frac{10}{78} = 0.128$

» » toluene $= \frac{10}{92} = 0.109$

» » naphthalene $= \frac{10}{128} = 0.078$

Total moles $= 0.315$

$$\text{Moles of air} = \frac{PV}{RT} = \frac{1 \times 10}{0.082 \times 303} = 0.403$$

Since the solution is assumed to be ideal, then Raoult's law can be applied to each of the components in the solution.

$$p = p^0 x \text{*}$$

$$\text{Partial vapour pressure of benzene} = 118.5 \times \frac{0.128}{0.315} = 48.2 \text{ mm}$$

$$\text{Partial vapour pressurne of toluene} = 36.7 \times \frac{0.109}{0.315} = 12.7 \text{ mm}$$

,, ,, ,, naphthalene = 0 mm

,, ,, ,, air = 760 - (48.2 + 12.7) = 699.1 mm

But from Dalton's law of partial pressures :

$$p_{benzene} : p_{toluene} : p_{air} = n_{benzene} : n_{toluene} : n_{air}$$

where p is the partial pressure of the component and n is the number of moles of vapour of the component carried by the air.

$$\therefore \frac{\text{partial pressure of toluene}}{\text{,, ,, ,, air}} = \frac{\text{moles of toluene}}{\text{,, ,, air}}$$

$$\text{or} \quad \frac{12.7}{699.1} = \frac{\text{moles of toluene}}{0.403}$$

$$\therefore \text{Moles of toluene vaporized} = \frac{0.403 \times 12.7}{699.1}$$

$$= 0.00732$$

---

* The mole fraction of a component in a solution is given the symbol x, while in vapour it is given the symbol y.

$\therefore$ Grams of toluene vaporized $= 0.00732 \times 92$

$= \underline{0.673}$ g

Answer

52. Aqueous solutions of dichloroacetic acid (molecular weight 129) of strength (a) 0.1 molal and (b) 0 01 molal have freezing points -0.278 and $-0.033°C$ respectively. On the basis of Arrhenius theory, what is the degree of ionization in each of these solutions ?

(Molal boiling point constant K_f for water $= 1.85°C$)

SOLUTION

12.9 g of dichloroacetic acid in 1000 g water lowers the freezing point 1.85°C.

$\therefore$ For the 0.1 molal solution :

12.9 g dichloroacetie acid in 1000 g water lowers the freezing point by Δt_f °C

$$\Delta t_{f,\ calc.} = 1.85 \times \frac{12.9}{129} = 0.185\,°C$$

Similarly for the 0.01 molal solution.

$$\Delta t_{f,\ calc.} = 1.85 \times \frac{1.29}{129} = 0.0185°C$$

From Arrhenius theroy we can deduce :

$$\frac{\Delta t_{f,\ obs.}}{\Delta t_{f,\ calc.}} = i \quad \text{also } \alpha = \frac{i-1}{n-1}$$

where 'i' is van't Hoff's factor, 'n' is the number of ions resulting from the ionization of one molecule and 'α' is the degree of ionization.

a) For the 0.1 molal solution :

$$i = \frac{0.278}{0.185} = 1.503$$

$$\text{and } \alpha = \frac{1.503 - 1}{2 - 1} = \underline{0.503}$$

Answer

b) For the 0.01 molal solution :

$$i = \frac{0.033}{0.0185} = 1.783$$

$$\therefore \quad \alpha = \frac{1.783 - 1}{2 - 1} = \underline{0.783}$$

Answer

53. Calculate the osmotic pressure of 0.312 g urea in 100 cc of water at 25°C. The molecular weight of urea is 60.

SOLUTION

Van't Hoff's law for osmotic pressure is :

$$\pi V = n R T$$

where π is the osmotic pressure. V is the volume of solution in litres containing n moles of the solute, R is the gas constant and T the absolute temperature.

$$\therefore \pi = \frac{w}{M} \cdot \frac{RT}{V}$$

$$= \frac{0.312}{60} \cdot \frac{0.082 \times (273+25)}{0.1}$$

$$= \underline{1.27} \text{ atm}$$

Answer

54. Sodium chloride in 0.2 molar solution is dissociated to the extent of 80% at 18°C. What will be the concentration of a urea solution (NH_2CONH_2) which is isotonic with the salt solution ?

SOLUTION

$$\alpha = \frac{i-1}{n-1}$$

since n for NaCl = 2 and α = 0.8

$$\therefore i = \alpha (n-1) + 1$$

$$= 0.8 + 1 = 1.8$$

The osmotic pressure of the solution $\pi = \frac{i\,n\,R\,T}{V}$

$$\pi = 1.8 \times 0.2 \times 0.082 (273 + 18)$$

$$= 8.59 \text{ atm}$$

The isotonic urea solution has the same osmotic pressure.

Since urea does not ionize, then i = 1

$$\therefore \quad 8.59 = n \times 0.082 \times 291$$

$$\therefore \quad n = \frac{8.59}{0.082 \times 291} = 0.36 \text{ mole/l}$$

Amount of urea = 0.36 × 60 = 21.6 g/l

Answer

55. The osmotic pressure of 0.5 N solution of NaCl is 20.29 atmospheres at 18°C. Calculate the degree of dissociation of the salt.

SOLUTION

$\pi V = nRT$ for n moles of the solution in V litres of solution.

If the solute is ionized then the osmotic pressure increases according to the number of units present.

The degree of dissociation $\alpha = \frac{i - 1}{n - 1}$

$$\text{where } i = \frac{\text{the observed osmotic pressure}}{\text{the calculated osmotic pressure}}$$

If one mole of the solute is dissolved in 1 litre of the solution, then :

$$\pi = \frac{1 \times 0.082 \times (18 + 273)}{1}$$

$$= 23.86 \quad \text{atm}$$

$$\therefore i = \frac{20.29}{23.86 \times 0.5} = 1.7$$

Since n = 2

$\therefore \quad \alpha = 1.7 - 1 = \underline{0.7}$

Answer

56. A 0.08 molal solution of monochloroacetic acid (molecular weight 94.5) is 13% ionized. Calculate (a) the boiling point (b) the freezing point and (c) the vapour pressure at 25°C of this solution. The vapour pressure of water at 25°C is 23.756 mm. (The molal boiling point constant of water is 0.520 and the molal freezing point constant is 1.85).

SOLUTION

$$\alpha = \frac{i - 1}{n - 1} = 0.13$$

n for monochloroacetic acid is 2

$\therefore \quad i = 0.13 + 1 = 1.13$

$$i = \frac{\triangle t_{b,\ obs.}}{\triangle t_{b,\ calc.}} = \frac{\triangle t_{f,\ obs.}}{\triangle t_{f,\ calc.}} = \frac{(p^0 - p)_{obs.}}{(p^0 - p)_{calc.}}$$

The observed elevation of boiling point $= 1.13 \times 0.80 \times 0.52$
$= 0.047°C$

$\therefore$ The boiling point is $\underline{100.047°}$ C

Answer (a)

The observed depression of freezing point $= 1.13 \times 1.85 \times 0.08$
$= 0.167°C$

$\therefore$ The freezing point is $- \underline{0.167°C}$

Answer (b)

Since $\frac{p^o - p}{p^o} = \frac{n_2}{n_1 + n_2}$

$\therefore\ p^0 - p = p^0 \frac{n_2}{n + n_2}$

Since $n_2 << n_1$, then n_2 in the denominator can be omitted.

$\therefore$ For the molal solution at 25°C, provided no ionization takes place :

$$p^0 - p = 23\ 756 \times \frac{\frac{1}{1000}}{18}$$

$$= \frac{23.756 \times 18}{1000} = 0.4277 \text{ mm.}$$

The observed lowering of vapour pressure for the given solution = 1.13 × 0.08 × 0.4277 = 0.0387 mm.

$\therefore$ The vapour pressure of the solution = 23.76 – 0.0387

= 23.7173 mm.

Answer (c)

57. The freezing point of a solution of 0.684 g of cane sugar in 100 g of water is – 0.037°C and that of a solution of 0.585 g of sodium chloride in 100 g of water is —0.342°C. Calculate the molal freezing point constant of water, the apparent molecular weight of sodium chloride and its degree of dissociation.

SOLUTION

Molecular weight of cane sugar $C_{12}H_{22}O_{11}$= 342

Moles of cane sugar = $\frac{0.684}{342}$ = 0.002 moles in 100 g water

$\therefore$ The molal freezing constant of water $K_f = 0.037 \times \frac{10}{0.002}$

$= \underline{1.85^0C}$

Answer

0.585 g NaCl in 100 g water produces 0.342°C depression

x g « « 1000 g water « 1.85°C depression

$$\therefore \quad x = 0.585 \times \frac{1000}{100} \times \frac{1.85}{0.342} = 31.5$$

$\therefore$ The apparent molecular weight of NaCl = $\underline{31.5}$

Answer

58.5 g NaCl in 1000 g water produces 1.85°C depression

0.585 NaCl in 100 g water « $\triangle t_f$ depression

$$\triangle t_{f,\ calc.} = 1.85 \times \frac{0.585}{58.5} \times \frac{1000}{100} = 0.185^0C$$

The vant Hoff's factor $i = \frac{\triangle t_{f,\ obs.}}{\triangle t_{f,\ calc.}} = \frac{0.342}{0.185}$

$= 1.848$

The degree of ionization of NaCl $\alpha = \frac{i - 1}{n - 1}$

Since n for NaCl = 2

$$\therefore \quad \alpha = \frac{1.848 - 1}{2 - 1} = \underline{0.848}$$

Answer

PROBLEMS FOR PRACTICE

1. By dissolving 0.116 g of anthranilic acid (Mol. wt. 137) in 20g of naphthalene (M.P. 80.1°C) the freezing point in lowered by 0 278°C.

Assuming that anthranilic acid molecules are not associated or dissociated, calculate the molal freezing point constant for naphthalene. (6.89)

2. The boiling-point of pure acetone is 56.38°C at normal pressure. A solution of 0.707 g of a compound in 100 g of acetone boils at 56.88°C. What is the molecular weight of the compound? Use data in table II. (24.18)

3. A solution of calcium ferrocyanide $Ca_2Fe(CN)_6$ containing 313.9 g in 1000 g of water, has a vapour pressure of 4.434 mm at O°C. Calculate the osmotic pressure of the solution if the vapour pressure of water at O°C is 4.580 mm. (40.4)

4. The vapour pressure of sucrose ($C_{12}H_{22}O_{11}$) solution containing 1 mole in 1000 g of water at O°C is 4.489 mm. Find the osmotic pressure of the solution. (22.4)

5. The density of an aqueous solution of sodium chloride containing 8.000 g of salt per 100 g of solution is 1.8541 g/cc at 25°C. Calculate the concentration of this solution on the (a) molar (b) molal scales. (1.44) (1.49)

6. The vapour pressure of the immiscible liquid system diethylaniline-water is 760 mm at 99.4°C. The vapour pressure of water at that temperature is 744 mm. How many grams of steam are necessary to distil 100 g of diethylaniline $C_6H_5N\cdot(C_2H_5)_2$. (563)

7. A solution of 0.855 g of a metal in 100 g of mercury has, at a given temperature, a vapour pressure of 752.6 mm, that of pure mercury at the same temperature being 758 mm. Calculate the molecular weight of the metal, taking that of mercury as 200. (240)

8. A solution of 9.21 g of Hg $(CN)_2$ dissolved in 100 g of water has a vapour pressure of 755.2 mm at 100°C. Find the molecular weight of the dissolved salt. What inference may be drawn as to the electrolytic dissociation of Hg $(CN)_2$ in water? (259.72)

9. The vapour pressure of ether at 25°C is 537 mm. What is the vapour pressure of a solution containing 2g of benzaldehyde (C_6H_5CHO) in 100 g of ether $(C_2H_5)_2O$ at this temperature? (529.61)

10. The vapour pressure of a solution containing 13 g of a nonvolatile solute in 100 g of water at 28°C is 27.371 mm. Calculate the molecular weight of the solute. The vapour pressure of water at this temperature is 28.065 mm. (92)

11. The boiling point of chloroform can be measured with a particular apparatus with an accuracy of 0.01°C. Calculate the number of grams of an impurity of mol. 100 which would be required to raise the boiling point of 50 g of chloroform by this amount. (0.0138)

12. If 68.4 g of sugar (mol. wt. 342) is dissolved in 1000g of water, what are (a) the vapour pressure and (b) the osmotic pressure at 20°C? (c) What is the freezing point? (d) What is the B.P. of this solution?

The density of the solution at 20°C is 1.024 g/cc.

The vapour pressure of water at 20°C is 17.863 mm. (17.3) (4.61) (– 0.372) (100.102)

13. Given a 0 01 molal solution of urea in water at25°C, calculate :

a) The B. P. of the solution.

b) The vapour pressure of the solution if the vapour pressure of pure water is 23.756 mm.

c) The osmotic pressure (assuming that the density of the solution is practically 1 0 g/cc)

(100.51) (23.7517) (0.2445)

14. The vapour pressure of water at 25°C (23.756 mm) is lowered 0.071 mm by the addition of 1.53 g of a nonvolatile substance to 100 g of water. Calculate the molecular weight of the solute using Raoult's law. (92)

15. Purified nitrogen gas is slowly bubbled through a solution of 3.00 g of a nonvolatile organic compound dissolved in 200 g of benzene and then bubbled through pure benzene. The solution is found to be 2.1450 g lighter while the pure benzene suffered a loss in weight of 0.0160 g. What is the apparent molecular weight of the dissolved substance ? (157.5)

CHAPTER V.

CHEMICAL EQUILIBRIA

58. If the velocity constant for the hydrolysis of ethyl acetate at 25°C according to the equation :

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH$$

is 2.5×10^{-4} litre mole^{-1}, and the velocity constant for the back reaction (esterification) in the same units is 6.25×10^{-5}.

Calculate the value of the equilibrium constant.

SOLUTION

At equilibrium :

$$k_1 [CH_3COOC_2H_5] [H_2O] = k_2 [CH_3COOH] [C_2H_5OH]$$

where k_1 and k_2 are the velocity constants for the forward and back reactions.

$$\therefore \frac{k_1}{k_2} = \frac{[CH_3COOH] [C_2H_5OH]}{[CH_3COOC_2H_5] [H_2O]}$$

The right hand side of the equation is equal to the equilibrium constant K.

$$\therefore K = \frac{k_1}{k_2} = \frac{2.5 \times 10^{-4}}{6.25 \times 10^{-5}} = \underline{4.00}$$

Answer

It should be noticed that K in this case is dimensionless,

59. A mixture of nitrogen and hydrogen in the molar ratio 1 : 3 is heated to 500°C under 10 atmospheres till equilibrium is attained. At equilibrium the percent molar ratio of ammonia in the mixture is 1 2%. Find the pressure at which the mixture is in equilibrium at the same temperature and containing 10.4 molar percent of ammonia.

SOLUTION

Let the initial number of moles of nitrogen and hydrogen be a and b. If x is the number of moles of nitrogen consumed in the reaction, then at equilibrium :

N_2	+	$3H_2$	$\rightleftarrows$	$2NH_3$	Total moles
(a - x)		(b – 3x)		2x	a+b – 2x

From Dalton's law, the partial pressures of the gases in the mixture at equilibrium are :

$$p_{N_2} = p \frac{a - x}{a+b-2x}$$

$$p_{H_2} = p \frac{b - x}{a+b-2x}$$

$$p_{NH_3} = p \frac{2x}{a+b-2x}$$

where P is the total pressure of the mixture.

$$K_p = \frac{p^2NH^3}{PN_2 \cdot P^3H_2} = \frac{\left(P \frac{2x}{a+b-2x}\right)^2}{\left(P \frac{a-x}{a+b-2x}\right)\left(P \frac{b-3x}{a+b-2x}\right)^2}$$

$$= \frac{(4x^2)(a+b-2x)^2}{p^2(a-x)(b-3x)^3}$$

If a = 1 and b = 3 moles.

$$\therefore \quad \frac{2x}{a+b-2x} = \frac{1.2}{100}$$

$\therefore$ x = 0.0237 mole.

$$\therefore \quad K_p = \frac{(4\times0.0237^2)\ (4-2\times0.0237)^2}{100\ (1-0.0237)\ \ (3-3\times0.0237)^3}$$

$$= 1.43 \times 10^{-5}$$

$$\text{If} \quad \frac{2x}{a+b-2x} = \frac{10.4}{100}$$

$$\frac{2x}{1+3-2x} = \frac{10.4}{100}$$

$\therefore$ x = 0.1884 mole

Since K_p is constant at constant temperature and substituting for x in the equilibrium constant equation,

$$\therefore \quad 1.43\times10^{-5} = \frac{(4\times0.1884^2)\ (4-2\times0.1884)^3}{p^2(1-0.1884)(3-3\times0.1884)^3}$$

$\therefore$ $P^2 = 1 - 11\times10^4$ and P = 105 atm

Answer

60. One mole of a gas AB occupies a 40 litres vessel at 400°K. The percentage dissociation is 2%. Calculate:

a) the total pressure at equilibrium in atmospheres,

b) the constants K_p and K_c.

SOLUTION

If the degree of dissociation at equilibrium is α, then :

$$AB \rightleftharpoons A + B$$

$$\frac{1-\alpha}{v} \qquad \frac{\alpha}{v} \qquad \frac{\alpha}{v}$$

where $\frac{1-\alpha}{v}$, $\frac{\alpha}{v}$ and $\frac{\alpha}{v}$ are the molar concentrations of A B, A and B at equilibrium.

$$K_c = \frac{[A]\,[B]}{[AB]}$$

where [A], [B] and [AB] represent the respective molar concentrations.

$$\therefore \; K_c = \frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)\,v}$$

$$\because \; \alpha = 0.02$$

$$K_c = \frac{0.02}{(1-0.02)\times 40} = 1.02 \times 10^{-5}$$

Answer (b)

Since $K_p = K_c\,(RT)^{\Delta n}$ where Δn is the difference between the number of moles of products and reactants.

$$\Delta n = 2 - 1 = 1$$

$$\therefore \; K_p = 1.02 \times 10^{-5} \times 0.082 \times 400 = 3.35 \times 10^{-4}$$

Answer (b)

$$K_p = \frac{P_A \cdot P_B}{P_{AB}}$$

where $P_{AB,}$ and P_B are the partial pressures of the three constituents AB, A and B respectively.

$$P_{AB} = P\,\frac{1-\alpha}{1+\alpha}\,,\ P_A = p\,\frac{\alpha}{1+\alpha}\ \text{and}\ p_B = p\,\frac{\alpha}{1+\alpha}$$

where P is the total pressure at equilibrium.

$$\therefore\ K_p = \frac{P\,\frac{\alpha}{1+\alpha}\cdot P\,\frac{\alpha}{1+\alpha}}{P\,\frac{1-\alpha}{1+\alpha}} = P\,\frac{\alpha^2}{1-\alpha^2}$$

$$\therefore\quad P = K_p\,\frac{1-\alpha^2}{\alpha^2} = \frac{3.35\times 10^{-4}\times(1-0.0004)}{0.0004}$$

$$= \underline{0.837}\ \text{atm}$$

Answer (a)

<u>Another solution :</u>

Sincs PV = nRT for an ideal gas,

then assuming the gaseous mixture at equilibrium to be ideal,

$\therefore$ n is the number of moles in the gaseous mixture, and

$$P = \frac{n\ R\ T}{v}$$

$$AB \rightleftarrows A + B$$

$$1-\alpha \qquad\qquad \alpha \qquad \alpha$$

If we start with one mole of AB, if α is the degree of dissociation, then, at equilibrium there are $(1 - \alpha)$ moles undissociated AB, α moles A and α moles B. The total number of moles is $(1 + \alpha)$ which is n. The total volume of the mixture is $v = 40$ litres and $\alpha = 0.02$.

$$\therefore \quad P = \frac{1.02 \times 0.082 \times 400}{40} = \underline{0.837} \quad \text{atmospheres}$$

Answer (a)

$$K_p = \frac{p_A \cdot p_B}{p_{AB}}$$

$$\text{but : } P_A = P\,\frac{\alpha}{1+\alpha},\ p_B = P\,\frac{\alpha}{1+\alpha} \text{ and } p_{AB} = P\,\frac{1-\alpha}{1+\alpha}$$

$$\therefore \quad K_p = \frac{P\,\frac{\alpha}{1+\alpha} \cdot P\,\frac{\alpha}{1+\alpha}}{P\,\frac{1-\alpha}{1+\alpha}} = \frac{P+\alpha^2}{1-\alpha^2}$$

$$= \frac{0.837 \times (0.02)^2}{1 - (0.02^2)} \qquad = \underline{3.35 \times 10}$$

Answer (b)

$$\therefore \quad K_p = K_c\,(RT)^{\Delta n}$$

$$\therefore \quad K_c = \frac{K_p}{(RT)^{\Delta n}} \quad \text{but } \Delta n = 2 - 1 = 1$$

$$\therefore \quad K = \frac{3.35 \times 10^{-4}}{0.082 \times 400} = \underline{1.02 \times 10^{-5}}$$

Answer (b)

61. Water vapour reacts with red hot iron according to the equation :

$$3\ Fe + 4\ H_2O \rightleftharpoons Fe_3\ O_4 + 4\ H_2$$

At equilibrium at 200°C the partial pressures of water vapour and hydrogen are 4.6 and 95.8 mm respectively. Calculate K_p for the reaction.

If the partial pressure of water vapour is 6.9 mm, what is the partial pressure of hydrogen gas ? Find the partial pressures of the two gases if the total pressure is 760 mm.

SOLUTION

$$3\ Fe_{(s)} + 4\ H_2O_{(g)} \rightleftharpoons Fe_3\ O_{4(s)} + 4\ H_{2(g)}$$

$$\therefore\ K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4} = \left(\frac{95.8}{4.6}\right)^4 = \underline{1.88 \times 10^5}\ *$$

Answer

The value of K_p is constant as long as the temperature is constant.

It follows, therefore, that the partial pressure of hydrogen at 6.9 mm partial pressure of water vapour is :

$$P_{H_2} = \sqrt[4]{1.88 \times 10^5 \times 6.9^4}$$

$$= \underline{143.6}\ mm$$

Answer

* Partial pressures of solid reactants and products are neglected in the equilibrium constant relationship.

Assuming the initial moles of water vapour α are moles, and 4 x moles are consumed in the reaction at equilibrium, then 4 x moles of hydrogen will be formed.

$$\therefore\ K_p = \frac{P^4_{H_2}}{P^4_{H_2O}} = \frac{P^4 \cdot (4x)^4}{P^4\ (\alpha - 4x)} = \left(\frac{4x}{\alpha - 4x}\right)^4$$

Since the total pressure P has no effect on the reaction as shown above, the ratio of the partial pressures of the two gases is the same at constant temperature for any value of the total pressure.

$$\therefore\ P_{H_2O} = 760 \times \frac{6.9}{6.9 + 143.6} = \underline{34.8}\ \text{mm}$$

$$\text{and}\ P_{H_2} = 760 - 34.8 = \underline{725.2}\ \text{mm}$$

Answer

62. The equilibrium constant in terms of partial pressures at 750°C for the reaction :

$$\tfrac{1}{2}\ SnO_{2(s)} + H_{2(g)} = \tfrac{1}{2}\ Sn_{(s)} + H_2O_{(g)}$$

is 2.85 The equilibrium constant at 750°C for the reaction :

$$H_{2(g)} + CO_{2(g)} = CO_{(g)} + H_2O_{(g)}$$

is 0.771. Calculate K_p for the reaction :

$$\tfrac{1}{2}\ SnO_{2(s)} + CO_{(g)} = \tfrac{1}{2}\ Sn_{(s)} + CO_{2(g)}$$

at the same temperature.

For the reaction :

$$\tfrac{1}{2}\ SnO_{2(s)} + H_{2(g)} = \tfrac{1}{2}\ Sn_{(s)} + H_2O_{(g)}$$

$$K'_p = 2.85 = \frac{p_{H_2O}}{p_{H_2}} \quad \ldots\ldots (1)$$

For the reaction :

$$H_{2(g)} + CO_{2(g)} = CO_{(g)} + H_2O_{(g)}$$

$$K''_p = 0.771 = \frac{p_{CO} \cdot p_{H_2O}}{p_{H_2} \cdot p_{CO_2}} \quad \ldots\ldots (2)$$

Dividing equation (1) by equation (2) :

$$\frac{K'_p}{K''_p} = \frac{p_{CO_2}}{p_{CO}} = \frac{2.85}{0.771} = 3.7 \quad \ldots\ldots (3)$$

For the reaction :

$$\tfrac{1}{2}\ SnO_{2(s)} + CO_{(g)} = \tfrac{1}{2}\ Sn_{(s)} + CO_{2(g)}$$

$$K_p = \frac{p_{CO_2}}{p_{CO}} \quad \ldots\ldots (4)$$

From (3) and (4) :

$$\therefore\ K_p = \frac{p_{CO_2}}{p_{CO}} = \underline{3.7}$$

Answer

63. When sulphur dioxide is oxidized to sulphur trioxide in the presence of a catalyst at 727°C the following relation holds :

$$K_p = 1.85 = \left(\frac{p_{SO_3}}{p_{SO_2}} \right) \times \frac{1}{\sqrt{p_{O_2}}}$$

a) What ie the ratio of SO_3 to SO_2 when the partial pressure of oxygen at equilibrium is 0.3 atm ?

b) What is the ratio of SO_3 to SO_2 when the partial pressure of oxygen is 0 6 atm at equilibrium ?

c) What is the effect on the ratio SO_3/SO_2 if the total pressure of the mixture of gases is increased by forcing in nitrogen under pressure ?

SOLUTION

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightleftarrows SO_{3(g)}$$

At 727°C $$K_p = \frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{\frac{1}{2}}} = 1.85$$

(a) $$\frac{\text{Moles of } SO_3}{\text{Moles of } SO_2} = \frac{p_{SO_3}}{p_{SO_2}} = 1.85 \times p^{\frac{1}{2}}_{O_2}$$

$$= 1.85 \times (0.3)^{\frac{1}{2}} = \underline{1.01}$$

Answer (a)

(b) $$\frac{p_{SO_3}}{p_{SO_2}} = 1.85 \times (0.6)^{\frac{1}{2}} = \underline{1.43}$$

Answer (b)

(c)

$$K_p = \frac{\left(\frac{n_{SO_3}}{\Sigma n} \cdot P\right)}{\left(\frac{n_{SO_2}}{\Sigma n} P\right)\left(\frac{n_{O_2}}{\Sigma n} P\right)^{\frac{1}{2}}}$$

$$= \frac{n_{SO_3}}{n_{SO_2} \cdot (n_{O_2})^{\frac{1}{2}}} \left(\frac{P}{\Sigma n}\right)^{-\frac{1}{2}}$$

where Σ n is the total number of moles at equilibrium.

At constant volume, an increase in Σ n due to the addition of nitrogen will result in an exactly proportional increase in the total pressure P and therefore the ratio $\frac{P}{\Sigma n}$ will remain the same.

∴ The position of the equilibrium will remain unchanged i.e. the ratio of SO_3/SO_2 will not be affected by the addition of nitrogen :

64. At 1273° K anp at total pressure of 30 atm the equilibrium in the reaction:

$$CO_{2(g)} + C_{(s)} \rightleftarrows 2\ CO_{(g)}$$

is such that 17 molar per cent of the gas is CO_2.

a) What percentage would be CO_2 if the total pressure were 20 atm ?

b) What would be the effect on the equilibrium of adding nitrogen until the partial pressure of nitrogen is 10 atm ?

c) At what pressure will 25 per cent of the gas be CO_2 ?

SOLUTION

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$$

Let the total moles at equilibrium be 100 moles.

$\because$ Moles of CO_2 at equilibrium = 17 moles.

and ,, ,, CO ,, ,, $= 100 - 17 = 83$

$$K_p = \frac{p^2_{CO_2}}{p_{CO}} = \frac{\left(\frac{83}{100} \times P\right)^2}{\frac{17}{100} P}$$

$$= \frac{(0.83)^2 P}{0.17}$$

At a total pressure of 30 atm $K_p = \frac{(0.83)^2 \times 30}{0.17}$

$$= 121.5$$

(a) Let x be the molar percentage of CO_2 at a total pressure of 20 atm .

$\therefore$ Molar percentage of CO = 100 − x

$$K_p = \frac{\left(\frac{100 - x}{100}\right)^2 P^2}{\frac{x}{100} P}$$

$$= \frac{(100 - x)^2 P}{100 x}$$

$$121.5 = \frac{(100 - x)^2 20}{100 x}$$

$$607.5 x = 10^4 - 200 x + x^2$$

$$\therefore x^2 - 807.5\,x + 10^4 = 0$$

$$\therefore x = \frac{807.5 \pm \sqrt{(807.5)^2 - 4 \times 10^4}}{2}$$

$$\therefore x = 795 \text{ or } 12.5$$

The first value is impossible as a molar percentage.

$\therefore$ Molar percentage of CO_2 = 12.5.

Answer (a)

$$\text{(b)}\ K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{\left(\frac{n_{CO}}{\Sigma n} P\right)^2}{\frac{n_{CO_2}}{\Sigma n} P} = \frac{n^2_{CO}}{n_{CO_2}} \left(\frac{P}{\Sigma n}\right)$$

when Σn = total number of moles. At equilibrium, adding nitrogen will cause P and Σn to increase in the same ratio and, therefore, will have no effect on the equilibrium.

(c) If 25per cent of the gas at equilibrium is CO_2 :

$$\therefore K_p = \frac{\left(\frac{100-25}{100}\right)^2 P^2}{\frac{25}{100} P} = \frac{(0.75)^2}{0.25} P = 121.5$$

$$\therefore P = \frac{121.5 \times 0.25}{(0.75)^2} = \underline{54} \text{ atm}$$

Answer (c)

65. The reaction $CO_{2(g)} + H_{2(g)} \rightleftarrows CO_{2(g)} + H_2O_{(g)}$ was investigated by passing mixtures of CO_2 and H_2 over a catalyst at 900°C at 1 atm pressure. The resulting gas was chilled quickly to room temperature by passage through a capillary and was analyzed. In one experiment the partial pressures were as follows :

CO_2 = O. 2142, H_2 = 0.2549, H_2O = 0.2654 and CO = 0.2654 atm. Calculate the number of moles of hydrogen present in another equilibrium mixture containing 0.2272 mole of CO, 0.2272 moles of H_2O and 0.4850 moles of CO_2.

SOLUTION

$$K_p = \frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot p_{H_2}} = \frac{\left(\frac{n_{CO}}{\Sigma n} P\right)\left(\frac{n_{H_2O}}{\Sigma n} P\right)}{\left(\frac{n_{CO_2}}{\Sigma n} P\right)\left(\frac{n_{H_2}}{\Sigma n} P\right)}$$

$$= \frac{n_{CO} \cdot n_{H_2O}}{n_{CO_2} \cdot n_{H_2}}$$

∴ From the data given :

$$K_p = \frac{0.2654 \times 0.2654}{0.2142 \times 0.2548} = 1.285$$

Since the temperature is constant, the value of K_p will be the same.

$$\therefore \ 1.285 = \frac{0.2272 \times 0.2272}{0.4850 \times n_{H_2}}$$

$$\therefore \ n_{H_2} = \underline{0.0825} \text{ mole}$$

Answer

66. For the the reaction : $N_2O_4 \rightleftharpoons 2NO_2$, K_p at 25°C is 0.141. What pressure would be expected if 1 gram of liquid N_2O_4 is allowed to evaporate into a litre vessel at this temperature? Assume that N_2O_4 and NO_2 are perfect gases.

SOLUTION

Mol. wt. of N_2O_4 = 92

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)}$$

$$\frac{1}{92} - x \qquad 2x$$

Total moles at equilibrium = $\frac{1}{92} + x = 0.0109 + x$

where x is the number of moles N_2O_4 dissociated.

Since $K_p = K_c\ (RT)^{\triangle n}$

and $K_p = 0.141$, $\triangle n = 1$, $T = 298°K$

$\therefore\ 0.141 = K_c\ (0.082 \times 298)$

$\therefore\ K_c = 0.00578$

But $K_c = \frac{[NO_2]^2}{[N_2O_4]}$

$\because$ The volume of the vessel = 1 litre

$\therefore\ [NO_2] = \frac{2x}{1} = 2x$ mole/litre

$[N_2O_4] = \frac{0.0109 - x}{1} = (0.0109 - x)$ mole/litre

$\therefore\ K_c = \frac{(2x)^2}{0.0109 - x} = \frac{4x^2}{0.0109 - x} = 0.00578$

$\therefore\ 4x^2 + 0.00578\,x - 6.28 \times 10^{-5} = 0$

$$\therefore x = \frac{-0.00578 \pm \sqrt{(0.00578)^2 - 4 \times 4 \times 6.28 \times 10^{-5}}}{2 \times 4}$$

$$= 0.0033$$

The negative value of x is meaningless.

$\therefore$ Total moles at equilibrium $= 0.0109 + 0.0033$

$= 0.0142$

$$P\ V = n\ R\ T$$

$$P \times 1 = 0.0142 \times 0.082 \times 298$$

$$\therefore \quad P = \underline{0.347} \text{ atm}$$

answer

67. The value for the dissociation constant K_p for the dissociation of phosphorous pentachloride at 250°C is 1.78. Calculate the degree of dissociation at equilibrium if 0.04 mole of PCl_5 is allowed to evaporate in a vessel containing 0.2 mole of chlorine, previously put in it, under the following conditions.

a) A constant pressure of 2 atmospheres.

b) A constant volume of 4 litres.

Compare the results obtained with those obtained under the same conditions in absence of chlorine.

SOLUTION

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad \text{Total moles at equilibrium}$$

$$(a-x) \qquad x \qquad x \qquad\qquad a + x$$

$$K_p = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}}$$

$$\therefore \; K_p = \frac{P\frac{x}{a+x} \cdot P\frac{x}{a+x}}{P\frac{a-x}{a+x}} = \frac{Px^2}{a^2 - x^2}$$

In absence of Cl_2

a. At a pressure of 2 atm :

Substituting for the values of Kp and a in the above equation :

$$1.78 = \frac{2\,x^2}{0.04^2 - x^2}$$

$\therefore$ The degree of dissociation $= \frac{0.02745}{0.04} = \underline{0.686}$

Answer (a)

b. At a volume of 4 litres :

$$K_p = K_c \; (RT)^{\triangle n}$$

since $\triangle n = 2 - 1 = 1$

$$\therefore K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{a-x}{v}} = \frac{x^2}{v\,(a-x)}$$

Substituting for K_c, v and a in the above equation :

$$0.0415 = \frac{x^2}{4\,(0.04 - x)}$$

$\therefore$ x = 0.0334

$\therefore$ The degree of dissociation $= \frac{0.0334}{0.04} = \underline{0.85}$

Answer (b)

In presence of Cl_2 :

a. At a pressure of 2 atmospheres :

$$1.78 = \frac{2x\ (x + 0.2)}{0.04^2 - x^2}$$

$\therefore$ $x = 0.00669$

$\therefore$ The degree of dissociation $= \frac{0.00669}{0.04} = \underline{0.1673}$

Answer (a)

b. At a volume of 4 litres :

$$0.0415 = \frac{x\ (x + 0\ 2)}{4\ (0.04 - x)}$$

$\therefore$ $x = 0.0065$

$\therefore$ The degree of dissociation $= \frac{0.0065}{0.04} = \underline{0.1625}$

Answer

68. If 3.6 g of PCl_5 is heated to 200°C, it volatilizes completely and the vapour occupies a volume of one litre under 1 atm. At the same time it dissociates partially into PCl_3 and Cl_2. Calculate the degree of dissociation and the dissociation constant K_c of phosphorous pentachloride at this temperature. Express the concentrations in moles per litre.

SOLUTION

$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2	Total moles at equil.
$1 - \alpha$	α	α	$1 + \alpha$

where α is the degree of dissociation.

The total number of moles resulting from the dissociation of one mole of PCl_5 is $(1 + \alpha)$, but starting with $\frac{w}{M}$ moles of PCl_5 the total number of moles at equilibrium will be $\frac{w}{M}(1+\alpha)$

Assuming ideal gas conditions :

$$n = \frac{w}{M}(1 + \alpha) = \frac{PV}{RT}$$

$$\therefore \quad \alpha = \frac{MPV}{wRT} - 1 = \frac{208 \times 1 \times 1}{3.6 \times 0.082 \times 473} - 1 = \underline{0.49}$$

Answer

Since the concentration of each of the components in the mixture at equilibrium is equal to its number of moles divided by the total volume in litres, then :

$$[PCl_3] = \frac{\alpha \frac{w}{M}}{1} = \alpha \frac{w}{M} \text{ mole/litre.}$$

$$\text{Similarly } [Cl_2] = \alpha \frac{w}{M} \text{ mole/litre.}$$

$$\text{and } [PCl_5] = (1-\alpha)\frac{w}{M} \text{ mole/litre.}$$

$\therefore$ The dissociation constant at 200°C :

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{w\,\alpha^2}{M(1-\alpha)}$$

$$= \frac{(0.49)^2 \times 3.6}{208 \times 0.51 \times 1} = \underline{0.00815}$$

Answer

PROBLEMS FOR PRACTICE

1. Carbon dioxide gas dissociates to carbon monoxide and oxygen to the extent of 0.003 % at 1000°C and under atmospheric prssure. If oxygen gas is passed over carbon at 1000°C, the gaseous mixture, at equilibrium, consists of 99.3 % carbon monoxide and 0.7 % carbon dioxide. Find the partial pressure of oxygen if the total pressure is one atm. (7.9×10^{-19})

2. Water vapour dissociates at 1981°C and under atmospheric pressure to the extent of 1.77 %. Find K_p, K_c and the partial pressures of the constituents of the mixture.

(2.85×10^{-6}) (1.54×10^{-8}) (0.9733) 0.01755) (0.00877)

3. What is the degree of dissociation of nitrogen tetroxide at 35°C and under 10 atm, if the equilibrium constant K_p. is 0.310. How far does the result agree with Le Chatelier's principle if the degree of dissociation for the same reaction at the same temperature but under one atm is 0.270 ? (0.088)

4. Water vapour is 1.01 % dissociated at 1000°C and under one atm. Calculate the equilibrium constant of the dissociation K_p. (5.15×10^{-7})

5. Calculate the concentration of nitrogen dioxide in a solution of 0.5 mole nitrogen tetroxide in 450 cc chloroform at 8.2°C if the dissociation constant $K_c = 1.08 \times 10^{-2}$. (0.00852)

6. The following reaction takes place at 850°C and under one atm.

$$C_{(s)} + CO_{2(g)} \rightleftarrows 2\ CO_{(g)}$$

If the composition of the mixture at equilibrium is 93.77% carbon monoxide and 6.23% carbon dioxide, calculate :

a) the equilibrium constant K_p.

b) the compostion of the mixture at equilibrium at 2 atm (3.577) (61.4%)

7. The equilibrium constants at 200°C are given for the following reactions :

1. $H_{2(g)} + D_{2(g)} \rightleftarrows 2HD_{(g)}$ $K_1 = 3.27$
2. $H_2O_{(g)} + D_2O_{(g)} \rightleftarrows 2HDO_{(g)}$ $K_2 = 3.18$
3. $H_2O_{(g)} + HD_{(g)} \rightleftarrows HDO_{(g)} + H_{2(g)}$ $K_3 = 3.4$

Find the equilibrium constant for :

$$H_2O_{(g)} + D_{2(g)} \rightleftarrows D_2O_{(g)} + H_{2(g)} \quad (11.89)$$

8. Under what pressure must PCl_5 be placed at 250°C in order to obtain a 30 per cent conversion into PCl_3 and Cl_2 ? For the reaction :

$$PCl_{5(g)} \rightleftarrows PCl_{3(g)} + Cl_{2(g)} \quad , K_p = 1.78 \quad (18.0)$$

9. For the gaseous reaction $COCl_2 = CO + Cl_2$ at 100°C, the dissociation constant K_p is 6.7×10^{-9}. Calculate the partial pressure of carbon monoxide in equilibrium with phosgene at this temperature under a total pressure of 2 atm. The dissociation

is so slight that the partial pressure of phosgene may be taken as equal to the total pressure. (1.16×10^{-4})

10. Amylene C_5H_{10} and acetic acid react to give the ester according to the reaction ;

$$C_5H_{10} + CH_3COOH \rightleftharpoons CH_3COOC_5H_{11}$$

What is the value of K_c if 0.00645 mole of amylene and 0.001 mole of acetic acid mixed in 845 cc of a certain inert solvent react to give 0.000784 mole of ester ? (540)

11. The vapour density of nitrogen peroxide N_2O_4 at 49.7°C and under 182 mm pressure is 1.89, while the density of undissociated peroxide is 3.18, Find the degree of dissociation and the value of K_p . At what pressure (mm) is the gas half dissociated ? (0.6825) (0.8354) (476.2)

12. When one mole of carbon dioxide is heated with one mole of hydrogen in a one litre vessel at 1005°C, 0.56 mole of water is formed. Find the equilibrium constant K_p. (1.619)

13. When 1.19 moles hydrogen gas are mixed with 0 69 mole iodine at 450 mm pressure 1.26 moles of hydrogen iodide are formed at equilibrium. Find the amount of hydrogen iodide present in the equilibrium mixture if 2 moles of hydrogen are mixed with one mole of iodine at the same temperature. (1.86)

14. If the percentage dissociation of N_2O_4 gas at 25°C and under atmospheric pressure is 20%, what is its degree of dissociation at the same temperature and under $\frac{1}{2}$ atm ? (0.2587)

15. If the equilibrim constant K_c for the esterification

of acetic acid with ethyl alcohol according to the equation :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is 4, find the quantity of ethyl alcohol present at equilibrium, when one mole of acetic acid reacts with ;

a) 0.5 mole ethyl alcohol.

b) 8 moles alcohol.

c) one mole alcohol in presence of one mole water.
(0.423) (0.967) (0.543)

16. When one mole of phosphorous pentachloride is heated under constant pressure in a vessel previously evacuated, the degree of dissociation is 0.70 What is the degree of dissociation if 1.13 moles of chlorine are introduced into the vessel before dissociation ? (0.5)

17. If 9.2 g of nitrogen peroxide (N_2O_4) occupy 2.95 litres at 27°C and under atmospheric pressure, to what extent does it dissociate ? (19.84 %)

18. If the percentage dissociation of phosporous pentachloride is 80 at 250°C and under atmospheric pressure, find :

a) the equilibrium constant

b) the density of the dissociated gas. (1.778) (57.88)

19. The value of Kp for reversible reaction :

$$N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$$

is 1.44×10^{-5} at 500°C calculate K_c for the reaction.
(5.79×10^{-2})

20. A mixture of 1.24×10^{-2} moles hydrogen and 2.46×10^{-2} moles iodine is heated at 457.6°C to equilibrium. Calculate the number of moles of hydrogen iodide formed if the equilibrium constant K_p for the reaction at the given temperature is 48.7. (3.08×10^{-5})

21. For the reaction $SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftarrows SO_{3(g)}$

$K_p = 1.7 \times 10^{12}$ at 25°C. Calculate K_p and K_c at 25°C for the reaction :

$$2\,SO_{3(g)} \rightleftarrows 2\,SO_{2(g)} + O_{2(g)} \quad (0.35 \times 10^{-24}) \; (1.4 \times 10^{-26})$$

22. Nitrogen tetroxide N_2O_4 dissociates into NO_2 according to the reaction :

$$N_2O_{4(g)} \rightleftarrows 2\,NO_{2(g)}$$

If the average molecular weight of partially dissociated nitrogen tetroxide at 1 atm and 55°C is 61.2, calculate :

a) the degree of dissociation.
b) K_p.
c) the degree of dissociation at 0.1 atm and 55°C.

(0.503) (1.36) (0 879)

23. Hydrogen and nitrogen in the ratio 3 : 1 by volume react at 355°C and 50 atm to give a mixture containing 25.11% ammonia. Calculate the equilibrium constant. (1.9×10^{-2})

24. If the equilibrium constant K_c for the reaction :

$$2\,SO_{2(g)} + O_{2(g)} \rightleftarrows 2\,SO_{3(g)}$$

is 274 at 728°C, find K_p for the reaction at the same temperature. (3.34)

CHAPTER AI

ELECTROLYTIC CONDUCTANCE AND ION EQUILBIRIA

69. The ratio of distribution of aniline between benzene and water is 10.1 : 1. When a litre of aniline - hydrochloride solution, containing 0.0997 mole of the salt is shaken with 59 cc of benzene at 25°C, it is found that 50 cc of benzene takes up 0.0648 g of aniline. Find the degree of hydrolysis of aniline hydrochloride in the solution and calculate the dissociation constant of aniline as a base.

SOLUTION

Molecular weight of aniline ($C_6H_5NH_2$) $= 93$

Moles of aniline dissolved in 50 cc benzene $= \frac{0.0648}{93}$

Moles of aniline dissolved in 59 cc benzene $= \frac{0.0648}{93} \times \frac{59}{50}$

$= 0.00082$ mole

$\therefore$ Aniline dissolved in 1000 cc aqueous solution $= \frac{0.0648}{93 \times 50}$

$\times 1000 \times \frac{1}{10.1} = 0.00138$ mole

$\therefore$ Total amount of aniline $= 0.00082 + 0.00138$

$= 0.0022$ mole $=$ total HCl

Amount of unhydrolysed aniline · HCl $= 0.0997 - 0.0022$

$= 0.0975$ mole

$\therefore$ Aniline hydrochloride + water $\rightleftharpoons$ aniline + HCl

$$\begin{matrix} c(1-\alpha) & & c\alpha & c\alpha \end{matrix}$$

where α is the degree of hydrolysis and c is the initial concentration in moles per litre.

$$K_h = \frac{[\text{aniline}]\,[\text{HCl}]}{[\text{aniline}\cdot\text{HCl}]}$$

where K_h is the hydrolysis constant.

$$\therefore K_h = \frac{[\text{aniline in water}]\,[\text{HCl in water}]}{[\text{unhydrolysed aniline} \cdot \text{HCl}]}$$

$$= \frac{0.00138 \times 0.0022}{0.0975} = 3.117 \times 10^{-5}$$

$$K_h = \frac{c\alpha \, . \, c\alpha}{c\,(1-\alpha)} = c\alpha^2$$

Since α is negligible with respect to 1 :

$$\therefore \alpha = \sqrt{\frac{K_h}{c}}$$

$$\therefore \alpha = \sqrt{\frac{3.117 \times 10^{-5}}{0.0997}} = \underline{0.01768}$$

Answer

For the salt of a strong acid and a weak base :

$$K_h = \frac{K_w}{K_b}$$

$$\therefore K_b = \frac{K_w}{K_h} = \frac{10^{-14}}{3.11 \times 10^{-5}} = \underline{3.208 \times 10^{-10}}$$

Answer

70. How many moles of dry sodium acetate salt should be added to one litre of 0.1 N hydrochloric acid to change the pH value to 4.4?

(The ionization constant for acetic acid $K_a = 1.8 \times 10^{-5}$)

SOLUTION

The pH of 0.1 N hydrochloric acid solution is $- \log [H^+]$

of the solution. Since the acid is a strong electrolyte it ionizes completely to give 0.1 g ion of H^+ per litre.

$$\therefore \quad pH = -\log 0.1 = 1$$

Hydrogen ion concentration for a solution of pH 4.4 is $[H^+] = 10^{-4.4} = 3.98 \times 10^{-5}$ g ion per litre. Sodium acetate salt should be added to hydrochloric acid solution so that part of it reacts with all the acid to give acetic acid and a certain excess remains in solution so that the final result is the change of pH from 1 to 4.4.

$$\therefore \quad \text{Salt added} = 0.1 + c_s \text{ g equiv}$$

where c_s is the excess salt present.

After the addition of sodium acetate the solution will consist of acetic acid of concentration c_a = 0.1 g equiv per litre and sodium acetate c_s g equiv. per litre

$$\begin{array}{cccccc} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ c_\alpha (1-\alpha') & & c_a \alpha' & & c_a \alpha' \\ CH_3COONa & \longrightarrow & CH_3COO^- & + & Na^+ \\ c_s & & c_s & & c_s \end{array}$$

Acetic acid, being a weak acid i.e. a weak electrolyte, ionizes partially and its degree of ionization is small. Applying Ostwald's law of dilution :

$$K_a = \frac{c_a \alpha' . c_a \alpha'}{c_a (1 - \alpha')}$$

where α is the degree of ionization of acetic acid, while α′ is its degree of ionization in presence af excess sodium acetate,

c_a is the concentration of the acid in g equiv per litre and K_a is the ionization constant.

Sodium acetate, being a salt, ionizes completely. If its concentration is c_s g equiv per litre, the acetate ions will be c_s g ions per litre. The acetate ions, being common, depress the ionization of acetic acid. Its degree of ionizatian becomes α' much smaller than α. The total concentration of the acetate ions will not be much different from c_s. Applying Ostwald's law, we find:

$$K_a = \frac{c_a \alpha' \cdot c_s}{c_a (1 - \alpha')} \quad \text{or} \quad K_a = \frac{[H^+] \cdot c_s}{c_a (1-\alpha')}$$

Neglecting α' in comparison to 1, we get :

$$[H^+] = K_a \frac{c_a}{c_s}$$

Substituting for K_a, c_a and $[H^+]$:

$$3.98 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{0.1}{c_s}$$

$\therefore \quad c_s = 4.5 \times 10^{-2}$ g equiv.

$\therefore$ The total sodium acetate to be added $= 0.045 + 0.1$

$= 0.145$ g equiv/litre (or mole/litre)

Answer

71. If 5.85 g sodium chloride are dissolved in a litre of saturated silver chloride solution, calculate the weight of silver chloride which precipitates. The solubility of silver chloride at room temperature is 1×10^{-5} mole/litre.,

SOLUTION

Molecular weight of AgCl = 108 + 35.5 = 143.5

Molecular weight of NaCl = 23 + 35.5 = 58.5

Moles of sodium chloride = $\frac{5.85}{58.5} = 0.1$

The solubility product $S_{AgCl} = [Ag^+]\ [Cl^-]$

In aqueous solution $[Ag^+] = [Cl^-] = [AgCl] = 1 \times 10^{-5}$ mole per litre

$\therefore\ S_{AgCl} = (1 \times 10^{-5})^2 = 1 \times 10^{-10}$

$\therefore\ [Ag^+] = \frac{1 \times 10^{-10}}{[Cl^-]}$

When sodium chloride is added, it ionizes completly and the chloride ions given are of the same concentration as NaCl.

The chloride ions due to the soluble AgCl are very low in concentration with respect to those resulting from the ionization of NaCl and could be omitted.

$\therefore\ [Ag^+] = \frac{1 \times 10^{-10}}{0.1} = 10^{-9}$ g ion/liter

Since silver ions are the result of the complete ionization of AgCl in solution,

$\therefore\ [AgCl] = [Ag^+] = 10^{-9}$

AgCl precipitated $= 10^{-5} - 10^{-9} \simeq 10^{-5}$ mole/litre

$= 10^{-5} \times 143.5 =$ 0.001345 g/litre

Answer

Note : All silver chloride is nearly precipitated.

72. The specific conductance of a saturated solution of silver bromide at 20°C is 1.576×10^{-6} ohm^{-1} cm^{-1}. The specific conductance of the water used in the solution is 1.519×10^{-6} ohm^{-1} cm^{-1}.

Assuming that silver bromide is completely ionized, find the solubility and the solubility product of silver bromide.

The equivalent conductances at infinite dilution for KBr, KNO_3 and $AgNO_3$ are 137.4, 131.3 and 121.0 cm^2 ohm^{-1} equiv^{-1} respectively.

SOLUTION

The specific conductance of AgBr = the specific conductance of the solution – the specific conductance of water.

$$= 1.576 \times 10^{-6} - 1.519 \times 10^{-6}$$

$$= 0.057 \times 10^{-6} \text{ ohm}^{-1}\text{ cm}^{-1}$$

Since AgBr is assumed to be completely ionized, its equivalent conductance calculated from the specific conductance becomes equal to the equivalent conductance at infinite dilution Λ_0 .

$$\Lambda_0 \text{ for AgBr} = \lambda_{0_{Ag^+}} + \lambda_{0_{Br^-}}$$

$$= (\lambda_{0_{Ag^+}} + \lambda_{0_{NO_3^-}}) + (\lambda_{0_{K^+}} + \lambda_{0_{Br^-}}) - (\lambda_{0_{K^+}} + \lambda_{0_{NO_3^-}})$$

$$= \Lambda_{0_{AgNO_3}} + \Lambda_{0_{KBr}} - \Lambda_{0_{KNO_3}}$$

$$= 121 + 137.4 - 131.3$$

$$= 127.1 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$$

$$\therefore \Lambda_0 = \frac{1000\text{ K}}{c}$$

where K is the specific conductance and c the concentration of the conducting solution in moles per litre. (the equivalent weight of AgBr is the same as its molecular weight.)

$$\therefore 127.1 = \frac{1000 \times 0.057 \times 10^{-6}}{c}$$

$$\therefore c = \frac{1000 \times 0.057 \times 10^{-6}}{127.1} = 4.49 \times 10^{-7} \text{ mole/litre}$$

$\therefore$ The solubility of AgBr = $\underline{4.49 \times 10^{-7}}$ mole/iltre

Answer

Since AgBr is completely ionized,

$\therefore [AgBr] = [Ag^{+}] = [Br^{-}] = 4.49 \times 10^{-7}$

$\therefore$ The solubility product $S_{Ag\,Br} = (4.49 \times 10^{-7})^2$

$= \underline{2.03 \times 10^{-3}}$

Answer

73. a) Calculate the solubility product for $Mg(OH)_2$ if the solubility of this base is 0.01166 g per litre, assuming that any base in solution is completely ionized.

b) If the ionization constants of acetic and formic acids are 1.8×10^{-5} and 21.4×0^{-5} respectively, what is the ratio between the strengths of the two acids ?

SOLUTION

a) $Mg(OH)_2 \longrightarrow Mg^{++} + 2\ OH^{-}$

The molecular weight of the base = 58.32

The solubility $= \dfrac{0.01166}{58.32} = 2 \times 10^{-4}$ mole/litre

$$S_{Mg(OH)_2} = [Mg^{++}]\,[OH^-]^2$$

$$= (2 \times 10^{-4})\,(2 \times 2 \times 10^{-4})^2$$

$$= \underline{3.2 \times 10^{-11}}$$

Answer (a)

b) $\alpha = \sqrt{\dfrac{K_a}{c_a}}$

The strength of the acid depends on its degree of ionzation

$$\therefore \frac{\text{strength of acetic acid}}{\text{strength of formic acid}} = \frac{\alpha_{acetic}}{\alpha_{formic}}$$

$$= \sqrt{\left(\frac{K_a}{c_a}\right)_{acetic} \Big/ \left(\frac{K_a}{c_a}\right)_{formic}}$$

Taking the two solutions of the same concentration for comparison,

$$\therefore \frac{\text{strength of acetic acid}}{\text{strength of formic acid}} = \sqrt{\frac{K_{a\ acetic}}{K_{a\ formic}}}$$

$$= \sqrt{\frac{1.8 \times 10^{-5}}{21.4 \times 10^{-5}}} = \underline{\frac{1}{3.45}}$$

Answer (b)

74. Calculate the pH value for the following aqueous solutions :

1) Hydrochloric acid of concentration 0.01 mole per litre.

2) Acetic acid of concentration 0.001 mole per litre.
(K_a = $1{\cdot}7 \times 10^{-5}$)

3) Ammonium hydroxide of concentration 1 mole per litre.
(K_b = $1{\cdot}8 \times 10^{-5}$)

4) A mixture of 0.01 mole acetic and 0.05 mole sodium acetate per litre.

5) A mixture of 0.005 mole acetic acid and 0.05 mole sodium chloride per litre.

SOLUTION

1) Hydrochloric acid, being a strong electrolyte, ionizes completely.

$$\begin{array}{llll} HCl & \longrightarrow & H^+ & + \; Cl^- \\ 0.01 & & 0.01 & \;\; 0.01 \end{array}$$

$$pH = -\log [H^+] = -\log 0.01 = \underline{2}$$

Answer (1)

2) Acetic acid, being a weak acid and, therefore, a weak electrolyte, ionizes partially and an equilibrium is established between the nonionized molecules and the ions.

$$\begin{array}{llll} CH_3COOH & \rightleftharpoons & CH_3COO^- & + \; H^+ \\ c_a(1-\alpha) & & c_a\alpha & \;\; c_a\alpha \end{array}$$

$$\therefore \; K_a = \frac{c_a\alpha \, . \, c_a\alpha}{c_a(1-\alpha)}$$

$$= \frac{c_a\alpha^2}{(1-\alpha)}$$

Since α is very small compared to one, it could be omitted

$$\therefore\ K_\alpha = c_\alpha \alpha^2 \qquad \text{or} \qquad \alpha = \sqrt{\frac{K_\alpha}{c_\alpha}}$$

and $[H^-] = c_\alpha \alpha = \sqrt{K_\alpha \cdot c_\alpha}$

$$= \sqrt{1.7 \times 10^{-5} \times 0.001} = 0.1304 \times 10^{-3}$$

g ion/litre

$$\therefore\ pH = -\log [H\ ] = -\log (1.304 \times 10^{-4})$$

$$= -(\bar{4}.1152) = -(-3.8848) = \underline{3.89}$$

Answer (2)

3) Ammonium hydroxide, being a weak base, i.e. a weak electrolyte, it is treated exactly in the same way as acetic acid.

$$NH_4OH \rightleftharpoons NH_4^- + OH^-$$

$$c_b(1-\alpha) \qquad c_b\alpha \qquad c_b\alpha$$

$$\therefore\ K_b = c_b\alpha^2$$

$$\therefore\ \alpha = \sqrt{\frac{K_b}{c_b}} = \sqrt{\frac{1.8 \times 10^{-5}}{1}} = 4.242 \times 10^{-3}$$

$$[OH^-] = c_b\ \alpha = 1 \times 4.242 \times 10^{-3}$$

$$pOH = -\log [OH^-] = -\log [4.242 \times 10^{-3}] = 2.37$$

But the ionic product of water $K_w = [H^+](OH^-) = 10^{-14}$

$$\therefore\ pK_w = pH + pOH = 14$$

$$\therefore\ pH = 14 - 2.37 = \underline{11.63}$$

Answer (3)

4)

$$CH_3COOH \rightleftarrows \boxed{CH_3COO^-} + H^+$$
$$c_\alpha (1-\alpha') \qquad c_a \alpha' \qquad c_a \alpha'$$
$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$
$$c_s \qquad c_s \qquad c_s$$

Acetic acid is partially ionized, but sodium acetate, being a salt, is completely ionized. If the salt concentration is c_s moles per litre, it gives c_s g ions per litre of acetate ions. This high concentration of the common acetate ion will depress the degree of ionization of the acid to a value α' less than α. The concentration of the acetate ions from the ionization of acetic acid ($c_a \alpha'$) is, therefore, negligible compared to that from the salt (c_s). Applying Ostwald's law of dilution to the equilibrium:

$$K_\alpha = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c_s \cdot (H^+)}{c_a}$$

$$\therefore \ (H^-) = K_a \cdot \frac{c_a}{c_s}$$

$$= 1.7 \times 10^{-5} \times \frac{0.05}{0.05} = 1.7 \times 10^{-5} \text{ g ion/litre}$$

$$\therefore \ pH = \underline{4.77}$$

Answer (4)

5) Sodium chloride in solution ionizes completely to Na^+ and Cl^- ions whic are not common with the ions of acetic acid and at the same time have no effect on the H^+ or OH^- ions in solution. This solution can, therefore, be treated as the pure acetic acid solution.

$$[H^+] = \sqrt{K_a \cdot c^a} = \sqrt{1.7\times10^{-5} \times 0.005}$$

$$= 2.916\times10^{-4} \text{ g ion/litre}$$

$$pH = \underline{3.54}$$

Answer (5)

75. The equivaleut conductance at infinite dilution for acetic acid is 388 cm^2 ohm^{-1} $equiv^{-1}$. The equivalent conductance of a solution of 0.3 g of the acid in 50 cc water is 46 cm^2 $ohn.^{-1}$ $equiv^{-1}$. Find the freezing point of this solution, the molal freezing point constant bein 1.86°C.

SOLUTION

Λ_0 = 388 cm^2 ohm^{-1} $equiv^{-1}$ and Λ = 4.6 cm^2 ohn^{-1} $equiv^{-1}$

$$\therefore \alpha = \frac{\Lambda}{\Lambda_0} = \frac{4.6}{388} = 0.01186$$

$$\text{but } \alpha = \frac{i - 1}{n - 1}$$

where " i " is vant Hoff's factor.

$$0.01186 = \frac{i - 1}{2 - 1}$$

$$\therefore \quad i = 1.01186$$

$$i = \frac{\Delta t_{f,\ obs.}}{\Delta t_{f,\ calc.}}$$

Mol. wt. of CH_3COOH = 60

60 g acetic acid in 1000 g water depress the freezing point 1.86°C
0.3 g acetic acid in 50 g water depresses the freezing point x°C

∴ x the calculated lowering of freezing point of the solution.

$$\Delta t_{f,\ calc.} = \frac{1.86 \times 0.8 \times 1000}{60 \times 50} = 0.186^{0}C$$

$$\because \quad \Delta t_{f,\ obs.} = i \times \Delta t_{f,\ calc.}$$

$$\therefore \quad \Delta t_{f,\ obs.} = 1.01186 \times 0.186$$

∴ The freezing point = − 0.188°C

Answer

76. The dissociation constant of a monobasic acid at a certain temperature is 21.4×10^{-5}. Find the degree of dissociation for a 0.1 N solution of the acid at the same tempe- rature. Find also the normality of the acid solution of pH 2.

SOLUTION

$$HA \rightleftharpoons H^{+} + A^{-}$$

$$c_{\alpha}(1-\alpha) \quad c_{\alpha} \quad c_{\alpha}$$

Let the concentration of the monobasic acid HA be c_a moles per litre, and the degree of dissociation α.

At equilibrium, applying Ostwald's dilution law, we get :

$$K_a = \frac{[H^{+}]\ [A^{-}]}{[HA]}$$

$$\therefore K_a = \frac{c_a \alpha \cdot c_a \alpha}{c_a (1-\alpha)} = \frac{c_a \alpha^2}{(1-\alpha)} = 21.4 \times 10^{-5}$$

∴ c_a = 9.1 N or 0.1 mole litre, since the acid is monobasic,

$$\therefore \alpha^2 = \frac{21.4 \times 10^{-5}}{0.1}$$

α is neglected in comparison with 1 as it is very small.

$$\therefore \alpha = \sqrt{21.4 \times 10^{-4}} = \underline{0\ 04626}$$

Answer

$\because pH = -\log [H^+] \qquad \therefore [H^+] = 10^{(-pH)}$

The hydrogen ion concentration of the acid solution of pH = 2 is, therefore, 10^{-2} g ion/litre.

But $[H^+] = c_a \alpha$ from the above equation.

$$\therefore c_a \alpha = 10^{-2}$$

$$\therefore K_a = \frac{c_a \cdot c_a \alpha}{c_a (1 - \alpha)}$$

Neglecting α with respect to 1, and substituting for K_a and $c_a \alpha$ with their respective values,

$$\therefore K_a = \frac{c_a \alpha \cdot c_a}{c_a} = \frac{10^{-2} \times 10^{-2}}{c_a} = 21.4 \times 10^{-5}$$

$$c_\alpha = \frac{10^{-4}}{21.4 \times 10^{-5}} = 0.4673 \text{ mole/litre}$$

$\therefore$ The solution is $\underline{0.4673}$ N

Answer

77. One hundred grams of of sodium chloride is dissolved iu 10000 litres of water at 25°C, giving a solution which may

be regarded in these calculations as infinitely dilute.

a) What is the equivalent conductance of the solution ?

b) What is the specific conductance of the solution ?

c) This dilute solution is placed in a glass tube of 4 cm diameter provided with electrodes filling the tube and placed 20 cm apart. How much current will flow if the potential drop between the electrodes is 80 volts ?

(Λ_0 for NaCl = 126.5 cm^2 ohm^{-1} $equiv^{-1}$)

SOLUTION

a) Since the solution is considered infinitly dilute its equivalent conductance = 126.5 cm^2 ohm^{-1} $equiv^{-1}$

Answer (a)

b) Equiv. wt. of NaCl = 58.5

$$\Lambda = KV_e$$

where V_e = volum in cc containing 1 g equiv of electrolyte .

$$126.5 = K \left(\frac{10000 \times 1000 \times 58.5}{100} \right)$$

$$\therefore K = \frac{126.5}{10^5 \times 58.5} = 2.16 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Answer (b)

c) $I = \dfrac{E}{R}$ (Ohm's law)

and $R = \dfrac{1}{K} \dfrac{l}{A}$ where l is the distance between the electrodes in cm and A is the area of the electrode in cm^2 .

$$\therefore\ I = \frac{E\ K\ A}{l} = \frac{80 \times 2.16 \times 10^{-5}\ (\pi \times 2^2)}{20}$$

$$= \underline{1.08 \times 10^{-3}}\ \text{amp}$$

Answer (c)

78. The resistance in a conductivity cell, containing 0.02 molar potassium chloride solution is 35.16 ohm. It is 179 ohm if the cell contains 0.1 molar acetic acid solution. What is the degree of ionization of acetic acid if its equivalent conductance at infinite dilution is 390 $cm^2\ ohm^{-1}\ equiv^{-1}$. (The specific conductance of a 0.02 molar potassium chloride solution is 0.002394 $ohm^{-1}\ cm^{-1}$)

SOLUTION

Since $R = \frac{1}{K} \cdot \frac{l}{A} = \frac{1}{K} \cdot K$

where $K = \frac{l}{A}$ which is constant for each cell.

$\therefore\ K = R \times K$

From the measurements on the 0.02 molar KCl solution :

$K = 35.16 \times 0.002394\ cm^{-1}$

K for 0.1 molar acetic acid solution

$$= \frac{K}{R} = \frac{35.16 \times 0.002394}{179}$$

$$= 0.0004701\ \ ohm^{-1}\ cm^{-1}$$

The equivalent conductance of a solution $\Lambda = K \times V_e$ where V_e is the volume in cc containing the equivalent weight.

$$\therefore \Lambda = 0.0004701 \times 10000 = 4.701 \text{ cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$$

$$\therefore \alpha = \frac{\Lambda}{\Lambda_0} = \frac{4.701}{350} = \underline{0.01343}$$

Answer

79. Ten amperes of current flowed for 1 hour through water containing a little sulphuric acid. How many litres of gas were formed at both electrodes at 27°C and 740 mm pressure ?

SOLUTION

$$H_2O_{(l)} = H_{2(g)} + \frac{1}{2} O_{2(g)}$$

From Faraday's law :

$$w = I \times t \times \text{equiv. wt.}$$

where w is the weight of gas liberated at the electrode in g, I the current passing in amp, t the time in sec during which the current flows and F is the faraday which equals 96500 coulombs.

$$w = \frac{10 \times 3600 \times 8}{96500} = 2.98 \text{ g}$$

$$PV = nRT$$

$$\left(\frac{740}{760}\right) \times V = \frac{2.98}{32} \times 0.082 \times 300$$

$\therefore$ Volume of oxygen at 27°C and 740 mm

$$= \frac{2.98 \times 0.082 \times 300 \times 760}{32 \times 740}$$

$= 2.36$ litres

Volume of H_2 = $2 \times$ volume of oxygen

$= 2 \times 2.36 = 4.72$ litres

Total volume of gas formed at both electrodes

$= 2.36 + 4.72 =$ 7.08 litres

Answer

PROBLEMS FOR PRACTICE

1. If the solubility of silver chloride at 18°C is 0.0015 g per litre, calculate:

a) the solubility product of the salt AgCl.

b) the salt remaining in solution after the addition ef 0.058 g sodium chloride per litre of solution.

(1.10 × 10^{-10}) (1.58 × 10^{-5})

2. The solubility of calcium sulphate at 20°C is 2.036 g per litre. The specific conductance of a saturated solution of the salt at the same temperature is 1908 × 10^{-5} ohm^{-1} $cm.^{-1}$. The ionic conductance for ($\frac{1}{2}$ Ca^{++}) at 18°C is 52 cm^2 ohm^{-1} $equiv^{-1}$ and its temperature coefficient is 0.0238 ohm^{-1} deg^{-1}. The ionic conductance for ($\frac{1}{2}$ SO_4^{--}) at 18°C is 68.3 cm^2 ohm^{-1} $equiv^{-1}$ and its temperature coefficient is 0.0227 ohm^{-1} deg^{-1}. Calculate :

a) the degree of ionization of calcium sulphate in its saturated solution,

b) the solubility product of the salt at 20°C.

(274 × 10^{-3}) (6.72 × 10^{-9})

3. At a certain temperature a litre of silver bromate $AgBrO_3$ dissolves 0.0031 mole per litre. Calculate the solubility of the salt after adding 0.0085 mole silver nitrate to the litre of solution, assuming the two salts to be completely ionized.

(3.96 × 10^{-3})

4. The specific conductance of a saturated solution of

silver chloride is 1.33×10^{-6} ohm^{-1} cm^{-1} at 20°C, and the equivalent conductance at infinite dilution is 125.5 cm^2 ohm^{-1} equiv^{-1} at the same temperature. Calculate the solubility product of silver chloride at 20°C. (1.12×10^{-10})

5. The solubility of calcium fluoride is 0.0002 mole per litre. What is the solubility product of calcium fluoride ?

(3.2×10^{-11})

6. The first ionization constant of carbonic acid is 3×10^{-7} at 18°C. Find the degree of ionization according to the equation,

$$H_2CO_3 \rightleftharpoons H^+ + HCO^-_3$$

at 20 litres per mole dilution. If the ionic conductance for hydrogen ions and bicarbonate ions at infinite dilution are 315 and 40.5 cm^2 ohm^{-1} equiv^{-1} respectively, calculate the specific conductance of the solution. (2.5×10^{-3}) (4355×10^{-5})

7. The equivalent conductance of an acetic acid solution containing one mole per 32 litres is 9.2 cm^2 ohm^{-1} equiv^{-1}. The ionic conductance at infinite dilution for the hydrogen and acetate ions are 318 and 71 cm^2 ohm^{-1} equiv^{-1} respectively. Calculate the ionization constant of acetic acid and the pH of a 0.02 N acetic acid solution. (1.75×10^{-5}) (3.13)

8. The equivalent conductance of a 0.01 N ammonium hydroxide solution at 18°C is 9.6 cm^2 ohm^{-1} and the equivalent conductance at infinite dilution for ammonium chloride is 130 cm^2 ohm^{-1} equiv^{-1}. If the ionic conductance at infinite dilution of the hydroxide and chloride ions are 174 and 66 cm^2 ohm^{-1} equiv^{-1} respectively, calculate :

a) the equivalent conductance at infinite dilution for ammonium hydroxide,

b) the degre of ionization of ammoium hydroxide,

c) the ionization constant. (238) (4.04×10^{-2}) (1.7×10^{-5})

9. At 25°C the equivalent conductance at infinite dilution of sodium monchloroacetate is 89.8 cm^2 ohm^{-1} $equiv^{-1}$. Calculate the equivalent conductance at infinite dilution at 25°C for monochloracetic acid. given that Λ^o_{HCl} and Λ^o_{NaCl} are 426.1 and 126.5 cm^2 ohm^{-1} $equiv^{-1}$ respectively. (389.4)

10. The equivalent conductance of an infinitely dilute solution of ammonium chloride is 149.7 cm^2 ohm^{-1} $equiv^{-1}$ and the ionic conductances of the hydroxide and chloride ions are 198.0 and 76.3 cm^2 ohm^{-1} $equiv^{-1}$ respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. (271.4)

11. At 25°C the equivalent conductance of propionic acid at infinite dilution is 385.6 cm^2 ohm^{-1} $equiv^{-1}$, and the ionization constant is 1.34×10^{-5}. Calculate the equivalent conductance of 0.05 N solution of propionic acid at 25°C. (6.32)

12. The molecular conductance of acetic acid at infinite dilution is 387 cm^2 ohm^{-1} $mole^{-1}$. At the same temperature but at the dilution of one mole in 1000 litres, the molecular conductance is 55 cm^2 ohm^{-1} $mole^{-1}$. Find the percentage ionization of 0.1 N acetic acid solution. (1.55)

13. The specific resistance of a solution of sulphuric acid containing 14.5 g acid per litre is 18 ohm cm. The equivalent conductance at infinite dilution is 384 cm^2 ohm^{-1} $equiv^{-1}$. What is the pH of the solution ? (0.5386)

14. The specific resistance of a 0.01 N lithium chloride solution is 1064 ohm cm. The equivalent conductance of the same compound at infinite dilution is 101 cm^2 ohm^{-1} equiv^{-1}. Find the degree of ionzation of the solution ? (0.931)

15. The specific conductance of a 0.5 N potassium fluoride solution is 0.0413 ohm^{-1} cm^{-1}. If the equivalent conductance at infinte dilution is 111,35 cm^2 ohm^{-1} equiv^{-1}, calculate the concentration of the fluoride ions. (0.371)

16. If the pH value of 0.1N acetic acid is 2.872, calculate the ionization constant of the acid. (1.8×10^{-5})

17. Chloroacetic acid $CH_2Cl.COOH$ is a monobasic acid, its ionization constant $K_\alpha = 1.6 \times 10^{-5}$. How many grams of the acid should be dissolved in 300 cc of solution in order to prepare 0.5 N solution ? What is the pH value of this solution ? (14.175) (1.09)

18. A conductivity cell cell was calibrated by filling it with a 0.02 N solution of KCl (K = 0.002768 ohm^{-1} cm^{-1}) and measuring the resistance at 25°C, it was found to be 457.3 ohms. The cell was then filled with a calcium chloride solution containing 0.555 gram of calcium chloride per litre. The measured resistance was 1050 ohms.

Calculate :

a. the cell constant for the cell,

b. the specific conductance of the calcium chloride solution,

c. the equivalent conductance of calcium chloride at this concentration. (1.266) (1.206×10^{-3}) (120.6)

19. A conductivity cell with two circular electrodes fixed horizontally, the distance between them is 1.72 cm and the circumference of each of the two is 1.34 cm. The cell is filled with 0.05 N sodium nitrate solution. If an E.M.F. of 0.5 volt allows 1.85 miliamperes of electricity to pass through the solution, find the equivalent conductance of the solution. (890)

TABLE 1

Heat of Formation at 25°C

$\Delta \overline{H}^{o}_{f}$ in kcal mole^{-1}

Elements and Inorganic Compounds *

$O_{3(g)}$	34.00	$NO_{2(g)}$	8.09	$Ag_2O_{(s)}$	− 7.31
$H_2O_{(g)}$	− 57.80	$NH_{3(g)}$	− 11.04	$AgCl_{(s)}$	− 30.36
$H_2O_{(l)}$	− 68.32	$HNO_{3(l)}$	− 41.40	$Fe_2O_{3(s)}$	− 196.5
$HCl_{(g)}$	− 22.06	$P_{(g)}$	75.18	$Fe_3O_{4(s)}$	− 267.0
$Br_{2(g)}$	7.34	$PCl_{3(g)}$	− 73.22	$Al_2O_{3(s)}$	− 399.90
$HBr_{(g)}$	− 8.66	$PCl_{5(g)}$	− 95.35	$UF_{6(g)}$	− 505
$HI_{(g)}$	6.20	$C_{(s,diamond)}$	0.45	$UF_{6(s)}$	− 517
$S_{(monoclinic)}$	0.07	$CO_{(g)}$	− 26.42	$CaO_{(s)}$	− 151.9
$SO_{2(g)}$	− 70.96	$CO_{2(g)}$	− 94.05	$CaCO_{3(s)}$	− 288.45
$SO_{3(g)}$	− 94.45	$PbO_{(s)}$	− 52.5	$NaF_{(s)}$	− 136.0
$H_2S_{(g)}$	− 4.82	$PbO_{2(s)}$	− 66.12	$NaCl_{(s)}$	− 98.23
$H_2SO_{4(l)}$	− 193.91	$PbSO_{4(s)}$	− 219.50	$KF_{(s)}$	− 134.46
$NO_{(g)}$	21.60	$Hg_{(g)}$	14.54	$KCl_{(s)}$	− 104.18

* Elements in states other than the standard state.

TABLE I (cont'd)

Organic Compounds

Methane, $CH_4(g)$	−17.89	n−Octane, $C_8H_{18}(g)$	−49.82	Acetaldehyde, $C_2H_4O_{(g)}$	−39.76
Ethane, $C_2H_6(g)$	−20.24	Benzene, $C_6H_6(g)$	19.82	Methanol, $CH_3OH_{(l)}$	−57.02
Propane, $C_3H_8(g)$	−24.82	Benzene, $C_6H_6(l)$	11.72	Ethanol, $C_2H_5OH_{(l)}$	−66.36
n−Butane, $C_4H_{10}(g)$	−29.81	Ethylene, $C_2H_4(g)$	12.50	Formic acid $HCOOH_{(l)}$	−97.8
iso−Dutane, $C_4H_{10}(g)$	−31.45	Propylene, $C_3H_6(g)$	4.88	Acctic acid, $CH_3COOH_{(l)}$	−116.4
n−Pentane, $C_5H_{12}(g)$	−35.00	1−Butene, $C_4H_8(g)$	0.28	Oxalic acid. $(COOH)_2(s)$	−197.6
n−Hexane, $C_6H_{14}(g)$	−39.96	Acetylene. $C_2H_2(g)$	54.19	Carbon tetrachloride, $CCl_4(l)$	−33.3
n−Heptane, $C_7H_{16}(g)$	−44.89	Formaldehyde $CH_2O_{(g)}$	−27.7	Glycine, $NH_2CH_2COOH_{(s)}$	−126.33

TABLE II

Molal Boiling-point and Freezing-Point Constants

Solvent	B.P. °C	K_b	F.P. °C	K_f
Acetic acid	118.1	2.93	17	3.9
Acetone	56.0	1.71	—	—
Benzene	80.2	2.53	5.4	5.12
Bromoform	—	—	7.8	14.4
Camphor	—	—	173	40
Chloroform	61.2	3.63	—	—
Cyclohexane	—	—	6.5	20
Ethanol	78.3	1.22	—	—
Ethylene bromide	—	—	10	12.5
Ethylether	34.4	2.02	—	—
Naphthalene	—	—	80	6.8
Tribromophenol	—	—	95	20.4
Water	100	0.51	0	1.860

TABLE III

Atomic Weights

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminium	Al	26.78	Manganese	Mn	54.94
Antimony	Sb	121.76	Mercury	Hg	200.61
Argon	A	39.94	Molybdenum	Mo	95.95
Arsenic	As	74.91	Neon	Ne	10.18
Barium	Ba	137.36	Nickel	Ni	58.69
Beryllium	Be	9.01	Nitrogen	N	14.00
Bismuth	Bi	209.00	Oxygen	O	16.00
Boron	B	10.82	Palladium	Pd	106.70
Bromine	Br	79.92	Phosphorus	P	30.98
Cadmium	Cd	112.41	Platinum	Pt	195.23
Calcium	Ca	40.08	Potassium	K	39.10
Carbon	C	12.01	Radium	Ra	226.05
Cerium	Ce	140.13	Radon	Rn	222
Cesium	Cs	132.91	Selenium	Se	78.96
Chlorine	Cl	35.46	Silicon	Si	28.09
Chromium	Cr	52.01	Silver	Ag	107.88
Cobalt	Co	58.94	Sodium	Na	22.99
Copper	Cu	63.54	Strontium	Sr	87.63
Fluorine	F	19.00	Sulphur	S	32,07
Gold	Au	197.00	Thorium	Th	232.05
Helium	He	4.00	Tin	Sn	118.70
Hydrogen	H	1.008	Titanium	Ti	47.90
Iodine	I	126.91	Tungsten	W	183.92
Iron	Fe	55.85	Uranium	U	238.07
Krypton	Kr	83.80	Vanadium	V	50.95
Lead	Pb	207.21	Xenon	X	131.3
Lithium	Li	6.94	Zinc	Zn	65.38
Magnesium	Mg	24.32	Zirconium	Zr	91.22

ترجمة رءوس المسائل المحلولة

الفصل الأول

١ — وجد بالتحليل الكيميائى أن كلوريد الرصاص يحتوى على ٧٤٫٥ ٪ رصاص ، ٢٥٫٥ ٪ كلور . فاذا كان الوزن الذرى للكلور ٣٥٫٤٥ والحرارة النوعية للرصاص ٠٫٠٢٩ سعر/جم تقريبا ، فحدد القانون الكيميائى لكلوريد الرصاص من بين القوانين المحتملة مثل : $Pb_2 Cl$ ، $Pb Cl$ ، $Pb Cl_2$ ، $Pb Cl_3$ ، $Pb_2 Cl_4$. ثم احسب الوزن الذرى للرصاص .

٢ — (أ) وجد أن الحرارة النوعية لعنصر فلزى M تساوى ٠٫٠٣٠٤ سعر / جم . وعندما سخن ٢٫٦٩٤ جم من البروميد اللامائى لهذا العنصر فى جو من الايدروجين تخلف ١٫٢٥٤ جم من العنصر . احسب التكافؤ والوزن الذرى للعنصر M .

(ب) وجد أن الحرارة النوعية لعنصر غازى G تساوى ٠٫٠٢٨٥ عند ضغط ثابت وتساوى ٠٫٠٢٣١ عند حجم ثابت ، ووزن ٣٠٠ سم^3 من الغاز عند درجة حرارة ١٦°م ، وضغط يعادل ٧٥٠ مم زئبق هو ١٫٦٢٤ جم . احسب عدد ذرات الجزىء من الغاز G ووزنه الجزيئى .

٣ — عومل ٢٫١٢٠ جم من كلوريد الباريوم بحامض كبريتيك فتحولت كلية إلى كبريتات الباريوم . وكان وزن كبريتات الباريوم الناتجة هو ٢٫٣١٨ جم . احسب الوزن المكافىء للباريوم . ما المقصود بالوزن المكافىء لعنصر ولشق ولمركب ؟

٤ — مرر الغاز الناتج من احتراق ٠٫٣٦٦٠ جم من كبريتيد فلز فى ماء البروم . وبعد غلى هذا المحلول واضافة كلوريد الباريوم نتج ٠٫٨٧٥٤ جم من كبريتات الباريوم . احسب الوزن المكافىء للفلز فى الكبريتيد .

٥ — اشرح ما تفهمه عن التشابه البلورى .

٠٫٧١٦٠ جم من كبريتات فلز مائى رسب ٠٫٧٠٠٢ جم من كبريتات الباريوم . وعند خلط كبريتـــات الفلز مع كبريتـات البوتاسيوم ثم البلورة نتج شبة متشابهة بلاوريا مع شبة البوتاس . احسب الوزن الذرى للفلز .

٦ — يشغل ٠٫٢ جم من ايدريد العنصر X عند درجة ١٠٠°م وضغط ٧٣٠ مم حجما قدره ٢١٨٫٥ سم^3 . احسب الكثافة البخارية للايدريد عند ١٠٠°م . وقد أمكن الحصول على ملح كالسيوم $Ca_n X_2$ بواسطة استبدال ايدروجين ايدريد الكلسيوم. وبعد التبخير فى وجود زيادة من حامض الكبريتيك المركز أنتج ١٫٣٤٣ جم من هذا الملح ٢٫٣٤٢ جم من كبريتات الكالسيوم . احسب الوزن المكافىء للعنصر X ثم استنبط التكافؤ والوزن الذرى للعنصر .

٧ — عند تسخين ١ جم من كبريتات لا مائية لفلز كان وزن الأكسيد المتخلف ٠٫٢٩٨ جم . فاذا كانت الحرارة النوعية لهذا الفلز هى ٠٫٢١ فاحسب الوزن الذرى لهذا العنصر .

٨ — الوزن الذرى للأكسجين ١٦ وللفضة ١٠٧٫٨٨ .

(١) المطلوب ايجاد الأوزان الذرية للكلور والبوتاسيوم من المعلومات الآتيـــة :

سخن ٣٫٦٧٦٨ جم من كلورات البوتاسيوم $KClO_3$ لتعطي كلوريد

بوتاسيوم KCl ذا وزن ثابت مقداره ٢٫٢٢٦٨ جم. ولما أذيب هذا الناتج في الماء وعومل المحلول بنترات الفضة تكون راسب من كلوريد الفضة وزنه وهو جاف ٤٫٣٠٠٢ جم .

(ب) أحسب الاوزان الذرية اذا أعطت كلورات البوتاسيوم بعد التحميص كلوريد بوتاسيوم وزنه ٢٫٢٣٥٠ جم نتيجة افقد جزء من المادة . ما الخطأ النسبي في الاوزان الذرية بالنسبة للنتائج التي أمكن حسابها في (ا) .

الفصل الثاني

٩ — احسب عدد الاطنان المترية من غاز ثاني أكسيد الكربون فوق ميل مربع من سطح الارض إذا كان الضغط الجوي يساوي ٧٦٠ مم ويحتوي الهواء على ٠٫٠٤٦ ٪ بالحجم من ثاني أكسيد الكربون .

١٠ — (ا) كم عدد جرامات الهواء في الجو المحيط بالارض إذا فرض أن الارض كروية الشكل وقطرها يساوي ١٢ مليون مترا وأن الضغط الجوي يساوي ٧٦٠ مم في أي مكان على سطح الارض ؟

(ب) كم عدد الجرام جزيئات من الهواء في الجو كله اذا فرض أن متوسط الوزن الجزيئي للهواء هو ٢٨٫٨ ؟

(حـ) كم عدد جزيئات الاكسجين في جو الارض إذا كان الاكسجين يمثل $\frac{1}{5}$ حجم الهواء ؟

١١ — أعطى ٠٫٧١٦ من مركب عضوي قانونه الاولى C_3H_6O

حجما قدره ٢٤٣٫٦ سم^٣ من البخار عند درجة ٢٠٠°م وضغط ٧٥٠مم . ما هو القانون الجزيئى للمركب ؟

١٢ — كم عدد الجزيئات فى قنينة حجمها لتر تحتوى على هواء عند ٢٠°م ومخلخلة إلى ضغط قدره ٠٫٠٠١ مم ؟

١٣ — احسب الكثافة البخارية والوزن الجزيئى لمادة ما من البيانات الآتية (طريقة ديماس) :

وزن القنينة فى الهواء ٢٣٫٤٤٩ جم
وزن القنينة وهى مليئة بالبخار عند ١٥٫٥°م ٢٣٫٧٢٠ جم
درجة حرارة الحمام عند لحام القنينة ١١٠°م
الضغط الجوى أثناء التجربة ٧٥٩ مم
وزن القنينة مليئة بالماء + طرف القنينة ٢٠١٫٤٤٩ جم
وزن لتر من الهواء عند م. ض . ء ١٫٢٩٣ جم

١٤ — قنينة زجاجية مجهزة بصنبور فرغت ووجد أن وزنها ٤٦٫٨٥٤٢جم بدون التصحيح لطفوية (bouyancy) الهواء . وعندما فتح الصنبور وسمح للهواء الجاف أن يملأ القنينة إزداد الوزن إلى ٤٧٫٠٤٦٥ جم . وكان الضغط الجوى ٧٤٥ مم ودرجة الحرارة ٢٧°م .

(ا) احسب الحجم الكلى للقنينة من متوسط الوزن الجزيئى للهواء وقدره ٢٨٫٨ .

(ب) احسب الوزن اذا ملئت القنينة بغاز ايدروجين جاف عند درجة الحرارة والضغط المذكورين

١٥ ـ ما حجم غاز الايدروجين اللازم ليتفاعل مع ٢٠٠ سم٣ من غاز النتروجين ليكون غاز النوشادر علما بأن غاز الايدروجين عند درجة ١٥°م وتحت ضغط ٨٠٠ مم ، وبينما غاز النتروجين عند درجة ٣١°م وتحت ضغط ٦٠٠ ؟ وما حجم غاز النوشادر الناتج عند م. ض. د. ؟

١٦ ـ اعتبر أن الهواء غاز مثالى واحسب بالضبط وزن ١ سم٣ من الهواء عند ٢٥°م ، ١ ضغط جوى اذا كانت الرطوبة النسبية للهواء ٧٠ ٪ وضغط بخار الماء عند ٢٥°م هو ٢٣٫٧ مم . علما بأن الهواء الجاف يحتوى على ٨٠ ٪ نيتروجين و ٢٠ ٪ اكسجين بالحجم .

١٧ ـ اذا كانت كثافة الهليوم ٠٫١٧٨٢ جم / لتر عند م. ض. د فاحسب كثافته عند ٢٥°م وتحت ضغط ٧٤٠ مم .

١٨ ـ ما كثافة خليط من الميثان والإيثان فى كل من الحالتين الآتيتين :

(ا) اذا كان الغازان موجودين بنسبة وزنية مساوية للنسبة بين وزنيهما الجزيئيين عند ١٠٠°م ، ٧٠٠ مم زئبق .

(ب) اذا كان الغازان موجودين بنسبة حجمية مساوية للنسبة بين وزنيهما الجزيئيين ، عند نفس الظروف السابقة .

١٩ ـ وجد أن وزن وعاء مفرغ يزيد بمقدار ٠٫٢٥٠٠ ، ٠٫٥٥٣٥ ، ٠٫٥٢٦٨ جم عندما يملأ بأكسجين أو كلور أو مركب من الاكسجين والكلور كل على حده على التوالى عند نفس درجة الحرارة والضغط . احسب من هذه المعلومات فقط الأوزان الجزيئية للكلور ولأكسيد الكلور . ماذا يمكنك استنتاجه عن عدد الذرات فى جزىء الكلور من هذه المعلومات ؟ ما هو قانون أكسيد الكلور؟

٢٠ — عومل جرام واحد من خليــط من فلزين ، كل منها يعطى ايدروجين مع الاحماض المخففه ، بحامض ايدرو كلوريك مخفف ، فتصاعد ٦٥٠ سم^{3} من الايدروجين عند ١٢°م ، ٧٧٠ مم احسب التركيب المئوى للخليط إذا كانت الأوزان المكافئة للفلزين هما ١٢ ، ٢٠ على الترتيب .

٢١ — خليط مكون من ١ر. حجم ايدروجين ، ٢ر. حجم نيتروجين سيحفظ عند ضغط ٧٦٠ مم ، ٢٦°م .

(أ) ما هو حجم الوعاء اللازم مع افتراض أنه ليس هناك أى تفاعل بين النيتروجروجين والايدووجين ؟

(ب) احسب الكسر الجزيئى للايدروجين .

(ح) ما هو الضغط الجزيئى للايدروجين ؟

٢٢ — أربعة أحجام من غاز ما تنتشر فى نفس الوقت اللازم لإنتشار ثلاثة أحجام من الاكسيجين . احسب الوزن الجزيئى للغاز .

٢٣ — احسب الوزن الجزيئى للهواء المشبع ببخار الماء عند درجة ٢٥°م وضغط جوى واحد علما بأن الضغط البخارى للماء عند ٢٥°م هو ٧ر٢٣ مم وأن الهواء الجاف يحتوى على ٨٠٪ نيتروجين ، ٢٠٪ اكسيجين بالحجم .

٢٤ — عندما بخر ٥ جرامات من كربامات النوشادر $NH_4CO_2NH_2$ عند ٢٠٠°م كان حجمها ٦٦ر٧ لترا تحت ضغط ٧٤٠ مم . احسب درجة التفكك حسب المعادلة الكيميائية الآتية :

$$NH_4CO_2NH_2 = 2NH_3 + CO_2$$

الفصل الثالث

٢٥ — تبلغ حراره تفكك فوق اكسيد الايدروجين بوساطة البلاتين الاسود — ١٣٠٦٠ سعـــرا . فاذا كانت حرارة تكوين الماء السائل هى — ٦٨٣٦٠ سعرا ، احسب حرارة تكوين فوق اكسيد الايدروجين .

٢٦ — تبلغ حرارة الذوبان لكبريتات المغنسيوم اللامائية — ٢٠٢٨٠ سعرا ، وكبريتات المغنسيوم أحادية الماء — ١٣٣٠٠ سعرا وكبريتـــات الماغنسيوم سباعية الماء + ٣٨٠٠ سعرا . احسب حرارة الأدرته للاتى :

(ا) كبريتات المغنسيوم اللامائية إلى أحادية الماء .

(ب) كبريتات المغنسيوم اللامائية إلى سباعية الماء .

(حـ) كبريتات المغنسيوم أحادية الماء إلى سباعية الماء .

٢٧ — اكتب المعادلة الكيميائية الحرارية لتكوين محلول حامض النيتروز واحسب حرارة تكوينه من المعادلات الموجودة بالنص الإنجليزى .

٢٨ — يعطى تفاعل الاوزون مع محلول يوديد البوتاسيوم كمية معينة من الحرارة كما أن تفـــاعل فوق اكسيد الايدروجين مع محـــلول يوديد البوتاسيوم يعطى كمية أقل من الحرارة . والفرق بين كميتى الحرارة بالنسبة على أساس جرام جزىء واحد من يوديد البوتاسيوم هو ٤ كيلو سعر . فاذا كانت حرارة تحلل فوق اكسيد الايدروجين هى ٢١٫٦ كيلو سعر . احسب حرارة تكوين الاوزون .

٢٩ — ينتج حجم معين من الميثان عند الاحتراق الكامل فى مسعر مغلق (ذى حجم ثابت) ٢٫٠١٩٤ حجم من الماء السائل ويتصاعد ١١٫٩٥ كيلو

سعر . احسب حرارة تكوين الميثان علما بان حـــرارة تكوين غاز ثانى اكسيد الكربون ــ ٩٤ كيلو سعر وأن حرارة تكوين الماء السائل هى ــ ٦٩ كيلو سعر .

٣٠ ــ إذا كانت حرارة تعـــادل كل من ايدروكسيد الصوديـوم وايدروكسيد الامونيوم مـع حامض الايـدروكلوريك هى ــ ١٣٦٨٠ : ــ ١٢٢٧٠ سعرا على التوالى . احسب حرارة تأين ايدروكسيد الامونيوم مع افترض أنها لا تتأين عمليا .

٣١ ــ حرارة تعادل حامض الايدروكلوريك مع ايدوكسيد الصوديوم هى ١٣٧٧٠ سعرا ومع حامض احادى كلورو الخليك هى ١٤٢٨٠ سعرا . فاذا أضيف جرام مكافىء واحـــد من حامض الايدرو كلوريك إلى جرام مكافىء من أحادى كلورو خلات الصوديوم فى محلول مخفف فامتصت حرارة تساوى ٤٥٥ سعرا . احسب كمية الخـلات التى تتحال حسب المعادلة التى فى النص الإنجليزى .

٣٢ ــ احسب حرارة تـــكوين ثانى كبريتيد الـكربون السائل وغاز كبريتيد الايدروجين مستخدما المعلومات الموجوده بالنص الإنجليزى .

٣٣ ــ احسب حرارة أدرته (hydration) جرام جزىء من كبريتات النحـاس اللامائية بوساطة ٥ جرام جزيئات من بخـــار الماء عند ٢٥°م مع العلم بأن حرارة تبخر الماء هى + ١٠٫٥٢ كيلو سعرا لـكل جرام جزىء من الماء . وأن حرارة إذابة كبريتات النحـاس اللامائى وكبريتات النحـاس خماسية الماء هى ــ ٢٨٫٩٧ ، ــ ١٢٫١٠ كيلو سعرا على التوالى .

٣٤ — بصهر كبريتات الصوديوم المائية عند درجة حرارة ما ، تكون محلول مشبع يحتوى على x جرام جزىء من الماء لكل جرام جزىء من كبريتات الصوديوم اللامائية كما ترسبت كبريتات الصوديوم اللامائية . وأثناء الانصهار امتص ١٦٥٠٩ سعرا لكل جرام جزىء كبريتات صوديوم مائية تحول إلى محلول مشبع وراسب من الكبريتات اللامائية . فاذا كانت x = ١٥ر٦ فالمطلوب إيجاد :

(ا) عدد الجرام جزيئات من الكبريتات فى المحلول المشبع والجرام جزيئات من الكبريتات اللامائية الناتجة من جرام جزىء من الكبريتات المائية .

(ب) الحرارة المتصاعدة عند تكوين الكبريتات المائية من جرام جزىء واحد من كبريتات الصوديوم اللامائية ومحلول مشبع من كبريتات الصوديوم .

٣٥ — حل ٠٨٧٤ر٠ جم من اليود محل ١٢ر٧ سم^{3} من الهواء فى جهاز فيكتور ماير عند ٢١ر٥°م وتحت ضغط ٧٢٣ مم . احسب الكثافة البخارية لليود ودرجة تفككه عند درجة حرارة التجربة . علما بأن ضغط بخار الماء عند ٢١ر٥°م = ١٩ر٢ مم .

٣٦ — حول ٠ر٩٦ جم من يوديد الايدروجين فى كل تجربة من خمس تجارب إلى بخار عند درجات الحرارة المعطاة وتحت ضغط ثابت ثم برد بسرعة وقدرت كمية اليود المنفصلة فى كل تجربة بمعايرتها بمحلول ٠ر١ عيارى من ثيو كبريتات الصوديوم . وحجوم المحلول العيارى المستخدمة عند درجات

الحرارة المختلفة مبينة كالآتى :

درجة الحرارة م°	٢٥٠	٢٩٠	٣٢٠	٣٦٠	٤٢٠
الحجم سم^٣	١٣٫٢٥	١٢٫٤	١٢٫٠	١٤٫٦	١٥٫٧

احسب النسبة المئوية لتفكك يوديد الايدوجين عند كل درجة حرارة ومثل الناتج بيانيا . ما هى استنتاجاتك من الرسم البيانى ؟

٢٧ — عند احتراق أول اكسيد الكربون والإيدروجين والكحول المثيلى احتراقا تاما فى أوعية مغلقة تحتوى الأكسيجين تصاعدت كميات الحرارة الآتية :

٦٧٧٠٠ ، ٦٨٤٠٠ ، ١٧٠٦٠٠ سعرا لكل جرام جزىء على الترتيب. احسب التغير الحرارى للتفاعل التالى باستخدام المعلومات السابقة .

$$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(l)}$$

وما هو الشغل المبذول من الجو على النظام (System) لكل جرام جزىء من الكحول المثيلى المتكون لو أجرى التفاعل تحت الضغط الجوى وعند ٣٠٠°م ؟

ماهو التأثير الناتج على حرارة التفاعل إذا أجرى التفاعل تحت ضغط ثابت أو عند حجم ثابت ؟

٣٨ — حرارة التكوين للمحاليل المخففه لكل من ايدروكسيد الصوديوم ونيترات الصوديوم وايون الإيدروكسيد فى المحلول هى — ١١٢٫٢٣٦ ، — ١٠٦٫٦٥١ ، — ٥٤٫٩٥٧ كيلو سعرا لكل جرام جزىء على الترتيب . احسب من هذه البيانات حرارة تكوين ايون النيترات فى المحلول المخفف .

٣٩ — احسب حرارة التخفيف التكاملية (integral) لإضافة ١٩٥ جرام جزىء من الماء الى جرام جزىء من كلوريد الإيدروجين الذائب فى ٥ جرام جزىء من الماء . هذا مع العلم أن حرارتى الذوبان التكامليتين لكلوريد الإيدروجين فى كل من ٥ جرام جرام جزىء من الماء و ٢٠٠ جرام جزىء من الماء هى — ١٥ر٢ ، — ١٧ر٧٤ كيلو سعر على الترتيب .

٤٠ — احسب التغير فى المحتوى الحرارى $\triangle H$ عند ٢٥°م لكل كيلو جرام من الوقود والمؤكسد فى التفاعلات المذكورة فى الوصف الإنجليزى . استخدم البيانات عن حرارات التكوين المعطاه فى الجدول رقم ١ .

٤١ — عند احتراق ١ر٧٣٥ جرام من السكروز فى مسعر حرارى ارتفعت درجة الحرارة بمقدار ٢ر٩٠٧°م . فاذا كانت حرارة احتراق السكروز هى ١٣٤٩ر٦ كيلو سعر جرام جزىء :

(ا) فما هى السعة الحرارية الكلية للماء والمسعر ؟

(ب) وإذا كان المسعر يحتوى ١٨٥٠ جراما من الماء (الحرارة النوعية للماء ١ر٠ سعرا / درجة / جرام) ، فما هى السعة الحرارية الحقيقية للمسعر ؟ يمكن إهمال أى تصحيحات لأكسدة سلك الإحتراق والنيتروجين المتبقى .

٤٢ — أحسب التغير فى المحتوى الحرارى ($\triangle H$) للتفاعلات المذكورة بالنص الإنجليزى .

ملحوظة : حرارات تكوين المركبات والأيونات يمكن إيجادها من جدول رقم ١ فى هذا الكتاب أو فى كتب الكيمياء الطبيعية .

الفصل الرابع

٤٣ — إذا كانت كثافة محلول نترات البوتاسيوم يحتوى على ١٢٩٫٦ جرام من الملح فى لتر من المحلول هى ١٫١٤٢٢ جرام / ملليلتر ، احسب التركيز بالدلالات الآتية :

(ا) بالجزيلية (عدد جرام جزىء من المذاب فى ١٠٠٠ جم من المذيب)

(ب) بالجزيئية (عدد جرام جزىء من المذاب فى لتر من المحلول)

(حـ) بالكسر الجزيئى

(ى) بالنسبة المئوية الوزنية .

٤٤ — تتبع محاليل غاز كلوريد الايدروجين فى كلوروبنزين قانون هنرى . فنى المحاليل المخففه نجد أن :

$$K = \frac{p}{m} = 0.438$$

حيث K ثابت هنرى ، p الضغط بالجو والتركيز m بالجزيليه . ماهو الضغط الجزئى لغاز كلوريد الإيدوجين بالمليمترات فوق محلول غاز كلوريد الايدروجين فى كلورو بنزين تركيزه ١ ٪ بالوزن ؟

٤٥ — اذا احتوى خزان سعته ١٠ لتر على غاز الميثان ولتر واحد من الماء حتى ضغط كلى مقداره ٤٧٠ مم ، وكانت درجة الحرارة ٢٥°م ، احسب كم جراما من غاز الميثان ذائبة فى الماء إذا علمت أن ثابت قانون هنرى لغاز الميثان عند درجة ٢٥°م هو :

$$K_2 = \frac{p_2}{x_2} = \frac{\text{الضغط الجزئى للغاز بالمليمتر}}{\text{الكسر الجزيئى للغاز فى المحلول}} = ٣١٫٤ \times ١٠^٩$$

وأن ضغط بخار الماء عند درجة ٢٥°م هو ٢٣٫٧٦ مم .

٤٦ — سحب تيار من الهواء الجاف خلال سلسلة من الانابيب تحتوى على ٤٫٢٥٧ جم من المادة (x) ذائبة فى ٥٢٫٦٨ جم من الكحول الإيثيلى ثم خلال سلسلة من الأنابيب المماثلة تحتـــوى على الكحولى الإيثيلى النقى على التتابع . وكان الهواء الداخل ومجموعتا الأنابيب عند نفس درجة الحرارة الثابته . فاذا كان النقص فى وزن مجموعة الانابيب الاولى هو ١٫٢٩٢ جم والنقص فى وزن مجموعة الأنابيب الثانية ٠٫٠٣١٣ جم ، احسب الوزن الجزيئى المادة (x) .

٤٧ — إذا كان الضغط البخارى فوق محلول يحتوى على ٦٫٦٩ جم من نيترات الكالسيوم فى ١٠٠ جم من الماء هو ٧٤٦٫٩ مم عند درجة ١٠٠°م ، فما هى درجة تفكك الملح ؟

٤٨ — إذا كانت درجة غليان خليط من ثانى بروميد الإيثيلين والمـــاء هى ٩١°م ، فما التركيب المئوى لما يقطر من الخليط أثناء عملية التقطير البخارى ؟ (ضغط بخار الماء المشبع عند ٩١°م هو ٥٤٥ مم) .

٤٩ — يتجمد محلول لمادة غير متطايرة فى الماء عند درجة — ٠٫٢٠٠°م ، فما درجة الغليان لهذا المحلول ؟ وما ضغطه البخارى عند درجة ١٠٠°م ؟

اعتبر أن ثابتى الغليان والتجمد الجزيئيان للماء هما ٠٫٥١ ، ١٫٨٦ على الترتيب .

٥٠ — أذيبت مادة هيدروكربونيه لها القانون $H(CH_2)_nH$ فى بروميد الإيثلين الذى يتجمد عند ١٠٫٠٠°م . وقد وجد أن المحلول المحتوى على ٠٫٨١ جم من

الهيدرو كربون ١٩٠ جم بروميد الإيثاين يتجمد عند ٤٧ر٩°م . احسب قيمة n .

٥١ — مزجت ١٠ جرامات من البنزين مع ١٠ جرامات من التولوين وكذلك ١٠ جرامات من النفتالين لتكون جميعها محلولا متجانسا فكم جراما من التولوين تتطاير بامرار ١٠ لترات من الهواء خلال المحلول عند درجة ٣٠°م إذا كان الضغط البخارى للتولوين ٣٦٫٧مم وللبنزين ١١٨٫٥مم عند هذه الدرجة وأن الضغط البخارى للنفتالين يمكن إهماله ، ذلك بفرض أن المحلول مثالى ؟

٥٢ — إذا درجات التجمد لمحاليل مائية لثانى كلورو حامض الخليك (وزنة الجزيئى ١٢٩) تركيزها (ا) ١ر. جرام جزيلى ، (ب) ٠١ر. جرام جزيلى هى - ٢٧٨ر. ، - ٠٣٢ر.°م على الترتيب، إحسب درجة التأين فى كل من المحلولين على أسس نظرية ارهينيس (الثابت الجزيلى لدرجة التجمد للماء ١٫٨٥)

٥٣ — احسب الضغط الأسموزى لمحلول اليوريا الذى يحتوى على ٣١٢ر. جرام فى ١٠٠ سم^3 من الماء عند درجة ٢٥°م . الوزن الجزيئى لليوريا ٦٠ .

٥٤ - إذا كان محلول كلوريد الصوديوم تركيزه الجزيئى ٢ر. يتفكك بنسبة ٨٠ ٪ عند درجة ١٨°م ، فما هو تركيز محلول اليوريا الذى يتساوى أسموزيا مع محلول الملح ؟

٥٥ — إذا كان الضغط الأسموزى لمحلول كلوريد الصوديوم ٥ر. عيارى هو ٢٠٫٢٩ جو عند درجة ١٨°م فاحسب درجة تفكك الملح .

٥٦ - إذا كانت النسبة المئوية لتأين محلول أحادى كلورو حامض الخليك (الوزن الجزيئى ٩٤٫٥) ٠٧ر. جرام جزيلى هى ١٣ ٪ . احسب :

ا ـ درجة الغليان ب ـ درجة التجمد حـ ـ الضغط البخارى للمحلول عند درجة ٢٥°م .

الضغط البخارى للماء عند درجة ٢٥°م هو ٢٣٫٧٥٦ مم ، والثابت الجزيئى لدرجة الغليان للماء هو ٠٫٥٢ والثابت الجزيئى لتجمد الماء هو ١٫٨٥ .

٥٧ — درجة تجمد محلول من ٠٫٦٨٤ جرام من سكر القصب فى ١٠٠ جرام من الماء هى ـ ٠٫٠٣٧٠٠°م ، ودرجة تجمد محلول من ٠٫٥٨٥ جرام من كلوريد الصوديوم فى ١٠٠ جرام من الماء هى ـ ٠٫٣٢٤٢°م. احسب الثابت الجزيئى لتجمد الماء ، واحسب الوزن الجزيئى الظاهرى لكوريد الصوديوم ودرجة تفككه .

الفصل الخامس

٥٧ — إذا كان ثابت السرعة لتميوء خلات الإيثيل عند درجة ٢٥°م حسب المعادلة :

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH$$

هو ٢٫٥ × ١٠⁻⁴ لتر / جزىء ، وثابت السرعة للتفاعل العكسى (الأسترة) بنفس الوحدات هو ٦٫٢٥ × ١٠⁻⁵ . احسب قيمة ثابت الإتزان .

٥٩ — سخن خليط مكون من النيتروجين والايدروجين بنسبة جزيئية ١ : ٣ إلى درجة ٥٠٠°م تحت ضغط ١ جو حتى وصل إلى حالة الاتزان . وكانت نسبة النشادر الجزيئية المئوية فى الخليط عند حالة الاتزان هى ١٫٢ . أوجد الضغط التى يصبح الخليط تحته فى حالة اتزان عند نفس درجة الحرارة ويحتوى على ١٠٫٤ نسبة جزيئية مئوية من النشادر .

٦٠ — جرام جزىء واحد من الغاز AB يشغل اناء حجمه ٤٠ لـتـرا عند درجة ٤٠٠° مطلقة . فاذا كانت نسبة تفكك الغاز هى ٢ ٪ فاحسب :

(أ) الضغط الكلى بالجو عند حالة الاتزان .

(ب) سابقتين K_p ، K_c .

٦١ — يتفاعل بخـــار الماء مع الحديد المسخن لدرجـة الاحمـرار طبقا للمعادلة :

$$3\ Fe + 4\ H_2O \rightleftarrows Fe_3O_4 + 4\ H_2$$

وعند الاتزان عند ٢٠٠°م ، كان الضغط الجزئى لكل من بخـــار الماء والايدروجين ٦ر٤ و ٨ر٩٥ مم على الترتيب . احسب الثابت K_1 للتفاعل . احسب الضغط الجزئى لغاز الايدروجين عندما يكون الضغط الجزئى لبخار الماء ٦ر٩ مم . احسب كذلك الضغط الجزئى لكل من الغازين عندما يكون الضغط الكلى ٧٦٠ مم .

٦٢ — فى التفاعلات الآتية ، إذا كان ثابت الاتزان عند ٧٥٠°م ، بمدلول الضغوط الجزئية ، للتفاعل (١) يساوى ٨٥ر٢، وللتفاعل (٢) يساوى ٧٧١ر٠ ، احسب ثابت الاتزان K_p للتفاعل (٣) عند نفس درجة الحرارة .

1) $\frac{1}{2}\ SnO_{2(s)} + H_{2(g)} = \frac{1}{2}\ Sn_{(s)} + H_2O_{(g)}$

2) $H_{2(g)} + CO_{2(g)} = CO_{(g)} + H_2O_{(g)}$

3) $\frac{1}{2}\ SnO_{2(s)} + CO_{(g)} = \frac{1}{2}\ Sn_{(s)} + CO_{2(g)}$

٦٣ — عند تأكسد ثانى أكسيد الكبريت إلى ثالث أكسيد الكبريت فى وجود عامل مساعد عند ٧٢٧°م . يخضع ثابت الاتزان للعلاقة التالية :

$$K_p = 1.85 = \left(\frac{P_{SO_3}}{P_{SO_2}}\right) \times \sqrt{\frac{1}{P_{O^2}}}$$

(ا) أحسب نسبة SO_3 إلى SO_2 عندما يكون الضغط الجزئى للاكسجين عند الاتزان ٣ر٠ جو .

(ب) أحسب نسبة SO_3 إلى SO_2 عندما يكون الضغط الجزئى الاكسجين عند الاتزان ٦ر٠ جو

(حـ) ما هو التأثير على نسب SO_3 إلى SO_2 إذا زاد الضغط الكلى لمخلوط الغازات ، نتيجة لإضافة نيتروجين إلى المخلوط تحت ضغط ؟

٦٤ — عند ١٢٧٣° مطلقة وضغط كلى ٣٠ جو يتم توازن التفاعل

$$CO_{2(g)} + C_{(s)} \rightleftarrows 2\ CO_{(g)}$$

بحيث تكون النسبة الجزيئية لثانى أكسيد الكربون فى المخلوط الغازى ١٧٪.

(ا) أحسب النسبة المئوية الجزيئية لثانى أكسيد الكربون إذا كان الضغط الكلى ٢٠ جو .

(ب) ماذا يكون تأثير أضافة نيتروجين حتى يصير ضغطه الجزئى ١٠ جو ، على التوازن ؟

(حـ) عند أى ضغط تكون النسبة الجزيئية لثانى أكسيد الكربون ٢٥٪

٦٥ — درس التفاعل .

$$CO_{2(g)} + H_{2(g)} = CO_{(g)} + H_2O_{(g)}$$

بامرار مخلوط من ثانى أكسيد الكربون والإيدروجين فوق عامل مساعد عند ٩٠٠°م وتحت الضغط الجوى ، ثم برد المخلوط الغازى الناتج بسرعة إلى درجة حرارة الغرفة بامراره خلال أنبوبة شعرية ، ثم حلل . وفى إحدى التجارب كانت الضغوط الجزيئية لثانى أكسيد الكربون والايدروجين وأول أكسيد الكربون وبخار الماء على الترتيب كما يلى : ٠ر٢١٤٢ ، ٠ر٢٥٤٩ ، ٠ر٢٦٥٤ و ٠ر٢٦٥٤ جو . أحسب عدد جرام جزيئات الايدروجين الموجودة فى مخلوط اتزان آخر يحتوى على الجرام جزيئات الآتية من أول أكسيد الكربون وبخار الماء وثانى أكسيد الكربون على الترتيب : ٠ر٢٢٠٢ ، ٠ر٢٢٧٢ و ٠ر٠٤٨٥٠

٦٦ — إذا كان ثابت الاتزان K_p للتفاعل التالى عند ٢٥°م = ٠ر١٤١

$$N_2O_4 \rightleftarrows 2\ NO_2$$

أحسب الضغط الذى تتوقعه إذا سمح لجرام واحد من N_2O_4 السائل أن يتبخر فى إناء حجمه لتر واحد عند هذه الدرجة من الحرارة بفرض أن كلا من NO_2 و N_2O_4 يتصرف كغاز مثالى .

٦٧ — إذا كانت قيمة ثابت التفكك K_p ، لتفكك خامس كلوريد الفوسفور عند ٢٥٠°م تساوى ١ر٧٨ أحسب درجة التفكك عن الاتزان عندما يسمح لـ ٠ر٠٤ جرام جزىء من PCl_5 بالتبخر فى اناء يحتوى على ٠ر٢ جرام جزىء من الكلور ، موجودة من الأصل ، تحت الظروف الآتية :

(أ) تحت ضغط ثابت يساوى ٢ جو .

(ب) عند حجم ثابت يساوى ٤ لترات .

قارن النتائج التى تحصل عليها بالنتائج التى يمكن الحصول عليها تحت نفس الظروف ، لكن فى غياب الكلور .

٦٨ — عندما يسخن ٢ر٦ جرام من خامس كلوريد الفوسفور إلى درجة حرارة ٢٠٠°، يتبخر كليـة ويشغل البخار حجما يساوى لترا واحـدا تحت الضغط الجوى وفى نفس الوقت يتفكك جزئيا إلى ثالث كلوريد الفوسفور وغاز الكلور . أحسب درجة التفكك وثابت التفكك K_c لخـامس كلوريد الفوسفور عند هذه الدرجة من من الحرارة .

عبر عن التركيز بعدد الجرام الجزيئات فى اللتر .

الفصل السادس

٦٩ — إذا كانت نسبة توزيع الأنيلين البنزين والمـاء تساوى ١ر١٠ إلى ١ر وبعد ٦ر ج لتر من محلول ايدرو كلوريد الأنيلين الذى يحتوى على ٠٩٩٧ر٠ جرام جزىء من هذا الملح مع ٥٩ سم^3 من البنزين عند ٢٥°م ، وجد أن ٥٠سم^3 من البنزين تحتوى ٠٦٤٨ر٠ جرام من الأنيلين . أوجد درجة تميؤ ايدرو كلوريد الأنيلين فى المحلول وأحسب ثابت تكك الأنيلين كقاعدة .

٧٠ — كم عدد الجرام جزيئات من خلات الصوديوم الجافة التى يجب إضافتها إلى لتر واحد من حامض الايدرو كلوريك $\frac{1}{10}$ عيارى حتى تصبح قيمـة الرقم الايدروجينى pH ٤ر٤ ؟ علمـا بأن ثابت التأين لحـامض الخليك يساوى ١ر٨ × ١٠$^{-5}$.

٧١ — أذيب ٥٨٥ر٥ جرام من كلوريد الصوديوم فى لتر واحد من محلول مشبع بكلوريد الفضة ، أحسب وزن كلوريد الفضة الذى يترسب علما بأن درجة ذوبان كلوريد الفضة فى الماء فى درجـة الحرارة العادية يساوى ١ × ١٠$^{-5}$ جرام جزىء فى اللتر .

٧٢ — التوصيل النوعى لمحلول مشبع ببروميد الفضة عند ٢٠°م يساوى ١٫٥٧٦ × ١٠^-٦ أوم^-١ سم^-١ . والتوصيل النوعى للماء المستخدم فى المحلول يساوى ١٫٥١٩ × ١٠^-٦ أوم^-١ سم^-١ . وبفرض أن بروميد الفضة تام التأين أحسب درجة وحاصل الإذابة لبروميد الفضة ، علما بأن التوصيل المكافىء عند التخفيف اللانهائى لكل من بروميد البوتاسيوم ونترات البوتاسيوم ونترات الفضة ١٣٧٫٤ و ١٣١٫٣ و ١٢١٫٠ سم^٢ أوم^-١ مكافىء^-١ على الترتيب .

٧٣ — (ا) أحسب حاصل الإذابة لإيدروكسيد الماغنسيوم ، إذا علم أن درجة الإذابة لهذه القاعدة هى ٠٫٠١١٦٦ جرام فى اللتر ، بفرض أن القواعد الذائبة تامة التأين .

(ب) إذا كان ثابت التأين لكل من حامض الخليك وحامض الفورميك هو ١٫٨ × ١٠^-٥ و ٢١٫٤ × ١٠^-٥ على التوالى ، ماهى النسبة بين قوتى هذين الحامضين ؟

٧٤ — أحسب قيمة الرقم الايدروجينى P_H للمحاليل الآتية : —

(ا) حامض ايدوكلوريد تركيزه ٠٫٠١ جرام جزىء فى اللتر .

(ب) حامض خليك تركيزه ٠٫٠٠١ جرام جزىء فى اللتر (ثابت التأين للحامض = ١٫٧ × ١٠^-٥)

(ح) ايدروكسيد امونيوم تركيزه جرام جزىء واحد فى اللتر (ثابت التأين للقاعدة = ١٫٨ × ١٠^-٥)

(ى) خليط يحتوى على ٠٫٠١ جرام جزىء من حامض الخليك و ٠٫٠٥ جرام جزىء من خلات الصوديوم فى اللتر .

(هـ) خليط يحتوى على ٠٠٥ر٠ جرام جزىء من حامض الخليك ٠٥ر٠ جرام جزىء من كلوريد الصوديوم فى اللتر .

٧٥ — التوصيل المكافىء عند التخفيف اللانهائى لحامض يساوى ٣٨٨ سم^{٢} أو م$^{-١}$ مكافى$^{-١}$. والتوصل المكافىء لمحلول يحتوى على ٣ر٠ جرام من الحامض فى ٥٠ سم^{٣} من الماء هو ٦ر٤ سم أو م$^{-١}$ مكافىء$^{-١}$. أحسب نقطة تجمد هذا المحلول ، علما بأن الثابت الجزيئى لدرجة تجمد الماء يساوى ٨٦ر١°م .

٧٦ — ثابت التفكك لحامض أحادى القاعدية عند درجة حرارة معينة يساوى ٤ر٢١ × ١٠$^{-٥}$. أحسب درجة تفكك الحامض فى محلول ١ر٠ عيارى عند نفس درجة الحرارة . أحسب كذلك عيارية محلول الحامض الذى رقمه الايدروجينى يساوى ٢ .

٧٧ — أذيب ١٠٠ جرام من كلوريد الصوديوم فى ١٠٠٠٠ لتر من الماء عند ٢٥°م ، معطيا محلولا يمكن اعتباره لانهائى التخفيف .

(ا) ماقيمة التوصيل المكافىء لهذا المحلول ؟

(ب) ماقيمة التوصيل النوعى لهذا المحلول ؟

(حـ) وضع هذا المحلول المخفف فى أنبوبة زجاجية قطرها ٤ سم مزودة بقطبين يملآن الأنبوبة ويبعدان عن بعضهما بمسافة ٢٠ سم . أحسب شدة التيار الذى يمر إذا كان الفرق فى الجهد بين القطبين ٨٠ فولت .

(Λ_0 لكلوريد الصوديوم = ٥ر١٢٦ سم^{٢} أو م$^{-١}$ مكافىء$^{-١}$)

٧٨ — إذا كانت المقاومة فى خلية توصيل كهربائى تحتوى على محلول كلوريد

بوتاسيوم تركيزه ٠٫٠٢ جرام جزىء فى اللتر، تساوى ٣٥٫١٦ أوم. وتساوى المقاومة ١٧٩ أوم إذا كانت الخلية تحتوى على محلول حامض خليك تركيزه ٠٫١ جرام جزىء فى اللتر . فما هى درجة تأين حامض الخليك علماً بأن التوصيل المكافئ لحامض الخليك اللانهائى التخفيف تساوى ٣٥٠ سم^{2} أوم$^{-1}$ مكافىء$^{-1}$، وأن التوصيل النوعى لمحلول كلوريد البوتاسيوم تركيزه ٠٫٠٢ جرام جزىء فى اللتر هو ٠٫٠٠٢٢٩٤ أوم$^{-1}$ سم$^{-1}$؟

٧٩ — مر تيار كهربائى شدته ١٠ أمبير لمدة ساعة خلال ماء يحتوى على قليل من حامض الكبريتيك كم لتراً من الغاز تكون عند كلى القطبين عند ٢٧°م وضغط ٧٤٠ مم ؟