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D. I. MENDELEYEV'S PERIODI

PERIODS	SERIES	ELEMENT I	II	III	IV	V
1	I	1 **H** 1,00797 1				
2	II	3 **Li** 6,939 1 2	4 **Be** 9,0122 2 2	5 **B** 10,811 3 2	6 **C** 12,01115 4 2	7 **N** 14,008 5 2
3	III	11 **Na** 22,991 1 8 2	12 **Mg** 24,312 2 8 2	13 **Al** 26,9815 3 8 2	14 **Si** 28,086 4 8 2	15 **P** 30,9738 5 8 2
4	IV	19 **K** 39,102 1 8 8 2	20 **Ca** 40,08 2 8 8 2	21 **Sc** 44,956 2 9 8 2	22 **Ti** 47,90 2 10 8 2	23 **V** 50,942 2 11 8 2
	V	29 **Cu** 63,54 1 18 8 2	30 **Zn** 65,37 2 18 8 2	31 **Ga** 69,72 3 18 8 2	32 **Ge** 72,59 4 18 8 2	33 **As** 74,9216 5 18 8 2
5	VI	37 **Rb** 85,47 1 8 18 8 2	38 **Sr** 87,62 2 8 18 8 2	39 **Y** 88,905 2 9 18 8 2	40 **Zr** 91,22 2 10 18 8 2	41 **Nb** 92,906 1 12 18 8 2
	VII	47 **Ag** 107,870 1 18 18 8 2	48 **Cd** 112,40 2 18 18 8 2	49 **In** 114,82 3 18 18 8 2	50 **Sn** 118,69 4 18 18 8 2	51 **Sb** 121,76 5 18 18 8 2
6	VIII	55 **Cs** 132,905 1 8 18 18 8 2	56 **Ba** 137,34 2 8 18 18 8 2	57 **La*** 138,91 2 9 18 18 8 2	72 **Hf** 178,49 2 10 32 18 8 2	73 **Ta** 180,948 2 11 32 18 8 2
	IX	79 **Au** 196,967 1 18 32 18 8 2	80 **Hg** 200,59 2 18 32 18 8 2	81 **Tl** 204,37 3 18 32 18 8 2	82 **Pb** 207,19 4 18 32 18 8 2	83 **Bi** 208,980 5 18 32 18 8 2
7	X	87 **Fr** [223] 1 8 18 32 18 8 2	88 **Ra** [226] 2 8 18 32 18 8 2	89 **Ac**** [227] 2 9 18 32 18 8 2	(Th)	(Pa)

*LANTHA

58	59	60	61	62	63	64
Ce 140,12 2 8 20 18 8 2	**Pr** 140,907 2 8 21 18 8 2	**Nd** 144,24 2 8 22 18 8 2	**Pm** [147] 2 8 23 18 8 2	**Sm** 150,35 2 8 24 18 8 2	**Eu** 151,96 2 8 25 18 8 2	**Gd** 157,25 2 8 25 18 8 2

** ACTI

90	91	92	93	94	95	96
Th 232,038 2 10 18 32 18 8 2	**Pa** [231] 2 9 20 32 18 8 2	**U** 238,03 2 9 21 32 18 8 2	**Np** [237] 2 8 23 32 18 8 2	**Pu** [242] 2 8 24 32 18 8 2	**Am** [243] 2 8 25 32 18 8 2	**Cm** [247] 2 9 25 32 18 3 2

Figures in square brackets are mass numbers of stablest isotopes

TABLE OF ELEMENTS

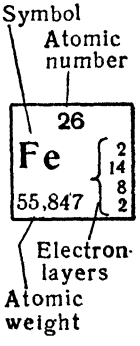
GROUPS					
VI	VII	VIII			0
	(H)				He 2 4,0026 2
8 O 6 2 15,9994	9 F 7 2 18,9984				Ne 10 20,183 8 2
16 S 6 8 2 32,064	17 Cl 7 8 2 35,453				Ar 18 39,948 8 8 2
24 Cr 1 13 8 2 51,996	25 Mn 2 13 8 2 54,9381	26 Fe 2 14 8 2 55,847	27 Co 2 15 8 2 58,9332	28 Ni 2 16 8 2 58,71	
6 34 Se 18 8 2 78,96	7 35 Br 18 8 2 79,909				36 Kr 8 18 8 2 83,80
42 Mo 1 13 18 8 2 95,94	43 Tc 1 14 18 8 2 [97]	44 Ru 1 15 18 8 2 101,07	45 Rh 1 16 18 8 2 102,905	46 Pd 0 18 18 8 2 106,4	
6 52 Te 18 18 8 2 127,60	7 53 I 18 18 8 2 126,9044				54 Xe 8 18 18 8 2 131,30
74 W 2 12 32 18 8 2 183,85	75 Re 2 13 32 18 8 2 186,2	76 Os 2 14 32 18 8 2 190,2	77 Ir 2 15 32 18 8 2 192,2	78 Pt 1 17 32 18 8 2 195,09	
6 84 Po 18 32 18 8 2 [210]	7 85 At 18 32 18 8 2 [210]				86 Rn 8 18 32 18 8 2 [222]
(U)					

NIDES 58-71

65 Tb 2 8 27 18 8 2 158,924	66 Dy 2 8 28 18 8 2 162,50	67 Ho 2 8 29 18 8 2 164,930	68 Er 2 8 30 18 8 2 167,26	69 Tu 2 8 31 18 8 2 168,934	70 Yb 2 8 32 18 8 2 173,04	71 Lu 2 8 32 18 8 2 174,97

NIDES

97 Bk 2 8 27 32 18 8 2 [247]	98 Cf 2 8 28 32 18 8 2 [249]	99 Es 2 8 29 32 18 8 2 [254]	100 Fm 2 8 30 32 18 8 2 [253]	101 Md 2 8 31 32 18 8 2 [256]	102 No 2 8 32 32 18 8 2 [255]	103 Lw 2 9 32 32 18 8 2 [257]



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В. И. Семишин

ПРАКТИКУМ ПО ОБЩЕЙ ХИМИИ

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ГОСУДАРСТВЕННОЕ
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ХИМИЧЕСКОЙ ЛИТЕРАТУРЫ
МОСКВА

V. Semishin

LABORATORY EXERCISES IN GENERAL CHEMISTRY

Translated from the Russian by
BORIS BELITSKY

PEACE PUBLISHERS MOSCOW

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INTRODUCTION

Laboratory exercises are an integral part of a course of chemistry. To perform them profitably, the student should first study the subjects listed in small print at the beginning of each exercise. The questions included enable him to make certain that such preparation for each exercise has been sufficiently thorough. It is especially important to solve the problems included, which are based on the subject-matter of the exercise. Atomic weights approximated to one decimal should be used in solving the problems.

All laboratory work should be done by students individually. The student should be familiar with the laboratory routine, and he should follow it unswervingly.

From the very first exercise thought should be given to the time-saving factor. The student should endeavour to organise his work in such a way that during lengthy operations not requiring his undivided attention (filtration, evaporation, calcination, etc.) he could perform other experiments.

Reagents should always be taken in the quantities indicated. The stoppers of reagent bottles should be promptly replaced, and the bottles should be put back where they belong. *A reagent taken in excess should never be poured back into the bottle.* Used reagents should be poured down the drain; in the case of fuming reagents, however, this should be a drain fitted with a ventilated hood, while spent reagents of considerable value should be collected in special vessels.

No work requiring a ventilated hood should be done without it, on an unhooded laboratory table.

The results of all the experiments conducted should be recorded in a notebook, a margin being left for the instructor's comments. All records should be clear and concise. The conditions in which the experiment is conducted should be specified, and the phenomena observed described. The chemical process should be expressed by proper equations, and a sketch or diagram of the apparatus used should be added if necessary.

Exhaustive written answers should be given to all the questions put in the exercises.

All calculations should be done by means of a table of logarithms or slide rule. If the treatment of the experimental data involves atomic weights, their values should be approximated to two decimals.

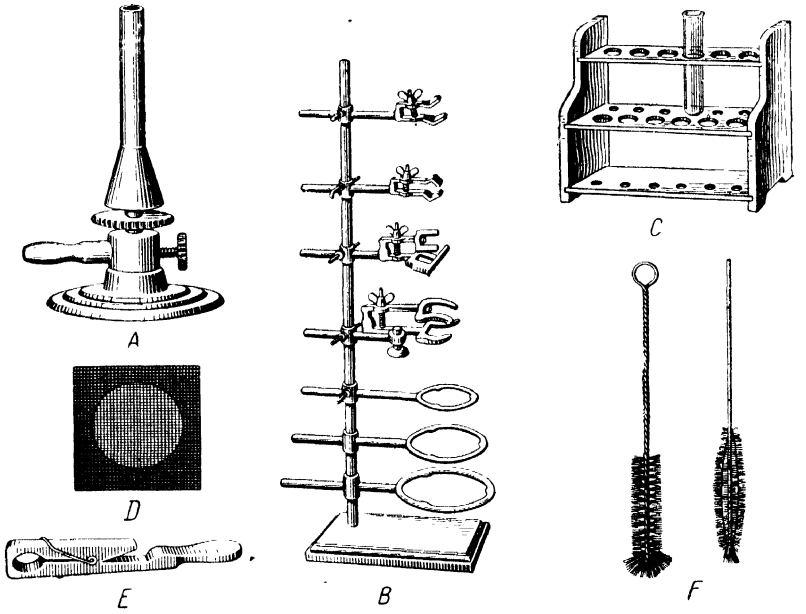
The results of an experiment should be entered in the student's notebook before a new experiment is begun.

On completing a laboratory exercise, the student should submit his notebook with the results of all the experiments to the instructor. Before leaving the laboratory, the student should put his workplace in order and wash his hands.

The instructor should be informed at once of any accident in the laboratory.

THE STUDENT'S LABORATORY EQUIPMENT

Each workplace should have laid on: gas, hot and cold water, electricity (a. c. and d. c.), suction, and a drain. In addition, each student should be provided with the following objects:



A — burner; *B* — ringstand; *C* — test-tube rack; *D* — wire gauze with asbestos centre; *E* — test-tube holder; *F* — brushes for cleaning utensils.

Exercise 1

HEATING AND WEIGHING

LABORATORY WORK

Apparatus and materials: gas burner; crucible tongs; 5-7 cm of nichrome wire about 1 mm in diameter; porcelain crucible cover; watch glasses, weighing bottles, and crucibles; glass tube about 20 cm in length and 5-6 cm in diameter; test tubes; pins; matches; sheets of paper 10×10 cm; potassium bromide; anhydrous sodium sulphate, and an object for test weighing.

Heating

Many chemical processes can be accelerated by heating. This is effected by electric appliances (furnaces and heaters) or burners (spirit, petrol, and gas), depending upon the laboratory equipment and the nature of the process studied.

1. Gas Burner. Take the burner shown in Fig. 1 apart: unscrew the gas tube (2) from the base (1); unscrew the disk (3) from the lower,

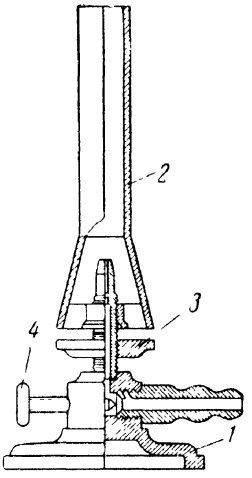


Fig. 1. Gas burner (Teclu burner)

1 — base; 2 — tube; 3 — disk regulating flow of air; 4 — valve regulating supply of gas.

wider part of the tube, which is called the gas-mixing chamber. Examine each part and ascertain the purpose of the disk and of the valve (4).

Reassemble the burner* and draw a diagram of it in your notebook, designating the names of all the parts.

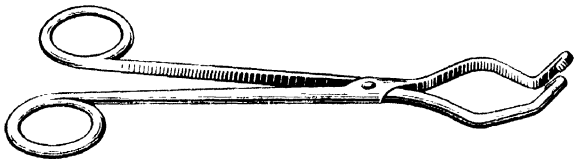


Fig. 2. Crucible tongs

Connect the burner to a gas-supply tap by means of rubber tubing; screw in the disk close to the chamber; turn on the gas by turning the cock 90°, and light the burner.

Now turn the valve slowly and observe the changes in the size of the flame. What purpose does the valve serve?

By means of a pair of crucible tongs (Fig. 2) take a porcelain crucible cover and introduce it into the flame. What is formed on the surface of the cover? How is such a flame called? Is the burning of the gas in such a flame complete? **

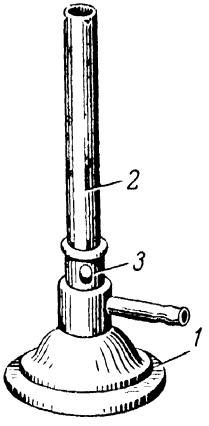


Fig. 3. Gas burner (Bunsen) with ring

1 — base; 2 — tube; 3 — ring regulating flow of air.

Turn the disk slowly, observing the changes in the flame, until a sharply defined inner cone appears within it. Introduce a clean porcelain crucible cover into the middle of the outer cone. Is any carbon black formed now? How is such a flame called? What does the disk serve for?

Other types of gas burners are sometimes used in the laboratory too (Fig. 3).

2. Flame Flash-back. By turning the valve smoothly reduce the height of the flame to about 2 cm, after which turn the disk until it is fully released from the tube. The flame has now flashed back, i. e., combustion takes place within the burner (verify this!). This causes the flame over the tube either to disappear or to become elongated and luminous, combustion being often accompanied by a whistling sound. If the burner is made of a copper alloy, the flame may after a time acquire a green tinge.

When the flame flashes back, it means that the burning of the gas is incomplete, with the result that the air in the laboratory becomes

---

* Screw the disk on so that its smooth side faces upwards.

** Hot objects should be placed on asbestos millboard or on a ceramic plate.

poisoned. Moreover, since combustion takes place inside the tube, the latter becomes very hot, which may cause the rubber tubing feeding the gas to the burner to catch fire.

When a flame flash-back occurs, turn off the gas, allow the burner to cool (beware of burning your hands!), and then light it again in accordance with the rules (see p. 12).

Why is a flash-back of the flame undesirable?

3. Gas-poisoning Hazard. The gas used in the laboratory (which is the same gas as that used in industry and for household needs) is chiefly *coke-oven gas*, either pure or mixed with *natural gas*. Coke-oven gas is prepared by the gasification of coal, while natural gas is obtained by tapping natural deposits (in the U.S.S.R. there are big deposits at Saratov on the Volga, Dashava in the Ukraine, and elsewhere). These gases have the following average composition (in %):

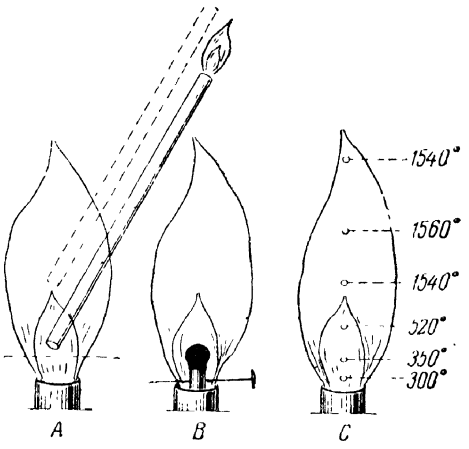


Fig. 4. Structure of gas burner flame

	H_2	CH_4, C_2H_6	C_xH_y	CO	H_2O	N_2	CO_2	O_2
Coke-oven gas	57	23	2	7	0.5	7.5	2	1
Natural gas (Saratov)	—	95.2	1.3	—	—	3.3	0.2	—

The carbon monoxide contained in coke-oven gas is highly poisonous. A mere 0.3% of it in the air can cause fatal poisoning in 12-15 minutes. *For this reason always keep an eye on gas burners. Before leaving the laboratory, make sure the gas is turned off.*

4. Flame Structure. Quickly introduce a sheet of paper for 2-3 seconds into the lower part of the small *nonluminous* flame (broken line in Fig. 4 *A*). Observe the appearance of a ring of charring. Introduce a glass tube into the flame, as shown in the figure, and light the gas at its upper end. Lift the tube slowly, and note the position of its lower end when the burning at the upper end ceases. Put out the

burner by turning off the gas, and insert a match, attached to a pin, into the tube of the burner (Fig. 4 *B*). Now turn on the gas and light the flame. Does the match ignite? Lifting the pin by the tongs, move the match into the upper cone of the flame. What happens now? What conclusions can be drawn about the burning of the gas in the inner and the outer cone on the basis of these experiments?

5. Flame Temperature. Draw a diagram of the burner flame in your notebook. Mark all the points and corresponding temperatures shown in Fig. 4 *C*. Introduce a nichrome wire, whose end has been joined to a glass tube, into the various zones of the flame, and observe the colour of the heated wire. Depending upon the temperature to which it is heated, the wire acquires the following colours:

dark red at 500°	orange at 1100°
red at 700°	white at 1500°

In the diagram mark the points corresponding to the experimentally observed temperatures of 700 and 1100°.

Put 1 g of powdered potassium bromide (m. p. 728°) into a dry test tube and heat it for some time in the hottest zone of the flame. Does the salt melt? Now conduct a similar experiment with 1 g of anhydrous sodium sulphate (m. p. 884°). Does this salt melt? On the basis of these experiments state the average temperature achieved in practice when heating objects with a gas burner.

Rules for using a gas burner

1. Drive in the disk close to the wide part of the gas tube.
2. Turn on the gas and light the burner.
3. Screw out the disk slowly until a sharply defined inner cone appears in the flame.

Weighing

Weighing is one of the most important operations in quantitatively estimating the results of a chemical process, as well as in determining the numerical values of certain characteristics of a substance (its equivalent, its atomic and molecular weights, etc.). The reliability of the quantitative assessment of the data of a chemical experiment depends to a considerable extent upon the accuracy of weighing. Three types of balances are used by the student in the laboratory of inorganic chemistry: the technical balance (for rough weighing), the chemical balance (for weighing to 0.01 g), and the analytical balance (for weighing to 0.0001 g).

1. Chemical Balance. The chemical balance (Fig. 5) is mounted on an uncovered base with special screws for adjusting the balance according to the plumb weight attached to the pillar (1). After adjustment according to the plumb weight the balance should not be shifted.

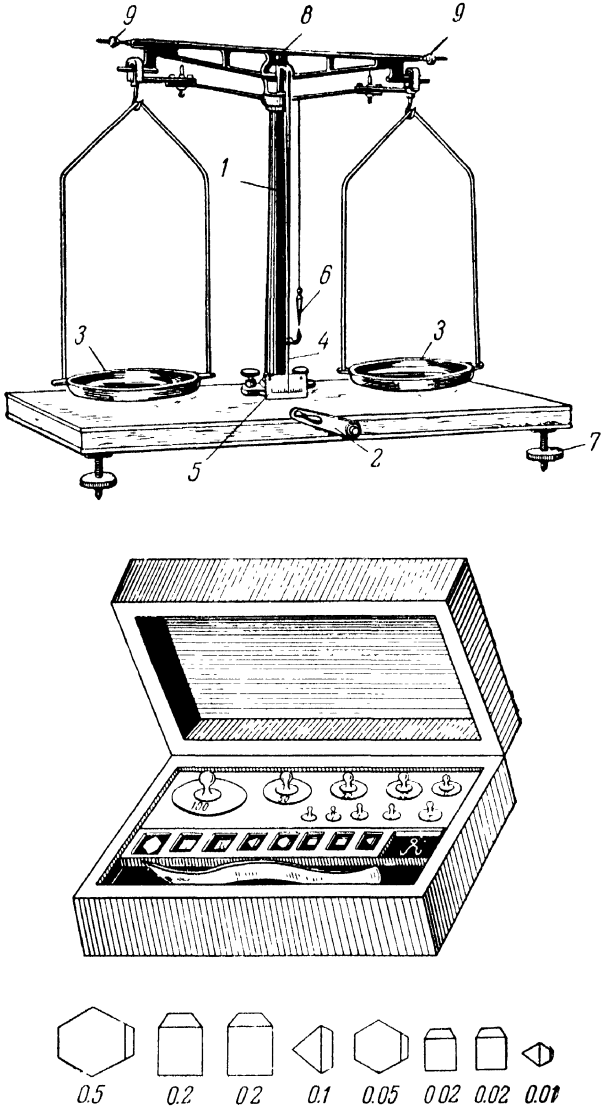


Fig. 5. Chemical balance and weights

1 — pillar; 2 — catch; 3 — pans; 4 — pointer; 5 — graduated scale; 6 — plumb weight; 7 — screws for levelling the balance; 8 — beam; 9 — screws for balancing empty pans.

Before weighing, the balance should be checked. By shifting the catch (2) smoothly to the right, the balance is made operational: the beam is lowered so that the edge of its central prism rests upon its support and begins to swing together with the pans (3) suspended

from side prisms of the beam. If the pointer (4) now swings back and forth across the graduated scale (5) an equal number of divisions away from the middle line each way (or one or two divisions more in one direction than in the other), the balance may be considered adjusted correctly. After the balance has been checked, the beam should be arrested; this is done by moving the catch back into the non-operational position.

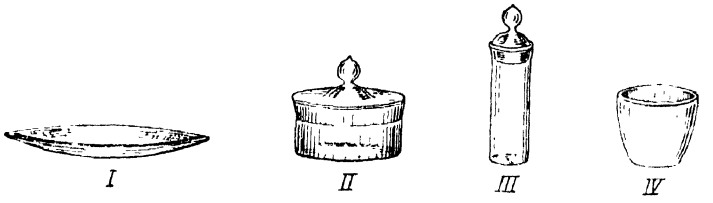


Fig. 6. Vessels for weighing
I — watch glass; II and III — weighing bottles; IV — crucible.

2. Rules for Weighing. The objects that are being weighed and the weights may be placed on the balance pans or removed from them only after the balance has been arrested.

Solids are weighed on watch glasses, in weighing bottles, crucibles, or on sheets of clean paper, whereas liquids are weighed in weighing bottles (Fig. 6) and beakers only.

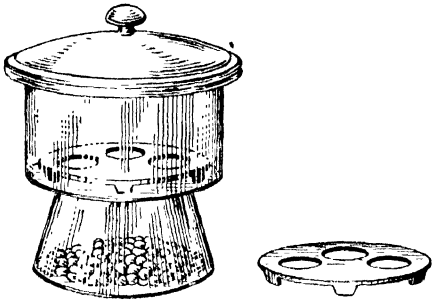


Fig. 7. Desiccator and porcelain plate

Hot crucibles or casseroles should, before weighing, be cooled in desiccators to room temperature (for about 15 minutes). A desiccator (Fig. 7) is a thick-walled glass vessel with a ground-in lid; placed in the bottom part is a substance capable of absorbing water vapour (see p. 27).

The object to be weighed should be placed on the left-hand pan of the balance; a weight approximately equal to the weight of the object should then be placed *by means of forceps* on the right pan. If the weight is too big, it should be replaced with another of the next lower denomination, and so on until the object is counterbalanced by the weights (the pointer should swing an equal number of divisions to the right and left of the middle line on the scale). The weights should now be added up; this is done by adding up the grams, decigrams, and centigrams separately. The weight of the object to 0.01 g should then be recorded by the student in his notebook.

A 100 g set of weights is decimally constituted (this system was proposed by D. Mendeleyev):

Grams	50	20	20	10
	5	2	2	1
Fractions of a gram	0.5	0.2	0.2	0.1
	0.05	0.02	0.02	0.01

The weights of such a set can be combined to make up any weight ranging from 0.01 to 111.10 g (with an accuracy to 0.01 g).

All weighing for one and the same experiment should be done on the same balance and with the same set of weights.

After the weighing, the weights should be replaced in their respective nests in the box with the aid of forceps. After operations the balance and the weights should always be left in order.

3. Absolute and Relative Error. The absolute error $\pm e$ in weight determination is the difference between the true weight W and the experimentally obtained weight w:

$$\pm e = W - w$$

In practice it is more customary to calculate the relative error expressed in per cent. This is the ratio of the absolute error to the true weight multiplied by one hundred:

$$e\% = \frac{e}{W} \cdot 100 = \frac{W - w}{W} \cdot 100$$

4. Weighing an Object. Obtain an object for test weighing from the laboratory assistant and weigh it to an accuracy of 0.01 g. Record the result in your notebook as follows:

Name of object	Weight, g
Plastic disk No. 17	8.74

Check the weight of the object together with the laboratory assistant and, in the event of a discrepancy, calculate the relative error.

1. An object weighed on a chemical balance has been counterbalanced exactly by two weights: 20 and 2 g. How should the exact weight of the object be written down?
2. The weight of an object weighed on a chemical balance is written down as 11.270 g. Is this correct?
3. Two weights—1 and 10 g—were used on a chemical balance. For which of them is the relative error of weighing larger and why?

Exercise 2

SOLUTION, FILTRATION, AND HYDROMETRY

SUBJECTS FOR STUDY

Mechanical mixtures and chemical compounds; laws of definite proportions, multiple proportions, and weight equivalents, which govern the composition of chemical compounds; compounds of constant and variable composition, and percentage and molar concentration of solutions.

In conducting chemical experiments, it is often necessary to dissolve substances, filter liquids, wash precipitates, and determine the concentration of solutions by means of a hydrometer.

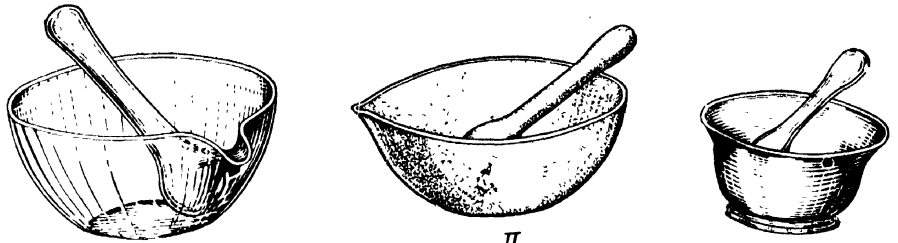


Fig. 8. Mortars for grinding
I — glass; *II* — porcelain; *III* — metal.

1. Dissolving Solids. Substances in the form of large crystals are sometimes ground to a powder prior to dissolving. The grinding is done in porcelain, glass, agate, or metal mortars (Fig. 8). When grinding caustic alkalis or highly poisonous substances, the face should be protected by a mask with a respirator; the hands, by rubber gloves. Highly poisonous substances should be ground in a ventilated hood.

Approximate volumes of solvents are determined in measuring cylinders or glasses (Fig. 9) and expressed in millilitres (ml).

The substance to be dissolved and the solvent are placed in a beaker (or flask) and mixed with a glass rod. In most cases it is advisable to heat the solution (Fig. 10) in order to speed up the process. Aqueous solutions are prepared with distilled water.

2. Filtration. Substances which have not dissolved in the solution are separated from it by filtration.

Various porous materials, such as filter paper, cotton wool, cloth, porous plates of glass or porcelain, finely divided charcoal and asbestos, and glass wool, can serve as filters. The material most commonly used in the laboratory is filter paper, which is employed for making two types of filters: ordinary and folded.

. To make an ordinary filter (Fig. 11), a square sheet of filter paper (*A*) is folded in half twice (*B*, *C*). The ends of the filter are then cut neatly by scissors, as shown by the broken line in Fig. 11 (*D*). The filter is finally opened up into a cone (*E*).

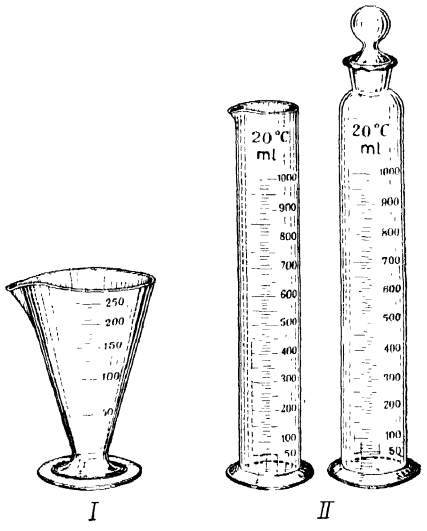


Fig. 9. Measuring vessels

I — measuring glass; *II* — measuring cylinders.

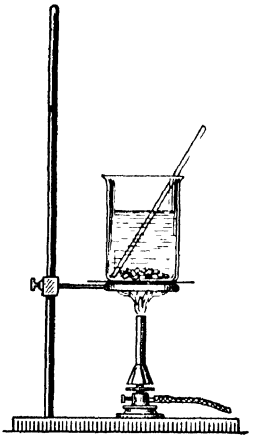


Fig. 10. Dissolving solids in water

To make a folded filter, at first follow the same procedure (*A-D*); then unfold the filter (*F*) and fold each segment in half twice towards each other (*G-I*); now turn the filter over (*J*) and, after it has been folded twice more (*K*, *L*), it may be opened up to assume its final shape (*M*). In this case it is more convenient to trim the ends after folding. The trimming should be done in such a way that the top of the filter is 3-5 cm below the upper rim of the funnel.

The ordinary filter should be fitted into the funnel, held in position with a finger, and moistened with distilled water, which is allowed to drip away. Chemical funnels should form a 60° cone; the ordinary filter in this case fits snugly into the funnel. If the angle is bigger or smaller than 60°, air gaps form between the wall of the funnel and the filter, and this slows down filtration (Fig. 12). The stem of the funnel should be filled with liquid during filtration; the presence of air bubbles in it likewise delays filtration.

The speed of filtration depends upon temperature, since with a rise in temperature there is a decrease of the internal friction of the liquid in the filter pores (for example, the internal friction of water

at 100° is nearly 85% lower than at 0°). If possible, liquids should therefore always be filtered *hot*.

It is customary to use ordinary filters wherever the precipitate has to be retained for further operations, since it is easier to remove the precipitate from such a filter. If, on the other hand, the solution only

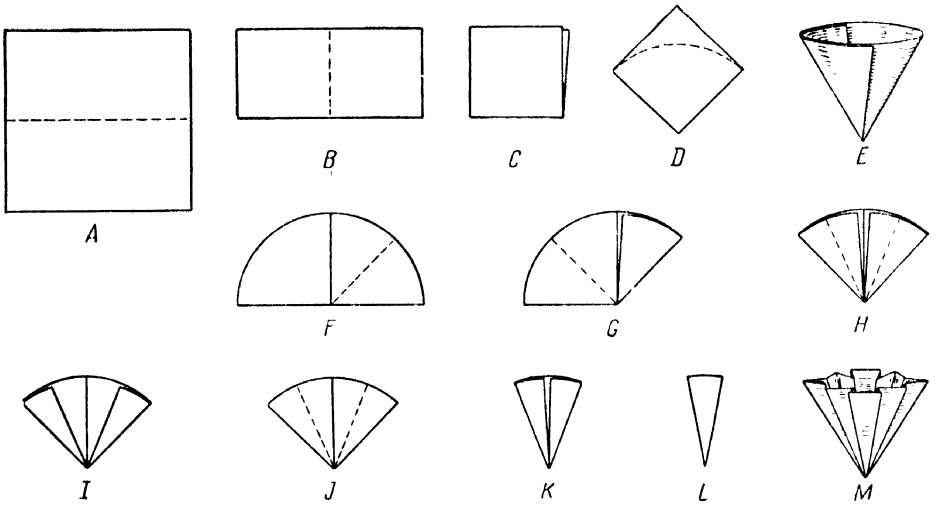


Fig. 11. Making filters

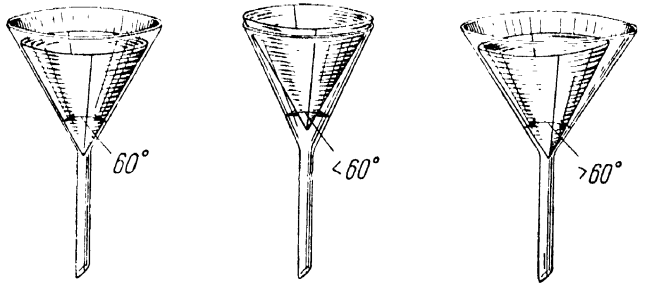


Fig. 12. Funnels for filtration

is needed for subsequent operations, a folded filter is used; filtration in this case proceeds faster, owing to a greater filtering area.

Two filtration techniques are in common use: either the liquid is transferred to the filter with the precipitate or the liquid is poured off from the precipitate into the filter (*decantation*). In the former case, the liquid is stirred with the precipitate and poured into the filter down a glass rod (Fig. 13); the filter should be filled to such an extent that the level of the liquid is 2-3 mm below the filter rim.

In the latter case, the liquid is poured off carefully down a rod into the filter without disturbing the precipitate.

To prevent splashing, the stem of the funnel should rest against the side of the receiving vessel. When the entire liquid has been filtered, the precipitate should be washed.

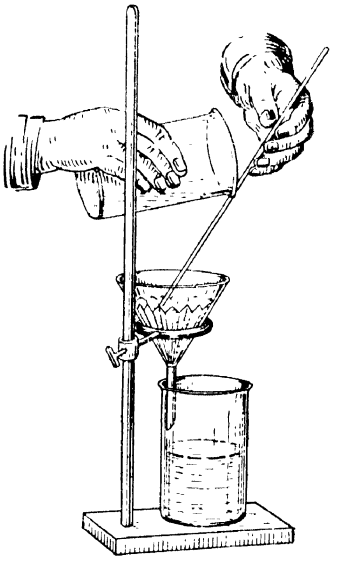


Fig. 13. Filtration

3. Washing the Precipitate. The precipitate transferred to the filter is washed by means of a wash bottle (Fig. 14), which is a flat-bottom flask with a stopper that has two bent tubes passing through it. If air is blown orally into the shorter tube, the water in the flask will be forced by the pressure to issue in a thin stream from the other tube. The filter loaded with the precipitate is filled with the washing liquid (in most cases, cold or hot water), which is allowed to drain through the paper. This washing is repeated two or three times, a new portion of water not being poured into the filter until the previous portion has drained away. The last drops of the filtrate are collected in a test tube and tested with reagents to make sure that the soluble impurities have been washed out from the precipitate.

When the precipitate is left in the beaker, it is washed by decantation. For this purpose the washing liquid is poured into the beaker, stirred with a rod, and, after the precipitate has settled, transferred to the filter down a rod. After 2-3 washings, the wash water is tested for impurities.

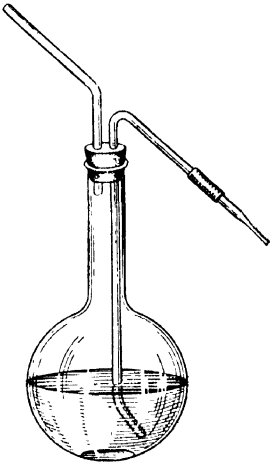


Fig. 14. Wash bottle

4. Concentration of Solutions. The concentration of the dissolved substance (solute) is determined by the amount of it contained in a definite weight or volume of the solution.

Percentage concentration is expressed by the number of weight units of the solute in 100 weight units of the solution.

Molar concentration (M) is expressed by the number of mols of the solute in 1 litre of the solution.

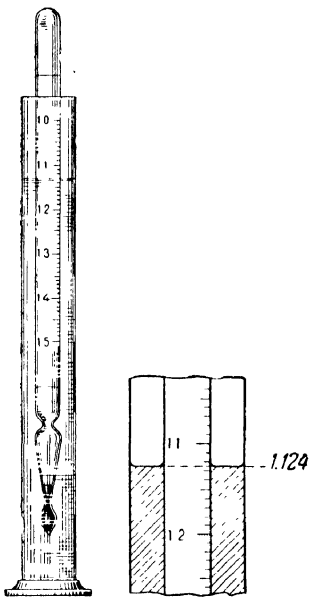


Fig. 15. Position of hydrometer in cylinder with solution and reading the hydrometer scale

Other units expressing the concentration of solutions are defined in Exercise 10.

5. Determining the Concentration of Solutions by the Relative Density*. The relative density of solutions changes with their concentration; for this reason the concentration of a substance in solution can be determined by its relative density, use being made of suitable reference tables. Relative density is affected by temperature and should therefore be determined at the temperatures specified in the tables (or else allowance should be made for variation from the standard temperature indicated).

The symbol γ_4^{20} in reference books means** that the relative density has been determined at 20° and referred to the weight of water at 4°, the temperature of its maximum density. Relative density can be determined by means of a pycnometer, by hydrostatic weighing, etc. For technical purposes the relative density is in most cases determined by a hydrometer.

The hydrometer (Fig. 15) is a hollow glass float with a graduated upper part and a weighted (usually with lead shot) lower part. The weight keeps the instrument in a vertical position when it is immersed in a liquid. The hydrometer is calibrated for a definite temperature, which is indicated on the scale. The divisions of the scale correspond to relative densities. By means of a set of hydrometers the relative density of a liquid can quickly be determined.

For this purpose the test solution, first heated or cooled to the temperature indicated in the tables of relative densities, is poured into a 250-300 ml dry narrow cylinder. The hydrometer (clean and dry) is then lowered into the cylinder with the solution so that it should not touch the walls of the vessel. The reading of the hydrometer scale is taken according to the lowest point of the level of the liquid in the cylinder. The scale is read downwards with an accuracy of $\pm$ 0.003.

In Fig. 15 the hydrometer reading corresponds to a relative density of 1.124. It may happen that the table of relative densities does not

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* The ratio of the weight of 1 ml of a solution to the weight of 1 ml of water at the temperature of its maximum density (4°) used to be called *specific gravity*.

** Some reference books use the symbol d_4^{20}.

give the value 1.124, but gives close values, as in the case of a solution of sulphuric acid:

Relative density	Concentration (%)
1.120	17.01
1.130	18.31

In such cases the percentage concentration is found by the method of interpolation, i. e., by determining an intermediate quantity according to two known extreme quantities. The following procedure is used:

1. The respective differences are found for the two consecutive values of relative densities and of concentrations taken from the table:

$$\begin{array}{ll} 1.130 \ldots\ldots & 18.31\% \\ 1.120 \ldots\ldots & 17.01\% \\ \hline 0.010 \ldots\ldots & 1.30\% \end{array}$$

2. The difference is found between the hydrometrically determined value and the smaller of the two table values:

$$1.124 - 1.120 = 0.004$$

The proportion is set up:

$$0.010 \ldots\ldots\ldots 1.30\%$$
$$0.004 \ldots\ldots\ldots x$$
$$x = \frac{1.30 \cdot 0.004}{0.010} = 0.52\%$$

3. The quantity obtained is added to the smaller of the two concentration values taken from the table:

$$17.01 + 0.52 = 17.53$$

QUESTIONS

1. What is meant by the analysis and synthesis of a substance? Give three examples each of analysis and synthesis. What are these processes used for?
2. Give examples of compounds of constant composition and of variable composition; explain the difference between them.
3. What conclusions can be drawn from the law of multiple proportions?
4. In what cases are ordinary filters used, and in what cases are folded filters used?
5. What is decantation?

6. Give the equations of the reactions that serve to check wash water for sulphates and chlorides.

7. Could a hydrometer be calibrated in such a way that the divisions of its scale would correspond to the percentage content of a substance in a solution instead of corresponding to relative densities?

Problems *

1. Three samples consisting of sulphur and iron were found, upon analysis, to have the following respective percentage compositions:

	I	II	III
Fe	63.6	60	46.6
S	36.4	40	53.4

Which of these correspond in composition to chemical compounds?

2. Three compounds of chromium and oxygen contain 76.5, 68.4, and 52% of chromium respectively. Show by calculations that these proportions of the elements in the compounds conform to one of the basic laws of chemistry.

3. A copper oxide contains 79.9% of copper and 20.1% of oxygen. How much copper can be obtained from 15.9 g of the oxide?

4. When a metal is burned, 2.07 g of it combines with 2.4 g of oxygen. What amount of hydrogen can be obtained from water if 1.38 g of this metal reacts with the water?

5. In the formation of zinc sulphide, 32.1 g of sulphur is used up for every 65.4 g of metallic zinc. How much of which substance will be left over if 30 g of zinc and 30 g of sulphur are taken for the reaction?

6. Determine the molar concentration of a 17.1% solution of nitric acid which has a relative density of 1.1.

7. A laboratory prepared 4.7 kg of a 7.6% solution of soda. How much soda and how much water were used?

8. What amount of table salt containing 98.5% NaCl is needed to prepare 5,000 kg of an 8% solution?

9. Calculate the percentage concentration of sodium hydroxide in the solution if 3.4 kg of caustic soda (commercial sodium hydroxide) which analyses 97.2% NaOH was dissolved in 8.6 kg of water.

10. The relative density of a KOH solution at 15° is 1.054. With the aid of Table VII calculate the percentage concentration of the solution.

LABORATORY WORK

Apparatus and materials: test-tube rack and test tubes; 250 ml measuring cylinder; 300 ml narrow measuring cylinder for determining relative density; 200 ml beaker; 250 ml flat-bottom flask; wash bottle; funnel 7 cm in diameter; glass rod; hydrometer with a 1.0-1.2 relative density scale; thermometer for 100°; spatula; scissors; sheets of paper 8 × 8 cm; filter paper; mixture of table salt and sand; 0.1 N solution of silver nitrate, and 0.1 N solution of nitric acid.

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* Atomic and molecular weights approximated to one decimal should be used in solving the problems throughout all the exercises.

Preparation of sand and table salt mixture. The sand for the mixture is first washed with water and dried; the salt is ground in a mortar to a powder and mixed thoroughly with the sand. Several mixtures with different NaCl contents are needed.

Determining the Percentage Content of NaCl in a Mixture. Weigh about 20 g of a sand and table salt mixture to an accuracy of 0.01 g. The mixture should be weighed on a watch glass or in a weighing bottle weighed in advance on a chemical balance. It should be placed on the watch glass or in the weighing bottle with a spatula (Fig. 16). The weighed mixture should be poured into a beaker, and 100 ml of distilled water, measured in a cylinder, should be added. The beaker with the liquid should then be heated to boiling point, the contents being stirred with a glass rod.

Prepare a folded filter, place it in a funnel, moisten it with distilled water, and filter the solution, collecting the filtrate in a beaker or a flask. During filtration heat the water in the wash bottle to boiling point. After the whole of the liquid has been filtered, pour 10-12 ml of hot water into the beaker, shake it, allow the precipitate to settle, and transfer the solution to the filter. Wash the filter thrice with hot distilled water, collecting the last 2-3 ml of the filtrate in a test tube (the average-sized test tube has a volume of 15 ml). Add 2-4 drops of nitric acid solution and as many drops of silver nitrate to the liquid in the test tube (write the equation of the reaction). If no precipitate is formed and the liquid does not become cloudy, the washing may be considered completed; otherwise it should be continued.

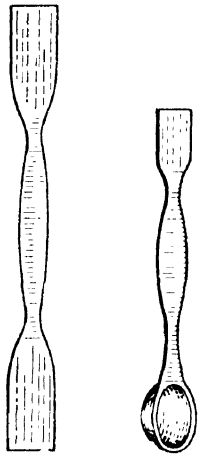


Fig. 16. Spatulas

Now add the wash water to the solution, transfer the solution to a measuring cylinder, and cool it to 20°. By adding water, bring the volume of the solution up to 250 ml. Then transfer the solution to a narrow cylinder and stir it thoroughly. Lower a dry hydrometer into the solution *slowly* and take a reading, first becoming familiar with the calibration of the hydrometer and the value of a single division on its scale. Take the average of 3-4 readings *. After the relative density determination, the hydrometer should be rinsed with clean water, dried, and put away in its case.

On the basis of the relative density of the solution, determine its percentage concentration, making use of Table I (p. 329). If the table

* For example, the average of three readings will be:

1.024 1.027 1.026

average: 1.026

does not list the exact value of the relative density obtained, find the quantity sought from the two closest values given in the table (a smaller and a bigger) by the method of interpolation.

Record the results of the experiment in your notebook as follows:

Weight of mixture in g	Volume of solution in ml	Relative density according to hydrometer at 20°	Percentage concentration (from table or found by interpolation)	Quantity of salt in solution in g

To determine the quantity of salt in the solution, it is necessary to calculate the weight of the solution in g from its volume and relative density, the quantity sought finally being established from the percentage concentration.

Knowing the weight of the salt and the weight of the mixture, calculate the NaCl content in the initial mixture to 0.1%.

From the percentage concentration of the NaCl solution and its relative density calculate the molar concentration.

Exercise 3

DETERMINING THE MOLECULAR WEIGHT OF A GAS (VAPOUR)

SUBJECTS FOR STUDY

Equation of state of a gas; reducing the volume of a gas to N. T. P.; Avogadro's Law and conclusions from it; gram-molecule; gas constant and Mendeleyev-Clapeyron Equation; density of gases and the density of one gas in terms of another; relation between the density of a gas (vapour) and its molecular weight; partial pressure.

1. The Molecular Weight and Density of a Gas. *Molecular weight* is a number indicating how many times heavier a molecule of a given substance is than 1/12 of a carbon atom.

A gram-molecule (*mol*) is the quantity of a substance equal in grams to its molecular weight.

A gram-molecule of any substance in the gaseous or vaporous state under normal conditions (*N. T. P.**) *occupies a volume of 22.4 litres.*

The volume of a gas is reduced to N. T. P. by the equation of state of a gas:

$$v_0 = \frac{vpT_0}{p_0T} \qquad \text{(I)}$$

* An abbreviation for *normal temperature and pressure* (i. e., 0° C and 760 mm Hg). Another abbreviation used to express this in British and American literature is S. T. P. (*standard temperature and pressure*).— *Tr.*

The conversion from the international hundred-degree scale (°C) to the absolute scale (°K) is effected by the formula:

$$T = 273 + t$$

where T is the temperature in °K, while t is the temperature in °C.

The ratio $\frac{v_0 p_0}{T_0}$ from the equation of state of a gas *is constant for one gram-molecule of any gas.* It is called *the universal gas constant* and is denoted by the letter R. Its value and dimension depend upon the system of units chosen:

$$R = \frac{v_0 p_0}{T_0} = \frac{22.4 \cdot 1}{273} = 0.082 \text{ l} \cdot \text{atm/deg}$$

$$R = \frac{v_0 p_0}{T_0} = \frac{22{,}400 \cdot 760}{273} = 62{,}369 \text{ ml} \cdot \text{mm/deg}$$

The value and dimension of R should always be in keeping with the dimensions adopted for pressure and volume.

By substituting the gas constant into equation (I), we obtain the Mendeleyev-Clapeyron Equation:

$$pv = RT \qquad \text{(II)}$$

If n mols of the gaseous substance are taken, the Mendeleyev-Clapeyron Equation assumes the form:

$$pv = nRT \qquad \text{(III)}$$

But n, the number of mols of the gas, is equal to the ratio of m, the weight of the gas in grams, to M, the weight of a gram-molecule:

$$n = \frac{m}{M}$$

When this expression for n is substituted into equation (III), we obtain

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

from which

$$M = \frac{mRT}{pv} \qquad \text{(IV)}$$

This formula makes it possible to calculate the molecular weight of a gas provided the weight m of a certain volume v of it is known, as well as its pressure p and temperature T.

If we know the *density* of the gas (absolute density) D_a, i. e., the weight in g of 1 litre of the gas at N. T. P., the molecular weight M

can be calculated by means of the formula:

$$M = 22.4D_a \qquad (V)$$

It is more convenient, however, in determining molecular weight, to make use of the *density of one gaseous substance in terms of another.*

The density D of one gas in terms of another is the ratio of the weight of one to the weight of an equal volume of the second at the same temperature and pressure.

The molecular weight of a gaseous substance is equal to its density in terms of another gas multiplied by the latter's molecular weight:

$$M_A = M_B \cdot D \qquad (VI)$$

Example. Calculate the molecular weight of a gas if equal volumes of it and of chlorine under the same conditions weigh 0.240 and 1.065 g respectively.

First, it is necessary to determine the density of the gas in terms of chlorine:

$$D_{Cl} = \frac{0.240}{1.065} = 0.225$$

Since the molecular weight of chlorine is 70.9, the molecular weight of the gas

$$M = 70.9 \cdot 0.225 = 15.95 \approx 16$$

The density of a gas is usually determined in terms of hydrogen or air. The molecular weight of hydrogen is 2.016. Air is 14.38 times heavier than hydrogen, and its mean molecular weight is 28.99. The formulae for determining molecular weight are therefore:

$$M = 2.016D_H \approx 2D_H$$
$$M = 28.99D_{air} \approx 29D_{air}$$

The above formulae make it possible to calculate the molecular weights of gaseous substances and those *liquid and solid substances* that are vaporised at low temperatures without chemical decomposition.

The molecular weight is an important characteristic of a pure substance. Impurities alter the density of a gas (vapour) and lead to errors in molecular weight determination.

Accordingly, all the necessary steps should be taken, in experimentally determining the molecular weight of a gas, to remove possible impurities from the gas. Chemically pure products should be used in determining the molecular weights of highly volatile liquids and solids.

2. Gas Purification. Gaseous impurities are removed by passing a gas through certain substances (often in the form of solutions) that react chemically with the impurity, but not with the principal gas. If, for instance, it is necessary to remove CO_2 from a mixture of CO and CO_2, the mixture is passed through a solution of an alkali or a car-

bonate of an alkali metal. The carbon dioxide in such cases reacts according to one of the following equations:

$$2KOH + CO_2 = K_2CO_3 + H_2O$$
$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3$$

The CO_2 admixture is in this way removed from the carbon monoxide.

Water vapour is removed from gases by passing it through bottles containing dehydrating agents (concentrated sulphuric acid, calcium chloride, zinc chloride, alkalis, phosphorus pentoxide, etc.). Dehydrating agents are not equally effective: phosphorus pentoxide and magnesium perchlorate are the best (Table 1).

Table 1

Effectiveness of Dehydrating Agents in Drying Air

Dehydrating agent	Residual humidity of gas in mg/l	Dehydrating agent	Residual humidity of gas in mg/l
P_2O_5	$2 \cdot 10^{-5}$	NaOH (molten)	0.16
$Mg(ClO_4)_2$	$5 \cdot 10^{-4}$	CaO	0.20
KOH (molten)	0.002	H_2SO_4 (95.6%)	0.30
H_2SO_4	0.003	$CaCl_2$ (molten)	0.36
$CaSO_4$	0.004	$CuSO_4$	1.40

Gases cannot be dried by means of substances that react with them. For instance, ammonia cannot be dried by sulphuric acid, or hydrogen chloride by calcium oxide, to mention only two such cases. The types of apparatus used for drying gases are shown in Fig. 17.

3. Partial Pressure. The pressure of each component of a mixture of gases is called the *partial pressure* of that gas. If a gas is collected over water, there will be a mixture of the gas and of water vapour over its surface; the degree to which the water vapour saturates the gas will depend upon the temperature.

(a) If the water in the cylinder in which the gas has been collected and in the vessel into which the cylinder has been lowered is *at the same level* (Fig. 18, *I*), the sum of the gas pressure p' and the water vapour pressure h equals the atmospheric pressure p:

$$p' + h = p$$

To determine the gas pressure proper, i. e., its partial pressure, the partial pressure of the water vapour has to be subtracted from the

total pressure:

$$p' = p - h$$

When the volume of a gas collected over water is reduced to N. T. P., the difference $p—h$ should be substituted for p in the equation of state, which, accordingly, becomes:

$$v_0 = \frac{v\,(p - h)\,T_0}{p_0 T}$$

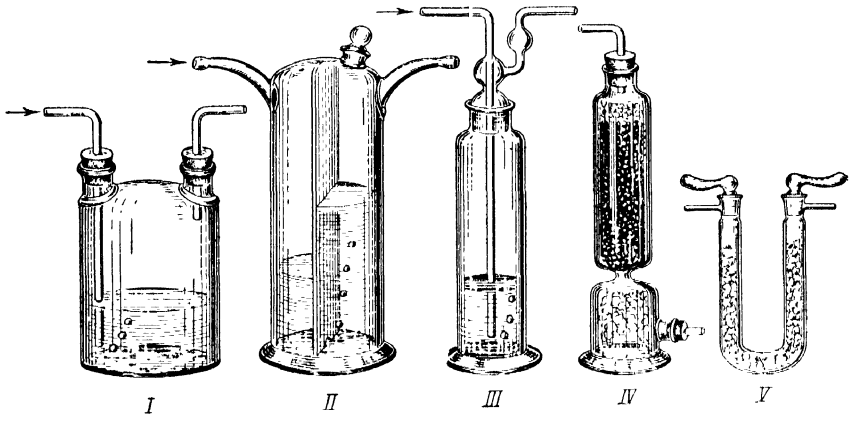


Fig. 17. Types of apparatus for drying gases
I, *II*, and *III*—bottles with dehydrating agents; *IV* — drying tower; *V* — U-tube.

The pressure of the water vapour, which is commonly called the *aqueous vapour tension*, depends upon the temperature (Table 2).

Table 2

Aqueous Vapour Tension h (in mm Hg) at Temperature t (°C)

t	h	t	h	t	h	t	h
10	9.2	16	13.6	22	19.8	28	28.3
11	9.8	17	14.5	23	21.1	29	30.0
12	10.5	18	15.5	24	22.4	30	31.8
13	11.2	19	16.5	25	23.8	40	55.3
14	12.0	20	17.5	26	25.2	50	92.5
15	12.8	21	18.6	27	26.7	100	760.0

(b) If the water in the cylinder and in the vessel is *at different levels* (Fig. 18, *II*), the atmospheric pressure is balanced by the sum of

the gas pressure p', the aqueous vapour tension h, and the pressure of the column of water p_w (the latter, converted to pressure in mm Hg, equals the height of the column in mm divided by the density of mercury, i. e., by 13.6 g/cm^3):

$$p' + h + \frac{p_w}{13.6} = p$$

The partial pressure of the gas can then be expressed:

$$p' = p - \left(h + \frac{p_w}{13.6}\right)$$

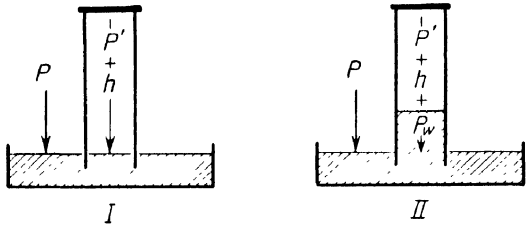


Fig. 18. Determin ng the pressure of a gas collected over water

The equation for reducing the volume of a gas to N. T. P. then becomes:

$$v_0 = \frac{v\left[p - \left(h + \frac{p_w}{13.6}\right)\right] T_0}{p_0 T}$$

This equation is used in experiments in which it is not possible to bring the water in the cylinder and in the vessel to the same level.

If the gas is collected over some liquid other than water (a salt solution), it is necessary to use the value of h for that solution.

QUESTIONS

1. How should the formula for the molecular weight of a gas be written if its density is determined in terms of nitrogen or carbon dioxide?
2. Which is the heavier: dry carbon dioxide or an equal volume of the gas containing water vapour, other conditions being identical? How can the same question be decided for methane (dry and containing water vapour)?
3. Knowing the volume of a gas at N. T. P., but not its density, how can we establish its weight?

4. By means of the corollaries to Avogadro's Law determine the weight of an atom of nitrogen and the weight of a molecule of chlorine dioxide.

5. Which of the substances listed in Table 1 can be used to remove water vapour from carbon dioxide?

6. What is the partial pressure of carbon monoxide collected in a cylinder over water at 17° and 752 mm Hg if the water in the cylinder and in the vessel is at the same level (use the data in Table 2)?

Problems

1. Equal volumes of chlorine and of nitric oxide weigh 3.16 and 1.34 g respectively. Calculate the molecular weight of nitric oxide from its density in terms of chlorine, knowing that the molecular weight of the latter is 70.9.

2. One litre of a gaseous substance at N. T. P. weighs 0.76 g. A litre of air and a litre of hydrogen under the same conditions weigh 1.293 and 0.09 g, respectively. Calculate the molecular weight of the gas by three different methods.

3. A gaseous substance at 770 mm Hg and 27° occupies a volume of 320 ml and weighs 0.5 g. Calculate its molecular weight.

4. Given the molecular weights of oxygen and nitrogen, calculate the mean molecular weight of air on the assumption that it consists of 24% of oxygen and 76% of nitrogen by weight.

5. Calculate the mean molecular weight of a gaseous mixture consisting of 60% of carbon monoxide and 40% of hydrogen by weight, knowing that their molecular weights are 28 and 2 respectively.

6. Calculate the molecular weight of a gas and its density in terms of air if 0.62 litre of the gas weighs 1.24 g at 21° and 750 mm Hg.

7. Calculate the molecular weight of a substance and the density of its vapour in terms of nitrogen if 355 ml of the substance in the vaporous state weighs 1.1 g at 20° and 770 mm Hg.

8. The density of liquid chlorine is 1.5 g/cm^3. How many litres of gaseous chlorine can be obtained from 80 ml of liquid chlorine?

9. What is the weight of 410 ml of acetylene collected at a temperature of 17° and a pressure of 740 mm Hg if it is known that its molecular weight is 26?

10. Calculate the weight of the oxygen in a $5 \times 2.6 \times 2$ m air-filled chamber containing 21% by volume of oxygen if the temperature in the chamber is 17° and the pressure is 752 mm Hg.

LABORATORY WORK

Apparatus and materials: Kipp gas generator for preparing carbon dioxide or oxygen (with two wash bottles for gases); the apparatus shown in Fig. 21; bottles with water; 250 to 500 ml measuring cylinders; room thermometer; dry 250 ml flat bottom flask with stopper and rubber band; barometer; glass ampoules; marble in lumps; manganese dioxide catalyst; 1 : 6 hydrochloric acid; concentrated sulphuric acid; 3% hydrogen peroxide solution; saturated solution of sodium bicarbonate; chloroform; carbon tetrachloride, and a metal ruler.

Preparation of manganese dioxide catalyst. Add water to a mixture of 150 g of cement and 70 g of granular manganese dioxide until it acquires a thick doughy consistency. Then divide the mass into big lumps and leave them to dry overnight.

1. Kipp Gas Generator. Gases are often prepared by means of the *Kipp gas generator*, an apparatus consisting of three glass bulbs,

usually of spherical shape (Fig. 19). Two of the bulbs are interconnected. In the bottom one there is an outlet with a stopper, through which the spent liquid is drained. The middle bulb also has an outlet with a stopper, through which a glass tube with a tap has been passed. Inserted into the top opening of this bulb is a funnel ground to fit the opening; the funnel widens upwards into a bulb, while its lower tip reaches the bottom of the generator.

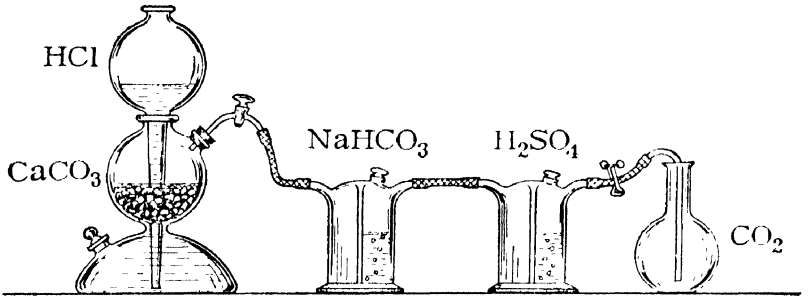


Fig. 19. Arrangement for preparing and purifying carbon dioxide

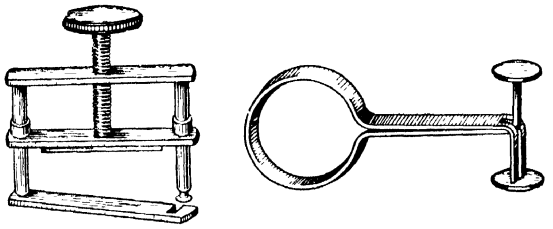
To prepare carbon dioxide, lumps of marble are placed into the middle bulb, while hydrochloric acid is poured into the top one. When the tap is opened, acid runs down the funnel into the bottom bulb and rises into the middle bulb to come in contact with the marble. When the tap is shut, the gas which is formed forces the acid out of the middle bulb and into the upper one through the bottom one; this brings the reaction to a halt.

The Kipp apparatus can be used to generate several other gases. For example, it can be used to prepare oxygen from a 3% solution of hydrogen peroxide, which decomposes to evolve oxygen under the catalytic action of manganese dioxide.

2. Determining the Molecular Weight of Carbon Dioxide. Weigh a dry stoppered flask with air on a chemical balance (weight w_1). The stopper should be inserted into the neck of the flask to a definite point marked by a rubber band. Now lower into the flask a glass tube attached to the Kipp gas generator producing carbon dioxide (Fig. 19). The gas is first washed and dried by being passed through two wash bottles for gases with a solution of sodium bicarbonate and concentrated sulphuric acid respectively. Remove the clip (Fig. 20) from the rubber tubing. Open the tap of the Kipp gas generator and allow carbon dioxide to issue from it *slowly* for 7-8 minutes. Then stopper up the flask to the marking and weigh it (w_2). Pass carbon dioxide into the flask again for 3-4 minutes, after which weigh it once more (w_3). If the latter two weighings produce identical results or results that do not differ by more than 0.01 g, the filling of the flask may be consid-

ered completed. Otherwise repeat the filling procedure, until a constant weight of the flask is achieved. This done, record the temperature and the pressure by referring to a room thermometer and barometer.

To measure the volume of the flask, fill it to the marking with water at room temperature (why?); then pour the water into a measuring



I *II*

Fig. 20. Metal clips

I — screw clip; *II* — spring clip.

cylinder, determine its volume, and record the results of the experiment.

Results of experiment

Weight of flask with air and stopper	Weight of flask with CO_2 and stopper	Volume of flask in ml	Temperature t in °C	Pressure p in mm Hg
w_1=	w_2= w_3=			

By means of the equation of state of a gas reduce the volume of the gas in the flask to N. T. P. (v_0).

Knowing that *at N. T. P.* 1 litre of air weighs 1.293 g, calculate the weight of the air in the flask (w_4).

The difference w_1—w_4 will be the weight of the empty flask with the stopper (w_5).

The difference w_3—w_5 will be the weight of the carbon dioxide in the flask (w_6). From the weights w_6 and w_4 calculate the density of carbon dioxide in terms of air and the molecular weight of carbon dioxide (to the second decimal). Calculate the absolute error and the relative error of the experiment.

Make a sketch of the Kipp gas generator, explaining the principle of its operation.

Write the equation of the reaction of carbon dioxide preparation. Why is the CO_2 produced by the Kipp generator first washed with

a sodium bicarbonate solution and then with sulphuric acid? What does bringing something to a constant weight mean? What experimental data are necessary to calculate the molecular weight of a gas?

3. Determining the Molecular Weight of Oxygen. Conduct this experiment in the same way as the previous one. The oxygen needed for the experiment is produced in the Kipp generator and then dried by passage through a wash bottle for gases filled with concentrated sulphuric acid.

From the experimental data calculate the molecular weight of oxygen (to the second decimal) and determine the absolute and the relative error.

How is it possible to find out whether the air has been fully expelled from the flask?

If the flask had been filled with undried oxygen, would the figure obtained for the molecular weight be bigger or smaller than the true value?

4. Determining the Molecular Weight of Volatile Substances. A weighed quantity of a volatile substance (chloroform, acetone, carbon tetrachloride, ether, etc.) is heated to convert it into a vapour; the vapour expels from the apparatus an equal volume of air, which is measured in a eudiometer. From the known weight of the substance and its volume in the vaporous state, reduced to N. T. P., it is possible to calculate the molecular weight of the volatile substance.

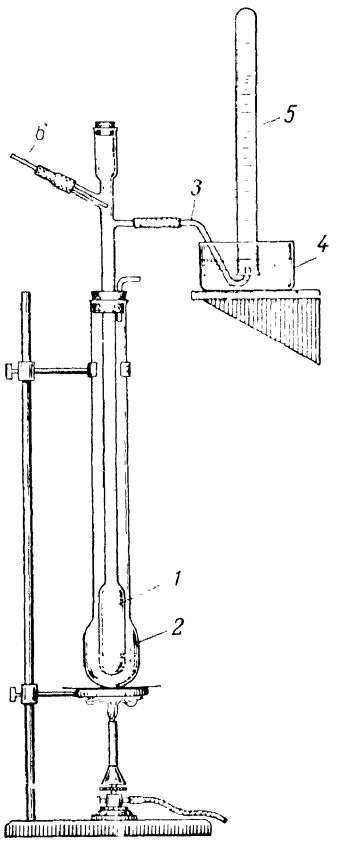


Fig. 21. Apparatus for determining molecular weight

1 — tube; 2 — bulb tube vaporiser; 3— side arm; 4 — vessel; 5 — eudiometer; 6 — rod for supporting ampoule.

The apparatus employed for the determination (Fig. 21) consists of a tube (1), a bulb tube vaporiser (2), a side arm (3), a vessel (4), and a eudiometer (5).

Pour 70-80 ml of water into the bulb tube vaporiser and heat it to boiling point. The air expanding in the tube is forced out through the side arm and bubbles through the water in the vessel.

Weigh a glass ampoule (Fig. 22*A*), heat its bulb *slightly* in the flame of a burner, and immerse the open capillary into the liquid whose molecular weight is to be determined. The cooling of the ampoule causes the liquid to be sucked up into it (Fig. 22*B*). When the

liquid has risen 5 mm above the tapered part of the ampoule, withdraw the ampoule from the jar and turn it over. Now weigh the ampoule with the liquid. There should be no more than about 0.20-0.30 g of the liquid. If there is more, turn the ampoule over and, by tapping your finger on the capillary tube, remove the excess liquid. Then weigh the ampoule again. Heat the capillary carefully on a small flame of a burner until it softens (Fig. 22*C*), draw it out quickly, and seal it (Fig. 22*D*).

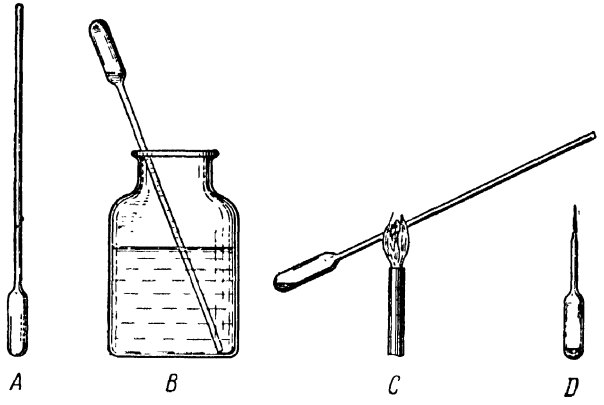


Fig. 22. Filling and sealing ampoules

Lower the ampoule, capillary downwards, into the upper part of tube *1*, so that it rests on rod *6*, and stopper up tube *1* tightly.

When no more air bubbles issue from tube *3*, place it under the eudiometer (make certain there are no more air bubbles!) and carefully pull rod *6*. This causes the ampoule to fall to the bottom and the thin capillary to break. The substance inside the ampoule is vaporised and displaces its own volume of air, which ascends the eudiometer.

When the escape of air from tube *3* ceases, it is removed from the water vessel. The volume of the displaced air and the distance from the level of the water in the vessel to the level of the water in the cylinder are measured (by means of mm ruler). These data, as well as the temperature t and barometric pressure p at which the experiment is conducted, are recorded. The value of h, the aqueous vapour tension, is found in Table 2 (p. 28).

From the experimental data calculate the molecular weight of the substance. Compare the value found with the value derived from the formula of the substance. Determine the relative error.

Note. If the experiment has to be repeated, air should be passed through tube *1* to remove the remaining vapour (consult instructor).

Results of experiment

Ampoule weight		Weight of substance in g	Volume of vapour in ml	t in °C	p in mm Hg	h in mm Hg	p_s in mm
with substance in g	empty in g						

Exercise 1

LABORATORY TECHNIQUES

SUBJECTS FOR STUDY

1. Selection and Treatment of Stoppers. The materials used for stoppers are the bark of the cork oak (these stoppers are simply called corks), rubber, and glass.

Corks should be selected in such a way that the diameter of the tapered end is slightly bigger than that of the vessel neck or tube. The cork chosen should be carefully squeezed along the circumference in a cork press (Fig. 23); after this it should fit the vessel neck tightly (not more than one-half to two-thirds of the cork being inserted).

Corks are bored by means of special cork borers (Fig. 24) or hand drilling machine (Fig. 25). In selecting the bore, it is necessary

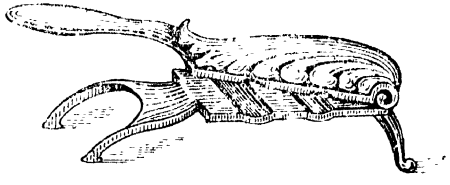


Fig. 23. Cork press

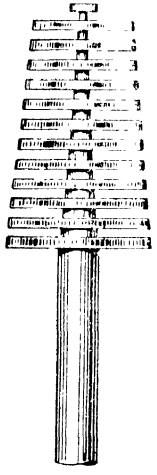


Fig. 24. Set of cork borers

to choose one with a diameter somewhat smaller than the diameter of the tube which is to be passed through the cork, or else the joint will not be airtight. The boring should be done from the tapered end

of the cork, which should be held in the left hand (Fig. 26). The borer, held in the right hand, should be centred and then turned to and fro, a slight pressure being applied to the cork. When the borer has passed through half the cork, it should be carefully withdrawn; the boring should then be resumed from the wide end of the cork. The borer should always be perpendicular to the end of the cork. When the boring is finished, the bits of cork left inside the hole should be pushed out by means of a ramrod. If the borers become blunted, they should be sharpened (consult the laboratory assistant).

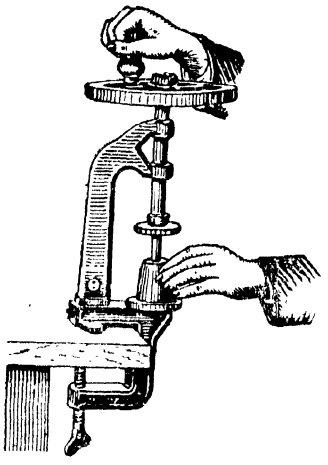


Fig. 25. Hand drilling machine

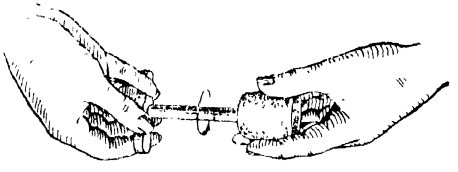


Fig. 26. Boring corks

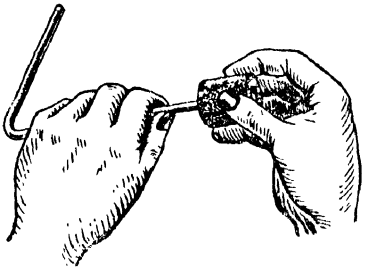


Fig. 27. Position of hands when inserting tube into stopper

When boring rubber stoppers, it is advisable to put a drop of alkali solution or glycerol on the stopper at the point of application of the borer; this acts as a lubricant and facilitates boring.

When the boring is done by means of a hand drilling machine, the bit should be fastened in a vertical position by a special nut and centred on the tapered end of the stopper*. A hole is then drilled in the stopper by turning the wheel.

When inserting a glass tube in the hole drilled, moisten the end of the tube with water. If the tube is bent, do not hold it at the bend, since the tube can break and cut your hand. The tube should be held as shown in Fig. 27.

2. Processing Glass Tubes. To prepare simple laboratory apparatus, it is enough to be proficient in cutting and drawing out glass tubes, rounding off the ends, and making capillaries. Tubes of small diame-

* To avoid blunting the drill, place a wide cork or a thin wooden plank underneath the stopper.

ter are cut in the following manner: a file or special knife is used to make a deep scratch at the place where it is required to cut the tube; the tube is then taken in both hands in such a way that the thumbnails are over the scratch; by bending and at the same time stretching the tube, it is broken at the scratch (Fig. 28).

Tubes are best bent over a gas burner with a dovetail nozzle (Fig. 29). This produces an extended flame which covers the required length

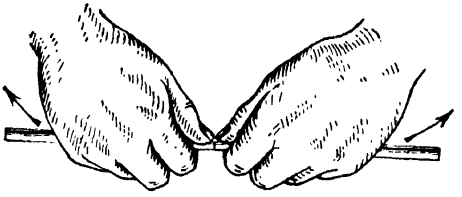


Fig. 28. Position of hands when breaking scratched glass tube

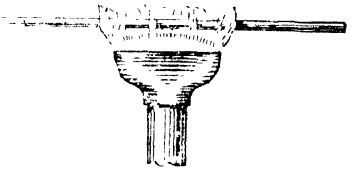


Fig. 29. Dovetail nozzle

of tube. While continuously rotated, the tube should be heated until it softens; it is then held at one end and allowed to bend under its own weight. The use of a dovetail nozzle is essential when working

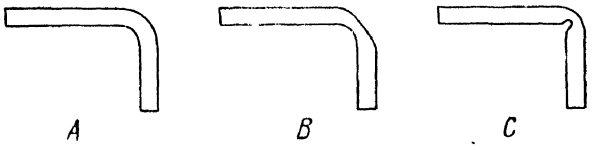


Fig. 30. Bent glass tubes

A — correctly bent; *B* and *C* — incorrectly bent.

with a nonluminous flame. The nozzle slit through which the gas issues should be even; uneven heating may produce incorrectly bent tubes (Fig. 30).

Tube ends are rounded off on a nonluminous flame until they become smooth. When the burner flame becomes yellow, this is a sure sign that edge melting has begun.

To draw out a tube, first heat it slightly over a flame, then introduce its middle part into the outer cone of the flame, and, while rotating it between the thumb and index finger, heat it until it softens. Now remove the tube from the flame and stretch it slowly outwards in both directions until it is of the required diameter.

Capillaries are drawn out in the same way except that the glass should be made softer and the stretching done somewhat faster (but not in a jerk!).

QUESTIONS

1. What advantage has a rubber stopper over a cork?
2. What conditions have to be observed in boring stoppers?
3. Why is it advisable to use a dovetail nozzle when bending glass tubes?
4. Why is it advisable to blacken the heated part of a tube over a smoking flame after treating it in a nonluminous flame?
5. How should a bent tube be inserted in the hole of a stopper?

LABORATORY WORK

Apparatus and materials: set of cork borers; knife for scratching tubes; round file; burner nozzle; scissors; 750 ml wide mouth reagent bottle; test tube with a hole in the bottom; straight funnel; refractory bulb tube; glass tube 5-6 mm in diameter; corks and rubber stoppers; rubber tubing 5 mm in diameter, and asbestos millboard.

1. Laboratory Apparatus Components. Assemble the apparatus shown in Fig. 31.

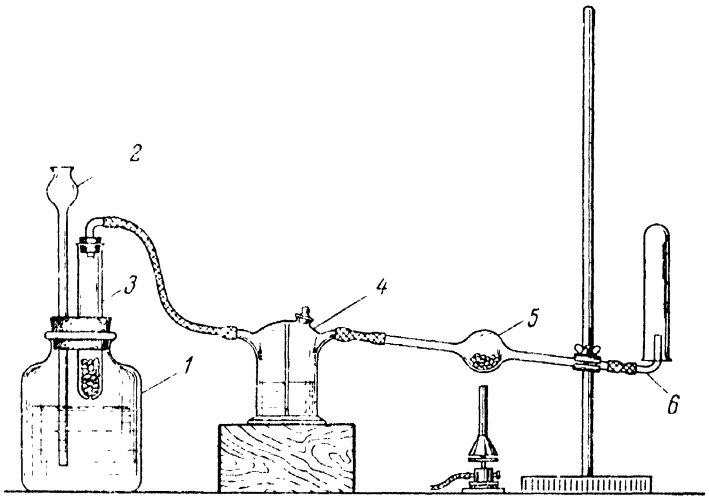


Fig. 31. Apparatus for reducing cupric oxide

1 — bottle; 2 — funnel; 3 — test tube; 4 — wash bottle for gases; 5 — bulb tube; 6 — gas-delivery tube.

The apparatus consists of a bottle (1) with a stopper through which a funnel (2) and a test tube (3) with a hole in the bottom have been passed. The test tube has a rubber stopper with a bent tube passed through it. This is connected by short lengths of rubber tubing with a wash bottle for gases (4) and a bulb tube (5). The latter is connected to a short length of glass tube (6) bent at a right angle.

To assemble the apparatus, it is necessary to prepare two glass tubes bent at a right angle and to select stoppers for the bottle (cork) and for the test tube (rubber).

2. Selection of Stoppers. Bore two holes in a cork: one for the funnel and the other for the test tube, selecting the borers accordingly. If the diameter of the biggest borer is smaller than that of the test tube, widen the hole in the cork by means of a round file. The hole should enable the test tube to be moved easily up and down. In the centre of the rubber stopper bore a hole equal in diameter to the glass tube chosen.

3. Preparation of Tubes. Cut two lengths of glass tube of about 15 cm each and one 30 cm length. Round off their ends and bend the short tubes at right angles*. *Do not place the heated glass tubes directly on the table: place them on asbestos millboard.*

4. Assembly of Apparatus. Insert one of the bent tubes in the rubber stopper so that its end should not protrude from the tapered end of the stopper.

Make certain that the apparatus assembled according to Fig. 31 is airtight. For this purpose pour water into bottle *1* so that it is half full, lower test tube *3* into it, and blow air orally into tube *6*; if the air bubbles through the water, the apparatus is airtight.

Show the apparatus to the instructor. If it is approved, take it apart and put the parts away for the next exercise.

5. Making of Capillaries. Make four capillaries from a glass tube. For this purpose, cut a 15-17 cm length of tube and draw out a capillary tube of 1.5 mm diameter from it. Mark it off carefully into 45 mm lengths and break it at the scratches.

This done, seal the capillaries at one end and show them to the instructor. If the capillaries are found satisfactory, put them away for Exercise 7.

Exercise 5

DETERMINING THE CHEMICAL FORMULA OF A SUBSTANCE

SUBJECTS FOR STUDY

Analysis of compounds; calculation of percentage compositions; atoms and atomic weights; determination of atomic weights; Dulong and Petit's rule and Cannizzaro's method; derivation of empirical formulae; true formulae of substances; qualitative and quantitative meaning of chemical symbols and formulae; equations of reactions, and stoichiometry.

* The straight tube and the capillaries will be needed for the first experiment in Exercise 7.

1. Atomic Weight. This is the most important characteristic of an element. *The atomic weight is a number indicating how many times an atom of a given element is heavier than 1/12 of a carbon atom.* Approximate values of atomic weights (for the heavier elements) can be determined on the basis of Dulong and Petit's rule: *the product of the specific heat of a simple substance in the solid state by the atomic weight of the element at average temperatures equals about 6.2.* The specific heat can be determined from the thermal balance equation. If a certain mass m_1 of a substance with a temperature t_1 and specific heat c_1 is placed in water whose mass is m_2 and temperature t_2 ($t_2 < t_1$), the temperatures level out to t_3. If we assume the specific heat of water to be 1, we get:

$$m_1 c_1 (t_1 - t_3) = m_2 \cdot 1 \, (t_3 - t_2)$$

whence:

$$c_1 = \frac{m_2 (t_3 - t_2)}{m_1 (t_1 - t_3)}$$

Example. 100 g of metallic vanadium is heated to 52° and then immersed in 120 g of water (at 16.8°). The water is thereby heated to 20°. Calculate the atomic weight of vanadium.

By substituting the figures given into the thermal balance equation, we obtain:

$$100 \cdot c \, (52—20) = 120 \cdot 1 \, (20—16.8) \text{ or } c = \frac{120 \cdot 3.2}{100 \cdot 32} = 0.12$$

The atomic weight (A) will then be:

$$A = \frac{6.2}{0.12} = 51.7$$

(the exact atomic weight of vanadium is 50.942).

To determine the atomic weight of an element according to Cannizzaro's method, we must take several volatile compounds of that element and, by analysis, establish their percentage composition and molecular weight. By then setting up a proportion, we find the weight of the element per molecular weight of its compound. After this has been done for several compounds, the least of the weights is assumed to be the atomic weight.

Example. Determine the atomic weight of phosphorus from the following data concerning its compounds.

	Molecular weight	Phosphorus content in %
Phosphorus hydride . . .	34	91.2
Phosphorus trichloride . .	137.5	22.5
Phosphorus hydride (liquid)	66	94.0

A proportion is set up for phosphorus hydride:
100 parts by weight contain 91.2 parts by weight of phosphorus
34 parts by weight contain x_1 parts by weight of phosphorus

$$x_1 = \frac{34 \cdot 91.2}{100} = 31$$

From similar proportions for the other two compounds we obtain:

$$x_2 = \frac{137.5 \cdot 22.5}{100} = 31 \quad \text{and} \quad x_3 = \frac{66 \cdot 94.0}{100} = 62$$

The smallest of the obtained values (i. e., 31) is assumed to be the atomic weight of phosphorus.

Approximate atomic weights can be calculated from Mendeleyev's Periodic Table as the arithmetic mean of the atomic weights of the neighbouring elements (to the left and right, as well as above and below the given element).

Example. Calculate the atomic weight of vanadium from the atomic weights of the neighbouring elements: phosphorus, arsenic, titanium, and chromium.
We find the arithmetic mean of the four atomic weights.

$$x = \frac{30.98 + 74.91 + 47.90 + 52.01}{4} = 51.45$$

(the exact atomic weight of vanadium is 50.942).

Atomic weights approximated to the first decimal can be found by the method of determining equivalents. Modern physical methods (mass spectrography) make it possible to determine the relative masses of atoms with an accuracy to the third and even the fourth decimal.

2. Chemical Formulae. The tiniest particle of a complex substance which retains all its chemical properties is called a molecule. Chemical formulae are conventional designations of the molecules of substances. By means of formulae we express the qualitative and quantitative composition of molecules. For instance, the formula N_xH_y indicates that a substance consists of nitrogen and hydrogen. This is its qualitative composition. Without knowing the values of x and y, we cannot say what the substance is. It might be NH_3, N_3H, or N_2H_4. To find the formula of the substance, we must determine the number of atoms in the molecule, or, in this particular case, determine the values of x and y.

(a) *The simplest (empirical) formulae* give the *relative numbers* of atoms in the molecule.

To write the empirical formula of a substance, we must know its composition by weight and the atomic weights of its constituent elements.

Example. Find the empirical formula of a substance consisting of 87.5% of nitrogen and 12.5% of hydrogen, knowing that the approximate atomic weights of these elements are 14 and 1, respectively.

We denote the formula as N_xH_y and find the ratio of the number of atoms of one element to the number of atoms of the other:

$$x : y = \frac{87.5}{14} : \frac{12.5}{1} = 6.25 : 12.5 = 1 : 2$$

This means that the molecule of the substance contains twice as many hydrogen atoms as nitrogen atoms. Its empirical formula is therefore NH_2.

(b) *The true, or molecular, formula* gives not the relative, but the *actual number* of atoms in the molecule. To arrive at the molecular formula of a compound, we must know not only its percentage composition and the atomic weights of the constituent elements, but also the molecular weight. In the case of some substances the empirical formula and the molecular formula coincide.

Example. Find the molecular formula of the substance from the data of the previous example and the additional information that the density of its vapour in terms of air $D_{air} = 1.1$.

We first find the empirical formula of the substance, as in the previous example. Since the ratio $x : y = 1 : 2$, the molecular formula can be NH_2, or N_2H_4, or N_3H_6, etc.

From the formula $M = 29D_{air}$, we find the molecular weight $M = 31.9 \approx 32$.

If we assume that the empirical formula NH_2 is the molecular formula, the molecular weight adds up to $14 + 2 \cdot 1 = 16$. We know, however, that the molecular weight is double that figure. Consequently, the molecule contains twice as many atoms. The substance must therefore have the formula N_2H_4 and be hydrazine.

To find the formula of a simple substance, one must know its molecular weight and the atomic weights of its constituent elements.

Example. Determine the composition of a molecule of white phosphorus, knowing that its atomic weight is 30.98 and its absolute vapour pressure is 5.53 g/l.

First, we must calculate the molecular weight:

$$M = 22.4D_a = 22.4 \cdot 5.53 \approx 123.9$$

The number of atoms in the molecule is found from the ratio $123.9 : 30.98 = 4$. The composition of the molecule is therefore expressed be the formula P_4.

From the chemical formula of a gaseous substance we can find some of its quantitative characteristics: the percentage composition, the molecular weight, the density in terms of any other gas, and the absolute weight of the molecule.

Chemical formulae also make it possible to calculate the quantities (by weight and by volume) of the reactants and resultants of a reaction from its equation. All such calculations involving the use of chemical formulae and equations are called *stoichiometric*. The term *stoichiometric amounts* means amounts corresponding to the equation of the reaction.

3. Nomenclature of Inorganic Compounds. The following principles form the basis of the international nomenclature of *salts* in chemical literature.

The names of salts are formed from the name of the metal used adjectivally and followed by the name of the electronegative ion or anion *. Metals which form more than one oxide and give rise to corresponding series of salts have the different series distinguished by an inflecting suffix to the name of the metal. The suffix *ous* is used to indicate the lower and the suffix *ic* to indicate the higher condition of oxidation, as in the copper compounds—cuprous chloride (CuCl) and cupric chloride ($CuCl_2$). The name of the electronegative ion or anion is derived from the name of the element which forms it. In the case of salts of acids containing no oxygen, the name of the electronegative element is inflected by the suffix *ide*. In the case of salts of oxygen-containing acids, the termination *ite* is used for the lower valence of the element forming the acid, while the termination *ate* is used for the higher valence. Examples: CaS—calcium sulphide; $CaSO_3$—calcium sulphite; $CaSO_4$—calcium sulphate; Cu_2SO_4—cuprous sulphate, and $CuSO_4$—cupric sulphate.

For acid salts the name of the radical is inflected by the prefix *hydro* (or *bi*). Examples: NaHS—sodium hydrosulphide; $NaHSO_3$—sodium hydrosulphite (bisulphite), and $NaHSO_4$—sodium hydrogen sulphate (bisulphate).

For basic salts the name of the radical is inflected by the prefix *hydroxy* (salts containing the hydroxyl) or *oxy* (salts containing oxygen). Examples: $Bi(OH)_2NO_3$—bismuth hydroxynitrate (subnitrate) and $BiONO_3$—bismuth oxynitrate (bismuthyl nitrate).

QUESTIONS

1. Why has the oxygen unit for measuring atomic weights been given up in favour of the carbon unit?
2. For which elements do the atomic weights found according to Dulong and Petit's rule differ considerably from the real values?
3. From the formula of ammonia derive its quantitative characteristics (molecular weight, absolute density and relative density in terms of air, and percentage composition).
4. How are absolute weights of atoms and molecules calculated? Calculate the absolute weights of the copper atom and the phosphorus hydride molecule.
5. What is the qualitative and quantitative meaning of the equations:

$$2KOH + H_2SO_4 = 2H_2O + K_2SO_4 \text{ (weight units)}$$
$$4NH_3 + 5O_2 = 4NO + 6H_2O_{vapour} \text{ (volume units)}$$

* The names of some anions (acid radicals) are given on the inside back cover of the book.

6. Explain why Fe_2O_3 is called ferric oxide, while FeO is called ferrous oxide. Explain why H_3AsO_4 is called arsenic acid, while H_3AsO_3 is called arsenous acid.

7. Name the following salts:

Mg_3N_2, $Mg(NO_2)_2$, $Mg(NO_3)_2$, Na_2HAsO_3, NH_4VO_3, and $AlOHCl_2$

Problems

1. Calculate the atomic weight of carbon from the following data:

	Molecular weight	Carbon content in %
Carbon dioxide	44	27.3
Ethyl alcohol	46	52.2
Acetone	58	61.2
Benzene	78	92.3

2. Calculate the atomic weight of chlorine from the following data:

	Molecular weight	Chlorine content in %
Hydrogen chloride	36.5	97.3
Potassium chloride . . .	74.6	47.6
Silicon chloride	170.1	83.5
Chloroform	119.5	89.1

3. A piece of metal weighing 40 g was heated to 79.2° and immersed in 80 g of water at a temperature of 17.1°, the water thereby being heated to 20°. Calculate the atomic weight of the metal on the basis of Dulong and Petit's rule.

4. Vanadium consists of two stable isotopes: 0.23% of V^{50} and 99.77% of V^{51}. Calculate the mean atomic weight of vanadium.

5. Determine the formula of a substance containing 64.87% of C, 21.62% of O, and 13.51% of H, if the density of its vapour in terms of air is 2.56.

6. Determine the formula of a substance containing 24.24% of C, 4.05% of H, and 71.71% of Cl if its density in terms of air is 3.42.

7. The burning of a substance containing carbon, hydrogen, and chlorine yields 0.22 g of CO_2 and 0.09 g of water. When an identical amount of the same substance was analysed for chlorine content, 1.44 g of silver chloride was obtained. The vapour density of the compound in terms of hydrogen was found to be 42.5. Determine the formula of the substance.

8. The formula of a substance is P_2H_4. Determine its percentage composition, its density in terms of hydrogen and in terms of air, and its absolute density.

9. How much will the pressure in an oxygen-filled vessel diminish if 8.7% by volume of the oxygen is converted to ozone?

10. How much zinc will be dissolved in 1.5 kg of 35% hydrochloric acid, and what will be the volume of hydrogen evolved ($p = 770$ mm, $t = 17°$)?

LABORATORY WORK

Apparatus and materials: the parts of the arrangement shown in Fig. 31; desiccator with sulphuric acid; test tubes and rack; copper or iron wire 1.5-2 mm in diameter; absorbent cotton-wool; dilute (1 : 6) sulphuric acid; granulated zinc, and calcined granulated cupric oxide.

Note. The cupric oxide should be calcined thoroughly in an open crucible, cooled in a desiccator, and put in a jar with a ground-in lid.

Determining the Formula of Cupric Oxide *. Assemble the apparatus shown in Fig. 31, using the parts prepared in Exercise 4.

Weigh the bulb tube (5) and place about 1 g of granular cupric oxide in its bulb (if powdered cupric oxide clings to the inner surface of the tube, remove it with a wad of cotton-wool attached to a wire). Then weigh the tube again to 0.01 g and connect it up with the rest of the apparatus, as shown in Fig. 31, making sure that the tube is properly inclined.

Now place 15-20 lumps of zinc in the test tube and pour enough sulphuric acid into the bottle through the funnel to immerse one-third of the test tube into the acid. Lower the test tube into the acid. Upon coming in contact with the acid, the zinc begins to react with it, and the hydrogen evolved gradually forces the air out of the apparatus. Water vapour is removed from the hydrogen by passing the latter through a wash bottle containing sulphuric acid (see Fig. 31).

To make certain that all the air has been forced out of the apparatus, a test tube is placed over the end of the delivery tube (6). This test tube should be removed every 2 minutes and, without being turned over, held over the flame of a burner. Pure hydrogen burns quietly, whereas hydrogen mixed with air produces a slight explosion. If the evolution of hydrogen subsides, more acid should be added through the funnel.

After the air has been forced out, heat the bulb of the tube carefully, continuing reduction until the cupric oxide becomes red (the colour of metallic copper). If drops of water should form at the end of the bulb tube, heat that part of the tube slightly. Then remove the burner and allow the tube to cool with hydrogen flowing through it until room temperature is achieved (why?). Remove the test tube containing the zinc from the acid, disengage the tube with the copper in it, and, after cooling it for 10 minutes in a desiccator, weigh it (w_1). Attach the tube to the rest of the apparatus again, continue the reduction, and, after cooling, weigh the tube once more (w_2).

If the weights w_1 and w_2 are equal or differ by not more than 0.01 g, reduction may be considered completed. Otherwise, the process of reduction should be continued until a constant weight is reached.

From the data obtained calculate the percentage composition of cupric oxide and establish its empirical formula.

Write the equations for the reactions by which hydrogen was produced and the cupric oxide reduced.

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* The formulae of lead oxide, bismuth oxide, etc., can also be determined. The oxides of lead and bismuth are reduced to a drop of molten silvery metal.

Calculate the volume of hydrogen (reduced to N. T. P.) used up to reduce the amount of cupric oxide taken and the amount of zinc and sulphuric acid (24%) consumed.

Why should not the bulb tube be heated from the start of the experiment?

Why must the hydrogen entering the bulb tube be dried?

Why is the tube cooled with hydrogen flowing through it?

Why must reduction be repeated?

Exercise 6

DETERMINING CHEMICAL EQUIVALENTS

SUBJECTS FOR STUDY

The concept of chemical equivalents; hydrogen equivalents; relationship between equivalent, valence, and atomic weight; derivation of atomic weight from equivalent; equivalent of a compound; valence; determination of valence; formation of molecules, and electrovalent and covalent bonds.

Chemical Equivalents. A *chemical equivalent* is the weight of a substance which will replace or combine with 8 parts by weight of oxygen or 1.008 parts by weight of hydrogen. The quantity of a substance equal in grams (milligrams) to its equivalent is called a *gram-equivalent* (milligram-equivalent).

Substances react in equivalent amounts. If we know the equivalent and valence of an element, we can determine its atomic weight, as these quantities are linked by the following relationship:

$$\text{atomic weight} = \text{equivalent} \times \text{valence}\ *$$

Experimentally the equivalent of an element can be found *chemically*: by estimating the amount of hydrogen, oxygen, or other element of known chemical equivalent added or replaced by the given element.

Chemical equivalents can also be determined *electrochemically* on the basis of Faraday's Law, whereby the passage of 96,496 coulombs of electricity through an electrolyte solution always deposits one gram-equivalent of a substance on the electrodes.

The guiding principle in calculating the chemical equivalents of acids, bases, and salts from their formulae is the principle that the *chemical equivalent of an acid* is equal to its molecular weight divided by the basicity of the acid, i. e., by the number of hydrogen atoms contained in the acid molecule and capable of being replaced by a metal. Similarly, *the equivalent of a base* is equal to its molecular weight divided by the valence of the metal or the number of hydroxyl groups

* This relationship is inapplicable to inert gases.

in the molecule. The *equivalent of a salt* is equal to its molecular weight divided by the product of the number of atoms of the metal in the salt molecule by the valence of the metal.

Examples:

H_3PO_4 — mol. weight 98, equivalent $\frac{98}{3} = 32.7$

$Ca(OH)_2$ — mol. weight 74, equivalent $\frac{74}{2} = 37$

$Al_2(SO_4)_3$ — mol. weight 342, equivalent $\frac{342}{2 \cdot 3} = 57$

If we know in what amounts HCl and $AgNO_3$ interact and the equivalent of HCl, we can experimentally determine the equivalent of $AgNO_3$. Thus, if a parts by weight of HCl react with b parts of $AgNO_3$, we can, knowing that the equivalent of HCl = = 36.5, calculate the equivalent of $AgNO_3 = x$ from the proportion:

$$\begin{matrix} a - b \\ 36.5 - x \end{matrix} \quad x = \frac{36.5 \cdot b}{a}$$

QUESTIONS

1. Calculate the exchange equivalents of the following substances from their formulae:

SiH_4 Fe_2O_3 Na_3PO_4

2. Write the equation for the burning of SiH_4 and calculate the substance's equivalent. Compare this with the exchange equivalent and explain the discrepancy.

3. Determine the valence of As, P, N, and S in the compounds:

$H_4As_2O_5$ K_2HPO_4 $Al(NO_3)_3$ $ZnSO_4$

4. Write the structural formulae of the following compounds:

Cl_2O_7 H_2MnO_4 $Al(NO_3)_3$ $Na_2B_4O_7$ $Ca_3(PO_4)_2$
Na_2HPO_4 $Bi(OH)_2NO_3$

5. Give diagrams for the formation of the ionic molecule K_2S and the atomic molecule SiH_4. Explain the mechanism giving rise to electrovalent and covalent bonds.

Problems

1. When 1.11 g of a metal was dissolved in acid, 404.2 ml of hydrogen (measured at 19° and 770 mm) was evolved. Calculate the equivalent of the metal and its atomic weight, knowing that the metal is bivalent.

2. Calculate the equivalent of a metal if 3.4 g of its iodide contains 1.9 g of iodine, whose equivalent is 126.9.

3. Calculate the equivalent of a metal if 0.347 g of it releases 180 ml of hydrogen (at 15° and 748 mm) from water.

4. Silver nitrate is used to precipitate 1.49 g of potassium chloride, which contains 52.36% of potassium. The weight of the silver chloride obtained is 2.868 g. Calculate the equivalent of silver if the equivalent of potassium is 39.

5. Find the equivalent of phosphoric acid if 1.68 g of potassium hydroxide, whose equivalent is 56, is used up to neutralise 9.8 g of its 10% solution.

6. The heating of 4.3 g of a metal oxide yielded 580 ml of oxygen (at 17° and 850 mm). Calculate the equivalent of the metal, knowing that 1 litre of oxygen weighs 1.43 g at N. T. P.

7. Calculate the equivalent of $CaCO_3$, knowing that 20 g of 7.3% hydrochloric acid dissolves 2 g of it.

8. The reduction of 1.305 g of manganese dioxide by aluminium yields 0.825 g of manganese. Calculate the equivalent of the latter.

9. The heating of 0.954 g of a metal in oxygen yields 1.194 g of its oxide. Calculate the atomic weight of the metal, knowing it to be bivalent.

10. Calculate the atomic weight of a metal if 5.6 litres of oxygen (measured at N. T. P.) was used up in burning up 30.67 g of it. The specific heat of the metal is known to be 0.033.

LABORATORY WORK

Apparatus and materials: the arrangement shown in Fig. 33; drying cabinet; 10-25 ml measuring cylinder; 100 ml beaker; wash bottle; burette; funnel for burette; porcelain casserole; weighing bottle; watch glass; forceps; room thermometer; desiccator; barometer; marble in lumps; N solution (titrated) of hydrochloric acid; 1:3 hydrochloric acid; 1:1 nitric acid; metallic sodium; weighed amounts of the metals—zinc, magnesium, manganese, and aluminium; magnesium ribbon; ethyl alcohol; phenolphthalein solution, and filter paper (strips).

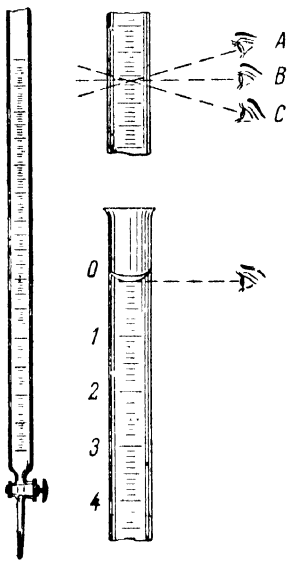


Fig. 32. Burette and how to take a burette reading

Note. The metals in the form of ribbon or shavings should be weighed on an analytical balance to 0.001 g. The amount of zinc should range from 0.030 to 0.040 g; the amounts of magnesium and aluminium, from 0.010 to 0.014 g; the amount of manganese should be 0.026 g. Each weighed amount should be wrapped in paper, and the weight written on it.

1. Determining the Chemical Equivalent of Calcium Carbonate. Weigh a clean 100 ml beaker on a chemical balance (weight w_1). Put several lumps of clean marble in it, and weigh it again (w_2). The marble should weigh 2.50-3.00 g.

Now measure 15 ml of a normal (N) solution of hydrochloric acid (a normal solution contains 1 gram-equivalent of a substance in a litre). To do this, first pour 3-4 ml of the acid solution into the burette through a funnel to wash the inner walls of the burette; pour the solution out through the stop-cock. Repeat this procedure with the same amount of the solution. Then fill the burette with the solution in such a way that there are no air bubbles left in the tip of the burette

(consult the instructor) and that the level of the liquid is slightly above the zero mark (remove the funnel from the burette). Burette readings may differ depending upon the position of the observer's eye in relation to the meniscus (Fig. 32). The eye should therefore always be on a level with the lower meniscus of the liquid (Fig. 32 *B*). Open the stop-cock gently to drain the extra acid, bringing the lower meniscus down to the zero graduation (Fig. 32). Now place the beaker with the weighed marble under the tip of the burette and, opening the stop-cock carefully once more, pour acid into the beaker until the lower meniscus descends to the mark 15.

The reaction which takes place in the beaker involves the evolution of the gas CO_2. Write the equation of the reaction. When the evolution of the gas bubbles slows down considerably, heat the beaker to 60-70°. Bubble formation will at first be speeded; when it stops, the reaction may be considered completed. Now pour the solution formed out of the beaker and wash the remaining lumps of marble twice with distilled water by the method of decantation. Dry the beaker with the remainder of the marble in a drying cabinet and, after cooling it in a desiccator, weigh it (w_3).

Record the results of the experiment as follows:

Weight of the beaker in g			Weight of the marble in g		Amount of marble to react in g	Acid	
empty	with marble		before reaction	after reaction		normality	amount taken in ml
	before exp.	after exp.					
w_1	w_2	w_3	$w_2 - w_1$	$w_3 - w_1$	$w_2 - w_3$		

From the experimental data calculate the chemical equivalent of calcium carbonate.

2. Determining the Hydrogen Equivalent of a Metal. The apparatus for the determination (Fig. 33) consists of two long tubes that are attached vertically to a stand and communicate by means of rubber tubing. One of the tubes is graduated (a burette); connected to it by a stopper is a test tube with a slight bulge in the upper part. The second tube is open at the top. The tubes are filled with water.

Before beginning the experiment, make sure that the apparatus is airtight. This is done by the following procedure. When the apparatus has been assembled, raise and lower the tube that is open at the top; the level of the water in the other tube should neither rise nor drop much, but should only fluctuate slightly. If this is not the case, insert the stoppers more tightly. Once the apparatus has been proved

airtight, adjust the level of water in the tubes at the same height and attach the tubes to the stand in this position. Record the level in the graduated tube with an accuracy to 0.05 ml (according to the lower meniscus).

Now pour 3-4 ml of dilute (1 : 3)* hydrochloric acid into the test tube by means of a funnel, taking care not to wet the bulge in the upper part of the test tube (if this should be wetted, dry it with filter paper). Now obtain a weighed amount of metal from the laboratory assistant, and record its weight in your notebook. Lift the test tube into the position shown by the broken line in Fig. 33 and carefully transfer the weighed metal into the bulge of the test tube, taking care that none of it should fall into the acid. Stopper up the test tube tightly again while it is still in this inclined position, and then shake it, allowing the metal to fall into the acid. The pressure of the hydrogen formed by the interaction of the metal and the acid forces the liquid out of the burette into the other tube.

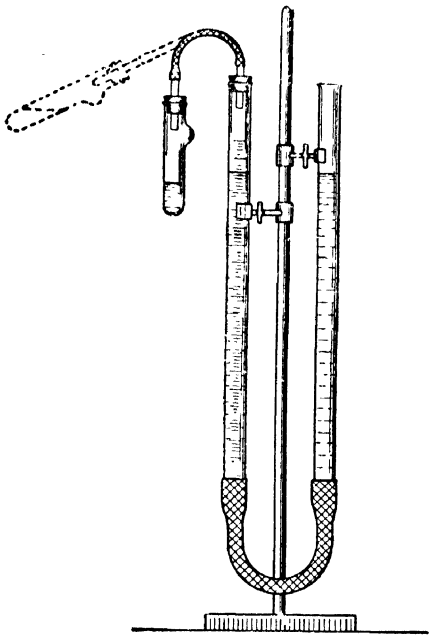


Fig. 33. Apparatus for equivalent determination

When the reaction ends, allow the test tube to cool and then *bring the water in the tubes to the same level* by lowering the tube open at the top. Record the new position of the level in the graduated tube. Record the readings of the thermometer and the barometer.

Results of experiment

Amount of metal in g	Conditions of experiment		Position of level in burette in ml		Volume of hydrogen in ml
	temperature in °C	pressure in mm	before exp.	after exp.	

* This designation means that the dilute acid was obtained by mixing one volume of concentrated acid with three volumes of water.

From the data of the experiment, calculate the equivalent of the metal. In the calculation, take into consideration the aqueous vapour tension (Table 2, p. 28), as the gas was collected over water. Will the equivalent of the metal be bigger or smaller if: (1) the metal contains impurities insoluble in acid; (2) no allowance is made for the aqueous vapour tension?

3. Determining the Oxygen Equivalent of a Metal. Weigh a dry porcelain casserole. Then weigh 0.18-0.22 g of magnesium ribbon in it. Subsequent operations should be conducted in a ventilated hood. Pour dilute (1 : 1) nitric acid in small portions (2-3 ml) into the casserole until the whole of the metal dissolves. When this has taken place, put the casserole on a wire gauze with an asbestos centre and evaporate slowly (without splashing) until there is no water left. Then heat the casserole with the dry salt, causing it first to melt and then to decompose, with the evolution of a brown gas and the formation of white magnesium oxide. Following this, cool the casserole in a desiccator and weigh it. To make sure that the salt has all been decomposed, repeat the calcination and weighing. If the results of two consecutive weighings are identical or differ by 0.01 g, decomposition is complete. From the weights of the metal and the resulting oxide, calculate the oxygen equivalent of the metal and the relative error of the determination.

Submit a report on the experiment with the results obtained for the equivalent and a brief description of the method to the instructor.

4. Determining the Chemical Equivalent of Chlorine from the Equivalent of Sodium. Weigh a dry porcelain casserole, pour 15 ml of ethyl alcohol into it, and cover it with a watch glass. Weigh a dry weighing bottle. Obtain a lump of dry metallic sodium from the laboratory assistant, place it quickly into the weighing bottle, close the bottle tightly, and weigh it again (the sodium should weigh about 0.20 g).

Now transfer the weighed sodium with forceps to the casserole and cover it at once with the watch glass. Write the equation for the interaction of the sodium with the alcohol. When the reaction ends, wash the splashes of the solution from the surface of the watch glass back into the casserole, using a small amount of water from a wash bottle for this operation. Add 1-2 drops of phenolphthalein to the solution. What is the colour of the solution now? Write the equation for the reaction of sodium ethylate with water.

Pour M HCl into a dry burette and add it to the solution in the casserole until the crimson colouration disappears. Place the casserole on a wire gauze with an asbestos centre and evaporate the solution over a small flame until there is no water left in the casserole. Cool the casserole in a desiccator for 7-10 minutes and weigh it. What is the substance obtained? Write the equation for the reaction that produced it.

From the weights of the sodium chloride and the sodium, knowing the chemical equivalent of sodium, calculate the chemical equivalent of chlorine and the relative error of the determination.

Exercise 7

DETERMINING THE PURITY OF A SUBSTANCE

SUBJECTS FOR STUDY

Pure substances and their properties; isolating individual substances from mixtures; purifying substances and determining the degree of their purity; grades of purity (commercially pure, analytical reagent, and chemically pure), and standard requirements with respect to chemical products.

Every pure substance has certain characteristic physical properties: colour, taste, odour, density, melting point and boiling point, hardness, viscosity, etc.

When we say that water is a colourless, odourless, and tasteless liquid that boils at 100° C, freezes at 0° C, has a density of 1 g/cm^3 at 4° C, etc., we are referring to pure water without any impurities, i. e., to the individual substance.

However, despite the exceptional progress made by reagent chemistry, it should not be thought that what is termed a "pure substance" does not contain minute impurities of other substances.

In the U.S.S.R. chemical products are manufactured in accordance with technical standards known as GOST (which is the Russian abbreviation for U.S.S.R. State Standard); these standards specify exact requirements with respect to the quality of such products as chemical reagents.

For instance, the following are the maximum permissible impurities, according to GOST, in the different reagent grades of *sodium hydroxide.*

Maximum Permissible Impurities (in %)

	Chemically pure	Analytical reagent	Pure
Chlorides	0.005	0.01	0.025
Sulphates	0.005	0.01	0.03
Phosphates	0.003	0.005	0.01
Silica	0.01	0.02	0.1
Heavy metals	0.003	0.003	0.003
Calcium	0.012	0.024	0.06
Sodium carbonate	1	2	4
Iron	0.0005	0.001	0.002
Substances precipitated by ammonia (Al_2O_3, Fe_2O_3)	0.01	0.02	0.1
Total nitrogen (nitrates, nitrites, ammonia, etc.)	0.001	0.001	0.001

Factory-made products are analysed at the factory laboratory; on the basis of the analysis and the relevant GOST, they are graded "chemically pure", "analytical reagent", "pure", or "commercially pure". The product is then packed and labelled accordingly.

The "chemically pure" substances are the purest. The amounts of impurities in them are so negligible that they can be detected only by special analytical techniques. Products marked "analytical reagent" may contain impurities in amounts that cannot prevent the use of these substances in chemical analysis.

Products marked "pure" contain greater amounts of impurities than products labelled "chemically pure" or "analytical reagents". The "commercially pure" products usually contain the most impurities. They are cheaper and are used for industrial purposes.

Of great practical importance is the development of techniques for isolating pure substances from natural materials and from industrial products or waste, as well as for testing the purity of substances.

Purity Testing Techniques. The purity of a substance of known composition can be tested either by physical methods (determination of density, melting point, boiling point, etc.) or by methods of chemical analysis (by treating a weighed amount of the substance with a reagent). In the latter case (*quantitative analysis*) the composition of the substance being tested is determined from the quantity (by weight or by volume) of the resultant substance or from the expenditure of the reagent. The detection of impurities may sometimes be confined to *qualitative analysis*, i. e., to employing reactions that in the case of a certain impurity yield products easily distinguishable by visible signs (the formation of a precipitate, a change in colour, etc.); the quantity of the impurity is not estimated in this case.

Below we shall consider some of the methods used in assessing the quality of a substance, namely, the determination of the melting and boiling points of a substance, the quantitative estimate of a substance according to the volume of a gas evolved when the product being tested is decomposed by reagents, and the qualitative analysis of a chemical product according to standards.

(a) The *melting point* of a substance is one of its most important characteristics; by means of this characteristic we can determine the purity of a solid crystalline * substance. The melting point is the temperature at which a solid substance, in conditions of equilibrium, passes into the liquid state.

In the case of a pure crystalline substance the temperature range from the moment melting begins (the appearance of a liquid phase) to its comlpetion usually does not exceed 0.5°. Substances containing impurities, on the other hand, do not have a sharply defined melting point; they usually melt over a range of several degrees.

* Amorphous substances do not have a distinct melting point.

Melting point determinations are carried out as follows. A finely ground powder of the substance being tested is packed tightly in a 2-3 mm layer into a capillary. Two capillaries are filled in this way. A capillary is then attached to a thermometer by a rubber band (Fig. 34*A*). The thermometer, fitted into the hole of a stopper, is then put into a dry test tube, which serves as something like an "air sleeve" to prevent overheating. The test tube is lowered into a beaker, flask, or special vessel (Fig. 34*B* and *C*) filled with water, paraffin butter, or concentrated sulphuric acid, depending upon the melting point of the substance. The beaker or flask is placed on the ring of a stand and heated slowly.

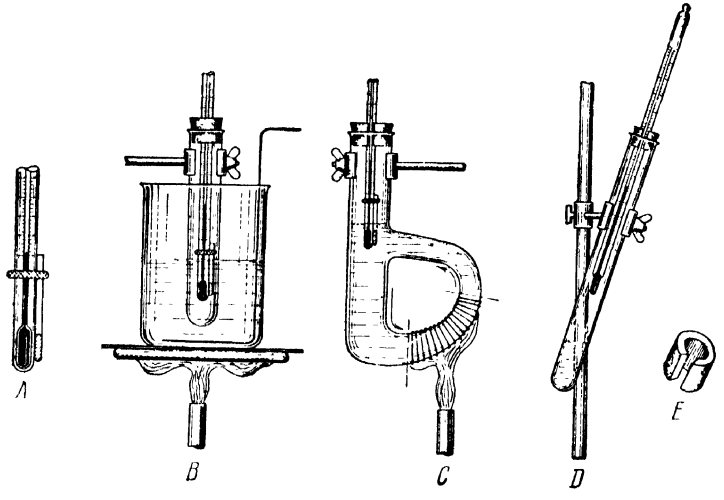


Fig. 34. Types of apparatus for melting and boiling point determination

Before beginning to melt, the substance usually shrinks, becoming disengaged from the walls of the capillary; after that a drop of liquid appears at the very bottom of the capillary. That is the moment to note the melting point on the thermometer.

The first capillary is used for a rough estimate. Let us assume that the melting point in this case was found to lie in the 75-80° range. The second capillary is then fixed in position and the heating conducted to 65°; after that the flame of the burner is reduced so that the temperature does not rise faster than 1° a minute. The liquid in the beaker is mixed with a stirrer. The temperature is now noted at which the substance begins to melt.

In the case of some substances, which decompose as they melt, the melting point cannot be regarded as a reliable indication of purity and is used only as an auxiliary characteristic.

Melting point determinations are also carried out in a special vessel of refractory glass, such as shown in Fig. 34*C*. The small flame of

the burner is applied to that part of the vessel which is covered with asbestos cord (between the broken lines in the figure). The heated layer of liquid moves counterclockwise in the vessel. Thanks to ideal conditions for the thermal movement of the liquid and for its mixing, melting point determinations can be carried out in such a vessel with a high degree of accuracy.

(b) The *boiling point* is another important characteristic of a chemically pure liquid substance. This is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure (i. e., 760 mm Hg).

The boiling point of a small quantity of a liquid can be determined in the apparatus shown in Fig. 34*D*. Pour 3-4 ml of the liquid into a dry test tube and throw a small lump of pumice or pieces of capillaries, sealed at one end, into the test tube so that the liquid should boil without bumping. Into a stopper with a slit (Fig. 34*E*) insert a thermometer in such a way that its lower end is 3 cm above the level of the liquid. The liquid in the test tube is then heated over a small flame until drops of condensing liquid begin to trickle continually from the end of the thermometer. This temperature is noted, after which the test tube is cooled and the determination repeated.

(c) *Determining the Purity of a Substance by the Chemical Method According to the Volume of Gas Evolved.* The substance to be tested is treated with a reagent whose interaction with the substance causes a gas to be evolved. The gas generated is collected over water, and its volume measured. The purity of the initial substance is determined from the volume of the gas, reduced to N.T.P., and the equation of the reaction.

If the gas evolved dissolves in water, it is collected over mercury, toluene, salt solutions, etc.

Example. Determine the degree of purity of calcite ($CaCO_3$) if 1 g of it, when treated with acid, yields 244 ml of carbon dioxide measured at 20° and 750 mm.

First, the volume of the gas should be reduced to N.T.P.:

$$v_0 = \frac{244 \cdot 750 \cdot 273}{760 \cdot 293} = 224 \text{ ml}$$

From the equation of the reaction

$$\underset{100\text{ g}}{CaCO_3} + 2HCl = H_2O + \underset{22.4\text{ lit}}{CO_2} + CaCl_2$$

it follows that 1 g of calcite should yield 224 ml of CO_2.

From a comparison of the volumes it is easy to see that the product tested is of 100% purity.

(d) *Determining Concentration and the Qualitative Analysis of a Substance According to Standards.* The technique of determining the concentration of a solution by the relative density, measured by a hydrometer, has been described in detail in Exercise 2. It should

be pointed out that the relative densities of aqueous solutions are usually greater than unity, while the relative densities of solutions of gaseous substances of low molecular weight (e. g., ammonia solution) are less than unity.

Qualitative reactions to determine the presence of impurities are conducted according to respective standards. To determine the presence of an impurity, a solution of the substance under test is treated with a characteristic reagent, i. e., a substance which reacts specifically with that impurity (forming a precipitate, generating a gas, or altering the colour of the solution).

Example. Ammonium nitrate which is chemically pure in accordance with the proper standard should not, in a solution of definite concentration, exhibit an acid reaction more pronounced than a certain permissible limit. To test whether a sample conforms to standard requirements, 5 g of it, weighed to 0.01 g, is dissolved in 50 ml of freshly boiled and cooled distilled water. A drop of 2% alcoholic solution of the indicator methyl-red is then added, which causes a red colouration to appear. If the colour turns to yellow upon the addition of not more than 2 ml of 0.01 M NaOH, the chemical conforms to standard requirements.

QUESTIONS

1. In what temperature range ought a chemically pure substance melt?
2. At what rate should heating be conducted in melting point determinations?
3. The testing of a substance by the method of chemical decomposition produces gaseous ammonia. Name a liquid over which the ammonia can be collected.
4. By means of what reaction is it possible to establish the presence of chlorides as an impurity in sulphuric acid?

Problems

1. Determine the degree of purity of calcium hydride (CaH_2) if the interaction of 7.6 g of it with water at 17° and 740 mm yields 8.75 l it of hydrogen.
2. The decomposition of 1.1 g of malachite yields 111.3 ml of carbon dioxide, measured at N.T.P. Determine the degree of purity of the malachite, which has the formula $Cu_2(OH)_2CO_3$.
3. It has been established by analysis that 32.2 g of sodium hydroxide contains an amount of sodium carbonate equivalent to 24 ml of M HCl. Determine the degree of purity of the sodium hydroxide.
4. Determine the degree of purity of tellurium if the burning of 12.76 g of it to tellurium dioxide requires 2.3 l it of oxygen, measured at 17° and 780 mm.
5. Determine the percentage content of impurities in pyrite if the burning of 15 t of FeS_2 yields 5,376 cu m of sulphur dioxide (reduced to N. T. P.). The equation for the burning process is:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

6. Determine the degree of purity of marble if 109.4 g of it upon decomposition yields 25 l it of carbon dioxide, measured at 15° and 780 mm.

7. Determine the carbon content in coal if 205.8 g of the coal at N.T.P. yields 1 cu m of a gas that contains 2% of CH_4, 29% of CO, and 2% of CO_2.

8. An alloy used in the manufacture of nibs contains—in addition to iron, tungsten, chromium, and nickel—the metal rhenium. The amount of rhenium in 26.5 g of the alloy is such that treatment with the proper reagents converts it to 0.72 g of perrhenic acid $HReO_4$. Determine the percentage content of rhenium in the alloy.

9. The decomposition of 2.88 g of aluminium carbide by hot water:

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$$

yields 1.23 lit of methane, collected at 20° and 770 mm. Determine the degree of purity of the aluminium carbide.

10. It has been established by analysis that 50 g of metallic thallium contains 3.5 milligram-equivalents of calcium, 5.4 milligram-equivalents of magnesium, and 6.1 milligram-equivalents of aluminium. Express the contents of the impurities in percentages.

LABORATORY WORK

Apparatus and materials: the arrangement shown in Fig. 34*B* and *D* and in Fig. 35; test tubes and rack; 250 ml measuring cylinder; 10 ml measuring cylinder; 200 ml beaker with stirrer; funnel; thermometer with 100° range; room thermometer; barometer; hydrometer with 0.8-1.0 relative density range; rubber bands for attaching capillaries to thermometer; powdered sodium thiosulphate; set of substances

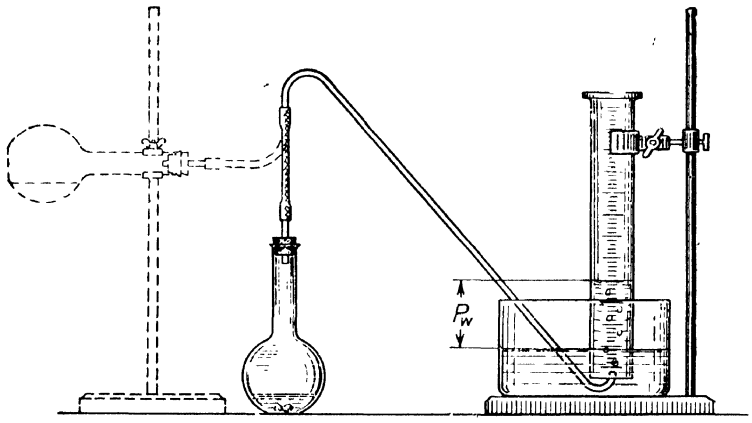


Fig. 35. Apparatus for purity determination

for melting point determinations; carbon tetrachloride; saturated solution of sodium chloride; 1 : 3 sulphuric acid; 0.5 N solution of cupric sulphate; zinc dust; 25% solution of ammonia; 10% solution of barium chloride; 2N solution of hydrochloric acid; 10% solution of acetic acid; 0.01 N solution of iodine; starch solution; hydrogen sulphide solution; lime water; red and blue litmus paper; cigarette paper; ruler with mm calibration, and weighed amounts of calcium carbide.

Note. The amounts of calcium carbide should weigh from 0.20 to 0.24 g. The hydrogen sulphide solution should preferably be prerared for each exercise, since it is easily oxidised by the oxygen of the air. The hydrogen sulphide prepared for this purpose in the Kipp gas generator should first be washed in a wash bottle for gases. Cloudy hydrogen sulphide solution should not be used.

1. Determination of Melting Point. (a) Two of the capillaries prepared in advance (Exercise 4) should be packed tightly with a 2-3 mm layer of finely ground sodium thiosulphate. This is done in the following manner. Some sodium thiosulphate powder is placed on a watch glass or on glossy paper. The open end of a capillary is then thrust into the powder, so that 5-6 mm of its length is filled with it. Following this, the capillary is dropped, sealed end first, into a 30 cm glass tube placed vertically on the table. When the capillary strikes the table, the substance moves towards its sealed end. By repeating this 5-6 times, the capillary is packed tightly. This done, the capillary is attached by a rubber band to a thermometer, and the thermometer is lowered into a beaker with water (Fig. 34).

By heating the first capillary, we now determine the approximate melting point of the substance. The second cappilary is then heated to a temperature 10° below the found approximate melting point; from there on heating is continued so that the temperature rises at a rate of 1° a minute until the first drop of the molten substance forms. The temperature at which this takes place is the melting point.

Determination	I approximate	II exact
Melting point in °C		

(b) Determine the melting point of an unknown substance received from the instructor. Record the results obtained in the above table and check them with the instructor.

2. Determination of Boiling Point. Fill the test tube in the apparatus shown in Fig. 34*D* with carbon tetrachloride to the level illustrated and carry out three determinations of its boiling point in accordance with the procedure described in the introduction to the exercise (see Para. b).

Determination	I	II	III
Boiling point in °C			
Average value $t°=$			

3. Determining the Purity of Calcium Carbide. Calcium carbide reacts readily with water:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

The acetylene evolved is collected over a saturated solution of sodium chloride in water (since acetylene is slightly soluble in water), and its volume is measured. From this volume and the weight of the calcium carbide taken, it is easy to determine the degree of purity of the CaC_2.

The apparatus (Fig. 35) consists of a long-necked flask with a stopper, through which a delivery tube has been passed, a measuring cylinder, and a vessel.

Pour a saturated solution of sodium chloride into the beaker until it is half full and into the cylinder until it is quite full. Cover the cylinder with a glass plate and place it upside down in the beaker. *Make certain that the apparatus is airtight.*

Now pour 10 ml of distilled water into the flask, trying not to wet the walls of its neck. Obtain a weighed amount of calcium carbide from the laboratory assistant and record its weight. Place the calcium carbide inside the neck of the flask, which is in a horizontal position (shown by broken line in Fig. 35), stopper up the flask quickly, place the end of the delivery tube under the cylinder, and let the lumps of calcium carbide slip into the water. The acetylene evolved is collected in the cylinder.

When the reaction terminates, remove the delivery tube from the vessel; by means of a ruler measure the distance from the level of the liquid in the vessel to its level in the cylinder (height p_w in Fig. 35); determine the volume of acetylene. Record the temperature and the pressure.

Table 3

Vapour Pressure h (mm Hg) over Saturated Solution of Sodium Chloride at Temperature t (°C)

t	h	t	h	t	h	t	h
11	7.4	16	10.3	21	14.1	26	19.0
12	7.9	17	11.0	22	15.0	27	20.2
13	8.5	18	11.7	23	15.9	28	21.4
14	9.1	19	12.4	24	16.9	29	22.6
15	9.7	20	13.2	25	17.9	30	24.0

From Table 3 find the vapour pressure h of the solution for the given temperature t.

Results of experiment

Weight of CaC_2 in *g*	Volume of the acetylene in ml	p_w in mm	p_{bar} in mm Hg	°C	*h* in mm Hg

Calculations:

(a) On the basis of the equation of state of a gas, reduce the volume of the acetylene to N.T.P., bearing in mind that the pressure of the acetylene

$$p = p_{bar} - \left(h + \frac{p_w}{13.6}\right)$$

(b) From the equation of the reaction calculate the volume o acetylene obtained from the given amount of calcium carbide (100% when treated with water.

(c) From the data of Paragraphs *a* and *b* calculate the percentage content of CaC_2 in the calcium carbide.

4. Determination of Zinc Dust Purity. This experiment, like the previous one, is conducted in the apparatus shown in Fig. 35. The vessel and the cylinder are filled with water, and 10 ml of 1 : 3 H_2SO_4 and 3 drops of a dilute solution of cupric sulphate are poured into the flask; 0.24-0.28 g of zinc dust is weighed in a packet of cigarette paper and placed inside the neck of the flask in the paper.

Record the results as in Experiment 3. From the experimental data determine the purity of the zinc dust.

5. Testing a Solution of Ammonia (*Ammonia Spirit*).

Excerpt from GOST 786-41:

"Ammonia Spirit, Medical.

"A transparent, colourless solution containing not less than 24% of ammonia (NH_3).

"It should pass tests for the absence of:

"(a) sulphates, in accordance with Para. 12.

"(b) carbonates, in accordance with Para. 13.

"(c) sulphides, in accordance with Para. 14, and

"(d) salts of the heavy metals, in accordance with Para.15."

"...Para. 12. *Test for Sulphates.* Dilute 5-8 ml of ammonia solution with 20 ml of distilled water, and add hydrochloric acid until the solution exhibits an acid reaction with respect to litmus. Heat the solution to boiling and add 2-3 ml of 10% barium chloride solution. Then cool the liquid and examine it in passing light. In the absence

of any trace of opacity, the product is regarded as satisfying requirements.

"Para. 13. *Test for Carbonates.* Dilute 10 ml of ammonia solution with 10 ml of water and add 40 ml of filtered lime water to the solution. Examine the liquid in transmitted light. In the absence of any trace of opacity, the product is regarded as satisfying the requirements.

"Para. 14. *Test for Sulphides.* Add a 10% solution of acetic acid to 5 ml of an ammonia solution until it exhibits a faintly acidic reaction with respect to litmus; then add 2 drops of an 0.01 N iodine solution. The appearance of a blue colour in the presence of starch points to the absence of sulphides in the product.

"Para. 15. *Test for Salts of the Heavy Metals.* Dilute about 5 ml of ammonia solution with 40 ml of distilled water and add 20-30 ml of hydrogen sulphide solution. If no dark (salts of iron, copper, etc.) or white (salts of zinc) precipitate is thrown down, there are no salts of the heavy metals present...."

Testing Procedure. Pour the solution to be tested into a 250-300 ml cylinder and make certain (by the naked eye) that it is transparent and colourless. Lower a dry hydrometer into the cylinder and measure the relative density to $\pm$ 0.003. After the measurement dry the hydrometer thoroughly. On the basis of the relative density value obtained, determine the percentage concentration of ammonia in the solution from the table on p. 331. If the experimental value of the relative density does not appear in the table, use the method of interpolation (see Exercise 2).

The qualitative reactions should be carried out with the reagents used to detect the corresponding ions (see Paras. 12-15 of the above excerpt from GOST). Record the results in your notebook and, by comparing them with the standard requirements, draw a conclusion concerning the quality of the solution tested.

RECORD OF AMMONIA SOLUTION TESTING

1. External appearance . . . . . .
2. Relative density shown by hydrometer (γ_4^{15}) . . .
3. NH_3 content . . . . . :
4. Qualitative reactions to detect: . . . . . .
   (a) sulphuric acid . . . . . .
   (b) carbonic acid . . . . . .
   (c) hydrosulphuric acid . . . . . .
   (d) salts of the heavy metals . . . . . .
   Conclusion . . . . . .

Date . . . . . .

Name . . . . . .

Exercise 8

THERMAL EFFECTS OF REACTIONS

SUBJECTS FOR STUDY

Energy transformations in chemical reactions; equivalence of different forms of energy; chemical energy and thermal energy; exothermal and endothermal reactions; thermal effects of reactions and thermochemical equations; Hess's Law, and the thermal effects of solution and hydration.

Every substance has not only a definite composition, but also a definite stock of chemical energy. Chemical reactions involve changes both in the composition of substances and, at the same time, in their stocks of energy. The difference between the chemical energy of the initial reactants and of the final reaction products is converted into an equivalent amount of some other form of energy: mechanical, radiant, thermal, or electric. Typical of most chemical reactions is the *transformation of chemical energy into thermal*; reactions in which heat is liberated are called *exothermal*, while those in which it is absorbed are termed *endothermal*.

Example.

$H_2 + S = H_2S + 4.8$ Cal. (Exothermal reaction)

$H_2 + Se = H_2Se - 18.5$ Cal. (Endothermal reaction)

The quantity of heat evolved or absorbed in a chemical reaction is called the *thermal effect of the reaction*. It is usually referred to one mol of the reaction product and expressed in large calories (*Cal.*). Chemical equations including the thermal effect value are called *thermochemical equations*. For example, the burning of carbon monoxide may be represented by the following thermochemical equation:

$$2CO + O_2 = 2CO_2 + 135 \text{ Cal.}$$

This may likewise be expressed by the equation:

$$CO + \frac{1}{2}O_2 = CO_2 + 67.5 \text{ Cal.}$$

It is general practice in thermochemistry to employ the latter type of equation, i. e., to refer the thermal effect to one gram-molecule of the *product*, using fractional coefficients if necessary.

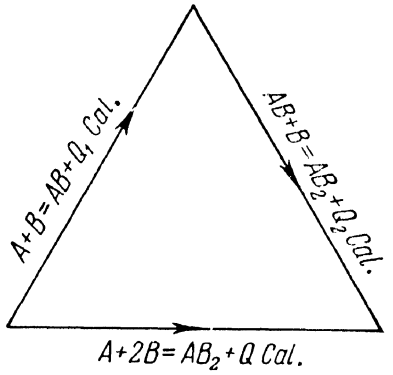
The thermal effects of the formation and decomposition of the same substance are equal in absolute value, but opposite in sign (first law of thermochemistry).

For instance:

$Pb + I_2 = PbI_2 + 41.77$ Cal. $\qquad PbI_2 = Pb + I_2 - 41.77$ Cal.

This law serves as the basis for calculating the thermal effects of various reactions important in practice (formation, decomposition, burning, solution, hydration, and neutralisation).

One and the same end product may be obtained from the same initial substances by different reactions. Let us assume, for example, that from the substances A and B it is necessary to prepare the product AB_2. The process may be conducted in different ways:



According to the second law of thermochemistry, established by the Russian scientist G. Hess (1836), *the quantity of heat evolved in a chemical process does not depend on whether the process takes place in a single stage or in several stages (provided volume and pressure remain constant)*. Consequently, for our case $Q = Q_1 + Q_2$. Since the thermal effect of some stages of the process may be negative, the general principle may be formulated as follows: *The algebraic sum of the thermal effects of a chemical process consisting of several stages is equal to the thermal effect of the same process taking place in a single stage.*

States and allotropic modifications of substances should be indicated in thermochemical equations, as the burning, say, of amorphous carbon, graphite, and diamond yields different quantities of heat (96.98, 94.23, and 94.45 Cal. respectively); similarly, the thermal effects of the formation of water, water vapour, and ice from their elements are not the same either (68.35, 57.84, and 69.95 Cal. respectively).

The quantity of heat in calories generated by the burning of 1 mol of a substance is called the *heat of combustion*. The burning of a compound substance may follow either of the two patterns.

1. The direct interaction of the molecules of the substance with oxygen (a single-staged process).
2. The decomposition of the molecule of the substance, with the subsequent burning of each component in oxygen (a process taking place in several stages: a, b, c, d...).

In accordance with Hess's Law, the thermal effect is the same in either of the two above cases, provided the end products of the reaction are identical in composition and number of molecules.

Example. Calculate the heat of combustion of acetylene, knowing that the heat of formation of liquid water is 68.35 Cal., the heat of formation of CO_2, 94.23 Cal., and the heat of formation of acetylene,—53.9 Cal.

It follows from the above data that acetylene C_2H_2 is an endothermal compound and that its decomposition is, therefore, accompanied by the liberation of heat.

Let us denote the unknown heat of combustion of acetylene as x Cal. We can then write:

1. $C_2H_2 + \frac{5}{2} O_2 = 2CO_2 + H_2O + x$ Cal.
2. (a) $C_2H_2 = 2C + H_2 + 53.9$ Cal.
   (b) $2C + 2O_2 = 2CO_2 + 2 \cdot 94.23$ Cal.
   (c) $H_2 + \frac{1}{2} O_2 = H_2O_{liq} + 68.35$ Cal.

From Hess's Law it follows that

$$x = 53.9 + 2 \cdot 94.28 + 68\ 35$$
$$x = 310.71 \text{ Cal.}$$

The heat of formation and the heat of decomposition are calculated in the same way.

Hydration is the process whereby the molecules of a substance that is being dissolved combine with the molecules of the solvent, specifically water. The process is accompanied by the evolution of heat, which is called heat of hydration. For instance, from the equation

$$ZnSO_4 + 6H_2O = ZnSO_4 \cdot 6H_2O + 19.3 \text{ Cal.}$$

it follows that 19.3 Cal. is evolved when a molecule of zinc sulphate combines with six molecules of water.

The process of solution may also be expressed as a thermochemical equation, e. g.:

$$ZnSO_4 \cdot 7H_2O + aq = ZnSO_4 \cdot aq - 4.26 \text{ Cal.}$$

Here aq denotes the solvent, water.

It is evident from the above equation that 4.26 Cal. is absorbed when one mol of the heptahydrate of zinc sulphate dissolves. It should be pointed out that an anhydrous salt forming a crystal hydrate dissolves in two stages: (a) hydration, and (b) the solution of the hydrate.

Example. Calculate the heat of hydration of anhydrous zinc sulphate, knowing that its heat of solution is 18.43 Cal., while the heat of solution of the hydrate $ZnSO_4 \cdot 7H_2O$ is —4.26 Cal.

Equations should be written, in which the heat of hydration is denoted as x:

1. $ZnSO_4 + aq = ZnSO_4 \cdot aq + 18.43$ Cal.
2. (a) $ZnSO_4 + 7H_2O = ZnSO_4 \cdot 7H_2O + x$ Cal.
   (b) $ZnSO_4 \cdot 7H_2O + aq = ZnSO_4 \cdot aq - 4.26$ Cal.

From Hess's Law it follows that

$$18.43 = x - 4.26$$
$$x = 22.69 \text{ Cal.}$$

QUESTIONS

1. Where is there a greater stock of chemical energy: in 1,000 atoms of hydrogen or in 500 molecules of it? Explain the reasons for the difference in the amount of energy in this case.
2. The formation of a gram-molecule of water is accompanied by the evolution of 68.35 Cal., while the formation of an equal amount of water vapour is accompanied by the evolution of only 57.84 Cal. Why the difference?
3. The same molar quantities of $MgSO_4$ and $MgSO_4 \cdot 7H_2O$ are dissolved in equal amounts of water. Why are the thermal effects different?
4. The values of the heat of formation for H_2O, P_2O_5, CO_2, and MgO are 68.35, 360.0, 94.23, and 146.1 Cal. respectively. If we take hydrogen, phosphorus, carbon, and magnesium *in equal quantities by weight*, in which case will burning produce the most heat?
5. Explain the thermochemical equation

$$P_{white} + \frac{3}{2}Cl_2 = PCl_3 + 70 \text{ Cal.}$$

To what amount of PCl_3 by weight is the thermal effect referred?

6. On the basis of Hess's Law write the thermochemical equations for the burning of the exothermal compound propane (C_3H_8) and for its decomposition to its elementary constituents, with their subsequent separate burning. Denote the separate thermal effects Q_1, Q_2, Q_3, and Q_4 respectively. Express Q_3 in terms of the other thermal effects.

Problems

1. The values of the heat of formation for SiO_2 and MgO are 203.3 and 146.1 Cal. respectively. Calculate the heat of the reaction

$$2Mg + SiO_2 = 2MgO + Si.$$

2. The heat of the formation of K_2O is 86.2 Cal. In the reaction between molecular quantities of K_2O and SO_2, 110.6 Cal. is evolved.

Calculate the thermal effect of the formation of SO_2, knowing that the heat of formation of K_2SO_3 from its elements is 267.7 Cal.

3. Calculate the heat of the reaction

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

It is known that the values of the heat of formation of SO_2 and SO_3 from their elements are 70.92 and 93.9 Cal. respectively.

4. Calculate the heat of the reaction

$$H_2S + \frac{3}{2} O_2 = H_2O_{vap} + SO_2$$

It is known that the heat of formation of H_2S from its elements is 4.8 Cal.; the heat of formation of SO_2, 70.9 Cal., and the heat of formation of H_2O_{vap}, 57.84 Cal.

5. Calculate the heat of formation of $CaCO_3$ from its constituent elements, knowing that the thermal effect of the reaction $CaCO_3 = CaO + CO_2$ equals —43.35 Cal. and the heat of formation of CaO and CO_2 from their constituent elements equals 151.7 and 94.23 Cal. respectively.

6. Given the thermochemical equations of the reaction:

$$MgSO_4 + aq = MgSO_4 \cdot aq + 20.3 \text{ Cal.}$$
$$MgSO_4 \cdot 7H_2O + aq = MgSO_4 \cdot aq - 3\,8 \text{ Cal.}$$

Calculate the heat of hydration of anhydrous magnesium sulphate.

7. The heat of formation of Al_2O_3 is 380 Cal. In the reaction

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe$$

the reduction of every 53.2 g of Fe_2O_3 is accompanied by the evolution of 60.5 Cal. Calculate the heat of formation of ferric oxide.

8. The reaction of the burning of benzene obeys the equation:

$$C_6H_6 + \frac{15}{2} O_2 = 6CO_2 + 3H_2O_{liq} + 782.3 \text{ Cal.}$$

Calculate its heat of formation from its constituent elements, knowing the heat of formation values for CO_2 and H_2O_{liq} (see Question 4).

9. The heat of formation values for H_2O_{vap} and CO_2 are known (see Questions 2 and 4); the heat of combustion of C_2H_2, with the formation of water vapour, is 300.2 Cal. Calculate the heat of formation of C_2H_2.

10. Calculate the heat of combustion of C_2H_6, knowing that its heat of formation is +20.24 Cal. and knowing the heat of formation values for water and CO_2 (see Question 4).

LABORATORY WORK

Apparatus and materials: sand bath with a thermometer up to 250°; porcelain crucible; crucible tongs; desiccator with sulphuric acid; calorimeter with cover; funnel and stirrer for calorimeter; 100 ml measuring cylinder; Dewar vacuum flask (or 50 ml beaker with heat-insulating jacket); Assman thermometer; glass stirring rod; powdered cupric sulphate; 0.5 M NaOH, and 0.5 M HCl.

Note. The Assman thermometer is used to measure the temperature of the air in determinations of air humidity by means of a psychrometer. It is graduated from —20° to +50°, with divisions of 0.1° (sometimes 0.2°).

Making the heat-insulating jacket. A heat-insulating jacket for a beaker is made from asbestos sheet that should first be soaked in water. The beaker is wrapped in the wet asbestos, wound with wire, and then dried.

1. Determining the Water of Crystallisation in Cupric Sulphate. The purpose of the experiment is to determine the number of molecules of water in the cupric sulphate molecule $CuSO_4 \cdot nH_2O$. To do so, it is necessary to heat a weighed amount of the hydrate, thereby expelling all the water of crystallisation and obtaining the anhydrous salt. The difference in weights is the weight of the expelled water, from which it is not difficult to derive the number of water molecules.

Weigh a clean, previously ignited crucible to 0.01 g. Put 1-1.2 g of finely ground cupric sulphate in it and weigh it again. The difference in weights gives the weight of the substance.

Now place the crucible (weighed with the sulphate) on a sand bath, so that $\frac{3}{4}$ of the crucible is submerged in the sand. Place a thermometer into the sand, so that its tip is level with the bottom of the crucible (Fig. 36).

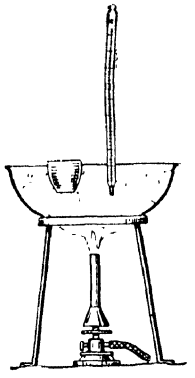


Fig. 36. Heating on a sand bath

Heat the sand bath to a temperature not higher than 220°, since at a higher temperature an undesirable side reaction may take place, with the formation of a basic salt (grey-coloured):

$$2CuSO_4 \cdot nH_2O = Cu_2(OH)_2SO_4 + SO_3 + (n - 1)H_2O$$

With the vaporisation of the water, the blue powder becomes pale; when the salt in the crucible turns white, the heating should be discontinued and the hot crucible put in a desiccator for cooling and then weighed (w_1). Afterwards the crucible should be placed on the sand bath again, heated for 10-15 minutes, and, after cooling, weighed again (w_2). If the weights w_1 and w_2 coincide or differ by not more than 0.01 g, i. e., if the crucible with the substance has been brought to a constant weight, ignition should be stopped. Otherwise the whole operation should be repeated. Record the experimental data (giving the weight after each ignition):

1. Weight of crucible with $CuSO_4 \cdot nH_2O$
   Weight of empty crucible . . . . . .
   Weight of $CuSO_4 \cdot nH_2O$ . . . . . .

2. Weight of crucible with $CuSO_4$ . . . .
   Weight of empty crucible . . . . . .
   Weight of $CuSO_4$. . . . . .

From the experimental data, calculate the number of water molecules in a molecule of cupric sulphate.

2. Determining the Heat of Neutralisation. Measure 100 ml of 0.5 M HCl in a cylinder and pour it into a beaker. Pour 100 ml of NaOH of the same concentration into another beaker. Place the beaker with the acid in a calorimeter (thick-walled battery jar) and cover it with a lid that has three orifices. Insert an accurate thermometer (with divisions of 0.1°) into the middle orifice, lowering it into the acid solution. Pass a funnel and a stirrer through the other orifices. After 10 minutes measure the temperature of the acid solution. Then quickly pour the alkali solution through the funnel and, while stirring the solution continuously, note the highest temperature of the solution to 0.1°.

Record the experimental data in the following manner:

HCl		NaOH		Temperature in °C	
concentration	volume in ml	concentration	volume in ml	initial	final

With the data obtained, carry out the following calculations:

(1) On the basis of the initial and the final temperature, as well as the over-all volume of the solution, calculate the quantity of heat in Cal. evolved in the course of the reaction (assume the relative density of the solution to be equal to 1, and the thermal capacity of the solution, equal to that of water).

(2) Write the equation for the reaction of neutralisation that takes place and calculate the thermal effect of the neutralisation of 1 gram-equivalent of the acid.

(3) Determine the relative error of the experiment, knowing that 13.7 Cal.is evolved when 1 gram-equivalent of a strong acid is neutralised by an equal amount of a strong alkali.

3. Determining the Heat of Solution of an Anhydrous Salt. Pour 25 ml of distilled water into a Dewar vacuum flask or into a beaker with a heat-insulating jacket. Place an Assman thermometer into the vessel (1 cm above its bottom), fixing the thermometer in position by a clamp attached to a ringstand. Note the temperature of the water to 0.1°. Now quickly transfer into the water the anhydrous cupric sulphate obtained in the first experiment and, while stirring the water, note the maximum temperature of the solution to 0.1°.

Since we know the temperature difference, the over-all mass of the solution (equal to the weight of the salt and the water), and the specific heat of the solution (which we assume to be equal to 1), we can calculate the amount of heat evolved in this process (the hydra-

tion of the anhydrous salt and its solution). This amount of heat can then be referred to one mol of the anhydrous salt.

Next, on the basis of Hess's Law, calculate the thermal effect of the reaction

$$1.\ CuSO_4 + aq = CuSO_4 \cdot aq + Q$$

it being known that the hydration of the anhydrous salt and the solution of the pentahydrate are expressed by the following thermochemical equations:

$$2.\ CuSO_4 + 5H_2O = CuSO_4 \cdot 5H_2O + 18.6\ Cal.$$
$$CuSO_4 \cdot 5H_2O + aq = CuSO_4 \cdot aq - 2.75\ Cal.$$

Compare the experimental and theoretical thermal effects and determine the relative error of the experiment in per cent.

Exercise 9

REACTION RATES AND CHEMICAL EQUILIBRIUM

SUBJECTS FOR STUDY

The rate of a chemical reaction and the effect of concentration and temperature on it; irreversible and reversible reactions; concentration and active mass; Law of Mass Action; chemical equilibrium constant; shifting of chemical equilibrium under the influence of various factors;

Le Chatelier's Principle; the rate of heterogeneous reactions and the effect of the solid phase surface; catalysis.

1. The Rate of Chemical Reactions. Substances interact chemically in the gaseous or the liquid state when their molecules collide.

The number of effective collisions depends upon the active mass of the substance, which is proportional to the total number of molecules per unit volume, or the *molecular (molar) concentration of the substance*, expressed in number of mols per unit volume (1 litre). With a change in volume, there is a change in concentration. The volume itself depends upon the pressure (in the case of gaseous substances) or upon the dilution of the solution. But even at equal concentrations different reactions may proceed at different rates, these depending upon the chemical nature of the reactants.

The rate of chemical reactions depends upon the nature of the interacting substances and is proportional to the product of their molecular concentrations.

When two substances, A and B, interact, the rate of the reaction (v) may be calculated by means of the equation

$$v = K[A] \cdot [B]$$

where K is the rate constant of the reaction, depending upon the nature of the interacting substances and upon the conditions in which the reaction takes place (temperature and pressure), while [A] and [B] are the molar concentrations of the substances. If $[A]=[B]=1$, K is numerically equal to the rate of the reaction. *The rate of a reaction is measured by the change in molar concentration per unit time (in a second or minute).*

Example. One litre of 2M acetic acid is mixed with one litre of 3M ethyl alcohol. Determine the rate of the reaction of the formation of the ester, ethyl acetate, at the initial moment. How will the initial rate change, if the solutions are each diluted by an equal volume of water before mixing?

The total volume of the mixture of the solutions is 2 lit.

The molar concentrations are: $[CH_3COOH]=1$ and $[C_2H_5OH]=1.5$.

The rate of the reaction is calculated according to the equation

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

$$v = K\cdot[CH_3COOH]\cdot[C_2H_5OH] = 1.5K$$

When the solutions are diluted, the total volume of the mixture becomes 4 lit. The molar concentrations will, accordingly, be:

$$[CH_3COOH] = 0.5 \quad \text{and} \quad [C_2H_5OH] = 0.75$$

$$v = K\cdot 0.5\cdot 0.75 = 0.375K$$

Consequently, when the solution is diluted by an equal volume of water, the reaction rate drops to $\frac{1}{4}$.

If two substances react in such a way that for every m molecules of the substance A there are n molecules of the substance B (where m and n are integers greater than 1), the reaction rate for the interaction $mA + nB$ will be:

$$v = K\,[A]^m\cdot[B]^n$$

In other words, the exponent of the concentration in the equation of the reaction rate is equal to the coefficient for that substance in the equation of the chemical reaction.

Example. How will the rate of the reaction $2H_2S + O_2$ change if the pressure is increased threefold?

If we denote $[H_2S]$ at the initial pressure as C_1 and $[O_2]$ as C_2, the reaction rate v can be expressed by the equation: $v = K\cdot C_1^2\cdot C_2$.

If the pressure is now trebled, the concentration of the reacting gases will increase accordingly: $[H_2S]=3C_1$ and $[O_2]=3C_2$. The reaction rate under the new conditions will be:

$$v = K\cdot(3C_1)^2\cdot 3C_2 = 27\cdot K\cdot C_1^2\cdot C_2$$

The reaction rate, hence, increases 27 times.

5. The Law of Mass Action. All chemical reactions can be divided into two types: irreversible and reversible reactions. Reactions proceeding in both opposite directions at the same time are called *re-*

versible, while those which proceed practically to the end in one direction are called *irreversible*. The number of irreversible reactions is limited; most reactions are in practice reversible.

A general equation for reversible reactions may be written as follows:

$$mA + nB \rightleftarrows pC + qD$$

The rates for the forward process ($\vec{v}_1$) and the back process ($\overleftarrow{v}_2$) are expressed by the respective equations:

$$v_1 = K' [A]^m \cdot [B]^n$$

$$v_2 = K'' [C]^p \cdot [D]^q$$

where [A], [B], [C], and [D] are the molar concentrations of the substances.

When equilibrium is established, the forward and back reactions do not cease; they continue in opposite directions at equal rates.

If $v_1 = v_2$, the right-hand parts of the above equations are likewise equal, i. e.:

$$K' [A]^m \cdot [B]^n = K'' [C]^p [D]^q$$

The Law of Mass Action may be formulated thus: *When equilibrium is attained, the product of the active masses of the reactants by the velocity constant of the forward reaction equals the product of the active masses of the resultants by the velocity constant of the back reaction.*

From the previous equation it follows that

$$\frac{K'}{K''} = \frac{[C]^p \cdot [D]^q}{[A]^m \cdot [B]^n}$$

The ratio of two constants is a constant; hence

$$K = \frac{[C]^p \cdot [D]^q}{[A]^m \cdot [B]^n}$$

The *chemical equilibrium constant* K is the ratio of the product of the molar concentrations of the resultants to the product of the molar concentrations of the reactants at the moment when equilibrium is attained.

In deriving the equilibrium constant, it is customary to have the product of the concentrations of the resultants as the numerator. For instance, for the reversible reaction

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$$

the equation for the equilibrium constant should be written as follows:

$$K = \frac{[H_2O]^2 \cdot [Cl_2]^2}{[HCl]^4 \cdot [O_2]}$$

If in such a system which has attained equilibrium, we were to increase the concentration of HCl, there would have to be either an increase in the numerator or a decrease of the second factor in the denominator, i. e., the quantity $[O_2]$. This could take place through a shift of the equilibrium from left to right, leading to the formation of additional quantities of H_2O and Cl_2. In the new steady state of equilibrium reached, the concentrations of all four substances will be different from the initial values, whereas the value of K will not have changed.

Consequently, to shift the equilibrium from left to right, it is necessary either to increase the concentration of one of the substances which appear to the left of the reversibility sign ($\rightleftarrows$) in the equation of the reaction or to reduce the concentration of one of the substances which appear to the right of that sign.

By means of the equation for the equilibrium constant, it is possible to determine the concentrations of substances at equilibrium, knowing the value of K and the initial concentrations, or vice versa.

If the initial concentration of substance A is denoted as $[A]_{intt}$, while the number of mols of this substance that has reacted by the time of equilibrium is denoted $[A]_{reac}$, the molar concentration at the moment of equilibrium $[A]_{eq}$ may be expressed as

$$[A]_{eq} = [A]_{intt} - [A]_{reac}$$

Example. For the system

$$CO + H_2O \rightleftarrows H_2 + CO_2$$

in equilibrium, $K = 1.0$ at 830°. Determine the concentrations of all the substances at equilibrium, knowing that the initial concentrations $[CO] = 2M$ and $[H_2O] = 3M$.

The equation for the equilibrium constant may be written thus:

$$\frac{[H_2] \cdot [CO_2]}{[CO] \cdot [H_2O]} = 1.0$$

The following table should now be drawn up:

	CO	H_2O	CO_2	H_2
Initial concentrations	2	3	—	—
Mols that have reacted	x	x	—	—
Mols formed	—	—	x	x
Concentration at equilibrium	$2-x$	$3-x$	x	x

In that case

$$\frac{x^2}{(2-x)(3-x)} = 1.0$$

From this it follows that

$$5x = 6 \quad \text{and} \quad x = \frac{6}{5} = 1.2$$

Consequently, at equilibrium:

$$[CO] = 2-1.2 = 0.8M$$
$$[H_2O] = 3-1.2 = 1.8M$$
$$[H_2] = [CO_2] = 1.2M$$

In the above example the coefficients of all the substances involved in the reaction are equal to 1, and determining the concentrations at equilibrium is therefore not difficult.

On the other hand, in the system

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$$

which is likewise in equilibrium, the coefficients are not equal to 1, and they must be taken into consideration in determining the molar concentrations at equilibrium. If x mols of HCl have reacted by the time equilibrium is attained, the number of mols of O_2 to react will have been $\frac{1}{4}$ of that amount, i. e., $\frac{x}{4}$, while the number of mols of H_2O and Cl_2 formed by that moment will be half the amount of mols of HCl, i. e., $\frac{x}{2}$.

3. Reaction Rates in Heterogeneous Systems. The relationships considered above apply only to homogeneous systems.

A *system* in chemistry is a part of space filled with a substance or mixture of substances and isolated from the surrounding medium. The parts of a system which have throughout the same physical properties, a uniform chemical composition, and an interface are termed *phases*.

Mixtures of gases, liquid water, and solutions are all examples of *homogeneous systems* (the number of phases is 1).

Heterogeneous systems are those which consist of several phases, e. g.:

water—ice—water vapour (the number of phases is 3);

water—oxygen—hydrogen (the number of phases is 2);

magnesium carbonate—magnesium oxide—carbon dioxide (the number of phases is 3).

The laws which govern reactions proceedeng in homogeneous systems do not apply in full to heterogeneous systems. For instance, in the heterogeneous system *gas—solid* the molecules of the gas can collide with the molecules of the solid only at the interface; hence, the concentration of the solid as a whole (the mass of the solid phase) has no effect on the reaction rate. When ferrous oxide is reduced by hydrogen

$$FeO + H_2 \xrightarrow{v} Fe + H_2O$$

the rate of the forward reaction is proportional only to the concentration of the hydrogen, i. e., $v = K'[H_2]$.

For a system in equilibrium such as

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O_{vap}$$

the equation for the equilibrium constant should be written thus:

$$\frac{[Fe]^3 \cdot [H_2O]^4}{[Fe_3O_4] \cdot [H_2]^4} = K_1$$

But since the concentrations of the solid phases $[Fe_3O_4]$ and [Fe] are constants, we can transfer them to the right-hand side of the equation and combine them with the constant K_1. This gives rise to a new constant, K:

$$\frac{[H_2O]^4}{[H_2]^4} = K_1 \cdot \frac{[Fe_3O_4]}{[Fe]^3} = K$$

The final equation for the equilibrium constant may therefore be written thus:

$$\frac{[H_2O]^4}{[H_2]^4} = K$$

In a heterogeneous system the reaction takes place at the interface; the reaction rate therefore increases with the *surface area of contact*. This is why solids react much more quickly in the pulverised state.

4. Effect of Temperature on Reaction Rate. Any rise in temperature speeds the reaction, as the absorption of energy increases the number of active molecules and the velocity of molecular movement; the number of molecules colliding per unit time therefore increases. Every 10° temperature increase just about doubles the reaction rate. In some cases, however, the reaction rate increases even more (e. g., 3-4 times).

If a temperature rise of 10° increases the reaction rate twofold* and if we denote the reaction rate at the ultimate temperature as v_{t_2} and the reaction rate at the initial temperature as v_{t_1}, the relationship between the rates may be expressed thus:

$$v_{t_2} = v_{t_1} \cdot 2^{\frac{t_2 - t_1}{10}}$$

Example. How much will the reaction rate increase as a result of a temperature rise from 10 to 100°, if every 10° increment doubles the rate?

$$v_{100^\circ} = v_{10^\circ} \cdot 2^{\frac{100-10}{10}} = v_{10^\circ} \cdot 2^9 = v_{10^\circ} \cdot 512$$

The rate thus increases 512 times.

* The number indicating how many times the reaction rate increases with a 10° rise in temperature is called the *temperature coefficient of the reaction.*

5. Shifting of Chemical Equilibrium. The direction in which the *equilibrium of a system shifts* whenever concentration, temperature, or pressure changes is determined by Le Chatelier's Principle. *If a reversible system in a state of mobile equilibrium is subjected to some external influence, the equilibrium shifts in such a way that the influence is reduced.*

Let us consider the following system at equilibrium:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 2 \cdot 11 \text{ Cal.}$$

In what direction will the equilibrium of the system be shifted if the pressure is increased and the temperature lowered?

The volume of the initial gases $N_2 + 3H_2$ is double the volume of the product $2NH_3$. The system will therefore react to an increase in pressure by an equilibrium shift towards the smaller gas volume.

The formation of ammonia is accompanied by the evolution of heat ($+ 2 \cdot 11$ Cal.), while the reverse process (ammonia decomposition) proceeds with the absorption of heat ($-2 \cdot 11$ Cal.). Consequently, the system will react to a drop in temperature by an equilibrium shift from left to right in the direction of the exothermic process, i. e., the evolution of heat.

Exercise. How does a rise in temperature and pressure affect the equilibrium of the following systems:

$$2N_2 + O_2 \rightleftarrows 2N_2O - 2 \cdot 19{,}65 \text{ Cal.}$$

$$H_2 + Br_2 \rightleftarrows 2HBr + 2 \cdot 8{,}65 \text{ Cal.}$$

$$2C + O_2 \rightleftarrows 2CO + 2 \cdot 26{,}42 \text{ Cal.}$$

6. Catalysis. *Catalysis* is a change in the speed of a chemical process under the influence of a foreign substance present in the reaction system, the composition and amount of the foreign substance remaining unchanged at the end of the reaction. Solid, liquid, and gaseous substances may alter the speed of a chemical process, i. e., act as catalysts.

In *homogeneous catalysis* the reactants and the catalyst constitute a one-phase system (e. g., the interaction of the gases NH_3 and HCl in the presence of H_2O vapours).

In *heterogeneous catalysis* the reactants and the catalyst form a two-phase system (e. g., the ignition of a mixture of oxygen and hydrogen on the surface of platinum black, a solid).

A catalyst does not initiate a chemical process; it has the *same effect* on the rate of both the forward reaction and the back reaction, thereby hastening the establishment of equilibrium in the system without, however, affecting that equilibrium in any way.

In heterogeneous catalysis relatively large amounts of reactants may react in the presence of small amounts of the catalyst. In homogeneous

catalysis the rate of the reaction is practically proportional to the amount of the catalyst.

The activity of catalysts and sometimes the specific character of their effect depend markedly upon temperature.

QUESTIONS

1. How will the rate of a reaction change with concentration? The concentrations of reactants *A* and *B* are given in the following table, together with the reaction time:

Concentration of substance *A* in mols/l	1	1	1	1
Concentration of substance *B* in mols/l	1	0.66	0.50	0.33
Reaction time in seconds	18	27	36	54

Plot a chart of the reaction rate as ordinate against the concentration as abscissa. What type of a line is the function? Should it pass through the origin of the coordinates?

2. Write the equations for the rates of the forward reactions:

$$2H_2 + O_2 \rightarrow \qquad 4NH_3 + 5O_2 \rightarrow \qquad 2Mg + O_2 \rightarrow$$

3. Give examples of homogeneous and heterogeneous systems. In what way do they differ?

4. Given the reversible system $CO_2 + H_2 \rightleftarrows H_2O + CO$. Will there be an identical shift of equilibrium in two such systems under the same conditions if 100 g of water vapour is added to one system, while 100 g of carbon monoxide is added to the other?

5. Considering the state of the substances in the system, write equations for the equilibrium constants of the following reactions:

$$CuO + H_2 \rightleftarrows H_2O + Cu$$

$$CaCO_3 \rightleftarrows CaO + CO_2$$

6. Under what conditions should the reaction

$$N_2 + O_2 \rightleftarrows 2NO - 43.06 \text{ Cal.}$$

be conducted to obtain a maximum yield of nitrogen oxide? (Apply Le Chatelier's Principle).

Problems

1. The equilibrium constant for the reaction $CO + Cl_2 \rightleftarrows COCl_2$ equals 39.4. If at equilibrium $[CO]=0.2$ and $[COCl_2]=0.8$ M, calculate the initial quantity $[Cl_2]$.
2. The equilibrium constant of the system $CO + H_2O \rightleftarrows H_2 + CO_2$ at a certain temperature is equal to 1. If the initial concentrations $[CO] = 1$ and $[H_2O] = 3$, what will be the concentrations of all the substances at equilibrium?
3. At 250° the equilibrium constant of the system $PCl_5 \rightleftarrows PCl_3 + Cl_2$ equals 0.0414. How many mols of PCl_5 were placed in a 1 litre vessel at that temperature, if the value of $[Cl_2]$ turned out to be 0.1 M?
4. The concentrations at equilibrium in the system $2N_2 + O_2 \rightleftarrows 2N_2O$ were found to be $[N_2]=0.72$, $[O_2]=1.12$, and $[N_2O]=0.84$. Determine the equilibrium constant.
5. The equilibrium constant of the system $H_2 + I_2 \rightleftarrows 2HI$ equals 40. How many mols of hydrogen have to be introduced into the system per mol of iodine to ensure that 60% of the iodine be converted to HI (at a constant volume of the system)?
6. Calculate the equilibrium constant of the system $N_2O_4 \rightleftarrows 2NO_2$ if the initial concentration of $N_2O_4=0.02$ and the dissociation at equilibrium is 60%.
7. Find the equilibrium constant of the system $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$ if at equilibrium $[H_2O]=[Cl_2]=0.14$, $[HCl]=0.2$, and $[O_2]=0.32$
8. The equilibrium constant of the system $H_2 + I_2 \rightleftarrows 2HI$ at 443° equals 50. At equilibrium the concentration of HI proved equal to 0.0315 mols/l, while the concentration of I_2 proved equal to 0.0114 mols/l. Calculate the hydrogen concentration at equilibrium.
9. Equilibrium in the reaction of acetic acid with ethyl alcohol is expressed by the equation:

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

How many mols of the ester are there in the system at equilibrium, if the equilibrium constant equals 4, and the initial concentrations of the alcohol and the acetic acid are 5 M and 2 M respectively.
10. One millimol of a substance reacts in 1 minute at 80°. How many millimols will react during the same time, if the temperature is raised first to 120° and then to 180° (the temperature coefficient of the reaction equals 2)?

LABORATORY WORK

Apparatus and materials: the set-up shown in Fig. 37; porcelain mortar; 250-400 ml beaker; 50 ml beaker; 3 burettes; 3 burette funnels; test tubes and rack; horn or glass spatula; thermometer up to 100°; metronome; stop watch; 25 ml measuring cylinder; splinters; 10×10 cm squared paper; filter paper; wax pencil; manganese dioxide in powdered form; 1:9 powdered mixture of manganese dioxide and ferric oxide; powdered ferric oxide; powdered silica; crystalline potassium chloride; potassium iodide; lead nitrate; chalk in lumps; ferric chloride saturated solution; potassium thiocyanate saturated solution; 2N HCl; 3% and 0.2% solutions of hydrogen peroxide; sodium thiosulphate solution containing 75 g of $Na_2S_2O_3$ per litre, and sulphuric acid solution (15 ml of H_2SO_4, relative density 1.84, per litre).

1. Reaction Rate in Homogeneous Systems. In the reaction between sulphuric acid and sodium thiosulphate

$$\text{(a)}\ Na_2S_2O_3 + H_2SO_4 = H_2S_2O_3 + Na_2SO_4$$
$$\text{(b)}\ H_2S_2O_3 = H_2O + SO_2 + S$$

the insoluble sulphur is precipitated in the form of slime. The time elapsing from the beginning of the reaction to the appearance of the

first traces of slime depends upon the concentration of the reactants and the temperature.

Fill three burettes with water, a solution of sodium thiosulphate, and a solution of sulphuric acid respectively. Fill four numbered test tubes with the number of millilitres of thiosulphate solution and water indicated in the table below. Pour 6 ml of sulphuric acid solution from a burette into each of four other test tubes.

Now pour the measured quantity of sulphuric acid into test tube No. 1, stir its contents quickly, and count the number of metronome beats from the moment when the liquids were combined until any slime appears. The reaction rate is inversely proportional to this period of time ($v = \frac{1}{T}$).

No. of test tube	Volume in ml		$Na_2S_2O_3$ concentration $\frac{a}{a+b}$	Time (No. of metronome beats) t	Reaction rate $v = \frac{1}{t}$
	$Na_2S_2O_3$ solution a	H_2O b			
1	6	0	1		
2	4	2	2/3		
3	3	3	1/2		
4	2	4	1/3		

Perform similar experiments with all the other test tubes. Draw a chart (this can be done conveniently on squared paper), plotting the concentration as abscissa against the reaction rate as ordinate *. A suitable scale is 3 cm for the minimum concentration and 8 cm for the maximum rate.

What kind of a line is the function?

Does it run through the origin of the coordinates? If so, why?

2. Effect of Temperature on Reaction Rate. Pour 4 ml of sodium thiosulphate solution from a burette into each of four clean numbered test tubes (1, 2, 3, 4) and pour 4 ml of sulphuric acid solution into each of four others (1*a*, 2*a*, 3*a*, 4*a*). Place all the test tubes into a beaker with water; five minutes later, after measuring the temperature of the water, combine the contents of test tubes 1 and 1*a*; count the number of metronome beats until any slime appears (do not forget to stir the solutions first).

Heat the beaker with the test tubes 10° above the original temperature and repeat the experiment, this time with test tubes 2 and 2*a*. Carry out similar experiments with the other test tubes, each time raising the temperature by another 10°.

* It is advisable to express v in decimals to hundredths and then multiply by 100.

Record the experimental results in the form of a table:

No. of test tube	Temperature of experiment in °C	Time (No. of metronome beats) t_1	Reaction rate $v = \frac{1}{t_1}$

Show the effect of temperature on the reaction rate by means of a chart, plotting the temperature as abscissa. A suitable scale is 2 cm for 10° and 8 cm for the maximum reaction rate.

What effect has temperature on the rate of the reaction studied?

Does the *rate—temperature* curve pass through the origin of the coordinates?

3. Chemical Equilibrium. A classic reversible reaction is that between ferric chloride and potassium or ammonium thiocyanate. The resulting solution of ferric thiocyanate $Fe(SCN)_3$ exhibits a red colouration whose intensity depends upon concentration. A shift of equilibrium is therefore easily detected by the changed intensity of the colour.

Pour 20 ml of water into a beaker and add 1-2 drops of saturated solutions of $FeCl_3$ and KSCN. Pour equal portions of the resulting red solution into four test tubes.

Write the equation of the reversible reaction and the equation of the equilibrium constant.

Add 2-3 drops of the saturated solution of $FeCl_3$ to the contents of one of the test tubes. Write up your observations and explain what has happened on the basis of the equation for the equilibrium constant.

Add 2-3 drops of the saturated solution of KSCN to the contents of another test tube. Explain the change observed. Why does a change in the concentration of KSCN cause a more pronounced shift of equilibrium than does a change in the concentration of $FeCl_3$?

Drop a small piece of solid potassium chloride into the third test tube and shake it vigorously. Compare the colours of the solutions in test tubes 3 and 4. Give an explanation.

What changes in concentration are required to shift the equilibrium to the right or to the left?

4. Reaction Rate in Heterogeneous Systems.

(a) Pour hydrochloric acid into two test tubes, filling $^1/_4$ of each. Take two lumps of chalk of equal size, grind one of them to a powder in a mortar, and transfer the powder to a sheet of paper. Then pour the powder into one test tube and, simultaneously, drop the lump of

chalk into another. In which of the test tubes does the reaction proceed faster? Why?

(b) Mix a few crystals of lead nitrate and potassium iodide in a mortar gently without grinding them with a pestle. Is there any change of colour?

Then grind the crystals vigorously with a pestle and note how the powdered mixture acquires a yellowish tinge. Write the equation of the observed process. Add a few drops of water by means of a dropping glass: the mixture instantly acquires a bright yellow colour. Explain the whole experiment.

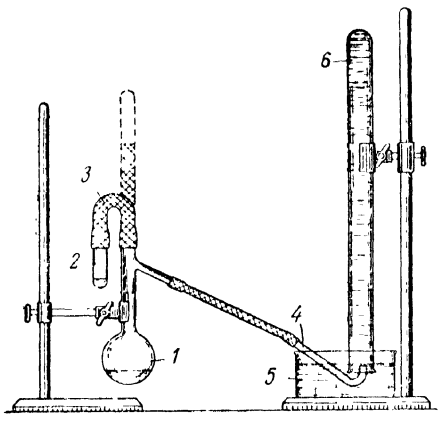


Fig. 37. Apparatus for hydrogen peroxide decomposition

1 — flask with side arm; 2 — test tube; 3 — rubber tubing; 4 — gas-delivery tube; 5 — vessel; 6 — eudiometer.

5. Effect of Catalysts on Reaction Rate. Pour 3 ml of a hydrogen peroxide solution into each of three test tubes. Add a pinch of manganese dioxide to one, an equal amount of ferric oxide to the second, and of silica to the third, all simultaneously. Observe the decomposition of the hydrogen peroxide with the evolution of oxygen (glowing splinter test). Does the process proceed at the same rate in each case? Write the equation of the reaction.

6. The Kinetics of the Catalytic Decomposition of Hydrogen Peroxide. The experiment is conducted in the set-up shown in Fig. 37. It consists of a flask (1), a small test tube (2), rubber tubing (3), a delivery tube (4), a vessel (5), and a eudiometer (6).

Fill the eudiometer with water and lower it into the vessel with water. Place the end of the delivery tube from the flask under it. Pour 40 ml of 0.2% hydrogen peroxide, measured in a measuring cylinder, into the flask, dry the interior of its neck with rolled up filter paper, and attach the rubber tubing to the neck.

Weigh 0.10-0.12 g of the powdered mixture of manganese dioxide and ferric oxide in a test tube. Connect the test tube with the rubber tubing. Then lift the test tube into a vertical position (as shown by the broken line in the figure); start the stop-watch as soon as the first bubble of oxygen emerges from the delivery tube. Note the volume of oxygen displaced at the end of every minute; conduct the experiment for 10 minutes. Then repeat it.

Plot the results of the experiment in the form of a curve representing the rate of the decomposition of the hydrogen peroxide as a func-

tion of time. In doing so, plot the time as abscissa (1 min. = 1 cm) and the volume of oxygen displaced every minute as ordinate (1 ml of oxygen = 1 cm).

Describe how the process proceeded during the interval of time in which it was observed.

Record the results of the experiment as follows:

	Time	1 min	2 min	3 min	.....	10 min
Total volume of O_2 in ml	Exper. 1					
	Exper. 2					
Volume of O_2 in ml for every minute	Exper. 1					
	Exper. 2					
	Average figures					

Exercise 10

PREPARATION OF SOLUTIONS

SUBJECTS FOR STUDY

The concentration of a solution and various ways of expressing it; percentage, molar, molal, and normal concentrations; titres; calculations in converting one type of concentration to another; the preparation of a solution according to a weighed amount and by diluting a concentrated solution.

The concentration of solutions is in most cases expressed by the amount of the solute by weight in a definite weight or volume of the solution or the solvent. More specifically, concentration is usually expressed in one of the following ways: as percentage concentration (%), as molar concentration (M), as molal concentration (*m*), or as normal concentration (N). In addition to this, the concentration of a solution may be expressed in terms of its titre (T). Percentage and molar concentrations were defined in Exercise 2. The molal concentration indicates how many mols of the solute are dissolved in 1,000 g of the solvent. The normal concentration is the number of gram-equivalents of the solute in 1 litre of the solution. Finally, the titre is the number of grams of the solute in 1 ml of the solution.

Since the percentage and the molal concentration involve weights of the solution, while the molar and the normal concentration, as well as the titre, involve volumes, a conversion of one type of concentration to another requires a knowledge of the relative density of the solution.

Example. Determine the molar concentration, the normal concentration, and the titre of a 40% solution of sulphuric acid with a relative density of 1.307.

First of all, find the amount of sulphuric acid contained in 1 litre of the solution (x).

One litre of the solution weighs $1{,}000 \cdot 1.307 = 1{,}307$ g. We can then set up the proportion:

$$100 - 40$$
$$1{,}307 - x$$

Hence.

$$x = \frac{1{,}307 \cdot 40}{100} = 522.8 \text{ g}$$

The titre of the solution is not difficult to determine: $T = \frac{522.8}{1{,}000} = 0.5228$. Since we know that the molecular weight of sulphuric acid is 98 and its equivalent is $\frac{98}{2} = 49$, we are able to determine the molar concentration $M = \frac{522.8}{98} = 5.33$ and the normal concentration $N = \frac{522.8}{49} = 10.66$.

It is evident from the above example that such a conversion involves first turning the known concentration into the amount of the solute and then turning that into the concentration sought.

Very common calculations are those connected with diluting solutions.

Example. What volumes of a 44% solution of KOH (relative density 1.46) and water should be mixed to prepare 80 lit of a 12% solution with a relative density o 1.10?

First, determine the amount of anhydrous KOH that the required solution should contain. The relative density of the solution is 1.10; the required amount, 80 lit. Its weight will therefore be $80 \cdot 1.10 = 88$ kg. From the required concentration we derive the weight of the anhydrous KOH needed to prepare the solution:

100 kg contains 12 kg of KOH

88 kg " x " " "

$$x = \frac{88 \cdot 12}{100} = 10.56 \text{ kg of KOH}$$

We then find what amount of the initial solution contains this quantity of the alkali:

44 kg of KOH is contained in 100 kg of the solution

10.56 " " " " " x " " " "

$$x = \frac{10.56 \cdot 100}{44} = 24 \text{ kg}$$

Since the relative density of the initial solution is known, it is not difficult to determine its volume:

$$v = \frac{24}{1.46} = 16.4 \text{ lit}$$

We now determine the volume of the water: $80 - 16.4 = 63.6$ lit.
Answer. We must take 16.4 lit of 44% KOH and 63.6 lit of water.

When weighed quantities (a, b) of several solutions of the same substance, with different percentage concentrations (A%, B%), are mixed, the concentration (x%) of the substance in the mixture is calculated by means of the formula:

$$a \cdot A + b \cdot B = (a + b) \cdot x$$

The formula is derived as follows. Let a grams of the solution of concentration A% be mixed with b grams of the solution of concentration B%. The weight of the resulting mixture will be $a + b$, while its concentration will be x%. In the first solution the quantity of the solid (100%) substance is $\frac{a \cdot A}{100}$, while in the second it is $\frac{B \cdot b}{100}$, in the mixture it will be $\frac{(a+b) \cdot x}{100}$. We may therefore write the sum:

$$\frac{a \cdot A}{100} + \frac{b \cdot B}{100} = \frac{(a + b) \cdot x}{100}$$

When we eliminate the common denominator, this yields the formula given above.

Example. Twenty kg of a 6% solution of sodium chloride is mixed with 12 kg of a 14% solution of the same salt. Find the concentration of the salt in the mixture.
Substitute the data given into the formula:

$$20 \cdot 6 + 12 \cdot 14 = (20 + 12) \cdot x$$

This yields

$$x = \frac{20 \cdot 6 + 12 \cdot 14}{20 + 12} = \frac{288}{32} = 9$$

The concentration of the salt in the mixture is 9%.

When given volumes of solutions are mixed, these should first be converted to weights by means of the relative densities; this makes it possible to use the same formula for the rest of the calculations.

In engineering the concentration of solutions is sometimes expressed in degrees Baumé. In the Baumé scale 0° corresponds to the relative density of water, while 10° corresponds to the specific gravity of a 10% solution of NaCl. Tables for converting degrees Baumé to relative density may be found on p.332. The following formulae may also be used for such conversion.

For liquids heavier than water the formulae are:

$$\gamma = \frac{144.3}{144.3 - Bé°} \quad \text{and} \quad Bé° = 144.3 - \frac{144.3}{\gamma}$$

For liquids lighter than water the formulae are:

$$\gamma = \frac{144.3}{144.3 + Bé°} \quad \text{and} \quad Bé° = \frac{144.3}{\gamma} - 144\,3$$

QUESTIONS

1. Define the concentration of a solution.
2. For what substances do the values of the molar and normal concentrations coincide?
3. Find the gram-equivalents of the following substances:

$$Pb(NO_3)_2 \qquad H_3PO_4 \qquad Cr_2(SO_4)_3 \cdot 18H_2O$$

4. The relative density of a solution is 1.184. Determine the concentration in degrees Baumé according to the formula and by means of the table (p. 332).
5. Derive the formula for finding the molal concentration of a solution from the molar concentration. Use the designations: *m* for molal concentration, M for molar concentration, *v* for the volume of the solution, γ for the relative density, and G for gram-molecule.

Problems

1. Eighteen litres of a 48% solution of sulphuric acid with a relative density of 1.38 is mixed with 2 litres of a 20% solution of the acid with a relative density of 1.143. Determine the percentage and the molar concentration of the resulting solution.
2. What weights of potassium hydroxide and water should be taken to prepare 75 lit of a 12% solution with a relative density of 1.1? Determine the titre of such a solution.
3. Determine the titre and percentage concentration of a 3 N solution of H_3PO_4 if its relative density is 1.055.
4. The titre of a nitric acid solution is 0.122; its relative density is 1.064. Determine its percentage and its normal concentration.
5. One litre of a solution contains 112 g of lead nitrate $Pb(NO_3)_2$; the relative density of the solution is 1.082. Determine the percentage, molar, and normal concentrations of the solution and its titre.
6. What volumes of water and of a 25% solution of ammonia (relative density 0.91) should be taken to prepare 1 litre of a 10% solution with a relative density of 0.96?
7. How many mols of ammonia are contained in 1 litre of a 12.74% solution of it with a relative density of 0.95?
8. Determine the percentage and the molar concentration of a nitric acid solution prepared by mixing 85 lit of a 60% solution (relative density 1.373) and 25 lit of a 24% solution (relative density 1.145).
9. Determine the concentration of a sulphuric acid solution, knowing that 4 kg of that solution, when mixed with 16 kg of a 40% solution of the same acid, produced 20 kg of a 36% solution.
10. Determine the titre and the normal concentration of a 25% solution of sodium nitrate with a relative density of 1.185.

LABORATORY WORK

Apparatus and materials: a 100 and a 250 ml measuring cylinder; 300 ml narrow cylinder for measuring relative density; 500 ml flat- bottom flask; hydrometer (for relative densities 1-1.4); glass stirrer (30 cm long glass tube with a bulb about 3 cm in diameter at the end); saturated solution of potassium sulphate; crystalline magnesium sulphate; 22.5 and 7.5% solutions of sodium chloride.

1. Preparation of a Solution from a Concentrated Solution and Water. Receive an individual assignment from the instructor: for example, to prepare 250 ml of a solution of K_2SO_4 with a relative density of 1.025 from the laboratory solution.

To carry out the assignment it is necessary to establish the percentage concentrations of the required solution and the available one.

In a reference book find the percentage concentration of the required solution on the basis of the given relative density (1.025). Determine the relative density of the laboratory solution by means of a hydrometer to ± 0.003 and note the temperature at which the measurement was made. In the reference book find the percentage concentration corresponding to that relative density. If the value recorded by the hydrometer is not given in the book, find the required concentration by the method of interpolation (explained in Exercise 2).

Now that all the data needed for the calculation are available determine the volumes of the laboratory solution and water that have to be mixed to give 250 ml of the required solution. To do this, first find the weight of the substance needed to obtain the required solution; then determine the weight of the laboratory solution containing the required amount of the substance; finally, knowing the relative density of the solution, determine its volume. The difference between the volume required and that found for the laboratory solution gives us the volume of the water.

When the calculation is finished, measure off the calculated amounts of the laboratory solution and water, pour them into a high cylinder, mix them thoroughly with a stirrer (tube with ball), and measure the relative density with a hydrometer.

Then wash the hydrometer with clean water, wipe it dry, and put it away. Pour the prepared solution into a special carboy. Establish (in per cent) the discrepancy between the calculated relative density and the experimental value. A considerable discrepancy points to an error either in calculations or in the experiment.

2. Preparation of a Solution from Two Solutions of Different Concentration. Receive an individual assignment from the instructor: for example, to prepare 250 ml of a 9 4% solution of NaCl from a 7.5% solution and a 22.5% solution of the same salt.

In the appropriate reference tables find the relative density values for all three solutions and calculate the volumes of the 7.5 and 22.5% solutions necessary to prepare the required solution. Measure off the

calculated amounts of the solutions, pour them together, mix them thoroughly, and determine the relative density of the prepared solution. Establish the discrepancy between the calculated and measured relative densities.

3. Preparation of a Solution from a Weighed Amount of a Solid Substance and Water. Receive an individual assignment from the instructor: for example, to prepare 250 ml of a 6.5% solution of $MgSO_4$.

To carry out the assignment, first calculate how much solid salt this is, considering that the salt crystallises with 7 molecules of water.

Weigh the calculated amount of salt, transfer it into a beaker, and dissolve it in half the required water (stir). When the salt dissolves, pour it into a cylinder, add water to bring the volume up to 250 ml, and mix the solution thoroughly. Determine the relative density of the solution by means of a hydrometer and establish the discrepancy between this value and that in the reference book.

Exercise 11

SOLUBILITY OF SUBSTANCES

SUBJECTS FOR STUDY

Solutions; processes that take place when a substance dissolves; crystallisation, the reverse process; saturated and supersaturated solutions; solubility and the solubility coefficient; solubility curves, and thermal effects of solution.

There is a limit to the ability of a solid substance to dissolve in a certain quantity of a solvent at certain conditions (temperature and pressure). An excess of the solid creates a saturated solution, i. e., a system consisting of two components in which there is mobile equilibrium between the liquid phase (the solution) and the solid phase (the solute).

The concentration of a saturated solution at given conditions is constant for every substance and is called its *solubility*. Solubility is usually expressed by the number of parts by weight of the anhydrous substance saturating 100 similar parts by weight of the solvent at given conditions. In some books the number indicating the solubility of a substance is termed the *solubility coefficient*.

Not infrequently solubility is expressed in percentages, i. e., by the number of parts by weight of the solute in 100 parts by weight of the saturated solution.

In practice the solubility of liquid and solid substances depends upon temperature, since their volume is not affected appreciably by pressure. This dependence can be expressed graphically in the form of a solubility curve (Fig. 38) by plotting the temperature as abscissa against the solubility as ordinate.

A solubility curve is a graphic representation of the solubility of a substance at different temperatures; it can be used for the calculations involved in purifying solids by the process of *recrystallisation*.

Example. It is required to recrystallise 1 kg of cupric sulphate (in terms of the anhydrous salt). Calculate the amount of water in which it should be dissolved and the yield of recrystallised salt if the cupric sulphate is dissolved at 100° and the solution then cooled to 15°.

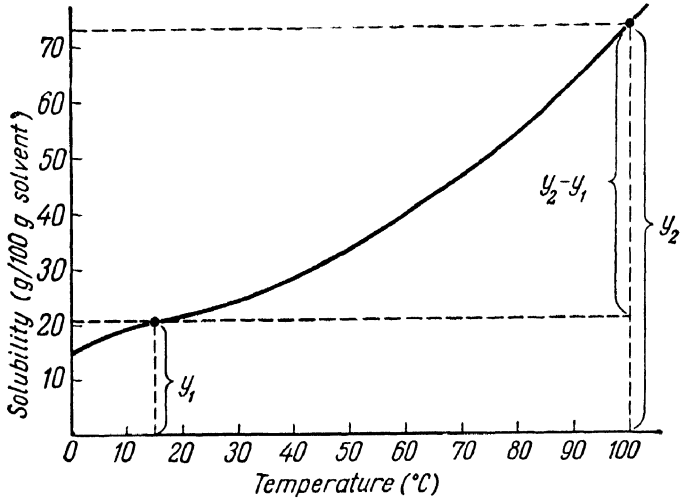


Fig. 38. Blue vitriol solubility curve

On the chart (Fig. 38) find the solubility of the salt at 100° and at 15°.

The solubility in 100 g of water at 100° is given by the ordinate $y_2 = 73.6$; the solubility at 15°, by the ordinate $y_1 = 20.5$.

Since dissolving 73.6 g of the anhydrous salt at 100° requires 100 g of water, to dissolve 1,000 g of the salt, we shall need x g of water:

$$x = \frac{100 \cdot 1{,}000}{73.6} = 1{,}359 \text{ g}$$

When the solution saturated at 100° is cooled to 15°, the number of grams of the salt precipitated will be equal to the difference between the ordinates on the chart:

$$y_2 - y_1 = 73.6 - 20.5 = 53.1$$

Since the cooling of a solution prepared from 73.6 g of the salt yields 53.1 g of the solid salt, the cooling of a solution prepared from 1,000 g of the salt will yield x grams (in terms of the anhydrous salt):

$$x = \frac{53.1 \cdot 1{,}000}{73.6} = 722 \text{ g}$$

The yield of the recrystallised salt will therefore be 72.2%.

Substances whose solubility is reduced by cooling can be crystallised by lowering the temperature of a saturated solution (recrystalli-

sation). Slow cooling causes the substance to form large crystals, while rapid cooling produces small crystals. The smaller crystals are a purer product with fewer impurities, since the growth of larger crystals is accompanied by the inclusion of minute quantities of the mother-liquid containing admixtures of foreign matter. A chemically pure substance is obtained by conducting recrystallisation (sometimes repeatedly) at a drastically reduced temperature of the solution with vigorous stirring *. Saturation is in most cases achieved at the temperature at which the solvent boils; ice, snow, or cold water is used for cooling solutions.

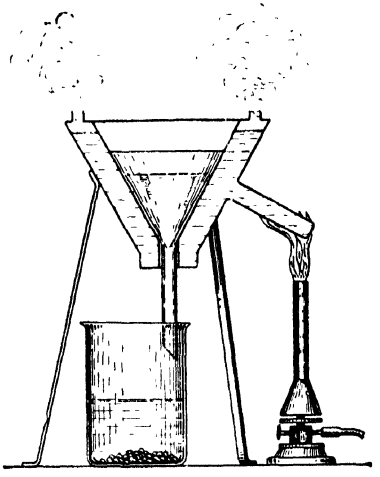


Fig. 39. Hot-water funnel

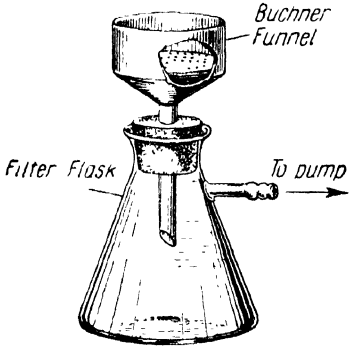


Fig. 40. Suction filter

An aqueous solution saturated at 100° often has to be filtered to remove various mechanical impurities (dust, turbidity, etc.). This is accomplished by means of a special hot-water funnel. If the filtering were done by the ordinary procedure, the drastic cooling of the solution in the funnel would cause crystallisation of the substance and hence clogging up of the filter pores; this would reduce the speed of filtration and, more important still, would result in partial loss of the substance.

A hot-water funnel (Fig. 39) is usually made of a copper alloy. It has double walls and a side arm (the latter is unnecessary in the event of electric heating). The space between the walls is filled with water through the inlet at the top. The side arm is heated by a burner. An

* Substances whose solubility rises with cooling, such as Li_2CO_3, $Ca(CH_3COO)_2$, and $Sr(CH_3COO)_2$, are recrystallised by the reverse procedure: a solution is saturated with such a substance at the lowest possible temperature and is then heated to boiling. The crystals formed are filtered off from the boiling solution.

ordinary glass funnel with a short stem and a plain paper filter is placed inside the hot-water funnel.

After the glass funnel has been warmed (this should take 10-15 minutes), 5-6 ml of boiling distilled water is poured into the filter and allowed to pass through it. A clean beaker is then placed under the filter, and the hot solution is poured into the filter. The beaker with the filtrate, in which some crystals have formed on account of cooling, is heated until they dissolve and then placed in a cooling medium (snow, ice, or cold water) and stirred vigorously; small crystals are precipitated.

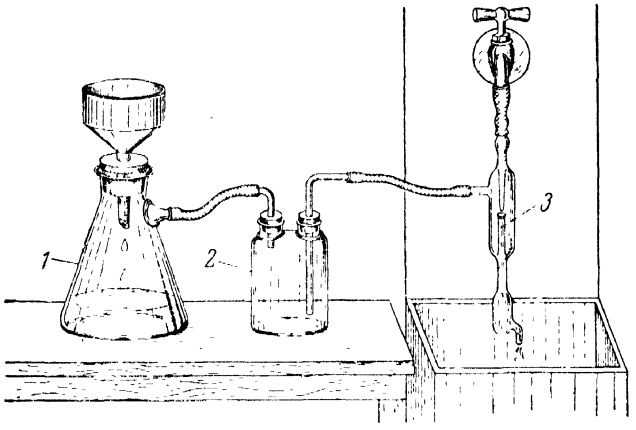


Fig. 41. Filtration with the application of suction

1 — flask with porcelain funnel for filtration; 2 — safety flask; 3 — filter pump.

The recrystallised substance is separated from the mother-liquid by filtration with the application of suction. This is necessary because ordinary filtration leaves a great deal of mother-liquid on the surface of the crystals (which contaminates the product with impurities) and they require prolonged drying.

The porcelain funnel used for this purpose and known as a Büchner funnel (Fig. 40) has a perforated bottom. Two pieces of filter paper are placed over the funnel, and its upper rim is traced on the paper by the blunt end of a pair of scissors. Two circular filters are then cut out: the first coinciding exactly with the traced circle, the second having a diameter 3-4 mm smaller. The smaller filter is put into the funnel first. When both filters are in the funnel, they should be moistened with water and their edges pressed tight to the rim with a finger so that there are no cracks. The stopper supporting the funnel is then fitted into a filter flask (Fig. 40), and this, through a safety flask, is connected to a suction pump (Fig. 41). Suction is applied, and the solution with the crystals is transferred from the beaker to the filter.

Suction should be continued until the dripping of the solution from the funnel ceases *. The remaining small quantity of the solution can be removed by pressing the material retained on the filter with a clean glass stopper (without discontinuing suction). When filtration is complete, the filter flask should first be disconnected from the safety flask; only then should suction be discontinued.

QUESTIONS

1. How will the solubility of $Na_2SO_4 \cdot 10H_2O$ be affected by a change of temperature? Why does the solubility curve of this compound have a point of inflection and what does it designate?
2. Three flasks contain a saturated, a supersaturated, and an unsaturated solution of the same substance respectively. How are we to determine which flask contains which solution?
3. Why does the solubility of most solids increase with a rise in temperature?
4. Plot a solubility curve on the basis of the solubility data for $CaSO_4$(see table on p. 329). Why is calcium sulphate listed among anomalously dissolving substances?
5. Plot a solubility curve for $Pb(NO_3)_2$ on the basis of the following data:

Temperature (in °C) . . .	10	20	30	50	60	70
Solubility	44.5	52.2	60.8	78.6	88.0	97.6

Determine the substance's solubility at 37°.
6. Who was the first scientist to study crystallisation processes?

Problems

1. The solubility of a salt at 80° is 64.7, while at 17° it is 13.8. What quantities of the solid salt and of water ought to be taken to obtain 1 kg of the salt, if it is recrystallised from a solution saturated at 80° and cooled to 17°?
2. A salt whose molecular weight is 168 forms a saturated solution at 18° that has a concentration of 3.4 M. If the relative density of the solution is 1.22, what is the solubility of the substance and the percentage concentration of the solution?
3. The solubility of K_2SO_4 at 40° is 13.1%. Determine the molar and the normal concentration of a solution saturated at 40°, if its relative density is 1.092.
4. A solution saturated at 100° is cooled to 14°, yielding 112 g of crystallised salt. How much water and how much salt were taken for the recrystallisation, if the solubility of the salt at 100° is 52.7, while at 14° it is 7.9?
5. Twenty millilitres of a saturated solution of ammonium sulphate weighs 20.94 g and contains 3.24 g of $(NH_4)_2SO_4$. Determine the solubility of the salt and the percentage, molar, and normal concentrations of the solution.
6. A salt has a solubility of 48.6 at 100° and of 16.4 at 20°. Recrystallisation, with cooling in that temperature range, yields 0.5 kg of recrystallised substance. What amounts of water and salt were taken for recrystallisation?

* If the filtrate is not required for subsequent work, there is no need for a safety flask.

7. It is known that 42.34 g of a solution contains 7.28 g of the solute. Determine the solubility of the solute and the percentage concentration of the solution.

8. Twenty kilograms of a salt solution saturated at 60° was cooled with snow. What amount of recrystallised salt was recovered if the solubility of the salt at 60° is 110, while at 0° it is 13.1? Calculate the yield in per cent.

9. A 9.92% saturated solution of K_2SO_4 has a relative density of 1.082. Determine the solubility of K_2SO_4 and the titre of the solution.

10. The percentage solubility of $K_2Cr_2O_7$ at 100° is 50.5, while at 10° it is 7.5. What amounts of $K_2Cr_2O_7$ and water should be taken to obtain 215 g of the pure salt recrystallised in the above temperature range?

LABORATORY WORK

Apparatus and materials: drying cabinet; hot-water funnel; Büchner funnel for filtration with the application of suction; desiccator; test tubes and rack; porcelain mortar; porcelain casserole 7 cm in diameter; 100 ml measuring cylinder; 500 ml beaker with stirrer; four 50 ml beakers; thermometer up to 100°; glass rod; scissors; 10 × 12 cm squared paper; filter paper; crystalline potassium bichromate; crystalline sodium thiosulphate; crystalline sodium acetate; crystalline cupric sulphate; 0.5 N solution of potassium iodide; 0.5 N solution of lead nitrate, and some salt whose solubility is to be determined (KCl, KNO_3, K_2SO_4, $K_2Cr_2O_7$, $Ba(NO_3)_2$, etc.).

1. Determining Solubility. This exercise should be carried out by a group of students, each determining the solubility at some one temperature. The individual assignments should be given by the instructor.

Weigh a porcelain casserole to 0.01 g.

Pour 10 ml of water into a small beaker, add 1-2 g of a finely ground salt, place the beaker into a wire ring, and lower it into a large beaker with water (Fig. 42). Heat or cool the large beaker to the required temperature and then adjust the flame of the burner so that the temperature of the water in the beaker remains constant.

If, after a certain time, all of the substance has dissolved, another portion is added, and so on until part of the solid salt remains undissolved. All this time the solution should be stirred and the temperature watched. The saturation of the solution, at a constant temperature, should be continued for 20-25 minutes.

Then remove the thermometer and the stirrer from the beaker. Allow the undissolved solute in the saturated solution to settle and quickly transfer the liquid to a weighed casserole, leaving the crystals in the beaker. Weigh the casserole with the solution.

Now place the casserole on a ring with wire gauze and heat it until all the water has been evaporated. Towards the end, conduct the evaporation over as small a flame as possible to avoid any splashing of the solution and consequent loss of the substance. Then place the casserole for 20-25 minutes into a drying cabinet (Fig. 43) heated to 115°.

Cool the casserole with the dry residue in a desiccator and weigh it. Repeat the drying of the residue and the weighing of the casserole (do this until the results tally!).

From the data of the experiment determine the weight of the solution that the casserole contained and then the weight of the dry salt

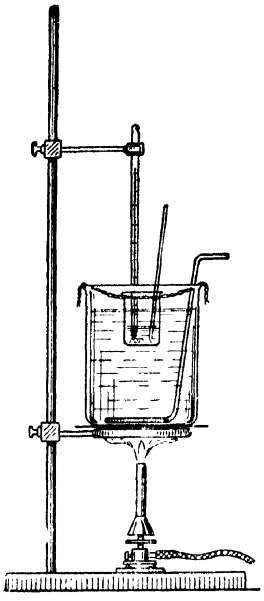


Fig. 42. Preparation of saturated solution

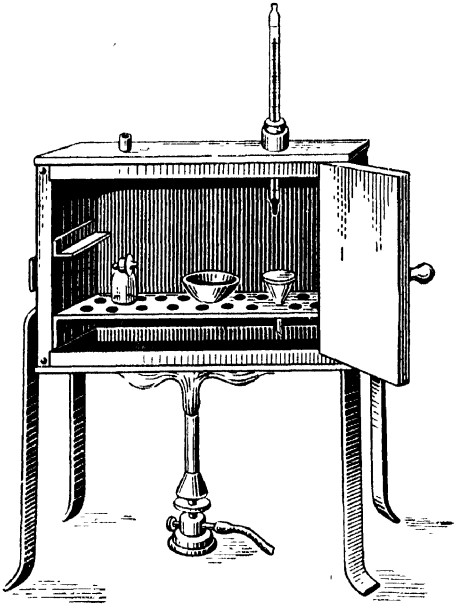


Fig. 43. Drying cabinet with gas heating

in it. Calculate the solubility coefficient and the percentage concentration of the solution.

Substance			Temperature		
Weight of casserole (in g)			Weight (in g) of		
with solution	with dry salt	empty	solution	dry salt	water

On the basis of the experiments carried out by all the students of the group, plot a solubility curve on squared paper, as shown in Fig. 44.

The broken line in Fig. 44 is an incorrectly plotted solubility curve; the solid line is the correctly plotted curve. It is evident from

the diagram that the experimental determinations of points *A*, *B*, and *C* were carried out with errors.

2. Purifying a Salt by Recrystallisation. Receive an individual assignment from the instructor: for instance, to prepare 5 g of recrystallised potassium bichromate in fine crystals.

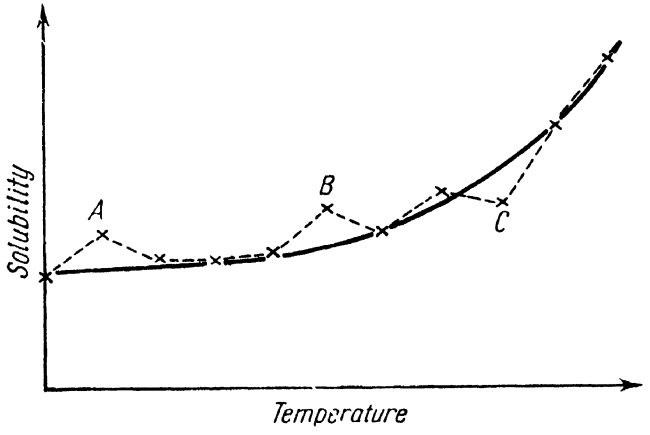


Fig. 44. Experimental solubility curve

Choose the temperature range for the proposed recrystallisation. On the basis of the initial and final temperatures, using the solubility table at the end of the book, calculate the amounts of the salt and water that should be taken to prepare the required amount of the recrystallised product.

Pour the calculated amount of water into a beaker. Weigh the required amount of the salt and pour it into the beaker with the water. Prepare a hot-water funnel for use. Heat the beaker with the water and salt on wire gauze with an asbestos centre until the water begins boiling and then pour it quickly into the filter in the funnel.

Heat the filtered solution, in which crystals have appeared with cooling, until the crystals dissolve; then cool the beaker, using snow or water from the tap. The solution should be stirred. The crystals formed should be removed by filtration with the application of suction, transferred from the funnel to filter paper, pressed in it to remove moisture, and then dried in the air for 20 minutes, with occasional stirring by a glass rod. Drying may be considered complete when the small crystals no longer cling to a dry glass rod.

Weigh the crystals and calculate the yield in per cent.

3. Preparing a Supersaturated Solution. (a) Pour 1 ml of water into a dry test tube containing 5-6 g of powdered sodium thiosulphate. Heat the contents of the test tube carefully until the entire salt dissolves by lowering the test tube into a beaker with hot water. Make

sure that there are no small crystals of the salt on the test tube wall. Close the test tube with some cotton wool and cool the solution slowly to room temperature.

Open the test tube and introduce a tiny crystal of the same salt (a "seed crystal") into it; this initiates crystallisation in the supersaturated solution. Hold the test tube in your hand and note that the solution grows warmer during crystallisation. Why is the precipitation of the solid phase from a supersaturated solution attended by the evolution of heat? Pour the solution with the crystals into a special bottle.

(b) Conduct a similar experiment with sodium acetate. Write up the experiment.

List the substances you know that can be used to prepare supersaturated solutions.

4. Effect of Surface Area on Rate of Solution. Pour 10 ml of distilled water into each of two small beakers. Weigh two 1 g amounts of cupric sulphate in large crystals. Grind one of the portions of cupric sulphate in a mortar to a fine powder. Transfer both portions into the beakers with water and observe the time (in minutes) which elapses before each portion dissolves completely.

Which crystals dissolve faster and why?

5. Effect of Temperature on Crystal Growth. Add 1 ml of a potassium iodide solution to an equal volume of a lead nitrate solution; this produces a yellow precipitate. Add 10 ml of water to the precipitate and heat until it boils. If the precipitate does not dissolve fully, add more water and continue the boiling. Pour the colourless solution into two test tubes, heat them to boiling point, and then place one into a rack for slow crystallisation, while the other is cooled with water. When the solutions have both cooled to room temperature, compare the size of the crystals. How should a saturated solution be cooled when it is desirable to obtain small crystals?

Exercise 12

SOLUTIONS OF FLUIDS

SUBJECTS FOR STUDY

Liquid-liquid systems with unlimited and limited solubility; critical solution temperature; solubility of gases; absorption coefficient; Henry's Law and Dalton's Law; solubility of gas mixture; partial pressures; thermal effect of the solution of gases and changes in their solubility with temperature.

Liquid-liquid systems can be divided into three groups:

(1) systems with an unlimited miscibility of the two components at ordinary conditions (e. g., *alcohol—water*);

(2) systems with a limited miscibility of the two components, which changes with temperature and at a definite temperature becomes unlimited (e. g., *phenol* *—*water*);

(3) systems with a limited miscibility of the two components, which at no temperature (pressure remaining ordinary) becomes unlimited (e.g., CCl_4—H_2O).

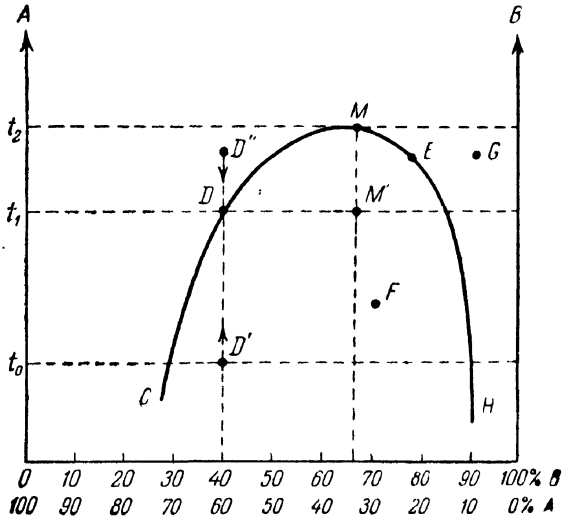


Fig. 45. Composition-property diagram for *phenol* (A) — *water* (B) system

Systems of the latter two types are heterogeneous: they are characterised by an interface separating the phases. When a system of the second type, with a definite content of the components, is heated, the interface will at a certain temperature disappear. This happens when complete miscibility is achieved. Should the proportion of the components be altered, miscibility is observed at a different temperature. The temperature above which the system is homogeneous whatever the proportion of the components is called the *critical solution temperature.*

When such a solution is cooled below a definite temperature, it breaks into phases and becomes heterogeneous again. If we prepare several solutions with differing contents of the two components by weight, a definite temperature of miscibility can be established for each solution. For the system *phenol—water* the miscibility temperatures at first, with a rise in phenol concentration, mount, but after

* In the presence of small amounts of water, phenol melts at room temperature.

a certain peak they begin to decline. If we plot the percentage composition of such systems as abscissa against the miscibility temperature as ordinate, we obtain a *composition-property* diagram (Fig. 45).

Let us take a solution (its temperature t_0 and 60% content of component A and 40% content of component B are designated on the diagram by point D') that is a heterogeneous system and start heating it (this is represented by the movement of point D' upwards along the broken line). Until the temperature reaches t_1 the system remains heterogeneous (with two phases). When the temperature t_1 is reached (point D), complete miscibility sets in and the system becomes homogeneous. At any point above D (such as D'') the system is homogeneous, but if it is cooled (movement from D'' downwards along the broken line), it will separate into two phases and become heterogeneous as soon as point D is reached. Point D is thus both the miscibility and the immiscibility temperature. Since the curve CMG is the geometric locus of points similar to D, it may be called the miscibility or immiscibility curve. The region above the curve is that of homogeneous solutions, while the region below the curve is that of the existence of the two-phase system. Thus, the system corresponding to the point M' on the isotherm t_1 will be heterogeneous. A special point on the curve is point M: at the temperature t_2 corresponding to this point the system is completely miscible irrespective of the concentration of the components (critical solution temperature). For the *phenol—water* system the critical solution temperature is 68.4°.

Gases dissolve in liquids with a considerable diminution of volume and evolution of heat. The thermal effects observed when some gases dissolve in water are given in Table 4.

Table 4

Heat of Solution of Some Gases in Water

Gas	Number of gram-mols of water per 1 mol of gas	Heat of solution (in Cal./mol)	Gas	Number of gram-mols of water per 1 mol of gas	Heat of solution (in Cal./mol)
H_2S	900	4.6	HF	200	11.56
Cl_2	1,000	4.9	NO_2	300	14.1
CO_2	1,700	5.88	HCl	400	17.47
SO_2	250	7.5	HBr	400	19.9
NH_3	200	8.35	HI	500	19.2

If a gas dissolves exothermically, while its generation from a solution is endothermic, then in a system such as

$$H_2S + H_2O \text{ (solvent)} \rightleftarrows \text{solution} + 4.6 \text{ Cal.}$$

a rise in temperature will, in accordance with Le Chatelier's Principle, cause equilibrium to shift in the direction of the endothermic process, i. e., in the direction of the evolution of gas from the solution. Consequently, *the solubility of a gas diminishes with a rise in temperature.*

The amount of gas that dissolves in a liquid also depends upon pressure. Under Henry's Law, *the amount of a gas (by weight) that dissolves in a liquid is directly proportional to the pressure of the gas.*

The solubility of a gas is expressed by the absorption coefficient; this is the number of volumes of a gas, reduced to N. T. P., that dissolve in a single volume of the solvent (Table 5).

Table 5

Coefficients for Absorption of Several Gases by Water at 0° C

Gas	Absorption coefficient	Gas	Absorption coefficient
Hydrogen	0.021	Chlorine	4.61
Nitrogen	0.023	Hydrogen sulphide	4.70
Oxygen	0.049	Sulphur dioxide	79.8
Methane	0.056	Hydrogen chloride	506.5
Carbon dioxide	1.713	Ammonia	1,176

When a mixture of gases is dissolved, *each gas,* in accordance with Dalton's Law, *dissolves in proportion to the share of the pressure it accounts for.* If we denote the pressure of the gas mixture as P_m and the pressures of the individual gases comprising the mixture as P_x, P_y, and P_z, we may write

$$P_m = P_x + P_y + P_z$$

The partial pressures of the gases (see p. 27) depend upon the content by volume of the gases in the mixture.

Example. Suppose there is a mixture consisting of 40% of oxygen and 60% of methane at a pressure of 1 atm. In what proportion (by volume) will these gases dissolve in water?

The partial pressures of oxygen and methane will be 0.4 and 0.6 atm respectively. Since the absorption coefficient for O_2 is 0.049 and for methane 0.056, their solubilities at their partial pressures are $0.049 \cdot 0.4 = 0.0196$ and $0.056 \cdot 0.6 = 0.0336$. The ratio of the volumes in the solution will be 0.0196:0.0336=1:1.71, whereas in the initial mixture it is 40:60=1:1.5.

Henry's Law and Dalton's Law are valid for gases of low solubility.

QUESTIONS

1. How many components and phases do the following systems have:

(a) $CaCO_3 \rightleftarrows CaO + CO_2$ (b) NH_3 + water $\rightleftarrows$ NH_3 solution

(c) $NaCl_{solid}$ + NaCl solution (d) kerosene + water

2. By referring to Fig. 45 describe the state of the system at points *E*, *F*, and *H*.

3. In the laboratory ammonia is often prepared by heating its 25% solution in water. Give a theoretical explanation of this method of preparing ammonia.

4. When a mixture of gases is dissolved, does the composition of the dissolved gases (by volume) depend upon the pressure of the mixture?

5. Why do bubbles of gas appear when a bottle of mineral or soda water is opened? When does the evolution of gas cease?

Problems

(for absorption coefficients see Table 5)

1. How many grams of carbon dioxide will dissolve in 1 cu m of water at 0° and 6 atm?

2. How much carbon dioxide (by weight) will be evolved at 15° from 0.5 litre of an aqueous solution if the pressure is changed from 3 to 1 atm? The absorption coefficient of CO_2 at 15° is 1.02.

3. How much ammonia (by volume) will be obtained if we boil an aqueous solution of it prepared by saturating 800 ml of water with gaseous ammonia at N.T.P. After boiling the solution has been found by analysis to have an 0.2 M concentration.

4. From the absorption coefficient of hydrogen determine the weight of the hydrogen that dissolves in 5 cu m of water at 0°.

5. A mixture of gases consisting of 52% by volume of CO and 48% of CO_2 is at a pressure of 1 atm washed in ice-cold water. Calculate the volumes (in litres) of both gases dissolved in 1 cu m of water and the percentage composition (by volume) of the gas mixture dissolved in the water. The absorption coefficient of CO is 0.035.

6. From the absorption coefficients of nitrogen, oxygen, and methane calculate the amounts by weight of each of them that dissolve in 1 cu m of ice-cold water at a pressure of 10 atm.

7. The absorption coefficient of acetylene in water at 20° is 1.03. while in a saturated solution of sodium chloride it is 0.05. How much acetylene by weight will dissolve in 100 lit of water and in 100 lit of the salt solution if the pressure is 12 atm?

8. Calculate the solubility of the gases in volume percentages from their mixture consisting of 33.3% of O_2, 42.4% of N_2, and 24.3% of CH_4. The total pressure of the mixture is 1 atm.

9. Solutions of hydrogen sulphide and sulphur dioxide have been saturated at 0°. What volumes of these solutions reacted if the reaction following the equation

$$2H_2S + SO_2 = 2H_2O + 3S$$

yielded 96 g of sulphur?

10. The reaction

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

has consumed 43.45 g of MnO_2. The chlorine generated is dissolved in water to prepare a solution saturated at 0°. What amount of water will this require?

LABORATORY WORK

Apparatus and materials: round flask with stopper and two tubes, as shown in Fig. 47; 1 litre beaker with stirrer; large crystalliser; 25 ml measuring cylinder; 20 ml calibrated test tube; set of test tubes with phenol solutions; thermometer up to 100°; spring or screw clips; rubber tubing 5 mm in diameter, and squared paper.

Note. The phenol used to prepare the solutions should be either colourless or faintly pink. Dark phenol should be distilled.To prepare the solutions pour the necessary amount of water into a flask and add the weighed quantity of phenol; the amounts should be calculated on the basis of the required concentration and the number of people working in the laboratory. Heat the flask until it contains a homogeneous solution; then increase the temperature by 10° and pour the solution into test tubes. If the solution in the flask becomes cloudy during the pouring, it should be heated again. The test tubes should be stoppered up with corks and numbered.

1. Determining the Critical Solution Temperature for Phenol in Water. The arrangement for determining the critical solution temperature (Fig. 46) consists of a large beaker heated by a burner and containing a glass stirrer and a thermometer up to 100° attached to the ringstand and lowered 5-6 cm below the level of the water in the beaker. The exercise also calls for a rack with numbered test tubes containing solutions of phenol in water with known proportions of the components by weight (see table).

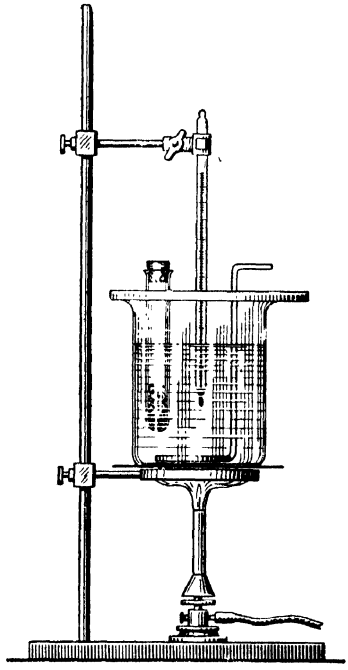


Fig. 46. Apparatus for studying phenol — water system

Place test tube No. 1 in the beaker with water and heat it over a small flame. From time to time shake the test tube vigorously without removing it from the beaker (take care not to break the beaker or the test tube!); every now and then also stir the water in the beaker with the stirrer. Note the temperature at which the milk-like solution suddenly becomes transparent (miscibility). Remove the burner from under the beaker. The water in the beaker now begins to cool, and at a certain temperature the solution in the test tube becomes cloudy (separates into phases). Note this temperature. The difference between the miscibility temperature and the immiscibility temperature should not exceed 1°. If it does, the experiment should be repeated.

Now lower test tube No. 7 into the beaker and shake the mixture in the test tube vigorously. If the system remains turbid, heat the

beaker and note the temperature at which the system becomes miscible; then allow the water in the beaker to cool and note the temperature at which the system becomes immiscible. If the system becomes transparent as soon as the test tube is lowered into the beaker and shaken, conduct the experiment in the reverse order: first cool the beaker, recording the immiscibility temperature, and then heat it to find the miscibility temperature.

In the same way conduct experiments with the rest of the solutions, taking the test tubes in the following order: No. 2 and No. 6, No. 3 and No. 5, and finally No. 4. Record the results in the form of the following table:

No. of test tube	Mixture contains				Temperature (in °C)		
	phenol (in g)	water (in g)	phenol (in % by weight)	water (in % by weight)	of miscibility	of immiscibility	mean
1	0.50	4.50					
2	0.85	4.15					
3	1.50	3.50					
4	2.00	3.00					
5	2.50	2.50					
6	3.00	2.00					
7	3.40	1.60					

On the basis of the experimental data plot a solubility diagram on squared paper. Draw an abscissa axis and two ordinate axes: the right-hand axis for pure water and the left-hand axis for pure phenol. A suitable scale for the abscissa is 1 cm = 10%; for the ordinate, 1 cm = = 10°. Plot the points and then connect them by drawing a smooth curve. Determine the coordinates of the peak.

2. Determining the Solubility of Air in Water. Fill a round flask (volume $\approx$ 500 ml), fitted with a cork through which two tubes have been passed (Fig. 47), with water from the tap. Do this by connecting one of the tubes (1) with the tap by means of rubber tubing.

When the water has filled the whole of the flask and the delivery tube (2), close the tube (1) leading to the tap by means of a clip. No bubbles of air should remain either in the flask or in the tube. Submerge the end of the delivery tube in a vessel (3) with water *. Lower the calibrated test tube (4), filled with water, into the vessel and place the end of the delivery tube under it.

After measuring the temperature of the water, place a burner under the gauze and heat the water in the flask to boiling point. Allow it to boil for 15-20 min and then note the level of the water in test

* It is better to fill the vessel and the calibrated test tube with a salt solution.

tube 4. Discontinue the heating, measure the volume occupied by air in the test tube and the volume of the flask with the delivery tube.

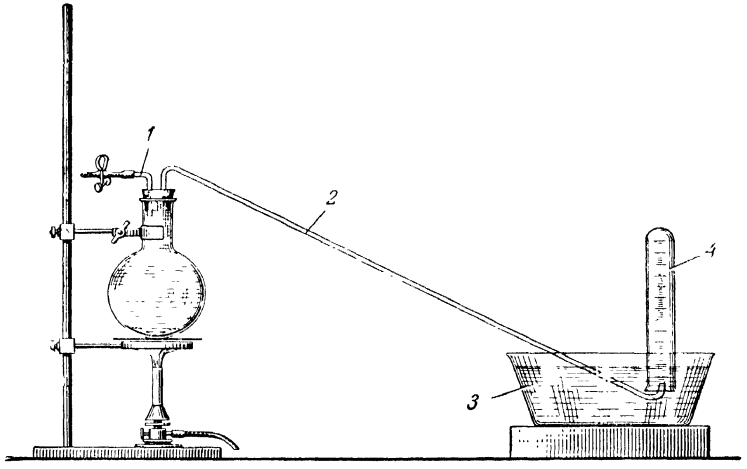


Fig. 47. Apparatus for determining the solubility of air in water

1— water-supply tube with clip; 2 — gas-delivery tube; 3 — vessel with water; 4 — calibrated test tube.

With the data of Table 6, the volume of the flask, and the temperature of the water from the tap, calculate the volume of the air that was dissolved in the water.

Table 6

Absorption Coefficient (α) of Air at Various Temperatures

°C	α	°C	α	°C	α
0	0.0292	13	0.0214	17	0.0197
10	0.0228	14	0.0210	18	0.0194
11	0.0223	15	0.0205	19	0.0190
12	0.0219	16	0.0201	20	0.0187

Compare the calculated volume of the air with the experimental value and explain the discrepancy.

Exercise 13

PROPERTIES OF SOLUTIONS

SUBJECTS FOR STUDY

Properties of solutions; osmotic pressure; vapour pressure of pure solvent and of solution; Raoult's Law; changes of the boiling and freezing points of a solution with concentration; cryoscopy and ebullioscopy, and the determination of a substance's molecular weight from the boiling and freezing points of its solutions.

Osmotic Pressure. The osmotic pressure of a solution is due to the presence of the solute particles. Quantitative measurements of the phenomenon made it possible to establish these regularities for *nonelectrolyte* solutions:

(1) Osmotic pressure is independent of the chemical nature of the solute and is directly proportional to its concentration (at a constant temperature).

(2) Osmotic pressure is directly proportional to the absolute temperature.

From the equation

$$P_{osm}V = nRT = \frac{m}{M}RT$$

in which the osmotic pressure of the solution P_{osm} has been substituted for gas pressure, we can determine P_{osm}, the molecular weight, and the other quantities involved.

If, in solving problems according to this formula, the volume is expressed in litres and the pressure in atmospheres, the quantity R has to be assumed equal to 0.082.

Example. Determine the molecular weight of cane sugar if 50 ml of a solution containing 2 g of sugar at 25° exhibits an osmotic pressure of 2.86 atm.

By substituting all the known quantities into the formula, we obtain:

$$M = \frac{2 \cdot 0.082\ (273 + 25)}{0.05 \cdot 2.86} = 341.7 \approx 342$$

The study of the physical properties of *nonelectrolyte* solutions (vapour pressure, boiling point, freezing point) revealed that *the relative lowering of the vapour pressure of a solution is independent of the chemical nature of the solute and is equal to the mol fraction of the solute* (Raoult's Law).

If the vapour pressure of the solvent at one and the same temperature is denoted as p_0 and the vapour pressure of the solution as p (it being stipulated that $p_0 > p$), the relative lowering of the vapour pressure will be $\frac{p_0 - p}{p_0}$. Raoult's Law can then be expressed mathematically thus:

$$\frac{p_0 - p}{p_0} = \frac{n}{n + N} \qquad (I)$$

where n is the number of mols of the solute; N is the number of mols of the solvent, and $\frac{n}{n+N}$ is the ratio of the number of mols of the solute to the total number of mols of the solute and the solvent, or the mol fraction of the solute.

The number of mols may be represented as $n = \frac{m_1}{M_1}$ and $N = \frac{m_2}{M_2}$, where m_1 and m_2 are the quantities by weight of the solute and the solvent, while M_1 and M_2 are their respective molecular weights expressed in grams (gram-molecules).

Substituting these values into formula (I), we obtain

$$\frac{p_0 - p}{p_0} = \frac{\frac{m_1}{M_1}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} \qquad \text{(II)}$$

Formula (II) makes it possible to determine the vapour pressure of the solvent and the solution, the amount of the solvent (m_2) and of the solute (m_1), and the gram-molecules (or molecular weights) of the solute (M_1) and the solvent (M_2).

Example 1. Pure water at 20° has a vapour pressure of 17.5 mm. Determine the vapour pressure of an aqueous solution of urea $CO(NH_2)_2$ at 20°, if 6 g of urea is dissolved in 178.2 g of water.

First it is necessary to determine the number of mols of urea:

$$n = \frac{6}{60} = 0.1$$

Then we determine the number of mols of water:

$$N = \frac{178.2}{18} = 9.9$$

The known quantities are substituted into formula (I):

$$\frac{17.5 - p}{17.5} = \frac{0.1}{0.1 + 9.9} = 0.01$$

Therefore

$$p = 17.5 - 0.175 = 17.325 \text{ mm}$$

Example 2. Determine the molecular weight of a substance if a solution of 1 g of it in 37.8 g of acetone at 30° has a vapour pressure of 275.2 mm. The vapour pressure of pure acetone at 30° is 281 mm.

First we determine the number of mols of the solute and of the acetone:

$$n = \frac{1}{M} \qquad N = \frac{37.8}{58} = 0.65$$

The known quantities are then substituted into formula (II):

$$\frac{281 - 275.2}{281} = \frac{\frac{1}{M}}{\frac{1}{M} + 0.65}$$

Hence

$$4.97M = 275.2 \quad \text{or} \quad M = 55.37$$

The following is a corollary to Raoult's Law: *A depression of the freezing point or elevation of the boiling point of a solution is independent of the chemical nature of the solute and is directly proportional to its molal concentration.*

This relationship is expressed by the formulae:

$$\Delta t_{fr} = K_c m \qquad \text{and} \qquad \Delta t_{boil} = K_e m$$

where m is the molal concentration, and K_c and K_e are proportionality coefficients.

From the above formulae it follows that at $m = 1$ the quantities Δt_{fr} and Δt_{boil} are numerically equal to the respective constants K_c and K_e.

If we take several *nonelectrolytes* and dissolve a gram-molecule of each in 1,000 g of one and the same solvent, the solutions, called *molal*, exhibit an identical depression of the freezing point or elevation of the boiling point. For each solvent the molal depression of the freezing point K_c and elevation of the boiling point K_e are *constants*; they are called the *cryoscopic* and the *ebullioscopic* constant respectively. The values of these constants for variuos solvents are given in Tables X and XI (p. 333).

By means of these constants, it is possible to determine the molecular weights of dissolved substances. Indeed, let a grams of a substance with the unknown molecular weight M be dissolved in b grams of a solvent. It has been established experimentally that the solution boils (or freezes) at a temperature Δt degrees higher (or lower) than the pure solvent does. From the data given it is easy to determine the molal concentration m of the solution, taking into account that the quantity $\frac{a}{M}$ denotes the number of mols of the solute in b grams of the solvent:

$$\frac{a}{M} \text{ ——— } b$$

$$m \text{ ——— } 1{,}000$$

$$m = \frac{a \cdot 1{,}000}{M \cdot b}$$

By substituting this value of m into one of the above formulae, we obtain:

$$\Delta t = \frac{K \cdot a \cdot 1{,}000}{M \cdot b} \qquad \text{or} \qquad M = \frac{K \cdot a \cdot 1{,}000}{b \cdot \Delta t}$$

Example 1. Determine the molecular weight of glucose if a solution containing 1.35 g of it in 100 g of water freezes at —0.139°. The cryoscopic constant of water is 1.86.

$$M = \frac{1.86 \cdot 1{,}000 \cdot 1.35}{100 \cdot 0.139} = 180$$

Example 2. What will be the boiling point of a solution of 3.46 g of urea $CO(NH_2)_2$ in 100 g of water? The ebullioscopic constant of water is 0.52.

$$\Delta t = \frac{K \cdot a \cdot 1{,}000}{M \cdot b} = \frac{0.52 \cdot 3.46 \cdot 1{,}000}{60 \cdot 100} = 0.3$$

The boiling point of the urea solution will be $100 + 0.3 = 100.3°$.

Cryoscopic and ebullioscopic methods provide important means of determining the molecular weights of substances that decompose upon vaporisation (when heated). It should be pointed out, however, that Raoult's Law applies only to dilute solutions of nonelectrolytes.

QUESTIONS

1. Do the concentrations of solutions change with temperature? If so, which and why?
2. How do we call solutions exhibiting the same osmotic pressure?
3. From what law does it follow that the melting point or the crystallisation point of a substance is lowered by the addition of an admixture of another substance?
4. At what concentration does a nonelectrolyte solution have an osmotic pressure of 1 atm?
5. The cryoscopic and ebullioscopic constants of water are 1.86 and 0.52 respectively. What do these figures express?

Problems

(for the values of K_c and K_e see Tables X and XI)

1. The vapour pressure of a solution of 1.8 g of glucose in 179.8 g of water at 29° is 29.97 mm and is 0.03 mm less than the vapour pressure of pure water. Calculate the molecular weight of glucose.
2. What is the freezing point of a solution of 18 g of cane sugar $C_{12}H_{22}O_{11}$ in 200 g of water?
3. A solution of 1.6 g of naphthalene in 40 g of benzene exhibits a boiling point elevation of 0.8°. Calculate the molecular weight of naphthalene.
4. What is the osmotic pressure exhibited at 17° by a solution containing 68.4 g of cane sugar dissolved in 3 litres?
5. Calculate the molecular weight of glucose if a solution of 16.2 g of it in 671 ml at 0° exhibits an osmotic pressure of 3 atm.
6. Aqueous vapour tension at 20° is 17.5 mm. Calculate the vapour pressure of a solution of 18.4 g of glycerol $C_3H_5(OH)_3$ in 176.4 g of water at the same temperature.
7. Determine the formula of a substance containing 94.38% of C and 5.62% of H, knowing that when 4.34 g of this substance is dissolved in 100 g of ethyl alcohol, the boiling point of the solution is 0.29° higher than that of pure alcohol.
8. How many degrees will the freezing point of benzene be depressed if 9.27 g of naphthalene $C_{10}H_8$ is dissolved in 225 g of it?
9. A solution of glucose $C_6H_{12}O_6$ and a solution of cane sugar $C_{12}H_{22}O_{11}$ exhibit the same osmotic pressure. How many grams of sugar are contained in 1 litre of the second solution if 1 litre of the first contains 9 g of glucose?
10. The boiling point of a solution of 1.28 g of sulphur in 50 g of carbon disulphide is 0.23° higher than the boiling point of pure carbon disulphide. Determine the number of atoms in a sulphur molecule.

LABORATORY WORK

Apparatus and materials: the arrangements shown in Fig. 34*D* and Fig. 48; beaker with heat-insulating jacket; 25 ml measuring cylinder; 10 ml pipette; glass rod; Assman thermometer; magnifying lens; weighing bottle or watch glass; crystalline calcium nitrate; commercially pure sodium chloride; weighed amounts of urea; snow or ice, and pumice stone.

The urea should be taken in amounts of about 0.050 g and weighed on an analytical balance to 0.001 g.

1. Determining the Molecular Weight of Urea. The method consists in experimentally determining the freezing points of a pure solvent and of a solution, and then calculating the molecular weight from the depression of the freezing point.

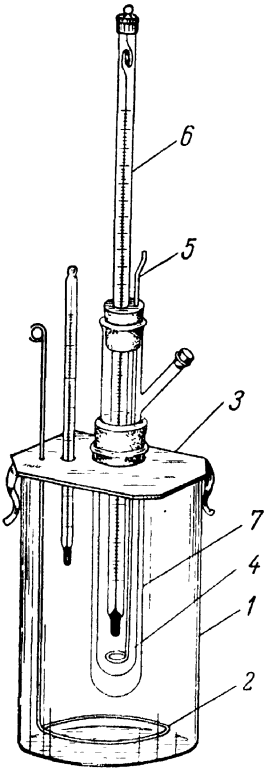


Fig. 48. Apparatu for determining the freezing point of a solution

1 — thick-walled beaker; 2 — stirrer for cooling mixture; 3 — lid; 4 — test tube with substance under investigation; 5 — stirrer for solution; 6 — Beckmann thermometer; 7 — test tube.

The depression of the freezing point of the solution is determined by means of an arrangement (Fig. 48) consisting of a thick-walled beaker (1) for the cooling mixture, a stirrer (2), a cover (3), two test tubes (4) and (7) of different diameters, a stirrer (5) for the solution, and a Beckmann thermometer (6).

Pour 10 ml of distilled water by means of a pipette into the inner test tube and close it with a stopper through which a stirrer and a Beckmann thermometer have been passed. The Beckmann thermometer should first be adjusted to the required temperature range*. Insert the test tube into a wider one, which serves as a jacket to prevent excessive cooling.

Put snow or ice in the beaker, add sodium chloride, and mix the contents thoroughly with the stirrer. To measure the temperature of the cooling mixture, lower an ordinary thermometer into it; see that the temperature remains at about —6°.

Now lower the test tube with the Beckmann thermometer into the cooling mixture. While stirring the water in the test tube with the stirrer, note the temperature (using a magnifying lens) at which crystals of ice appear. It is usual in such experiments for a slight supercooling to take place, with the temperature dropping below the freezing

* The thermometer should be adjusted in such a way that the mercury meniscus in melting ice is within the 1.750-2.250° range.

point. But after a certain drop, the mercury thread will abruptly rise and come to a stop at the freezing point of the solvent or the solution.

Record the temperature (to 0.005°). Then melt the ice in the test tube (by warming it with your hand) and repeat the experiment. The discrepancy between repeated determinations should not exceed 0.005°.

Next remove the test tube with the water and pour a weighed amount of urea (received from the laboratory assistant) into it; stir the contents until the urea dissolves. Then close the test tube with the stopper through which the thermometer and stirrer have been passed, lower the test tube into the cooling mixture, and, while stirring the solution, determine the freezing point of the solution. Warm the test tube with your hand, so that the crystals of ice melt, and repeat the determination.

Record the results of the experiment in the form of a table such as this:

Weight of water in g	Freezing point of water according to Beckmann thermometer			Weight of urea in g	Freezing point of solution according to Beckmann thermometer			Δt from experiment in °C
	I	II	average		I	II	average	

From the data obtained calculate the molecular weight of urea by means of the formula on p. 104.

2. Cooling Mixtures. Receive an individual assignment from the instructor: for example, to prepare a cooling mixture with a temperature of —13.6°.

With the aid of Tables 7 and 8, calculate the amount of salt that has to be mixed with 25 parts by weight of water or snow to reduce the temperature to that required.

Weigh the calculated amount of salt on a balance and measure off 25 ml of water in a cylinder. Pour the water into a beaker with a heat-insulating jacket, cool it to +13° and measure the temperature to ±0.2° (Assman thermometer).

Pour the weighed amount of salt into the beaker with water, stir the salt vigorously in the water, and note the lowest temperature reached (corresponding to the moment when all the salt dissolves).

To prepare a cooling mixture of snow and salt, transfer the weighed amount of salt (or mixture of salts) into the beaker with the weighed

Table 7

Salts Used to Prepare Cooling Mixtures

Salt	Salt + water		Salt + snow	
	parts by weight of salt to 100 parts by weight of water at 13°	lowest temperature in °C	parts by weight of salt to 100 parts by weight of snow	lowest temperature in °C
KNO_3	16	3.0	13	—2.9
KCl	30	0.6	30	—11.1
NH_4Cl	30	—5.1	25	—15.8
NH_4NO_3	60	—13.6	45	—17.3
$NaNO_3$	75	—5.3	50	—17.8
NaCl	36	—10.1	33	—21.2
$CaCl_2 \cdot 6H_2O$ . . .	250	—12.4	143	—55.0

Table 8

Mixtures of Salts Used to Prepare Cooling Mixtures

Composition of mixture (parts by weight of salt to 100 parts by weight of snow)	Lowest temperature in °C
$KNO_3(14) + NH_4Cl$ (26)	—17.8
$NH_4NO_3(52) + NaNO_3(55)$	—25.8
$KNO_3(9) + NH_4SCN$ (67)	—28.2
$NH_4NO_3(32) + NH_4SCN(59)$	—30.6
$HNO_3(2) + KSCN(112)$	—34.1
$NH_4SCN(57) + NaNO_3(57)$	—29.8

snow, mix thoroughly, and measure the lowest temperature of the mixture by a thermometer.

Compare the experimentally determined drop in temperature with the data of the table.

3. Determining the Boiling Point of a Pure Solvent and a Solution. Into the test tube of the arrangement shown in Fig. 34 *D* (p. 54) place a small lump of pumice stone and add 4 ml of distilled water. Determine the boiling point of the water by the thermometer. Does it differ from the true boiling point of water?

Weigh 3 g of calcium nitrate crystalline hydrate $Ca(NO_3)_2 \cdot 4H_2O$, put it into the test tube with water, and, when all the salt has dissolved, measure the boiling point of the solution by the procedure described in Para. "b" on p. 55.

How does a rise in the concentration of the solute affect the boiling point of a solution?

Exercise 14

ELECTROLYTES

SUBJECTS FOR STUDY

Theory of electrolytic dissociation; electrolytes and nonelectrolytes; degree of electrolytic dissociation; strong and weak electrolytes; electrolytic dissociation as a reversible process; equation for ionisation constant; electrolytic dissociation of water; ion product for water; pH-value and the acidity or alkalinity of a solution; determining [H·] and [OH′] in solutions of weak electrolytes.

1. Electrolytic Dissociation. Electrolytes are substances that, in a medium with a high dielectric constant (water, alcohols, etc.), break up into ions *. This process of the breaking up of a substance into ions is called electrolytic dissociation.

The dissociation of a substance into ions is accompanied by the *solvation* of the ions, i. e., their interaction with the polar molecules of the solvent. If the solvent is water, the term *hydration* is used for solvation.

The process of electrolytic dissociation ** should be expressed by equations such as these:

$$NaCN + mH_2O \rightleftarrows [Na \cdot nH_2O]^{\cdot} + [CN \cdot qH_2O]'$$

$$HCN + mH_2O \rightleftarrows [H \cdot H_2O]^{\cdot} + [CN \cdot qH_2O]'$$

In practice it is customary to use simplified equations:

$$NaCN \rightleftarrows Na^{\cdot} + CN'$$

$$HCN \rightleftarrows H^{\cdot} + CN'$$

Electrolytic dissociation is a *reversible* process, with unionised molecules as well as ions present at equilibrium. The ratio of the number of ionised molecules to the total number of the molecules of the electrolyte is called the degree of electrolytic dissociation, or, more often, the *degree of ionisation* (α).

For one and the same electrolyte, α increases with dilution; when the solution is highly dilute, the electrolyte is dissociated completely ($\alpha = 1$). Only solutions of the same normality can be compared as far as degree of ionisation is concerned. Sometimes the degree of ionisation is expressed as a percentage ($\alpha\,\% = \alpha \cdot 100$). According to their degree of ionisation, electrolytes are classified as strong, medium, or weak (Table 9).

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* Electrolytes in the molten state likewise break up into ions.

** Molecules break up into ions at the site of an ionic or markedly polar bond.

Table 9

Degree of Ionisation of Some Electrolytes in 0.1 N Solution

Strong electrolytes ($\alpha \geqslant 30\%$)	α %	Medium electrolytes ($\alpha = 2$-30%)	α %	Weak electrolytes ($\alpha < 2\%$)	α %
HNO_3	93	H_3PO_4	29	CH_3COOH	1.36
HCl	92	H_2SO_3	20	H_2CO_3	0.17
H_2SO_4	58	HF	8	H_2S	0.07
KOH	95			HCN	0.01
NaOH	93			NH_4OH	1.4
$Ba(OH)_2$	75				

Nearly all salts belong to the group of strong electrolytes. In an 0.1 N solution the various types of salts (M stands for the metal; X, for the acid radical) have roughly the following degrees of ionisation:

^{+1-1}MX	$^{+2-1}MX_2$	and	$^{+1-2}M_2X$	^{+2-2}MX	$^{+3-1}MX_3$	and	$^{+1-3}M_3X$
80-90%	70-80%			35-45%	60-65%		

The equilibrium arising in the solution of a *weak* electrolyte, say HCN, may be expressed by the equation:

$$HCN \rightleftarrows H^{\cdot} + CN'$$

If we apply to this equilibrium the Law of Mass Action, we get the following equation for the equilibrium constant:

$$\frac{[H^{\cdot}] \cdot [CN']}{[HCN]} = K_{ion}$$

In this case the equilibrium constant, i. e., the ratio of the product of the ion concentrations to the concentration of the undissociated, or unionised, molecules of the weak electrolyte at equilibrium, is called the dissociation constant, or, more often, the *ionisation constant.*

Unlike the degree of ionisation, the ionisation constant does not change when the solution is diluted.

TableXII (on p.334) lists the ionisation constants of some substances.

By increasing the concentration of the $H^{\cdot}$ ions or the CN' ions it is possible to shift the balance in an HCN solution, reducing its degree of ionisation.

2. Electrolytic Dissociation ol Water. Water is an exceedingly weak electrolyte, which dissociates according to the equation: $H_2O \rightleftarrows H^{\cdot} + OH'$.

The product of the hydrogen and hydroxyl ion concentrations is termed the *ion product for water* $[H^{\cdot}] \cdot [OH'] = K_w$. Its numerical value at 22° is $1 \cdot 10^{-14}$.

In pure water $[H^+] = [OH']$ and, accordingly, $[H^+] = \sqrt{1 \cdot 10^{-14}} = 1 \cdot 10^{-7}$. The value of $[H^+]$ may be used to express the acidity or alkalinity of a solution:

in an acid solution $[H^+] > [OH'] > 1 \cdot 10^{-7}$;

in a neutral solution $[H^+] = [OH'] = 1 \cdot 10^{-7}$, and

in an alkaline solution $[H^+] < [OH'] < 1 \cdot 10^{-7}$.

Instead of using the actual hydrogen ion concentration $[H^+]$, it is more customary to use the logarithm of that quantity, with its sign reversed. This is known as the hydrogen exponent or, simply, the pH-value: $pH = -\log [H^+]$. The following diagram shows the pH-value for solutions of varying acidity or alkalinity:

$$pH = \underset{\text{acidity increases}}{0\ 1\ 2\ 3\ 4\ 5\ 6} \quad \underset{\text{neutral}}{7} \quad \underset{\text{alkalinity increases}}{8\ 9\ 10\ 11\ 12\ 13\ 14}$$

Strong electrolytes break up into ions completely; for this reason $[H^+]$ or $[OH']$ in solutions of strong acids or alkalis may be assumed to be equal to the molar concentration of the acid or alkali.

Examples. (a) Determine the hydrogen ion concentration and the pH-value in an 0.01 M solution of HCl.

HCl is a strong electrolyte, and it therefore dissociates completely in solution:

$$\underset{0.01}{HCl} \longrightarrow \underset{0.01}{H^+} + \underset{0.01}{Cl'}$$

Consequently, the gram-ion concentration $[H^+]$ is numerically equal to the molar concentration of HCl:

$$[H^+] = 0.01 = 1.10^{-2};\ pH = -\log 1 \cdot 10^{-2} = 2^*$$

(b) Determine $[H^+]$ and pH for an 0.01 M solution of KOH.

The concentration of OH' ions is numerically equal to the KOH concentration (as in "a"):

$$[OH'] = 0.01 = 1 \cdot 10^{-2}$$

From the ion product for water we then find that

$$[H^+] = \frac{1 \cdot 10^{-14}}{[OH']} = \frac{1 \cdot 10^{-14}}{1 \cdot 10^{-2}} = 1 \cdot 10^{-12},\ \text{or}\ pH = 12$$

For solutions of weak monobasic acids and monovalent alkalis these quantities are determined somewhat differently. For example, in the case of acetic acid, in whose solution we have the equilibrium $CH_3COOH \rightleftarrows H^+ + CH_3COO'$, the equation for the ionisation constant will be:

$$\frac{[H^+] \cdot [CH_3COO']}{[CH_3COOH]} = K$$

* To calculate the pH-value exactly for solutions of strong acids and alkalis, it is necessary to use ion activities instead of ion concentrations.

Since acetic acid is a weak electrolyte, there will be but a small error involved in assuming $[CH_3COOH]$ to be equal to C, the total concentration of the acid. The equation therefore becomes:

$$[H^{\cdot}] \cdot [CH_3COO'] = K \cdot C$$

Furthermore, since $[H^{\cdot}] = [CH_3COO']$, we get

$$[H^{\cdot}]^2 = K \cdot C \text{ and } [H^{\cdot}] = \sqrt{K \cdot C}$$

Example. Determine $[H^{\cdot}]$ and pH for an 0.1 M solution of CH_3COOH, knowing that $K_{CH_3COOH} = 1.82 \odot 10^{-5}$.

By substituting the known quantities into the formula $[H^{\cdot}] = \sqrt{K \cdot C}$, we obtain:

$$[H^{\cdot}] = \sqrt{1.82 \cdot 10^{-5} \cdot 1 \cdot 10^{-1}} = 1.34 \cdot 10^{-3}$$

$$pH = -\log [H^{\cdot}] = -(\log 1.34 + \log 10^{-3}) = -(0.1271 - 3) \approx 2.87$$

Knowing $[H^{\cdot}]$, it is not difficult to calculate the degree of ionisation from the relationship $\alpha = \frac{[H^{\cdot}]}{C}$.

In this particular case

$$\alpha = \frac{1.34 \cdot 10^{-3}}{1 \cdot 10^{-1}} = 1.34 \cdot 10^{-2} \quad \text{or} \quad \alpha\% = 1.34\%$$

3. Dissociation by Steps. In the case of polybasic acids and polyvalent bases, all the hydrogen or hydroxyl ions in their molecules do not split off at once. Electrolytic dissociation proceeds by steps.

The following are examples of stepwise dissociation equations:

I step $H_2S \rightleftarrows H^{\cdot} + HS'$ $\quad$ $Co(OH)_2 \rightleftarrows CoOH^{\cdot} + OH'$

II step $\quad\quad\quad\quad\quad H^{\cdot} + S''$ $\quad\quad\quad\quad$ $Co^{\cdot\cdot} + OH'$

Two equations of ionisation constants may be written for ionic equilibrium in the H_2S solution:

$$\frac{[H^{\cdot}] \cdot [HS']}{[H_2S]} = K_1 = 9 \cdot 10^{-8} \quad \text{and} \quad \frac{[H^{\cdot}] \cdot [S'']}{[HS']} = K_2 = 4 \cdot 10^{-13}$$

A comparison of the values of K_1 and K_2 shows that K_1 is more than 225,000 times $(9 \cdot 10^{-8} : 4 \cdot 10^{-13})$ bigger than K_2, which may therefore be neglected in calculating $[H^{\cdot}]$ and the pH-value. For weak polybasic acids there will be a small degree of error involved in taking into account only the first step of ionisation.

Some salts, such as $Ca(NO_3)_2$, $FeCl_3$, and BeF_2, likewise dissociate stepwise in solutions, but their stepwise dissociation is less pronounced than that of polyvalent bases or polybasic acids.

4. Molecular Weights of Electrolytes. In determinations of the molecular weight of electrolytes according to the depression of the freezing point or the elevation of the boiling point of the solution, or according

to the osmotic pressure, use is made of formulae in which the coefficient $i>1$:

$$M = \frac{i \cdot K \cdot 1{,}000 \cdot a}{b \cdot \Delta t} \quad \text{and} \quad M = \frac{i \cdot m \cdot RT}{V \cdot P_{osm}}$$

The theory of electrolytic dissociation has made it possible to establish the physical meaning of the coefficient i. If we denote the number of the solute molecules as n and the degree of ionisation as α, then $n\alpha$ will be the number of ionised molecules, while $n—n\alpha$ will be the number of unionised molecules. The $n\alpha$ number of molecules that undergo ionisation give rise to $n\alpha\beta$ ions, where β is the number of ions arising from a single molecule of the solute.

Let us denote the ratio of the sum of the number of unionised molecules and the number of ions formed to the total number of molecules taken as i. In that case:

$$i = \frac{n - n\alpha + n\alpha\beta}{n} = 1 + \alpha(\beta - 1)$$

For a binary electrolyte $\beta = 2$ and $i = 1 + \alpha$; for a ternary electrolyte $\beta = 3$ and $i = 1 + 2\alpha$, etc.

In this way the quantity i, known as the van't Hoff factor, is a measure of the increase in the number of particles in an electrolyte solution. By means of this factor, it is possible to calculate the molecular weight of electrolytes according to the above formulae, provided their degree of ionisation is known.

Example 1. Calculate the molecular weight of potassium cyanide if a solution containing 2.48 g of that salt in 500 g of water freezes at —0.27° and if $\alpha=0.9$.

We find $i = 1+0.9=1.9$. The cryoscopic constant of water $K = 1.86$. By substituting all these values into the formula, we obtain

$$M = \frac{1.9 \cdot 1.86 \cdot 1{,}000 \cdot 2.48}{500 \cdot 0.27} = 65$$

Example 2. Calculate the osmotic pressure of the solution in the previous example at 17° (assuming the relative density of the solution to be 1).

$$P_{osm} = \frac{i \cdot m \cdot RT}{M \cdot V} = \frac{1.9 \cdot 2.48 \cdot 0.082 \cdot 290}{65 \cdot 0.502} = 3.42 \text{ atm}$$

QUESTIONS

1. What experimental data suggested the theory of electrolytic dissociation to Arrhenius?
2. Write the equations of electrolytic dissociation for the following substances:

$Fe_2(SO_4)_3$ $NaHCO_3$ $MgOHCl$ $KCr(SO_4)_2$

3. Why does a solution of hydrogen chloride in water have acidic properties, while a solution of the same substance in benzene does not exhibit such properties?

4. What are the factors that cause electrolytes to break up into ions in an aqueous solution?

5. Write the equation for the ionisation constant of hypochloric acid HOCl. What substances should be introduced to reduce the ionisation of this acid?

6. From the theoretical considerations outlined in the introduction to this Exercise derive the formula

$$[OH'] = \sqrt{K_{base} \cdot C_{base}}$$

for the ionisation reaction $NH_4OH \rightleftarrows NH'_4 + OH'$.

7. Write the ionisation equations for H_3PO_4 on the basis of the ionisation constant values. Show which of the negative ions will be present in the solution in a relatively higher concentration.

Problems

(for ionisation constants see Table XII on p. 334)

1. Taking into account the first step of the ionisation of H_2S, calculate $\alpha\%$ for an 0.01 M solution of it.

2. Calculate $[H^+]$ and $\alpha\%$ for an 0.05 M solution of hydrofluoric acid HF.

3. Calculate the degree of ionisation of a binary electrolyte solution containing 0.50 g of salt in 100 g of water. The solution boils at 100.04°; the molecular weight of the salt is 126.

4. Determine which solution has a higher pH-value: an 0.01 M solution of HCl or an 0.1 M solution of HCN.

5. Where is the pH-value greater: in an 0.0001 M solution of HNO_3 or in an 0.01 M solution of H_2S?

6. Calculate the $\alpha\%$ and the pH-value of a 4% solution of boric acid, assuming the relative density of the solution to be 1.

7. Calculate the osmotic pressure of an 0.1 M solution of $BaCl_2$ at 20°, its apparent degree of ionisation being 0.72.

8. Calculate the molecular weight of a binary salt ($\alpha\% = 82$) if 0.33 g of it is dissolved in 100 g of water and the boiling point of the solution is 100.026°.

9. What will be the freezing point of a solution of $CaCl_2$ containing 8.0 g of the salt in 400 g of water if $\alpha = 70\%$?

10. What will be the boiling point of an 0.2-molal solution of $CuSO_4$ if its degree of ionisation is 45%?

LABORATORY WORK

Apparatus and materials: the arrangement for determining conductivity shown in Fig. 49 and that for determining the conductivity of molten salts shown in Fig. 50; the arrangement for observing ion migration shown in Fig.51; the cryoscopy arrangement shown in Fig. 48; test tubes and rack; 10 ml measuring cylinder; 1 ml and 10 ml pipettes; crystalline sodium acetate; crystalline potassium nitrate; anhydrous acetic acid; crystalline ammonium chloride; recrystallised potassium chloride in weighed amounts; commercial sodium chloride; 0.5 N solution of potassium iodide; 5% solution of alcohol; 5% solution of sugar; 10% solution of hydrochloric acid; 5% solution of potassium nitrate; 5% solution of sodium hydroxide; 25% and 1% solutions of ammonia; solution of phenolphthalein; solution of methyl-orange; litmus solution; starch solution; distilled water; boiled distilled water; snow or ice.

Note. The potassium chloride should be weighed in amounts of about 0.050 g; the weighing should be done on an analytical balance to 0.001 g.

1. Conductivity of Electrolyte Solutions. The apparatus (Fig. 49) consists of a wide mouth bottle with a rubber stopper, through which a funnel and two carbon electrodes have been passed. The electrodes have metal caps with terminals at the top. A line should be drawn with a file at the bottom ends of the electrodes to serve as a mark for the amount of electrolyte poured in.

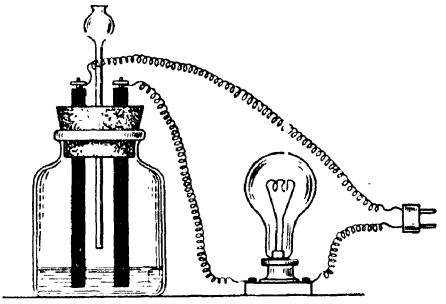


Fig. 49. Apparatus for determining th conductivity of solutions

Through the funnel pour distilled water into the bottle to the mark on the electrodes; plug in the apparatus and switch on the electricity. Does the lamp glow? The glowing of the lamp is a sign that there is an electric current in the circuit.

Repeat the experiment, filling the bottle consecutively with solutions of alcohol, sugar, hydrochloric acid, pottassim nitrate, and potassium hydroxide. Before each experiment wash the electrodes, the funnel, and the bottle thoroughly; rinse them with distilled water.

Which are the substances that conduct electricity in solution? What is an electrolyte? Write equations of electrolytic dissociation for the electrolytes tested. What are the ions characteristic of solutions of acids and alkalis?

2. Degree of Ionisation of an Acid. Pour concentrated acetic acid into the clean and dry bottle of the apparatus shown in Fig. 49 and switch on the electricity. Then add distilled water through the funnel, raising the electrodes over the stopper in such a way that the level of the solution in the bottle should not rise above the mark (in order to keep the effective surface of the electrodes constant). Note the changes in the glowing of the lamp. What accounts for these changes? Check your conclusions by calculating the values of α % for 0.1 and 0.001 N solutions of CH_3COOH.

3. Degree of Ionisation of Alkali and Salt. Pour a small amount of a 25% solution of ammonia (1 volume) into the bottle of the conductivity apparatus and switch on the electricity. Note the brightness of the lamp. Switch off the electricity. Carefully add glacial acetic acid ($\frac{1}{2}$ volume) in small portions. Stir the solution, cool it, and switch on the electricity. Note the change in the glowing of the lamp. Explain this, writing the necessary equations. Are salts weak or strong electrolytes?

4. Determining the Degree of Ionisation of a Salt. This experiment is conducted with the apparatus shown in Fig. 48, employing the same

procedure as that described in Para. 1 of Exercise 13. First determine the freezing point of the pure solvent—water. Two determinations should be made, and the freezing point should not differ by more than $\pm 0.005°$. An accurately weighed amount of recrystallised potassium chloride is then dissolved in the water. The freezing point of the solution should now be determined twice.

Since we know the weight of the salt taken for the experiment, its molecular weight, the weight of the solvent, its cryoscopic constant, and the depression of the freezing point of the solution, we are able

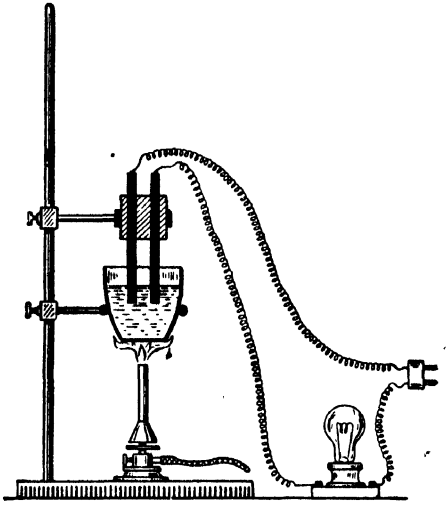


Fig. 50. Apparatus for determining the conductivity of molten salts

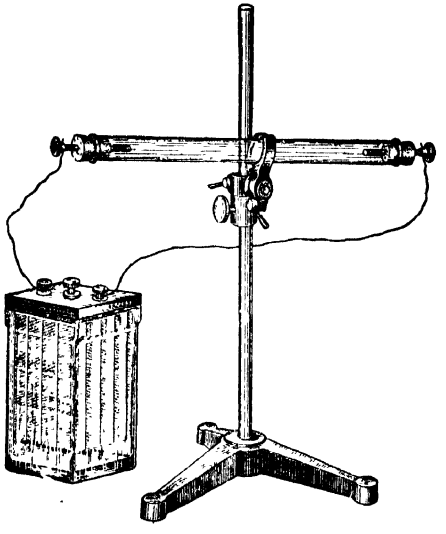


Fig. 51. Arrangement for observing ion migration

o calculate the van't Hoff factor, from which we derive the degree of ionisation. Compare the obtained value with the theoretical and establish the relative error of the determination.

5. Conductivity of Molten Electrolytes. Assemble the apparatus shown in Fig. 50. In the clamp attached to the ringstand fasten a stopper with two graphite electrodes passed through it. Lower the electrodes into a porcelain crucible containing finely ground potassium nitrate * and switch on the electricity. Does the lamp glow? Heat the crucible by means of a burner and note the appearance of current in the circuit when the salt melts (m. p. 336°).

6. Ion Migration. Hold the glass tube of the apparatus shown in Fig. 51 verticalli and close one end of it with a rubber stopper that

* Potassium nitrate may be replaced by other low-melting salts, such as tin chloride (m. p. 241°) or zinc chloride (m. p. 365°).

has a graphite electrode passed through it. Pour 1 ml of a potassium iodide solution, 1 ml of a starch solution, and 1 drop of an alcoholic solution of phenolphthalein into the tube; fill the tube to the top with distilled water, allowing for the closing of the tube with a second rubber stopper. Turn the closed tube over repeatedly to mix the solution.

Then fasten the tube in the clamp and connect thin wires from a storage battery or some other direct-current source to the terminals at the end of the graphite electrodes.

After a certain period of time a blue colouration appears at the positive electrode, while a crimson colouration appears at the negative electrode.

What accounts for these colourations at the electrodes? What ions migrated in the solution and in what direction? What are cations and anions?

7. Colour of Indicators. Pour 3 ml of distilled water into each of 9 clean test tubes. Add 1 drop of phenolphthalein into each of the first three, 1 drop of a methyl-orange solution into each of the next three, and 1 ml of a litmus solution into each of the remaining three. Now add 2-3 drops of a hydrochloric acid solution to 3 test tubes (one with phenolphthalein, another with methyl-orange, and the third with litmus). Add 2-3 drops of a sodium hydroxide solution to three other test tubes with different indicators.

Record the colour of the indicators in different solutions as follows:

Indicator	Type of solution		
	acid, pH < 7	neutral, pH = 7	alkaline, pH > 7
Phenolphthalein			
Methyl-orange			
Litmus			

8. Equilibrium in a Solution of a Weak Acid. Pour 4-5 ml of water into a test tube; add 1 drop of concentrated acetic acid and 2 drops of a methyl-orange solution. What colour does the solution acquire and why? Write the equation for the electrolytic dissociation of acetic acid and the equation for the ionisation constant.

Divide the solution into two equal parts and add a few crystals of sodium acetate to one half. Shake the test tube and compare the colours of the solutions in the two test tubes. Explain this in terms of the equilibrium constant.

What should be introduced into a solution of a weak acid to shift the equilibrium towards the formation of undissociated molecules?

9. Equilibrium in a Solution of a Weak Base. Carry out the same experiment as above, taking an ammonia solution instead of acetic acid, phenolphthalein instead of methyl-orange, and ammonium chloride instead of sodium acetate. Write up the experiment.

What should be introduced into a solution of a weak base to shift the equilibrium towards the formation of undissociated molecules? Formulate a general conclusion about the shifting of equilibrium in solutions of weak electrolytes.

Exercise 15

REACTIONS IN ELECTROLYTE SOLUTIONS

SUBJECTS FOR STUDY

Equilibrium in a *precipitate-solution* system; solubility product; formation of precipitates and their solution; Berthollet's Rule in the context of the theory of electrolytic dissociation; reactions between ions in solution; neutralisation; hydrolysis and particular cases of it; amphoteric electrolytes; properties of hydroxides and radius of positive ion charge.

1. Solubility Product. *The solubility product (SP) of a slightly soluble binary electrolyte is a quantity equal to the product of the concentrations of its ions in a saturated solution* *. For example, the solubility products of AgCl, $CaCO_3$, and $AlPO_4$ are expressed as follows:

$$SP_{AgCl} = [Ag^{\cdot}] \cdot [Cl'];\ SP_{CaCO_3} = [Ca^{\cdot\cdot}] \cdot [CO_3''];\ SP_{AlPO_4} = [Al^{\cdot\cdot\cdot}] \cdot [PO_4'''] $$

The solubility product characterises the solubility of slightly soluble substances at a *given temperature*; the smaller the solubility product, the less soluble the compound.

If $SP_{AgCl} = 1.7 \cdot 10^{-10}$ and $SP_{AgI} = 8.5 \cdot 10^{-17}$, it follows that AgCl is more soluble than AgI.

The solubility product is easily converted to the molar or ionic (gram-ions per litre) solubility. Let us consider, for instance, the case of barium sulphate, for which $SP_{BaSO_4} = [Ba^{\cdot\cdot}] \cdot [SO_4'']$. If we denote the ion concentration as x, we get: $SP = x \cdot x$, or $SP = x^2$, from which it follows that $x = \sqrt{SP}$. In this way from the solubility product we can determine the number of mols of $BaSO_4$ or the number of gram-ions of $Ba^{\cdot\cdot}$ or SO_4'' in 1 litre of a saturated solution. To determine the solubility in grams per litre (B), we must multiply the molar

* In accordance with the theory of strong electrolytes, the values of concentrations for the more soluble compounds ought to be replaced by *activity* values. These are products of the concentration by the activity coefficient.

or ionic solubility (x) by the molecular weight (M) or the ionic, atomic, or group weight (A):

$$B_{BaSO_4} = \sqrt{SP} \cdot M \qquad B_{Ba^{\cdot\cdot}} = \sqrt{SP} \cdot A_{Ba^{\cdot\cdot}} \qquad B_{SO_4''} = \sqrt{SP} \cdot A_{SO_4''}$$

Example. Calculate how many grams of AgI are contained in 500 ml of a saturated solution at 25° if $SP_{AgI} = 8.5 \cdot 10^{-17}$.

$$[Ag^{\cdot}] \cdot [I'] = SP = 8.5 \cdot 10^{-17}; \quad x = \sqrt{SP} = \sqrt{8.5 \cdot 10^{-17}} = 9.22 \cdot 10^{-9}$$

Since $M_{AgI} = 234.8$, the solubility of AgI equals $9.22 \cdot 10^{-9} \cdot 234.8$ g/l. Consequently, 500 ml contains

$$9.22 \cdot 10^{-9} \cdot 234.8 \cdot 0.5 = 1.08 \cdot 10^{-6} \text{ g AgI}$$

The formation and solution of precipitates can be explained in terms of SP values. A precipitate is thrown down when the product of the ion concentrations exceeds the solubility product; a precipitate dissolves when the product of the ion concentrations is less than the solubility product.

Example. How many times greater is the solubility of AgI in pure water than in an 0.01 M solution of NaI if $SP_{AgI} = 8.5 \cdot 10^{-17}$?

From the value of SP_{AgI} we derive the solubility of AgI in pure water:

$$\sqrt{SP} = \sqrt{8.5 \cdot 10^{-17}} = 9.22 \cdot 10^{-9} \text{ mols/l}$$

Sodium iodide is a strong electrolyte that breaks up into ions completely; therefore [I'] is equal to the total concentration of the salt, i. e., to 0.01, or $1 \cdot 10^{-2}$. Hence:

$$[Ag^{\cdot}] \cdot 1 \cdot 10^{-2} = 8.5 \cdot 10^{-17} \text{ and } [Ag^{\cdot}] = \frac{8.5 \cdot 10^{-17}}{1 \cdot 10^{-2}} = 8.5 \cdot 10^{-15} \text{ mols/l}$$

Since $[AgI] = [Ag^{\cdot}] = 8.5 \cdot 10^{-15}$, the ratio of the solubility of AgI in pure water to its solubility in a NaI solution will be $\frac{9.22 \cdot 10^{-9}}{8.5 \cdot 10^{-15}}$, i. e., the solubility of AgI in pure water will be 1,085,000 greater than in an 0.01 M solution of NaI.

2. Ionic Reactions. Chemical reactions in solutions of electrolytes are reactions not between molecules, but between ions.

In equations of reactions the ions of an electrolyte may be separated by a plus sign. For instance, sodium nitrate and sodium chloride may be written thus:

$$Ag^{\cdot} + NO_3'$$

and

$$Na^{\cdot} + Cl'$$

The interaction between these substances may be expressed by the equation:

$$Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl' = AgCl + Na^{\cdot} + NO_3'$$

From this equation it follows that only 2 of the 4 ions participating in the reaction actually interact. These are the $Ag^{\cdot}$ and Cl' ions; the $Na^{\cdot}$ and NO_3' ions do not take part in the reaction. Reactions are, however, possible in which all 4 ions take part, e. g.:

$$Zn^{\cdot\cdot} + SO_4'' + Ba^{\cdot\cdot} + S'' = ZnS + BaSO_4$$

3. Equations of Exchange Reactions in Solutions. Chemical reactions can be represented by equations of three types: (1) molecular, (2) ionic-molecular, and (3) ionic. For example:

(1) $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$

(2) $Ba^{\cdot\cdot} + 2Cl' + 2H^{\cdot} + SO_4'' = BaSO_4 + 2H^{\cdot} + 2Cl'$

(3) $Ba^{\cdot\cdot} + SO_4'' = BaSO_4$

The latter (ionic) equation indicates only the ions that take a direct part in the reaction. Henceforward, in writing the equations of the reactions between electrolytes in solutions, we shall use equations of the second type.

Reactions between ions may be referred to one of the following four types.

A. Reactions Proceeding with the Formation of a Precipitate

When writing the equations of reactions of this type, it is necessary to bear in mind the solubility of the substances involved (Table 10).

Table 10

Solubility of Some Substances in Water

(S stands for soluble; SS, slightly soluble; I, insoluble; DW, decomposed by water)

Anion	Cation														
	$Na^{\cdot}$	$K^{\cdot}$	$NH_4^{\cdot}$	$Ag^{\cdot}$	$Mg^{\cdot\cdot}$	$Ca^{\cdot\cdot}$	$Ba^{\cdot\cdot}$	$Fe^{\cdot\cdot}$	$Cu^{\cdot\cdot}$	$Zn^{\cdot\cdot}$	$Hg^{\cdot\cdot}$	$Pb^{\cdot\cdot}$	$Al^{\cdot\cdot\cdot}$	$Fe^{\cdot\cdot\cdot}$	$Cd^{\cdot\cdot}$
F'	S	S	S	S	I	I	SS	SS	I	SS	SS	I	S	S	SS
Cl'	S	S	S	I	S	S	S	S	S	S	S	SS	S	S	S
Br'	S	S	S	I	S	S	S	S	S	S	S	SS	S	S	S
I'	S	S	S	I	S	S	S	S	I	S	I	SS	S	S	S
OH'	S	S	S	SS	I	S	S	I	I	I	DW	I	I	I	I
NO_3'	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
S''	S	S	S	I	S	S	S	I	I	I	I	I	DW	I	I
CO_3''	S	S	S	I	I	I	I	I	DW	I	I	I	DW	DW	I
SO_4''	S	S	S	S	S	SS	I	S	S	S	S	I	S	S	S
CrO_4''	S	S	S	I	S	S	I	S	S	S	I	I	S	S	S
PO_4'''	S	S	S	I	I	I	I	I	I	I	I	I	I	I	I
$C_2H_3O_2'$	S	S	S	SS	S	S	S	S	S	S	S	S	S	S	S

To obtain an insoluble compound (precipitate), it is necessary to proceed from two soluble substances containing the required ions. In the equation of the reaction, the substance thrown down as a precipitate is represented by its molecular formula.

Below, for instance, are equations of reactions for the precipitation of ZnS and $AlPO_4$:

$$Zn^{\cdot\cdot} + SO_4^{\prime\prime} + 2K^{\cdot} + S^{\prime\prime} = ZnS + 2K^{\cdot} + SO_4^{\prime\prime}$$

$$Al^{\cdot\cdot\cdot} + 3Cl^{\prime} + 3Na^{\cdot} + PO_4^{\prime\prime\prime} = AlPO_4 + 3Na^{\cdot} + 3Cl^{\prime}$$

B. Reactions Proceeding with the Evolution of a Gas

The gases formed in ionic *exchange* reactions are *complex* gaseous substances. This group of substances, except for some gaseous fluorides, consists mainly of the hydrogen compounds of nonmetals: CH_4, SiH_4, NH_3, PH_3, AsH_3, SbH_3, H_2S, H_2Te, H_2Se, HF, HCl, HBr, HI, etc.

To obtain one of the above gases by an ionic exchange reaction, it is necessary to proceed from a compound of that particular nonmetal with a metal and a compound containing $H^{\cdot}$ ions (acid, water), e. g.:

$$2Na^{\cdot} + S^{\prime\prime} + 2H^{\cdot} + SO_4^{\prime\prime} = H_2S + 2Na^{\cdot} + SO_4^{\prime\prime}$$

If the initial substance (the compound of the nonmetal with a metal) has a low solubility in water, it is written in the equation in molecular form:

$$FeS + 2H^{\cdot} = SO_4^{\prime\prime} = H_2S + Fe^{\cdot\cdot} + SO_4^{\prime\prime}$$

Alternatively, the soluble part of the substance in the ionised state may be represented together with the insoluble part (precipitate) as a system in equilibrium:

$$\underbrace{Fe^{\cdot\cdot} + S^{\prime\prime}}_{\uparrow\downarrow\ FeS\ \text{precipitate}} + 2H^{\cdot} + SO_4^{\prime\prime} = H_2S + Fe^{\cdot\cdot} + SO_4^{\prime\prime}$$

C. Reactions Proceeding with the Formation of a Weak Electrolyte

Weak electrolytes include water, weak acids and bases, the acid radicals of polybasic acids containing the $H^{\cdot}$ ion, and the basic radicals of polyvalent bases containing $OH^{\prime}$ ions.

(*a*) *Neutralisation*. Neutralisation is a reaction in which the hydroxyl ions of a base (or basic salt) combine with the hydrogen ions of an acid (or acid salt) to form water (a weak electrolyte):

$$Na^{\cdot} + OH^{\prime} + H^{\cdot} + NO_3^{\prime} = H_2O + Na^{\cdot} + NO_3^{\prime}$$

$$K^{\cdot} + HSO_4^{\prime} + K^{\cdot} + OH^{\prime} = H_2O + 2K^{\cdot} + SO_4^{''}$$

$$AlOH^{\cdot\cdot} + 2Cl^{\prime} + H^{\cdot} + Cl^{\prime} \rightleftarrows H_2O + Al^{\cdot\cdot\cdot} + 3Cl^{\prime}$$

(*b*) *Displacement of Weak Acids from Their Salts by Strong Acids.* These reactions proceed owing to the formation of a weak acid (a weak electrolyte). The initial substances are the salt of a weak acid and a strong acid:

$$2Na^{\cdot} + SiO_3^{''} + 2H^{\cdot} + 2Cl^{\prime} = H_2SiO_3 + 2Na^{\cdot} + 2Cl^{\prime}$$

$$2K^{\cdot} + 2CN^{\prime} + 2H^{\cdot} + SO_4^{''} = 2HCN + 2K^{\cdot} + SO_4^{''}$$

If the resulting weak acid is a compound of low stability (such as H_2CO_3 or H_2SO_3), it decomposes to form water and an anhydride:

$$2Na^{\cdot} + CO_3^{''} + 2H^{\cdot} + 2Cl^{\prime} = H_2CO_3 + 2Na^{\cdot} + 2Cl^{\prime}$$

$$H_2CO_3 = H_2O + CO_2$$

(*c*) *Displacement of Weak Bases from Their Salts by Strong Bases.* Weak bases include magnesium, beryllium, and aluminium hydroxides, the hydroxides of the heavy metals, and ammonium hydroxide.

$$NH_4^{\cdot} + Cl^{\prime} + K^{\cdot} + OH^{\prime} = NH_4OH + K^{\cdot} + Cl^{\prime}$$

$$Cu^{\cdot\cdot} + SO_4^{''} + 2Na^{\cdot} + 2OH^{\prime} = Cu(OH)_2 + 2Na^{\cdot} + SO_4^{''}$$

(*d*) *Converting Normal Salts to Acid Salts.* Polybasic acids break up into ions stepwise. For example, carbonic acid dissociates according to the equation:

$$H_2CO_3 \rightleftarrows H^{\cdot} + \underbrace{HCO_3^{\prime}}_{H^{\cdot} + CO_3^{''}}$$

In this system the electrolytes are: H_2CO_3 at the first step and the $HCO_3^{\prime}$ ion at the second. The ionisation constants for each step are respectively:

$$K_1 = \frac{[H^{\cdot}]\cdot[HCO_3^{\prime}]}{[H_2CO_3]} = 3.5\cdot10^{-7} \qquad K_2 = \frac{[H^{\cdot}]\cdot[CO_3^{''}]}{[HCO_3^{\prime}]} = 5.6\cdot10^{-11}$$

From these values it is evident that the $HCO_3^{\prime}$ ion is a weaker electrolyte than is carbonic acid (the latter is a nearly 10,000 times stronger electrolyte).

The conversion of normal salts to acid salts is due to an interaction of ions that gives rise to the acid salt ion (a weak electrolyte):

$$\underset{\uparrow\downarrow}{\underset{MgCO_3}{Mg^{\cdot\cdot} + CO_3^{''}}} + H^{\cdot} + OH' + CO_2 = Mg^{\cdot\cdot} + 2HCO_3^{'}$$

$$\underset{\downarrow\uparrow}{\underset{Ca_3(PO_4)_2}{3Ca^{\cdot\cdot} + 2PO_4^{'''}}} + 2H^{\cdot} + SO_4^{''} = CaSO_4 + 2Ca^{\cdot\cdot} + 2HPO_4^{''}$$

(*e*) *Hydrolysis.* Hydrolysis is the interaction of a substance with ions of water, a reversible process. In pure water dissociated according to the equation $H_2O \rightleftarrows H^{\cdot} + OH'$ the concentrations of the $H^{\cdot}$ and OH' ions are equal, i. e., $[H^{\cdot}] = [OH']$, owing to which water is neutral (pH = 7). If one of the ions of a salt, in the course of hydrolysis, combines with one of the ions of water, this increases the relative concentration of the other ion of water; as a result, the salt solution becomes either acidic ($[H^{\cdot}] > [OH']$) or alkaline ($[H^{\cdot}] < [OH']$). The following are illustrations of both cases:

First Case

$$\left\{\begin{array}{l} KCN \rightleftarrows K^{\cdot} + CN' \\ \qquad\qquad + \\ H_2O \rightleftarrows OH' + H^{\cdot} \\ \qquad\qquad\quad \uparrow\downarrow \\ \qquad\qquad\quad HCN \end{array}\right. \quad pH > 7$$

Second Case

$$\left\{\begin{array}{l} NH_4NO_3 \rightleftarrows NH_4^{\cdot} + NO_3^{'} \\ \qquad\qquad + \\ H_2O \rightleftarrows OH' + H^{\cdot} \\ \qquad\quad \uparrow\downarrow \\ \qquad\quad NH_4OH \end{array}\right. \quad pH < 7$$

The equations for these reactions are written thus:

$$K^{\cdot} + CN' + H^{\cdot} + OH' \rightleftarrows HCN + K^{\cdot} + OH'$$

$$NH_4^{\cdot} + NO_3^{'} + H^{\cdot} + OH' \rightleftarrows NH_4OH + H^{\cdot} + NO_3^{'}$$

Salts formed by a strong base and a weak acid (*1*st case) exhibit an alkaline reaction in solution; salts formed by a weak base and a strong acid (*2*nd case) exhibit an acid reaction in solution.

Salts formed by a weak base and a weak acid undergo hydrolysis most readily of all, since the ions of these salts are bound up simultaneously by the ions of water to produce weak electrolytes. A case in point is the hydrolysis of ammonium acetate:

$$NH_4^{\cdot} + CH_3COO' + H^{\cdot} + OH' \rightleftarrows NH_4OH + CH_3COOH$$

Some salts of this type undergo practically irreversible complete hydrolysis, e. g.:

$$Cr_2S_3 + 6H^{\cdot} + 6OH' \rightarrow 3H_2S + 2Cr(OH)_3$$

$$Al_2(CO_3)_3 + 6H^{\cdot} + 6OH' \rightarrow 2Al(OH)_3 + 3H_2CO_3$$

$$\downarrow$$

$$3H_2O + 3CO_2$$

A salt of a polybasic acid or a polyvalent base upon hydrolysis yields an acid salt and a base or a basic salt and an acid:

$$2Na^{\cdot} + CO_3'' + H^{\cdot} + OH' \rightleftarrows Na^{\cdot} + HCO_3' + Na^{\cdot} + OH'$$

$$Sn^{\cdot\cdot} + 2Cl' + H^{\cdot} + OH' \rightleftarrows SnOH^{\cdot} + Cl' + H^{\cdot} + Cl'$$

$$\uparrow\downarrow$$

$$SnONCl$$

precipitate

The salts of weak polyvalent bases undergo hydrolysis stepwise. Ferric chloride, for instance, reacts with water thus:

$$Fe^{\cdot\cdot\cdot} + 3Cl' + H^{\cdot} + OH' \rightleftarrows FeOH^{\cdot\cdot} + 2Cl' + H^{\cdot} + Cl'$$

$$FeOH^{\cdot\cdot} + 2Cl' + H^{\cdot} + OH' \rightleftarrows Fe(OH)_2^{\cdot} + Cl' + H^{\cdot} + Cl'$$

Further hydrolysis is prevented by the build-up of $H^{\cdot}$ ions in the solution. Diluting the solution and increasing the temperature facilitates hydrolysis.

Salts formed by a strong acid and a strong base undergo practically no hydrolysis at all.

The study of the process of hydrolysis has shown that hydrolysis and neutralisation are reverse processes:

$$K^{\cdot} + OH' + H^{\cdot} + CN' \underset{\text{hydrolysis}}{\overset{\text{neutralisation}}{\rightleftarrows}} H_2O + K^{\cdot} + CN'$$

The compounds of certain nonmetals, such as PCl_5, PI_3, and SO_2Cl_2, undergo hydrolysis readily, the process being practically irreversible and giving rise to two acids:

$$PI_3 + 3H^{\cdot} + 3OH' \rightarrow H_3PO_3 + 3HI$$

$$SO_2Cl_2 + 2H^{\cdot} + 2OH' \rightarrow H_2SO_4 + 2HCl$$

(*f*) *Amphoteric Electrolytes.* The hydroxides of the heavy metals, as well as of magnesium, beryllium, and aluminium, are practically insoluble compounds, but dissolve in acids:

$$Fe(OH)_2 + 2H^{\cdot} + 2Cl' = 2H_2O + Fe^{\cdot\cdot} + 2Cl'$$

Some hydroxides dissolve not only in acids, but also in solutions of alkalis *, e. g.:

$$Sn(OH)_2 + 2H^{\cdot} + 2Cl' = 2H_2O + Sn^{\cdot\cdot} + 2Cl'$$

$$H_2SnO_2 + 2K^{\cdot} + 2OH' = 2H_2O + 2K^{\cdot} + SnO_2''$$

Such hydroxides are termed *amphoteric.*

It follows from the above equations that amphoteric hydroxides behave as bases in reactions with acids and as acids in reactions with alkalis. This dual behaviour is due to the fact that in solutions they can dissociate according to both the acid and the base pattern. The electrolytic dissociation of $Sn(OH)_2$, for example, can be summed up as follows:

$$Sn^{\cdot\cdot} + 2OH' \rightleftarrows Sn(OH)_2 \rightleftarrows 2H^{\cdot} + SnO_2''$$

Or, considering the stepwise character of dissociation, we can put down the process thus:

$$\begin{array}{ccccc} & SnOH^{\cdot} & + OH' & \rightleftarrows Sn(OH)_2 & \rightleftarrows H^{\cdot} + HSnO_2' \\ & \uparrow\downarrow & & & \uparrow\downarrow \\ Sn^{\cdot\cdot} & + OH' & & & \underbrace{\qquad\qquad}_{H^{\cdot}\quad SnO_2''} \end{array}$$

D. Reactions Proceeding with the Formation of a Complex Ion

A saturated solution of the compound, mercuric iodide, which dissolves in water with difficulty, contains $Hg^{\cdot\cdot}$ and I' ions, produced by electrolytic dissociation according to the equation:

$$HgI_2 \rightleftarrows Hg^{\cdot\cdot} + 2i'$$

These ions can be detected by the proper reagents. But if to this solution we add such an amount of potassium iodide that there are 2 molecules of it to every molecule of mercuric iodide, we will no longer be able to detect any $Hg^{\cdot\cdot}$ or I' ions. Instead there will be a new ion with new properties: $[HgI_4]''$. This is a complex ion consisting of 1 mercury ion and 4 iodide ions. It is extremely stable and practically does not dissociate. All other complex ions are, likewise, weak electrolytes. Unlike simple ions, they are usually designated by square brackets, e. g.: $[Ag(NH_3)_2]^{\cdot}$, $[Co(H_2O)_6]^{\cdot\cdot}$, and $[PtCl_6]''$.

The following equations illustrate the formation of a few complex ions:

$$AgCl + 2NH_3 = [Ag(NH_3)_2]^{\cdot} + Cl'$$

$$PtCl_4 + 2H^{\cdot} + 2Cl' = 2H^{\cdot} + [PtCl_6]''$$

$$AgCN + K^{\cdot} + CN' = K^{\cdot} + [Ag(CN)_2]'$$

* The solubility of amphoteric hydroxides in alkali solutions, with the formation of complex hydroxysalts, is dealt with in the introduction to Exercise 22.

QUESTIONS

1. On the basis of the *SP* values given in Table XIII (p.335) explain why ZnS dissolves in dilute hydrochloric acid, while HgS does not.
2. Why is $BaSO_4$ precipitated from a solution of barium chloride by the addition of dilute sulphuric acid, whereas the precipitation of $CaSO_4$ requires the addition of concentrated sulphuric acid?
3. Write ionic equations for the formation of the insoluble substances Ag_3PO_4, $HgCrO_4$, $CaCO_3$, $Cu(OH)_2$, and FeS.
4. Why does the neutralisation of a gram-equivalent of any strong acid by a gram-equivalent of any strong alkali (in solution) produce the same amount of heat?
5. Write the equations for the hydrolysis of the following salts: $AlCl_3$, K_2SO_3, $Cu(NO_3)_2$, and NH_4CN. State whether the solution in each case is acidic, neutral, or alkaline.
6. Write ionic-molecular eqautions to show how the amphoteric hydroxide $Be(OH)_2$ dissolves in an acid solution and in an alkali solution.
7. Why do not all salts in practice undergo hydrolysis?

Problems

(The *SP* values needed for solving some of these problems are given in Table XIII on p. 335.)

1. What amount of $BaCO_3$ in grams is contained in 5 litres of a solution saturated at 25°?
2. Calculate the *SP* of a binary electrolyte with a molecular weight of 140 if 200 ml of a saturated solution contains 0.00016 g of it.
3. How many times greater is the solubility of $PbSO_4$ in pure water than in an 0.01 M solution of $MgSO_4$?
4. A 500 ml saturated solution contains $0.79 \cdot 10^{-3}$ g of AgCl. Calculate the *SP* of the salt.
5. How many grams of $SrSO_4$ does a 400 ml saturated solution contain?
6. Will a precipitate of AgCl form when we combine equal volumes of 0.0002 M solutions of $AgNO_3$ and HCl?
7. Will $SrSO_4$ be precipitated when 0.05 litre of an 0.002 M solution of SrS is combined with an equal volume of an 0.002 M solution of $MgSO_4$?
8. What amount of water should be taken to dissolve 1 g of $CaSO_4 \cdot 2H_2O$ and obtain a saturated solution?
9. A saturated solution of AgCN is combined with an equal volume of an 0.02 M solution of KI. Will AgI be precipitated?
10. Will $MgCO_3$ be precipitated when 0.6 litre of an 0.01 M solution of $MgSO_4$ is combined with 0.4 litre of an 0.002 M solution of Na_2CO_3?

LABORATORY WORK

Apparatus and materials: test tubes and rack; 10 ml measuring cylinder; casserole; glass rod; ammonium acetate; potassium carbonate; iron sulphide; cupric sulphide, zinc sulphide; manganese chloride; sodium chloride; sodium phosphate; concentrated nitric acid; concentrated sulphuric acid; saturated solution of strontium chloride; saturated solution of calcium sulphate; saturated solution of calcium chloride; saturated solution of silver acetate; saturated solution of strontium sulphate; 20% solution of silver nitrate; 20% solution of sodium acetate; 10% solution of ammonia;

1:6 sulphuric acid; 2N solution of sodium hydroxide; N solution of sodium phosphate; 2 N solution of hydrochloric acid; 0.5 N solution of ferric chloride; 0.5 N solution of sodium sulphide; N solution of sodium sulphate; 0.5 N solution of zinc sulphate; N solution of magnesium sulphate; 0.5 N solution of cupric sulphate; N solution of barium chloride; 0.5 N solution of mercuric nitrate; 0.5 N solution of potassium iodide; 0.5 N solution of aluminium sulphate; 0.5 N solution of bismuth nitrate; phenolphthalein solution; neutral litmus solution; litmus paper, and boiled distilled water.

Preparation of Saturated Solution of Silver Acetate. Add a solution of 3.30 g of anhydrous soda salt in 75 ml of water to a solution of 10.6 g of silver nitrate in 50 ml of water. Filter off the precipitate formed, wash it on the filter three or four times with cold water, transfer it to a 1 litre beaker, add 8 ml of 80% acetic acid in 92 ml of water, and heat the contents of the beaker to a temperature not exceeding 50° (until the evolution of carbon dioxide in the form of bubbles ceases). Now pour 900 ml of water into the beaker, heat the solution to boiling point, and, after it has cooled, filter off the undissolved precipitate.

1. Conditions at Which Precipitates Form. (a) Mix 2 ml of a saturated solution of strontium chloride in a test tube with an equal volume of a saturated solution of calcium sulphate. What happens? Repeat the experiment with 2 ml amounts of saturated solutions of calcium chloride and strontium sulphate. Does a precipitate form? Account for the results of these experiments in terms of *SP* values (Table XIII).

(b) Pour 2 ml of a saturated solution of silver acetate into each of 2 test tubes. Add 2 ml of a 20% solution of silver nitrate to one and an equal volume of a 20% solution of sodium acetate to the other. What happens? Give an explanation of the results.

What are the conditions at which a substance is precipitated from a solution?

After the experiment pour the solutions with precipitates of silver salts into special bottles.

2. Dissolving Precipitates. Into each of 2 test tubes put a pinch of zinc sulphide and a pinch of cupric sulphide, taken separately on the end of a knife. Add 2 ml of water to each of the test tubes and shake them. Write the *SP* equations for both substances. Then add 3 ml of a hydrochloric acid solution to each of the test tubes. What happens to the precipitates? Give an explanation of this.

3. Ionic Reactions. (a) Choose from the available reagents those whose interaction can produce precipitates of magnesium phosphate, ferric hydroxide, and cupric sulphide. Bring about the necessary reactions and record the colours of the precipitates formed. Write ionic-molecular equations of the reactions.

(b) Pour 2 ml of a sodium sulphate, zinc sulphate, and aluminium sulphate solution respectively into 3 test tubes; add 2 ml of a barium chloride solution to each of them. Write three ionic-molecular equations and one over-all ionic equation. Which ion is a reagent for detecting the sulphate ion?

(c) Reactions proceeding with the evolution of a gas (conduct the experiment in a ventilated hood!). Treat a lump of ferric sulphide (in

a test tube) with 3 ml of a sulphuric acid solution, heating the test tube. Identify the gas evolved by its odour. Write the equation of the reaction.

(d) Treat about 0.5 g of table salt in a test tube with 2-3 ml of concentrated sulphuric acid. Observe the evolution of hydrogen chloride. Write the equation of the reaction. Why is not dilute sulphuric acid used for this reaction?

(e) Pour 5 ml of a 2 N solution of hydrochloric acid (measured in a cylinder) into a casserole and add 5 ml of a 2 N solution of sodium hydroxide first in small portions and then in drops. Stir the solution with a glass rod and test it with litmus paper (this should be done by putting a drop of the solution on small strips of red and blue litmus paper and observing the change in colour). Add alkali until the solution ceases changing the colour of either litmus paper. Evaporate the obtained neutral solution in the casserole. What is the residue? Taste it. Write the equation of the neutralisation reaction. What other two reactions of complex substances can produce sodium chloride? Write the equations of these reactions.

4. Hydrolysis. Pour 3 ml of a neutral litmus solution into each of six numbered test tubes. Introduce a few crystals of the following substances into five of the test tubes respectively: potassium carbonate, sodium phosphate, sodium chloride, aluminium chloride, and ammonium acetate. Shake the solutions and compare their colours with the colour of the litmus solution in the sixth test tube, examining them against the background of a sheet of white paper.

Record the results of the experiments as follows:

No. of test tube	Substance	Colour of litmus	Is the solution acidic, neutral, or alkaline?

What type of salts underwent hydrolysis? Write the equations of the hydrolysis reactions.

5. Shifting the Equilibrium of Hydrolysis. Pour several drops of a solution of bismuth nitrate into a test tube and dilute the solution gradually with distilled water. A precipitate forms. Write the equation of the hydrolysis reaction. Add a few drops of concentrated nitric acid to the test tube with the precipitate. What happens to the precipitate? Explain this on the basis of the equation for the equilibrium constant.

6. Effect of Temperature on Hydrolysis. Pour 4-5 ml of a sodium acetate solution and 1-2 drops of a phenolphthalein solution into a

test tube. Heat the solution until it boils and observe the appearance of a pink colour. Write the equation of the hydrolysis reaction and explain what happened. What factors influence equilibrium in hydrolysis and why?

7. Amphoteric Hydroxides. Prepare a precipitate of aluminium hydroxide and pour the solution with the precipitate into two test tubes. Add an excess of alkali to one and of acid to the other. Watch the precipitates dissolve. Write the equations of the three reactions carried out. Why do amphoteric hydroxides dissolve both in acids and in alkalis?

8. Reactions Proceeding with the Formation of a Complex Ion. (a) Prepare a cupric hydroxide precipitate by means of an exchange reaction between solutions of a cupric salt and sodium hydroxide. Write the equation of the reaction.

Pour the solution off from the precipitate and add an ammonia solution to the precipitate in the test tube. What happens? Write the equation of the reaction, which produces the complex ion $[Cu(NH_3)_4]^{\cdot\cdot}$.

(b) Add a few drops of a potassium iodide solution to a solution of a mercuric salt. What is formed? Write the equation of the reaction.

Write the equation for the solubility product of HgI_2. What should happen if the concentration of iodine ions is increased? Add an excess of a KI solution to the precipitate. Why does the precipitate dissolve?

Exercise 16

OXIDATION-REDUCTION REACTIONS

SUBJECTS FOR STUDY

Oxidation-reduction reactions from the electronic standpoint; oxidation-reduction characteristics of neutral atoms and ions; writing equations for oxidation-reduction reactions; effect of the pH-value.

Unlike ion-exchange reactions, oxidation-reduction reactions are marked by a transfer of electrons from one reactant to another, this altering the charge or valence of the interacting substances.

From the electronic standpoint a process involving the loss of electrons is termed *oxidation*, while a process involving the gain of electrons is termed *reduction*. Accordingly, substances that lose electrons in oxidation-reduction reactions are called *reducing agents*, while substances that gain, or receive, electrons are called *oxidising agents*.

Neutral atoms (molecules), elementary ions, and complex ions can take part in oxidation-reduction reactions.

The oxidation-reduction properties of neutral atoms and of ions can easily be explained on the basis of the Mendeleyev Periodic System of Elements (Table 11).

1. D. Mendeleyev's Periodic System of Elements. In 1869 the great Russian scientist Dmitry Mendeleyev discovered one of the most fundamental laws of nature: the Periodic Law of Chemical Elements. This Law he formulated thus: "*The properties of the elements (and, hence, of the simple and compound substances they form) are periodic functions of their atomic weights*".

The Law was embodied in the Periodic System of Elements, which has had a most profound influence on the progress of chemistry.

The most common method of representing the Periodic System is in the form of an eight-group table, such as is given on the inside cover of the book.

The elements are arranged in the Periodic System according to their atomic numbers (from 1 to 103). These numbers indicate the positive charge of the atomic nucleus (the number of protons) or the number of electrons in the electron layers of the atom.

Each period in the Periodic Table begins with an element whose atom contains but one electron in its outer layer; the periods end with elements whose atoms have 8 electrons in the outer layer (atoms of inert gases). The first period ends with the inert gas helium, which has two electrons in its outer layer. In all, there are 7 periods in the Table, the number of each period indicating the number of electron layers in the atom. The only exception is the fifth-period element *palladium*, whose atom has 4 electron layers.

According to the manner in which their electron sublevels are filled, the elements may be divided into four groups:

(a) The elements in whose atoms electrons are added to the *s* sublayer of the outer layer, or shell, are called *s*-elements. There are 14 such elements in the Table: the first two in each period.

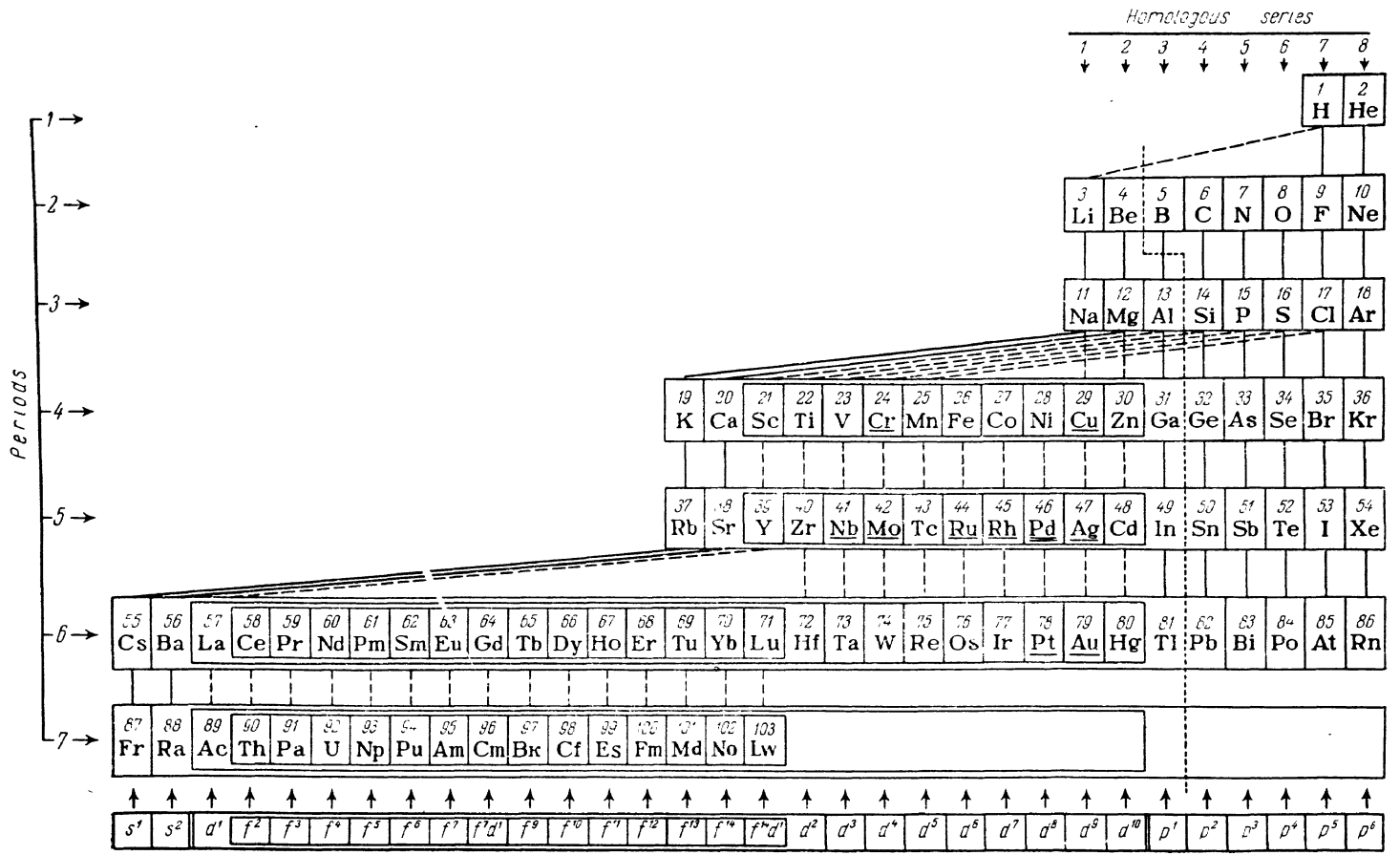
(b) The elements in whose atoms electrons are added to the *p* sublayer of the outer shell are called *p*-elements. The last 6 elements in each of five periods (2-6) are *p*-elements.

(c) The elements in whose atoms electrons are added to the *d* sublayer of the next to last layer are called *d*-elements. Since the *d* sublayer contains a maximum of 10 electrons, there are 10 such elements (atomic numbers 21-30, 39-48, 57, and 72-80) in each of periods 4, 5, and 6 and one element (number 89) in period 7, which makes a total of 31 elements. In their outermost shells these atoms usually have two electrons, seldom one (this is true of 9 elements, which are underlined by a single line in Table 11), while palladium has none because both of the *s*-electrons are in the *d* sublayer of the neighbouring layer (in Table 11 it is underlined with a double line).

(d) The rare-earth elements, or lanthanides, in whose atoms electrons are added to the *f* sublayer of the fourth shell. Since the *f* sublayer can hold a maximum of 14 electrons, there are 14 lanthanides in all (atomic numbers 58-71). They are situated in period 6, their atoms having 6 electron shells each. The outermost layer in these atoms has 2

D. I. Mendeleyev's Periodic System of Elements

Table 11



electrons ($6s^2$), while the one next to last (layer V) has 8 electrons. The *f* sublayer begins to be built up by two electrons at number 58 (Ce). The 64th element (gadolinium) and the 71st (lutetium), in addition to the *f*-electrons, add one electron each to the *d* sublayer of the fifth shell.

The actinides are elements whose atoms, like those of the lanthanides, build up the *f* sublayer, but of the fifth shell instead of the fourth. In elements 93-102 the distribution of electrons is similar to that in the above-situated (61-70) lanthanides. The six valence-electrons of uranium are distributed among the layers thus: $5f^3\ 6d^1\ 7s^2$. For the 5 valence-electrons of protactinium (91) and the 4 valence-electrons of thorium (90) there are two possible combinations of electron distribution: for protactinium $5f^2\ 6d^1\ 7s^2$ or $5f^1\ 6d^2\ 7s^2$ and for thorium $5f^1\ 6d^1\ 7s^2$ or $6d^27s^2$. Thirteen actinides are known at present (90-102).

The chemical properties of an element are related to the distribution of electrons in the atom. A number of elements with similar chemical properties due to an identical number of valence-electrons are called a *homologous series*, or a *series of analogues*. The elements of one and the same homologous series, or series of analogues, are connected in Table 11 by either a solid or a broken line.

The solid line is used to connect the analogues in the principal subgroups; the broken line, to connect the analogues in the subordinate subgroups, the lanthanides, and the actinides.

The similarity in the properties of the elements in the principal subgroups may be traced to the same number of electrons in the outer shells of the atoms of these elements. In the subordinate subgroups, however, the similarity of the elements depends not only on the outer electrons, but also on the electrons that are added (above eight) to the next layer. Thus, the element rhenium (Z=75), with the distribution of electrons in the atom)2)8)18)32)8 + 5)2, is an analogue of the element manganese (Z=25), which has the electron distribution)2)8)8 + 5)2. The actinides are chemically analogous to the lanthanides.

The study of atomic structure threw light on the underlying reason for periodicity. *The periodic change in the properties of the elements is related to a periodic recurrence of similar electron structure.*

2. Oxidation-reduction Properties of Neutral Atoms. All the elements can, according to their chemical properties, be divided into three groups: reducing agents, oxidising-reducing agents, and elements that are neither one nor the other.

(a) *The reducing agents* are elements whose atoms have from 1 to 3 electrons in the outer shell. In chemical reactions they do not receive electrons, but only give them up:

$$R - ne^- \rightarrow R^{+n}$$

In Table 11 these elements are situated to the left of the dotted line.

This group of elements consists primarily of metals, the exceptions being H, He, and B.

(b) *The oxidising-reducing agents* are elements whose atoms have 4, 5, 6, and 7 electrons in the outermost shell. They can either take up electrons (to 8), i. e., act as oxidising agents, or furnish electrons, i. e., act as reducing agents *. Thus, an atom with 6 electrons in its outer shell can react according to either of the following two equations:

$$R + 2e^- = R^{-2} \text{ (as an oxidising agent)}$$
$$R - 6e^- = R^{+6} \text{ (as a reducing agent)}$$

In Table 11 the elements of this group are situated to the right of the dotted line (the inert gases are an exception). Hydrogen and boron are likewise oxidising-reducing agents.

(c) *The inert gases* are elements whose atoms have 8 electrons in the outer shell (helium has 2). They neither receive nor give up electrons in chemical reactions and, consequently, exhibit neither oxidising nor reducing properties. Six elements make up this group.

The oxidising-reducing properties of neutral atoms are expressed in terms of ionisation potential and electron affinity.

The ionisation potential (unit: electron-volt, eV) is the work required to split off an electron from a neutral atom and can serve as a measure of an atom's reducing activity.

The electron affinity (usually expressed in Calories) is the energy of the addition of one electron to a neutral atom. It can serve as a measure of the relative oxidising activity of neutral atoms, which is inversely proportional to the reducing activity. Ionisation potential and electron affinity data can be used to characterise the changes in oxidation-reduction activity in the periods and homologous series of elements in the Periodic Table.

In the periods the ionisation potential, as a rule, increases from left to right, while the reducing activity declines and the oxidising activity mounts, owing to rising electron affinity. In the homologous series of the *s*-, *f*-, and *p*-elements the ionisation potential diminishes as we move downwards; the reducing activity increases and the oxidising activity falls off, since the electron affinity decreases. In the case of the *d*-elements, however, the change in ionisation potential is more complex. The strongest oxidising agents are in the upper right-hand part of the Table (fluorine, oxygen, chlorine, sulphur, etc.), while the reducing agents are concentrated in the lower left-hand part (francium, caesium, radium, barium, lanthanum, etc.).

3. Oxidation-reduction Properties of Elementary Ions**. Elementary ions can be charged either negatively or positively.

* Oxygen and fluorine are oxidising agents only; their atoms do not give up electrons in reactions.

** The radii of some ions are given in Table XVI (see Appendix).

(a) *Negative Ions.* The ions of this group are formed by the addition of one or several electrons to a neutral atom of a nonmetal.

For instance, a neutral atom of sulphur S^0, whose atomic number is 16, has the electron distribution)2)8)6. It can add another two electrons, becoming a doubly charged negative ion S^{-2} with the electron distribution)2)8)8.

In their outer shells elementary negative ions have 8 electrons; accordingly, they can only give up electrons and are reducing agents.

Examples: The reducing ions S^{-2}, I^{-1}, Br^{-1}, Se^{-2}, Te^{-2}, etc., in such compounds as H_2S, HI, HBr, H_2Se, and H_2Te, or in corresponding salts: Na_2S, KI, KBr, Na_2Se, and K_2Te.

(b) *Positive Ions.* The ions of this group can be divided into 2 subgroups according to their charge; there can be ions of maximum charge and ions of lower charge.

Positive elementary ions can have charges of 1 to 4 (free quadripositive ions are seldom encountered). Ions of maximum charge are formed when neutral atoms give up all their outer, or valence, electrons. For instance, the Al atom with the electron arrangement)2)8)3 or the Sn atom with the arrangement)2)8)18)18)4 can lose their respective 3 and 4 outer electrons to become Al^{+3} and Sn^{+4} with the electron arrangements)2)8 and)2)8)18)18. In their outer shells ions of maximum positive charge have either 8 or 18 electrons, which means that such ions can no longer relinquish electrons and can only recapture earlier lost electrons, acting as oxidising agents.

Examples: The oxidising ions Sn^{+4}, Pb^{+4}, Hg^{+2}, Ag^{+1}, etc., in various compounds.

Ions of lower charge are formed when neutral atoms give up only part of their outer electrons. The Sn atom, with the electron arrangement shown above, may lose only 2 electrons. In that case it turns into the bipositive ion Sn^{+2}, which has the electron distribution)2)8)18)18)2 and can therefore give up another 2 electrons, exhibiting reducing properties (or can recapture the earlier lost 2 electrons, in this case exhibiting oxidising properties). Consequently, ions of lower positive charge can act as *reducing* (as well as oxidising) agents. The reducing properties of the ions of this subgroup are more pronounced than their oxidising properties.

Reducing ions: Sn^{+2}, Ti^{+3}, Ce^{+3}, Fe^{+2}, etc.

4. Oxidising-reducing Properties of Composite Ions. Most composite ions are negatively charged (e. g., NO_3', CrO_4'', MnO_4', ClO_3', AsO_4''', NO_2', SO_3'', and SnO_2''); there are, however, a few positive composite ions as exceptions ($H_3O^{\cdot}$, $NH_4^{\cdot}$, $PH_4^{\cdot}$).

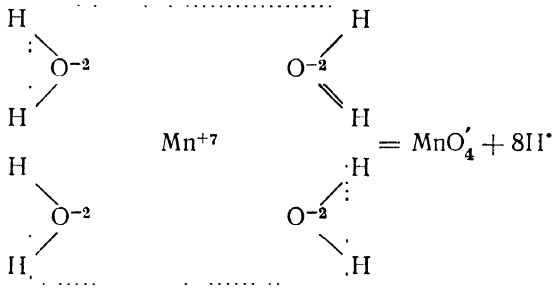
These ions are known to form in aqueous solutions as a result of the electrolytic dissociation of acids and salts. Nitric acid and potassium permanganate, for instance, are ionised thus:

$$HNO_3 \rightleftarrows H^{\cdot} + NO_3'$$

$$KMnO_4 \rightleftarrows K^{\cdot} + MnO_4^{\prime}$$

The chemical bond between $H^{\cdot}$ and $NO_3^{\prime}$, as well as between $K^{\cdot}$ and $MnO_4^{\prime}$, is ionogenic; it is for this reason that the HNO_3 and $KMnO_4$ molecules break up into such ions. Can the composite ions $NO_3^{\prime}$ and $MnO_4^{\prime}$ in turn break up (dissociate) into components? Experimental findings lead to the conclusion that composite negative ions practically do not dissociate, since the chemical bond between their component atoms is covalent (nonionogenic). The $NO_3^{\prime}$ and $MnO_4^{\prime}$ ions — and, hence, all other composite negative ions—act as monolithic groups.

As pointed out above, free positive ions of charges above +3 do not exist in aqueous solutions; indeed, even tripositive ions, if they have a small radius, turn into composite ions. This is due to the fact that if multipositive ions did form in an aqueous solution, they would at once, owing to the high specific density of the electric charge, combine with the oxygen ions of the water to form composite negative ions. This is what would happen to the heptapositive manganese "ion":



The heptapositive Mn "ion" polarises the oxygen ions to such a degree that the ionic bonds between them *are converted entirely to covalent bonds*, which produces a monolithic composite negative ion. This is corroborated by the hydrolysis of halogen anhydrides, such as PCl_5:

$$\underbrace{PCl_5}_{PO_4^{\prime\prime\prime}} + 4H^{\cdot}OH^{\prime} = H_3PO_4 + 5HCl$$

In other words, pentavalent phosphorus in an aqueous medium is at once converted to the composite negative ion $PO_4^{\prime\prime\prime}$. Hence, *there are no* free multipositive ions; as for Mn^{+7} in $MnO_4^{\prime}$ and P^{+5} in $PO_4^{\prime\prime\prime}$, they can be regarded as having a positive valence, but not charge. Elements with a high positive valence form composite negative ions of the types RO_4^{-m}, RO_3^{-n}, and RO_2^{-q}.

For instance, $MnO_4^{\prime}$ is an oxidising ion and in certain conditions may be reduced to the ion $MnO_3^{\prime\prime}$, adding three electrons. With respect

Table 12

Composition and Properties of Some Composite Negative Ions

Positive valence of element R				
R^{+3}	R^{+4}	R^{+5}	R^{+6}	R^{+7}
$NO_2^{'}$		$\underline{NO_3^{'}}$ *		
$AsO_3^{'''}$		$\underline{AsO_4^{'''}}$		
	$SO_3^{''}$		$\underline{SO_4^{''}}$	
	$SeO_3^{''}$		$\underline{SeO_4^{''}}$	
$CrO_2^{'}$			$\underline{CrO_4^{''}}$	
$ClO_2^{'}$		$ClO_3^{'}$		$\underline{ClO_4^{'}}$
$IO_2^{'}$		$IO_3^{'}$		$\underline{IO_4^{'}}$
$BrO_2^{'}$		$\underline{BrO_3^{'}}$		
	$MnO_3^{''}$		$MnO_4^{''}$	$\underline{MnO_4^{'}}$
rise in positive valence—oxidation →				
a shift of 1 box to the right—loss of 1 e^- decrease in positive valence—reduction				
← a shift of 1 box to the left—gain of 1 e^-				

* Oxidising ions are underlined; the rest are reducing ions.

to the $MnO_4^{'}$ ion the $NO_2^{'}$ ion is a reducing agent: it can give up 2 electrons, undergoing oxidation to the $NO_3^{'}$ ion.

5. Writing Equations of Oxidation-reduction Reactions of the Simplest Type. These are reactions between two substances only: a reducing agent (A) and an oxidising agent (B). The equation is therefore written:

$$mA + nB =$$

where m and n are coefficients. The problem of writing the full equation is a problem of finding these coefficients. They are found by applying the electron balance rule: *the total number of electrons lost by the reducing agent must equal the total number of electrons gained by the oxidising agent.*

Example. Write the equation of the reaction $Al + O_2 =$
This is done in 3 stages:

(1) First of all, it is necessary to identify the reducing and the oxidising agent. Aluminium is a metal of group III; its atom gives up 3 electrons, i.e., acts as a reducing agent. Oxygen, on the other hand, is a nonmetal and with respect to the reducing agent Al it acts as an oxidising agent: the O_2 molecule takes on 4 electrons.

(2) We can now write the skeleton electron balance:

$$\begin{array}{l|l} Al - 3e^- = Al^{+3} & 4 \\ O_2 + 4e^- = 2O^{-2} & 3 \end{array}$$

where 4 and 3 are additional factors that have to be introduced into the equation of the reaction to balance the number of electrons lost and gained.

(3) The equation is now written in its final form:

$$4Al + 3O_2 = 2Al_2O_3$$

Exercise. Write the equations of the following reactions:

(1) $P + O_2 =$ (2) $SO_2 + O_2 =$ (3) $Na + S =$
(4) $K + Br_2 =$ (5) $H_2S + I_2 =$ (6) $Mg + N_2 =$
(7) $FeCl_2 + Cl_2 =$ (8) $Al + CuSO_4 =$ (9) $Fe(NO_3)_2 + AgNO_3 =$

6. Writing Equations of Oxidation-reduction Reactions That Take Place in Aqueous Solutions. These equations are of the general type:

$$mA + nB + pC =$$

where A is the reducing agent, B is the oxidising agent, and C is the molecule of the medium. The coefficients m and n are found as explained above from the skeleton electron balance. The coefficient p is in most cases determined when writing the equation, after the coefficients m and n have been found.

Reactions in Acid Solutions

Example 1. Find the coefficients for the following reaction:

$$\underline{KNO_2} + \underline{\underline{KMnO_4}} + H_2SO_4 = \underline{KNO_3} + K_2SO_4 + \underline{\underline{MnSO_4}} + H_2O$$

To trace the whole process of the writing of the equation, we must break it up into steps:

(a) Underline the reducing ion and its oxidised form once, the oxidising ion and its reduced form twice. The NO_2^- ion is oxidised to the NO_3^- ion, while the MnO_4^- ion is reduced to the Mn^{++} ion.

(b) An additional skeleton electron balance is drawn up*, and the additional factors (the coefficients m and n) are found in this way:

	Least common multiple	Additional factors
$NO_2^- - 2e^- = NO_3^-$	10	5
$MnO_4^- + 5e^- = Mn^{++}$		2

* Tables 12 and 13 may be used to determine the number of electrons lost by the reducing agent and the number gained by the oxidising agent.

Table 13

Reducing and Oxidising Agents (Reductants and Oxidants)

Reducing agent	Number of electrons lost	Oxidised form of reductant	Conditions in which reaction is conducted	Oxidising agent	Number of electrons gained	Reduced form of oxidant	Conditions in which reaction is conducted
NO_2' *	$2e^-$	NO_3'		MnO_4'	$5e^-$	$Mn^{\cdot\cdot}$	Acid solution
S''	$2e^-$	S		MnO_4'	$3e^-$	MnO_2	Neutral or weakly alkaline solution
S''	$6e^-$	SO_2	In combustion reactions in the gaseous phase	MnO_4'	$1e^-$	MnO_4''	Strongly alkaline solution and shortage of reductant
S''	$8e^-$	SO_4''	Action of strong oxidants				
S	$6e^-$	SO_4''	Action of strong oxidants	MnO_2 ***	$2e^-$	$Mn^{\cdot\cdot}$	Acid solution
SO_3'' *	$2e^-$	SO_4''		Cr_2O_7''	$6e^-$	$2Cr^{\cdot\cdot\cdot}$	
AsO_3'''	$2e^-$	AsO_4'''		PbO_2	$2e^-$	$Pb^{\cdot\cdot}$	
$Mn^{\cdot\cdot}$	$2e^-$	MnO_2	In neutral or alkaline solution	NO_3'	$1e^-$	NO_2	Concentrated acid
				NO_3'	$3e^-$	NO	Dilute acid
MnO_2 *	$2e^-$	MnO_4''	In alkaline solution	NO_3'	$8e^-$	NH_3	Action of metals in alkaline solution
$Fe^{\cdot\cdot}$	$1e^-$	$Fe^{\cdot\cdot\cdot}$					
H	$1e^-$	$H^{\cdot}$		NO_2' ***	$1e^-$	NO	
Me	ne^-	Me^{+n}		O_2	$4e^-$	$2O^{-2}$	

CrO_2'	$3e^-$	CrO_4''	In alkaline solution	$O_2 \cdot O$	$2e^-$	$O_2 + O^{-2}$	
Cl'	$1e^-$	Cl		$[O_2]''$ ***	$2e^-$	$2O^{-2}$	
Br'	$1e^-$	Br		SO_4''	$2e^-$	SO_2	Concentrated acid
I'	$1e^-$	I		SO_3'' ***	$4e^-$	S	
Cl_2 *	$10e^-$	$2ClO_3'$	In boiling alkaline solution	$H^{\cdot}$	$1e^-$	H	
				Cl_2	$2e^-$	$2Cl'$	
Cl_2	$2e^-$	$2ClO'$	In cold alkaline solution	Br_2	$2e^-$	$2Br'$	
$[O_2]''$ *	$2e^-$	O_2		ClO'	$2e^-$	Cl'	
$Sn^{\cdot\cdot}$	$2e^-$	$Sn^{\cdot\cdot\cdot}$	In acid solution	ClO'	$1e^-$	Cl	Negative ion Cl' acts as reductant
SnO_2''	$2e^-$	SnO_3''	In alkaline solution				
Zn **	$2e^-$	ZnO_2''	In alkaline solution	ClO_3' ****	$6e^-$	Cl'	
$Ce^{\cdot\cdot\cdot}$	$1e^-$	CeO_2		ClO_3' ****	$5e^-$	Cl	Negative ion Cl' acts as reductant

* Reductants that can also exhibit oxidising properties.
** All the amphoteric bivalent metals react as zinc does, while the trivalent metals form the acid radicals MeO^- or MeO_3^{-3}.
*** Oxidants that can also exhibit reducing properties.
**** The ions BrO_3' and IO_3' react identically.

(c) Now substitute the coefficients found into the equation:

$$5KNO_2 + 2KMnO_4 + H_2SO_4 = KNO_3 + K_2SO_4 + MnSO_4 + H_2O$$

(d) From the coefficients found determine the number of molecules of the products, except the water:

$$5KNO_2 + 2KMnO_4 + H_2SO_4 = 5KNO_3 + K_2SO_4 + \\ + 2MnSO_4 + H_2O$$

Rule. In an acid solution all the ions of metals with charges of 1 to 3 combine with acid radicals to form salts.

(e) Count the number of sulphuric acid (medium) radicals in the right-hand side of the equation (in this case it is 3), in this way finding the coefficient for the acid molecules; insert it into the equation:

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + K_2SO_4 + 2MnSO_4 + H_2O$$

(f) From the number of hydrogen ions in the amount of acid taken determine the number of water molecules formed (in this particular case it is 3) and insert the last coefficient:

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + K_2SO_4 + \\ + 2MnSO_4 + 3H_2O$$

Note. The equation written is checked by counting the number of oxygen atoms in the left-hand and the right-hand side.

Steps "*c*", "*d*", "*e*", and "*f*" are performed mentally, and the equation need not be rewritten several times.

Example 2. Find the coefficients in the following equation:

$$FeSO_4 + KMnO_4 + H_2SO_4 = Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$$

After carrying out steps* "*a*", "*b*", "*c*", and "*d*" as in Example 1, we obtain:

$$10FeSO_4 + 2KMnO_4 + H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + \\ + 2MnSO_4 + H_2O$$

Then (step "*e*") count the number of sulphuric acid radicals in the right-hand side of the equation (it equals 18) and deduct from it the number of the same radicals contained in the reductant (it equals 10); the difference 18—10=8 yields the coefficient for the acid molecules. This element in writing equations should be borne in mind.

* The additional factors found have to be doubled because the molecule of the resulting ferric sulphate contains an even number of ferric ions.

Determine (step "*f*") the number of water molecules formed. The equation now assumes the final form:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Example 3. In this example the acid is the medium and plays the part of an oxidising or reducing agent. This being so, the formula of the acid should be written in the equation twice. Complete the equation:

$$Cu + HNO_3 + HNO_3 = Cu(NO_3)_2 + NO + H_2O$$

After carrying out all the steps, we obtain the final equation:

$$3Cu + 2HNO_3 + 6HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

From this equation it follows that out of the 8 molecules of nitric acid needed for the reaction, 2 are used for oxidation (the hydrogen ions of the oxidant and the medium are used to form water).

Exercise. Insert the coefficients in the following skeleton reactions:

(1) $K_2S + KMnO_4 + H_2SO_4 \rightarrow S + K_2SO_4 + MnSO_4 + H_2O$
(2) $KNO_2 + K_2Cr_2O_7 + HNO_3 \rightarrow KNO_3 + Cr(NO_3)_3 + H_2O$
(3) $FeSO_4 + KClO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + KCl + H_2O$
(4) $SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
(5) $NaI + PbO_2 + H_2SO_4 \rightarrow Na_2SO_4 + PbSO_4 + I_2 + H_2O$
(6) $SnCl_2 + K_2Cr_2O_7 + HCl \rightarrow H_2[SnCl_6] + KCl + CrCl_3 + H_2O$
(7) $KI + KNO_2 + H_2SO_4 \rightarrow I_2 + NO + K_2SO_4 + H_2O$
(8) $H_2S + K_2Cr_2O_7 + H_2SO_4 \rightarrow S + K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
(9) $FeSO_4 + HNO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO + H_2O$
(10) $Cu + H_2SO_4 + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$
(11) $Ag + HNO_3 + HNO_3 \rightarrow AgNO_3 + NO_2 + H_2O$
(12) $HCl + MnO_2 + HCl \rightarrow Cl_2 + MnCl_2 + H_2O$
(13) $S + HNO_3 \rightarrow H_2SO_4 + NO_2 + H_2O$

Reactions in Alkaline Solutions

Example 1. Complete the equation:

$$NaCrO_2 + Br_2 + NaOH = Na_2CrO_4 + NaBr + H_2O$$

After carrying out steps "*a*", "*b*", "c", and "*d*" as above, we obtain the following equation:

$$2NaCrO_2 + 3Br_2 + NaOH = 2Na_2CrO_4 + 6NaBr + H_2O$$

Rule. In an alkaline solution all the acid radicals formed (negative ions) combine with the positive ions of metals to form salts.

Count (step "*e*") the number of metal ions in the right-hand side of the equation that were part of the alkali molecule (in this case Na^+ ions) and deduct from them the number, if any, of the same ions that were part of the reductant or oxidant molecules (in this case 10-2). The difference yields the coefficient for the alkali:

$$2NaCrO_2 + 3Br_2 + 8NaOH = 2Na_2CrO_4 + 6NaBr + H_2O$$

From the number of hydrogen atoms in the left-hand side of the equation (step "*f*") we now find the coefficient for the water (provided no other hydrogen-containing compounds are formed in the reaction):

$$2NaCrO_2 + 3Br_2 + 8NaOH = 2Na_2CrO_4 + 6NaBr + 4H_2O$$

Exercise. Insert the coefficients in the following skeleton reactions:

(1) $Na_3CrO_3 + Cl_2 + NaOH \rightarrow Na_2CrO_4 + NaCl + H_2O$
(2) $MnO_2 + Br_2 + KOH \rightarrow K_2MnO_4 + KBr + H_2O$
(3) $NaCrO_2 + H_2O_2 + NaOH \rightarrow Na_2CrO_4 + H_2O$
(4) $MnO_2 + KClO_3 + KOH \rightarrow K_2MnO_4 + KCl + H_2O$
(5) $Bi_2O_3 + Br_2 + KOH \rightarrow KBiO_3 + KBr + H_2O$
(6) $Al + KNO_3 + KOH \rightarrow K_3AlO_3 + NH_3 + H_2O$
(7) $Zn + KNO_2 + KOH \rightarrow K_2ZnO_2 + NH_3 + H_2O$
(8) $Fe_2O_3 + NaNO_3 + NaOH \rightarrow Na_2FeO_4 + NaNO_2 + H_2O$

Reactions in Neutral Solutions

Equations of reactions of this type are written according to the same procedure, with molecules of water introduced instead of the acid or alkali.

Exercise. Insert the coefficients in the following skeleton reactions:

(1) $Fe(OH)_2 + O_2 + H_2O \rightarrow Fe(OH)_3$
(2) $Ni(OH)_2 + NaOCl + H_2O \rightarrow Ni(OH)_3 + NaCl$
(3) $MnSO_4 + KMnO_4 + H_2O \rightarrow MnO_2 + K_2SO_4 + H_2SO_4$
(4) $SO_2 + KMnO_4 + H_2O \rightarrow MnO_2 + K_2SO_4 + H_2SO_4$

7. Oxidation-reduction Equivalents. One and the same substance can take part both in exchange and oxidation-reduction (redox) reactions. Potassium chromate is a case in point. It can take part in the following two reactions:

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$$

(exchange reaction)

$$\overset{-1}{6KI} + \overset{+6}{2K_2CrO_4} + 8H_2SO_4 = 3\,I_2^0 + 5K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 8H_2O$$

(redox reaction)

The equivalents of potassium chromate in these reactions are different. To find its equivalent from the exchange reaction, we have to divide the molecular weight of potassium chromate by 2 (the valence of the salt's acid radical). The quantity obtained in this way is termed the *normal*, or *exchange, equivalent.* To find the *redox equivalent*, we have to divide the molecular weight of the substance by the number of electrons that are lost or gained by the reductant or oxidant molecule in the reaction. In the second reaction, for instance, the potassium chromate molecule (or, to be more exact, the $CrO_4^{''}$ ion) gains 3 electrons; hence, the equivalent equals the molecular weight divided by 3. In the case of some substances the exchange and redox equivalents may be equal.

QUESTIONS

1. Write two equations of redox reactions in each of the different types of solutions from the exercises above.
2. Calculate the values of the exchange and the redox equivalent of $KMnO_4$ in an acid solution.
3. The substances in the upper boxes of the table below are converted by reactions to the substances in the lower boxes:

1	2	3	4	5	6	7	8
H_2SO_4	$SnCl_2$	$Fe_2(SO_4)_3$	F_2	NiS	PH_3	NaClO	K_2HAsO_4
SO_2	$SnCl_4$	$FeSO_4$	KF	$NiSO_4$	H_3PO_4	NaCl	$KAsO_2$

Copy the table in your notebook and indicate in the vacant boxes in which cases the substance was oxidised and in which it was reduced.

4. With an eye to the fact that HI is both a reductant and an oxidant, write the equation for the oxidation of HI by potassium dichromate $K_2Cr_2O_7$.
5. On the basis of negative ion radii (Table XVI on p. 337) explain why hydrogen telluride is a stronger reducing agent than hydrogen sulphide is.

LABORATORY WORK

Apparatus and materials: test tubes and rack; copper shavings; iron nails; crystalline potassium permanganate; concentrated nitric acid; concentrated hydrochloric acid; 0.5 N solution of cupric sulphate; 0.5 N solution of potassium iodide; 2 N solution of sulphuric acid; N solution of potassium nitrite; 2 N solution of sodium hydroxide; 0.5 N solution of manganese chloride; 0.05 N solution of potassium permanga-

nate; 0.1 N solution of sodium metachromite; 0.3 N solution of potassium dichromate; 0.2 N solution of potassium iodate; 0.5 N solution of potassium sulphite; starch solution; chlorine water; bromine water; hydrogen sulphide water, and sandpaper.

Preparation of Starch Solution. In a mortar, grind 0.5 g of soluble starch with 5 ml of water; pour the mixture into 95 ml of boiling water. To protect the solution from decomposition by microorganisms, add a few grains of HgI_2 or salicylic acid. The starch solution should with iodine produce a blue colouration; a violet or reddish-brown colour of the starch, upon contact with iodine, indicates that the starch solution is unsatisfactory.

Preparation of Chromite Solution. Dissolve 8.9 g of chromic chloride or 16.5 g of potassium dichromate in 50 ml of water and add 10 ml of a 25% ammonia solution to the boiling solution. Filter off the precipitate and wash it with hot water until the Cl' and SO''_4 ions have been removed. Then dissolve the precipitate in 10 ml of a 40% solution of sodium hydroxide and dilute to 1 litre. Prepare the solution when needed.

Oxidation-reduction Reactions *. (a) Into a solution of cupric sulphate lower an iron nail whose surface has been cleaned with sandpaper. Keep the nail in the solution for 3-5 minutes. What happens?

(b) To 2-3 ml of a potassium iodide solution add an equal volume of chlorine water. Why does the colour of the solution change? Write the equation for the reaction that takes place. What is the substance that imparts the yellow colour to the solution?

(c) To 2-3 ml of hydrogen sulphide water add bromine water by drops. Observe how the solution loses colour and becomes turbid. Write the equation of the reaction that takes place.

(d) To 2-3 drops of a potassium iodide solution add 2 ml of an H_2SO_4 solution and 2-3 drops of a potassium iodate solution. The solution acquires a yellow colour, owing to the formation of free iodine. Write the equation of the reaction that takes place. Prove the presence of iodine in the solution, bearing in mind that the best reagent for free iodine is starch.

(e) To 2 ml of a potassium sulphite solution add an equal volume of dilute sulphuric acid and 1 ml of a potassium permanganate solution. The violet colour of the latter disappears. Write the equation of the reaction that takes place.

(f) Establish experimentally that potassium nitrite in an acid solution is a reducing agent with respect to potassium dichromate (the solution should be warmed).

(g) Add 2 ml of concentrated nitric acid (in a ventilated hood!) to a test tube containing some copper shavings. Observe the evolution of a gas (what is its colour?). Write the equation of the reaction that takes place.

(h) Pour 1 ml of concentrated hydrochloric acid on a few crystals of potassium permanganate in a test tube. After a short time observe the evolution of a gas in the test tube (what colour is the gas?). Write the equation of the reaction that takes place.

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* For every equation draw up a skeleton electron balance.

(i) To 1 ml of a sodium chromite solution add an equal volume of an alkali and 3 ml of bromine water. Boil the solution and note the change in its colour. Write the equation of the reaction that takes place.

(j) Add an alkali solution and then some bromine water to a $MnCl_2$ solution. Note the changes that occur and write the equations of the reactions (exchange and redox).

Exercise 17

HYDROGEN, OXYGEN, AND OZONE

SUBJECTS FOR STUDY

Hydrogen. Atomic structure and chemical properties; monoatomic hydrogen; molecular hydrogen; burning of hydrogen; hydrogen as a reducing agent, and methods of preparing hydrogen.

Oxygen. Atomic structure and chemical properties; reactions of oxidation and combustion; oxidation by oxygen in neutral and alkaline media; methods of preparing oxygen.

Ozone. Molecular structure and chemical properties; methods of preparation.

1. Hydrogen. Hydrogen is the lightest of the chemical elements; 1 litre of this gas at N. T. P. weighs 0.0899 g.

In chemical reactions hydrogen can be either a *reducing* or an *oxidising agent*:

$$H - 1e^- \rightarrow H^+ \qquad \text{or} \qquad H + 1e^- \rightarrow H^-$$

Its oxidant properties are manifested very seldom, only in reactions with certain metals.

Two hydrogen atoms combine to form a molecule with the evolution of a considerable amount of heat:

$$H + H \rightleftarrows H_2 + 104 \text{ Cal.}$$

Two hydrogen atoms have a greater store of internal energy than a hydrogen molecule. For this reason monoatomic hydrogen is much more active than molecular hydrogen. In chemical processes monoatomic hydrogen is often used for reactions of reduction (nascent hydrogen). Chemical reactions involving hydrogen are in most cases conducted at an increased temperature.

In the laboratory, hydrogen is prepared by the action of metals on water, dilute solutions of acids, or solutions of alkalis (amphoteric metals are used in the latter case). Only metals standing above hydrogen in the electromotive series (Table 15 on p. 164) can be used for this purpose.

The processes of hydrogen preparation may be expressed by equations such as these:

$$1.\ \overset{|\rightarrow|}{Ca + 2H^{\cdot}} + 2OH' = H_2 + Ca^{\cdot\cdot} + 2OH'$$

$$2.\ \overset{|\rightarrow|}{Zn + 2H^{\cdot}} + 2Cl' = H_2 + Zn^{\cdot\cdot} + 2Cl'$$

$$3.\ (a)\ \overset{|\rightarrow|}{Zn + 2H^{\cdot}} + 2OH' = H_2 + Zn(OH)_2\ (\text{or } H_2ZnO_2)$$

$$(b)\ H_2ZnO_2 + 2Na^{\cdot} + 2OH' = 2H_2O + 2Na^{\cdot} + ZnO_2^{\cdot\cdot}$$

$$\overset{|\rightarrow|}{Zn + 2H^{\cdot}} + 2OH' + 2Na^{\cdot} + 2OH' = H_2 + 2H_2O + 2Na^{\cdot} + ZnO_2^{\cdot\cdot}$$

Commercial zinc contains impurities (arsenic, phosphorus, sulphur, etc.). Accordingly, the hydrogen prepared by treating an acid with zinc contains gaseous impurities (arsenic hydride or phosphorus hydride, hydrogen sulphide, etc.). To free hydrogen from these gaseous impurities, it is passed through wash bottles containing solutions that oxidise these impurities.

A mixture of two volumes of hydrogen and one volume of oxygen is called detonating gas. The components of this mixture, when ignited, react with an explosion. It should be borne in mind that mixtures of these gases in other proportions (from 6 to 67% of hydrogen by volume) likewise explode when ignited.

2. **Oxygen.** Oxygen is the chemical element most widespread in nature. The electron arrangement of an oxygen atom is)2)6. In chemical reactions this atom builds up its outer shell to 8 electrons: $O + +2\ e^- = O^{-2}$. In doing so, it displays pronounced oxidant properties.

Like hydrogen, monoatomic oxygen is much more active than molecular oxygen, since two atoms combine to form a molecule with the evolution of a large amount of heat: $O + O = O_2 + 117.0$ Cal.

The atoms in the oxygen molecule are connected by two shared electron pairs:

$$:\ddot{O}::\ddot{O}:$$

At an ordinary temperature oxygen has a low reactivity, but upon heating this increases markedly. The oxygen molecule in oxidation processes can react in one of the following manners:

1. $O_2 + 4e^- = 2O^{-2}$ (the most general type of oxidising action of oxygen)
2. $O_2 + 2e^- = [O_2]^{-2}$ (when alkaline metals, except lithium, are burned; partly when hydrogen is burned with sharp cooling of the flame)
3. $O_2 + 1e^- = [O_2]^-$

The following are examples of oxidation:

$$S + O_2 = SO_2 + 70.92\ Cal.$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 210.8\ Cal.$$

$$2Na + O_2 = \overset{+1}{Na_2}\,[\overset{-2}{O_2}] + 119.2\ Cal.$$

$$K + O_2 = \overset{+1}{K}\,[\overset{-1}{O_2}] + 67.5\ Cal.$$

Compounds such as $Na_2[O_2]$ and $K[O_2]$, containing the ion $[O_2]^{-1}$ or $[O_2]^{-}$, are called metal peroxides.

In the laboratory, oxygen is in most cases prepared by decomposing certain oxides or salts of oxygen-containing acids (HgO, $KMnO_4$, $KClO_3$, KNO_3, etc.) by heating, sometimes in the presence of catalysts. Such reactions are called *intramolecular redox reactions* and are characterised by the transfer of electrons inside the molecule from one component to another. The following process, for example, takes place in the decomposition of potassium chlorate:

$$2\overset{+5\ -2}{KClO_3} = 2KCl + 3O_2 \qquad (e^- \leftarrow)$$

Oxygen can also be prepared from solutions of hydrogen peroxide and the peroxides of alkaline metals.

Since oxygen is somewhat heavier than air, it can be collected in upright cylinders.

Oxygen can be detected qualitatively in the laboratory by means of a glowing splint, which bursts into flame in oxygen.

3. **Ozone.** Ozone is an allotropic modification of oxygen; its molecule consists of three atoms. The question of the linkages between the oxygen atoms in the ozone molecule is still somewhat obscure, but on the strength of the fact that ozone is broken down in reactions to molecular and monoatomic oxygen ($O_3 = O_2 + O$), the formula of ozone may be written thus: $[O_2 \cdot O]$. Since monoatomic oxygen is much more active than molecular oxygen, ozone too is a more active oxidant than oxygen is. In reactions ozone acts thus:

$$\underset{\text{reducing agent}}{X} + [O_2 \cdot O] = \overset{+2}{X} + \overset{-2}{O} + O_2 = XO + O_2 \qquad (\rightarrow)$$

The ozone molecule thus gains two electrons, e. g.:

$$2\overset{-1}{NaI} + [O_2 \cdot O] + H_2O = I_2 + 2NaOH + O_2$$

Ozone is an endothermic compound, which decomposes according to the equation:

$$2O_3 = 3O_2 + 2 \cdot 34.5\ Cal.$$

Ozone is produced in ozonisers by the action of a silent electric discharge on dry oxygen.

QUESTIONS

1. Write the equations for the reactions whereby oxygen is prepared from $KMnO_4$ and from Ag_2O.
2. One of the industrial methods of preparing hydrogen consists in passing steam over red-hot iron. Write the equation of the reaction and the equation of the equilibrium constant.
3. What are hydrides? How can the charge of their hydrogen ion be confirmed experimentally?
4. Draw a diagram of the apparatus used to prepare oxygen from air, adding a brief explanation of each stage of the process.
5. What is the significance, in the liquefaction of gases, of the critical temperature?
6. By means of what reactions can oxygen be distinguished from ozone?
7. How was it proved that an ozone molecule consists of three oxygen atoms?

Problems

1. The daily output of an oxygen plant is 20,000 cu m of the gas reduced to N. T. P. How many steel bombs will the plant require daily for its output if the bombs have a 40 lit capacity, withstand a pressure of 150 atm, and are kept in premises where the temperature is 15°? What volume of air has to be passed through the compressor daily (assuming the performance of the compressor to be ideal?)
2. In the steam-iron method a single operation yields 80 cu m of hydrogen. Determine the daily expenditure of iron and the amount of Fe_3O_4 produced if 3 operations daily are conducted at the plant.
3. Calculate the volume of the resulting gaseous mixture and the number of grams of metallic silver that it can oxidise if 500 lit of air are passed through an ozoniser, 7% of the oxygen (by volume) being converted to ozone.
4. Two hundred grams of barium peroxide is decomposed by heating. What will be the yield of oxygen (by volume) at $p = 700$ mm and $t^0 = 27°$?
5. At 1200° one volume of iron dissolves 0.65 volume of hydrogen (at N. T. P.). Determine the weight of the hydrogen that can dissolve in 1 t of iron with a density of 7.9 g/cu cm.
6. An industrial plant has a daily output of 186 kg of sodium peroxide. What are its requirements in metallic sodium (by weight) and in 25 lit oxygen bombs, in which the oxygen is at 150 atm and 13°?
7. In a weakly alkaline medium 10 lit of ozonised oxygen is absorbed by a solution of potassium iodide. The potassium iodide combines quantitatively with the ozone to form KIO_3. Determine the percentage composition of the gaseous mixture (by volume), the yield being 10.7 g of potassium iodate.
8. A mixture consisting of 1 litre of hydrogen and 0.5 litre of oxygen at N. T. P is ignited. Determine the pressure of the water vapour formed, the temperature during the explosion reaching 2300°.
9. How much calcium hydride must react with water for the hydrogen evolved to reduce 32 g of ferric oxide?
10. What volume of air, taken at N. T. P. and containing 12% of ozone, is needed to oxidise 280 ml of an 0.1 N solution of sodium iodide in an acid medium?

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 52, the test tube having a hole in the bottom; the apparatus shown in Fig. 54; gas-holder with oxygen; Kipp gas generator; barometer; room thermometer; metal ruler; wash bottle for gases; test tubes and rack; two deflagrating spoons; two glass cylinders; 250 ml measuring cylinder; stopper with gas delivery tube; two glass covers for the cylinders; funnel; glass vessel; splints; potassium chlorate; manganese dioxide; potassium permanganate; ammonium persulphate; granulated zinc; coal in lumps; sulphur in lumps; diethyl ether; concentrated nitric acid; 1:6 dilute sulphuric acid; 0.1 N solution of potassium permanganate; 0.5 N solution of potassium iodide; 0.5 N solution of lead acetate; 2 N solution of sodium hydroxide; N solution of sodium sulphide; 0.5 N solution of manganese chloride; solution of indigo or indigo carmine, and cotton wool.

Note. It is best to use an 0.5% solution of indigo carmine, which dissolves readily in water. In the absence of indigo carmine, prepare a 1% solution of indigo in concentrated sulphuric acid. At first the solution will be green, but with the passage of time it will turn blue.

The apparatus shown in Fig. 54 may be replaced by an ozoniser.

1. Preparation and Burning of Hydrogen. (a) Place 5-6 granules of zinc in the test tube of the apparatus shown in Fig. 52; close the test tube with a stopper through which a straight delivery tube with a drawn tip has been passed. Lower the test tube into the sulphuric acid solution in the flask. When all the air has been displaced (check this as in Exercise 5), light the hydrogen that is being evolved and hold a dry funnel over the flame for a time. Note what forms on the glass of the funnel. Remove the test tube from the acid solution. Write the equations for the reactions of the preparation of hydrogen and its burning. Could any metal be used instead of zinc to prepare hydrogen in this way?

(b) Pour 3-4 ml of a 30% solution of sodium hydroxide into a test tube, put 2-3 aluminium shavings in it, and close the test tube with a stopper through which a straight gas delivery tube has been passed. Heat the test tube slightly. Collect the gas evolved in another test tube, held upside down, and ignite it. Write the equation of the reaction that has taken place. Name 4-5 metals that could be used instead of aluminium in this reaction.

2. Explosion of Detonating Gas (conduct this experiment with caution!). Fill with water a 100 ml cylinder* for collecting gases, cover the cylinder with a flat piece of glass, and immerse it upside down in a vessel with water. To the straight gas delivery tube of the apparatus used in the previous experiment attach a bent tube. Place the end of this bent tube in the vessel with water so that it is right under the cylinder. Lower the test tube with the zinc into the acid solution and fill two-thirds of the cylinder with the hydrogen evolved. Then fill the rest of the cylinder with oxygen from a gas-holder (Fig. 53). Cover the cylinder with the gaseous mixture with the glass, lift it out of the vessel, wrap it tightly in a towel, bring it up to the flame of a burner, and, removing the glass, light the gas. What happens?

* Do not substitute a flask or bottle for the cylinder in this experiment!

What is called detonating gas? Draw a diagram of a gas-holder and give a brief explanation of the principle on which it operates.

3. Activity of Monoatomic and Molecular Hydrogen. Pour 7-8 ml of a sulphuric acid solution into a test tube and add 2-8 drops of a dilute solution of potassium permanganate. Shake the solution and pour it, in equal portions, into two test tubes. Put a small lump of

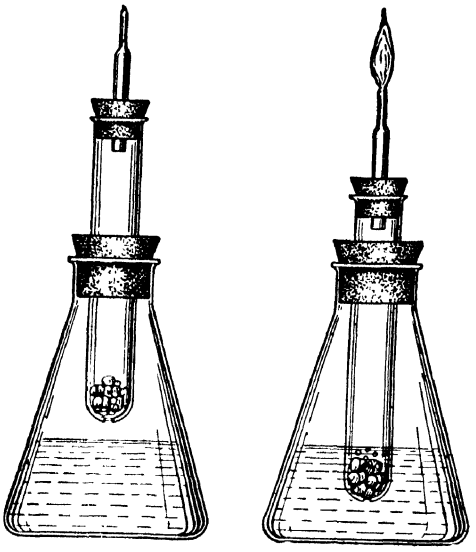


Fig. 52. Set-up for preparing hydrogen

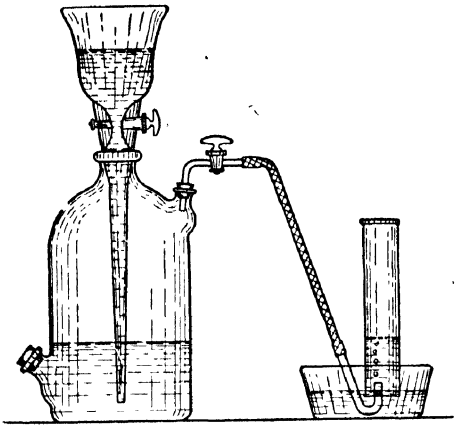


Fig. 53. Filling a cylinder with oxygen from a gas-holder

zinc into one of the test tubes, and pass a stream of hydrogen slowly through the other from the Kipp gas generator (to free the hydrogen from possible reductant impurities, pass it through a wash bottle for gases that contains an oxidising mixture). Why does the solution in the first test tube lose its colour? Write the equation for the reaction of the reduction of potassium permanganate by monoatomic hydrogen in an acid solution.

4. Preparation of Oxygen. (a) Fasten a dry test tube, which contains 0.5 g of crystalline potassium permanganate, vertically in a clamp and heat it over a burner. By means of a glowing splint determine whether the gaseous product of decomposition is oxygen. Write the equation for the reaction of decomposition of potassium permanganate. What type of a reaction is it?

(b) Conduct the same experiment, substituting potassium chlorate for potassium permanganate. When the salt melts, carry out the glowing splint test. Does the process of the decomposition of potassium chlorate proceed intensely? Remove the burner and add a pinch of manganese dioxide to the test tube. Observe the abundant evolution

of gas; test it with a glowing splint. Write the equation for the reaction of the decomposition of potassium chlorate. What role does manganese dioxide play in this reaction?

5. Oxidising Properties of Oxygen. (a) Fill two small cylinders with oxygen from a gas-holder, having the oxygen displace water from the cylinders *. In one of them burn a small lump of sulphur in a spoon, lighting the sulphur in advance**. In the second cylinder burn a small lump of coal heated red-hot on a burner. Observe the intensity with which these substances burn in pure oxygen and in the air. Why is combustion more intense in oxygen? Write the equations of the reactions that have taken place.

(b) Precipitate some manganous hydroxide in a test tube by means of an exchange reaction. Observe its colour. Then pass a stream of oxygen slowly from a gas-holder through the solution and note the change in the colour of the precipitate. Write the relevant equations. What is the difference between oxidation and combustion?

6. Determining the Absolute Density of Oxygen. Put 1.6-1.7 g of potassium permanganate into a dry test tube, stopper it up with a thin wad of cotton wool, and weigh it. Fasten the test tube, in a horizontal position, in a clamp attached to a ringstand. Close the test tube with a rubber stopper with a delivery tube (the wad of cotton wool should be next to the end of the stopper); lower the delivery tube into a vessel with water. Fill a 250 ml cylinder with water, cover it with a piece of glass, and turn it over into the vessel. Fasten the cylinder by means of a large clamp attached to the ringstand.

By means of a small flame heat the test tube, but not the part of it containing the potassium permanganate. When air ceases bubbling through the vessel, place the end of the delivery tube under the cylinder and start heating the potassium permanganate carefully. When about 160 ml of oxygen has collected in the cylinder, stop heating the test tube and immediately remove the stopper with the gas delivery tube from it.

Measure the volume of the oxygen generated and the height of the column of water in the cylinder above its level in the vessel. Note the room temperature and the barometric pressure. When the test tube has been cooled to room temperature, weigh it.

From the data obtained determine the absolute density of the oxygen and calculate the relative error.

7. Preparation of Ozone and Its Properties. (a) Pour 5 drops of diethyl ether into a large dry test tube and close it with a stopper.

---

* The oxygen can also be prepared in the Kipp gas generator from a 3% solution of hydrogen peroxide, which decomposes under the influence of a catalyst made from manganese dioxide (see Exercise 3). The yield is almost theoretical: from 1.7 litres of 3% hydrogen peroxide it is possible to obtain about 17 litres of oxygen.

** The spoon with the remainder of the sulphur should be ignited in a ventilated hood.

After the ether has evaporated, heat an iron wire until it is red-hot (the handle of a deflagrating spoon can serve as such a wire); insert the wire into the test tube with the ether vapour. Remove the wire after 5-10 seconds. Notice the odour of the ozone formed. Pour a few drops of a potassium iodide solution into the test tube. What happens? Write the equation for the reaction of the oxidation of potassium iodide by ozone in a neutral solution.

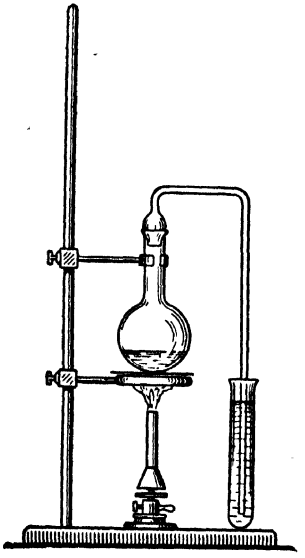


Fig. 54. Apparatus for preparing ozone

(b) Conduct this experiment *in a ventilated hood*! Pour 3-4 ml of an indigo solution into one test tube and conduct an exchange reaction between lead acetate and sodium sulphide in another. The reaction in the second test tube produces a black precipitate of lead sulphide (pour off the excess solution from the precipitate). Now put 2 g of crystalline ammonium persulphate in the flask of the apparatus shown in Fig. 54 and add 10 ml of concentrated nitric acid to it. Close the neck of the flask with a ground-in tube and lower its other end into the indigo solution.

Heat the flask on a small flame and note the disappearance of the blue colour after a time.

Pass ozone into the test tube containing the PbS precipitate. What is the black precipitate converted to? Write the equation for the reaction of the oxidation of PbS by ozone. What effect has ozone on dyes?

Exercise 18

WATER AND HYDROGEN PEROXIDE

SUBJECTS FOR STUDY

Water. Separation of mechanical admixtures from water; distillation of water; structure of water molecule and its polarity; chemical reactions involving water; hydration, and the catalytic action of water.

Hydrogen peroxide. Its molecular structure; chemical properties; methods of preparation; peroxides of metals; some idea of peracids.

1. Water. Water in nature contains mechanical admixtures, and these may be separated by filtration. Soluble impurities are separated by distillation, which is carried out by means of a distillation

apparatus consisting of a flask for boiling the water, a condenser for condensing the steam to water, and a receiver for the distilled water.

Fig. 55 shows the arrangement used in the laboratory, consisting of a round flask (1), a condenser (2), an adapter (3), and a receiver (4).

The distilled water obtained by distillation in such an apparatus contains dissolved gases and a negligible amount of silicates (resulting

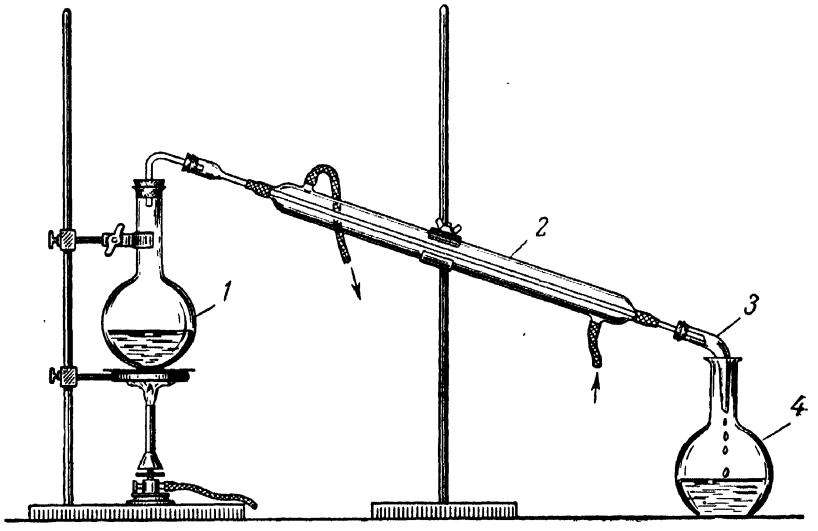


Fig. 55. Distillation of water

1 — round-bottom flask; 2 — condenser; 3 — adapter; 4 — receiver.

from the leaching of the glass by steam). This is the water usually employed in the laboratory for preparing solutions, but the dissolved gases can hamper certain experiments.

They can be removed by prolonged boiling. For this purpose a 1 litre flask is three-quarters filled with distilled water, several pieces of capillary tubing are placed in it (what for?), and the water is boiled for 30-40 minutes. After that the flask is removed from the wire gauze with the asbestos centre and is stoppered up tightly, the stopper having a tube containing soda lime (to absorb CO_2).

All chemical reactions involving water may be divided into two groups:

(1) oxidation reactions, and

(2) addition and exchange reactions.

Examples.

(1) Oxidising action of water:

$$3Fe + 4H_2O \rightleftarrows 4H_2 + Fe_3O_4$$

(2) Interaction with oxides:

$$CaO + H_2O = Ca(OH)_2$$

Formation of aquo-complexes:

$$CoCl_2 + 6H_2O = [Co(H_2O)_6]Cl_2$$

Hydrolysis:

$$K_2CO_3 + HOH \rightleftarrows KHCO_3 + KOH$$

Exceptionally important is the catalytic action of water. Many reactions are greatly accelerated by the presence of traces of water and do not proceed at all without it.

2. **Hydrogen Peroxide (H_2O_2).** A study of hydrogen combustion with flame cooling, as well as of the properties and structure of the metal peroxides, which are salts of hydrogen peroxide, justifies the assumption that hydrogen peroxide has the formula $\overset{+1}{H}_2[\overset{-2}{O}_2]$.

Hydrogen peroxide is a weak electrolyte (weak acid), which dissociates into ions:

$$H_2O_2 \rightleftarrows H^{\cdot} + HO_2^{\prime}$$
$$\downarrow\uparrow$$
$$H^{\cdot} + [O_2]''$$

Hydrogen peroxide has both oxidant and reductant properties. The $[O_2]^{-2}$ ion receives 2 electrons (as an oxidising agent), turning into negative oxygen ions: $[O_2]^{-2} + 2e^- = 2O^{-2}$. For example:

$$PbS + 4H_2[O_2] = PbSO_4 + 4H_2O$$

In other reactions the $[O_2]^{-2}$ ion can display reductant properties giving up 2 electrons and forming a neutral oxygen molecule, e. g.,

$$5H_2[O_2] + 2KMnO_4 + 3H_2SO_4 = 5O_2 + 8H_2O + K_2SO_4 + 2MnSO_4$$

Since peroxides can be oxidants and reductants, electrons can be transferred from one molecule to another:

$$H_2[O_2] + H_2[O_2] = O_2 + 2H_2O$$

Hydrogen peroxide is an unstable compound, and in due course (especially rapidly in the presence of catalysts, such as silicon compounds, metal oxides and dioxides, and colloidal metals) it decomposes to oxygen and water. The process of decomposition is hastened by illumination. Oxidation-reduction reactions in which molecules,

atoms, or ions of one and the same substance act both as a reductant and as an oxidant are termed *autooxidation-autoreduction, or disproportionation, reactions.*

In the laboratory hydrogen peroxide is usually prepared by treating barium peroxide with sulphuric acid.

In practice it is customary to use either a 3% aqueous solution of hydrogen peroxide (employed medicinally as a disinfectant) or a 30% aqueous solution, or perhydrol.

QUESTIONS

1. Write the structural formula of water and explain why a molecule of water has a dipole moment.
2. Do steam, water, and ice differ in their percentage or molecular composition?
3. How can it be proved that there are 8 parts by weight of oxygen to 1 part by weight of hydrogen in water?
4. Why is perhydrol stored in bottles whose inner walls have been coated with paraffin wax?
5. Give examples of chemical reactions that can serve to distinguish ozone from hydrogen peroxide.
6. How can the oxide and peroxide of sodium be prepared from the metal?
7. Write the equation of the reaction between potassium iodide and hydrogen peroxide in an acid solution.
8. What distinguishes metal dioxides from peroxides?
9. What substances serve to stabilise hydrogen peroxide?

Problems

1. Determine the empirical and the molecular formula of a substance that has the composition: 5.92% of H and 94.08% of O. A solution containing 2.55 g of this substance in 500 g of water freezes at —0.279°.
2. Calculate the molecular weight of steam, knowing that at the b. p. of water it contains 3.5% of double molecules.
3. What volume of oxygen will be evolved in the complete decomposition of 400 g of a 3% solution of hydrogen peroxide?
4. Determine the percentage concentration of the resulting solution if 8.75 kg of a 3% solution of hydrogen peroxide is mixed with 0. 75 kg of perhydrol.
5. What will be the b. p. of a solution of 82 g of glycerol in 660 g of water? The formula of glycerol is $C_3H_5(OH)_3$.
6. What will be the osmotic pressure exhibited by a solution containing 100 g of perhydrol in 2 litres? The temperature of the solution is 17° (the electrolytic properties of the dissolved substance may be disregarded).
7. Calculate the pH-value and the α% of a solution of 6 g of acetic acid in 0.5 litre.
8. What amounts of 3% hydrogen peroxide (its relative density being assumed equal to 1) and water have to be mixed to yield 750 ml of an 0.1 M solution? Calculate the $[H^+]$ and pH of the solution.

9. How much of a 3% solution of H_2O_2 and crystalline $KMnO_4$ will have reacted in an acid solution to produce 1.12 litres of oxygen at N. T. P.?

10. What amounts of barium peroxide (by weight) and carbon dioxide (by volume) will be used up to produce 1 kg of a 3% solution of H_2O_2?

LABORATORY WORK

Apparatus and materials: Kipp gas generator for preparing hydrogen sulphide and drying bottles (with $CaCl_2$); the apparatus shown in Fig. 55; stopper with gas delivery tube bent at a right angle; test tubes and rack; 100 ml beaker; two cylinders with glass covers; 50 ml measuring cylinder; 10 ml pipette; large crystalliser; funnel; glass spatula; two glass rods; deflagrating spoon; manganese dioxide; cupric chloride; potassium bromide; mercuric oxide; sodium peroxide; barium peroxide; iron filings; cobaltous chloride; sulphur in lumps; 2 N solution of sulphuric acid; N solution of potassium dichromate; 0.5 N solution of potassium iodide; N solution of sodium sulphide; 0.5 N solution of sodium sulphate; 0.5 N solution of sodium chloride; 1% solution of silver nitrate; 0.5 N solution of barium chloride; 1% solution of fuchsin; 0.5 N solution of lead nitrate; 0.1 N solution of sodium chromite; 2 N solution of sodium hydroxide; 0.05 N and 2 M solutions of potassium permanganate; 5% solution of ammonia; solutions of litmus, phenolphthalein, and methyl-orange; 3% solution of hydrogen peroxide; acetone; ether; snow or ice; ethyl alcohol; pieces of coloured cloth; filter paper; splints, and sand.

1. Reaction for Detecting Hydrogen Peroxide. Mix 2 ml of a hydrogen peroxide solution and an equal volume of a sulphuric acid solution in a test tube; add a layer of ether 0.5 cm high. Take a clean glass rod, dip it into a bottle with a potassium dichromate solution, and then lower it into the test tube. Chromium peroxide is formed at once (note its colour!); careful shaking of the test tube causes it to dissolve in the ether.

2. Preparation of Hydrogen Peroxide. Hydrogen peroxide is prepared by treating barium peroxide with dilute sulphuric acid. Calculate the amounts of barium peroxide and of 2 N sulphuric acid needed to obtain 0.5 g of H_2O_2. Measure off the calculated amount of sulphuric acid, pour it into a beaker, and place the beaker into a crystalliser with snow to be cooled. Weigh the required amount of barium peroxide and pour it in small portions into the beaker with the cooled solution of sulphuric acid, stirring it with a glass rod. Leave the mixture for 30-40 minutes in the snow, stirring the contents of the beaker from time to time. Filter the liquid through a small filter and test the filtrate for the presence of hydrogen peroxide.

3. Oxidant Properties of H_2O_2. (a) Add a solution of hydrogen peroxide to a solution of potassium iodide that has been acidified by the addition of an equal volume of dilute sulphuric acid. What is the substance formed? Write the equation of the reaction that takes place.

(b) Add a solution of an alkali and hydrogen peroxide to a sodium chromite solution and heat it. How does the colour of the solution change? Write the equation of the reaction that takes place.

(c) Add an equal volume of sodium sulphide solution to 2 ml of a lead nitrate solution; heat the solution to boiling point and, when the

black precipitate has settled, pour off the solution. Add 3 ml of 3% hydrogen peroxide to the precipitate and heat the solution slightly. How does the colour of the precipitate change? Write the equation of the reaction that takes place.

4. Reductant Properties of H_2O_2. (a) Pour 1 ml of a *concentrated* solution of potassium permanganate, 2 ml of a sulphuric acid solution, and 1-2 ml of a hydrogen peroxide solution into a test tube. Introduce a glowing splint into the test bube. What happens? Write the equation of the reaction that takes place.

(b) Add 5-6 drops of an ammonia solution and a pinch (on the tip of a knife) of powdered mercuric oxide to 3-4 ml of 3% hydrogen peroxide. What happens? Write the equation of the reaction that takes place.

5. Catalytic Decomposition of Hydrogen Peroxide. Pour 2-3 ml of a hydrogen peroxide solution into a test tube and add a pinch of manganese dioxide (on the tip of a penknife). Introduce a glowing splint into the test tube. What happens? Write the equation of the reaction that takes place.

6. Bleaching by Means of Hydrogen Peroxide. Place a small bit of coloured cloth into a test tube. Add 1 ml of a 5% solution of ammonia (what for?) and 2 ml of a hydrogen peroxide solution. Observe the change in the colour of the cloth after a time.

7. Interaction of Sodium Peroxide and Water. Pour 3 ml of water into a test tube and add a pinch of sodium peroxide to it. Establish experimentally what gas issues from the test tube and what has been formed in the solution. Write the equations of the reactions of hydrolysis and decomposition that take place.

8. Decomposition of Sodium Peroxide. Heat 0.5 g of sodium peroxide in a dry test tube. Continue this until a glowing splint ceases to flare up inside the test tube. What is the substance remaining in the test tube? Use it for experiment 9.

9. Interaction of Oxides and Water. Pour 4-5 ml of water into a cooled test tube with the substance obtained in the previous experiment. Test the solution with various indicators. What is the substance formed? Write the equation of the reaction that takes place.

10. Oxidant Properties of Water. Place a small quantity of wet sand at the bottom of a refractory test tube (1); fasten the test tube in a horizontal position, as shown in Fig. 56. By means of a small glass spatula, put some iron filings on the wall of the test tube (2). Close the test tube with a stopper through which a gas delivery tube bent at a right angle has been passed. Another test tube (3) is placed over the end of the delivery tube. Warm the reaction test tube where the iron filings are and then heat it until they are red-hot. From time to time heat the sand to remove part of the water. After a time show that there is hydrogen in the test tube used as a gas collector. Write the equation for the interaction of iron with steam.

11. Hydration of Cations and Formation of Aquo-complexes. (a) Dissolve a few crystals of cobaltous chloride hexahydrate in 2-3 ml of water and note the colour of the solution. Dissolve the same amount of crystals in 2-3 ml of ethyl alcohol, heating the solution. Account for the difference in the colours of the alcohol and the aqueous solution. Dilute the alcohol solution with water, and observe the change in the colour of the solution. Sprinkle a few drops of the aqueous solution on a piece of filter paper, and dry the filter paper over a burner. Does the pink colour remain? What colour are the Co^{++} and $[Co(H_2O)_6]^{\cdot\cdot}$ ions? Write the equation of the reactions that take place.

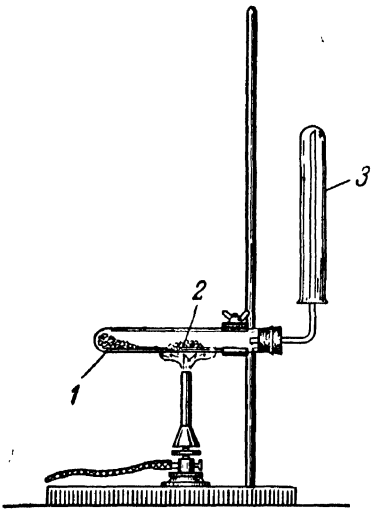


Fig. 56. Set-up for preparing hydrogen by the action of steam on iron

1 — refractory test tube; 2 — iron fillings; 3—test tube for collecting gas.

(b) Pour 3 ml of acetone into each of two dry test tubes. Dissolve a few crystals of potassium bromide in one of them and about 1 g of cupric chloride in the other; the colour of the latter solution should be a grassy green. Now pour half of the cupric chloride solution into the potassium bromide solution; a brownish solution of cupric bromide is formed. Add water by drops to both solutions and observe the appearance of the blue colouration typical of the hydrated cupric ions $[Cu(H_2O)_4]^{\cdot\cdot}$. Write the equation of the hydration reactions that take place.

Can the colour of Me^{+n} ions in a solid salt serve as any indication of the colour of solutions of that salt?

12. Catalytic Action of Water (experiment to be conducted in a ventilated hood!). Prepare two identical cylinders with glass covers. In one of them burn a small quantity of sulphur. Fill the other one with hydrogen sulphide from the Kipp gas generator (to dry the gas pass it through drying bottles filled with granulated calcium chloride). Place one cylinder on top of the other orifice to orifice, remove the glass lids, and mix the gases. Observe whether any changes take place. Move the upper cylinder slightly, pour a few drops of water from a pipette into the bottom cylinder, and mix the gases again thoroughly. Observe the formation of a light yellow deposit of sulphur on the walls of the cylinders. Write the equation of the reaction that takes place. What is the role of the water in this reaction?

13. Distillation of Water. Pour 100 ml of water from the tap into a beaker and add 2-3 ml of a sodium chloride solution and the same amount of a sodium sulphate solution. By means of the proper rea-

gents prove the presence of chloride and sulphate ions in the solution. Assemble the apparatus shown in Fig. 55. Pour the water from the beaker into the flask and add 10 ml of a fuchsin solution. Boil the water in the flask, collecting the distillate in the receiver. Pour the first 10 ml of the distillate down the drain. Discontinue distillation when a second portion (10-20 ml) of the distillate has collected in the receiver.

Does the distillate have a colour? Prove the absence of chloride or sulphate ions in the distillate.

Exercise 19

GENERAL PROPERTIES OF METALS AND ALLOYS

SUBJECTS FOR STUDY

General properties of metals; alloys; physico-chemical analysis; cooling curves; fusibility diagrams; eutectic mixtures; solid solutions; intermetallic compounds.

Electric current generated by chemical reactions; normal electrode potentials of metals; electromotive series; displacement of hydrogen by metals and displacement of some metals by others; galvanic cell.

Electrolysis and Faraday's Laws; electrolysis of different types of compounds; principal methods of preparing metals.

1. Physico-chemical Analysis. The methods of *physico-chemical analysis*, which determine changes in the physical properties of a system with changes in the concentration of the components, serve to establish that the two or more components have formed a new chemical compound.

The physical property studied most frequently is the melting (crystallisation) point of a system; the technique of studying its change with changes in the concentration of the components of the system is known as *thermal analysis*, or the *fusibility method*.

(a) *The melting point* is one of the most important constants of a chemically pure substance. When chemically pure cadmium is heated, it melts at 321°; if the molten metal is heated, say, to 340° and then cooled, at 321° it will begin to crystallise. This means that for one and the same substance the melting point and the crystallisation point coincide. The transition from the liquid to the solid state is accompanied by the release of the latent heat of fusion, and for this reason the temperature of the system remains constant until the entire liquid phase has been turned into the solid phase. If the process of crystallisation or melting is studied as a function of time, the variation of the temperature with time may be expressed graphically by means of *cooling or heating curves*. Fig. 57 shows the cooling and heating curves for Cd. Both curves, it will be observed, have temperature

halts, or breaks, at 321° (lines parallel to the abscissa), which indicate phase conversion (solid phase ⇄ liquid phase) *.

If a second component, say Zn (m. p. 419°), is added to Cd, the crystallisation point of Cd drops. The cooling curve (1) in Fig. 58 has a far less pronounced temperature halt at point *B* (2.5% Zn), since there is only partial crystallisation of the principal component (Cd)

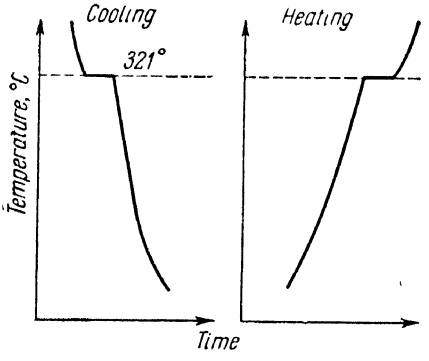


Fig. 57. Cadmium cooling and heating curves

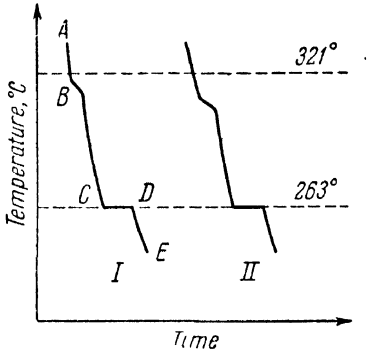


Fig. 58. Cooling curves for Cd with impurities: I—2.5% Zn; II—5% Zn.

here; a second and more pronounced temperature halt (*C* — *D*) corresponds to the simultaneous crystallisation of both components (Cd + + Zn). The *AB* section of the curve refers to the liquid phase; the *BC* section, to a system consisting of a solid and a liquid phase in equilibrium, and the *DE* section, to a system consisting of the two solid phases Cd and Zn.

If the Zn concentration is increased to 5%, the first temperature halt (Fig. 58, II) shifts even further downward, whereas the position of the second is unchanged.

The picture will be the same in systems where Zn is the principal component. If to that metal we add mounting quantities of Cd, the crystallisation point of Zn will gradually be lowered (Table 14).

The variation of the crystallisation (melting) point with the composition of the system may be represented graphically: the values characterising the composition (weight or molecular ** percentages for compounds and atomic percentages for simple substances) are plotted as abscissae against the temperatures as ordinates. Such a graph is called a *fusibility diagram* (Fig. 59).

The fusibility diagram of the Zn-Cd system, based on the data of Table 14, has the form of a V-curve (Fig. 59) and points to the *absence of chemical interaction between the components.*

* Supercooling is disregarded.

** Molecular percentages are expressed in the molar fraction multiplied by 100.

Table 14

Melting Points of Zn-Cd System

Weight composition in %		M. p. in °C	Weight composition in %		M. p. in °C
Zn	Cd		Zn	Cd	
100	—	419	40	60	305
90	10	402	25	75	277
80	20	381	16.5	83.5	263
70	30	362	10	90	282
60	40	343	5	95	300
50	50	324	0	100	321

(b) *Fusibility Diagram Analysis.* At point A' in the diagram the system has the constitution: 70% Zn and 30% Cd; at the given temperature (470°) it is in a liquid state (melt). If the system is cooled (movement from A' downward), there is no change in it until the temperature corresponding to the point K' is reached. At this point the Zn undergoes partial crystallisation, the system is converted from a homogeneous to a heterogeneous one, a solid phase appears, and the Zn concentration in the remaining liquid phase diminishes. With further cooling, changes in the composition of the liquid phase follow the curve $A'E$, which is part of the AE branch, until the point E (263°) is reached, where the Zn and Cd mixture crystallises.

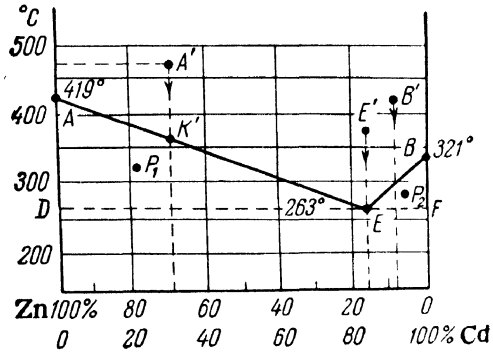


Fig. 59. Fusibility diagram for Zn-Cd system

If we take the system at any point above the BE branch (say, at B'), cooling will produce the same change, but the primary crystallisation product will be Cd. Finally, if a system consisting of 83.5% of Cd and 16.5% of Zn is heated, for example, to 375° (E') and then cooled, a mixture of both components will crystallise simultaneously at 263° (D).

This most readily melting mixture of the two components is termed a *eutectic*, while its melting point is termed the *eutectic temperature* (denoted by the letter E). The line DF parallel to the abscissa and passing through E is called the eutectic horizontal.

The part of the diagram above the *AEB* curve is called the *liquidus*, i. e., the area of liquid melts or solutions. The areas *AED* and *BEF* correspond to systems in which the solid and the liquid phase are in equilibrium: $Zn_{sol} + (Zn + Cd)_{molt}$ are in equilibrium at P_1, while $Cd_{sol} + (Cd + Zn)_{molt}$ are in equilibrium at P_2.

The part of the diagram below the eutectic horizontal is called the *solidus*, i. e., the area of solid phases.

The Zn-Cd system is not the only one with a eutectic point (*E*)—this is also characteristic of the systems Pb-Sn, Pb-Sb, Cd-Bi, Al-Si, and others. It should be added that such systems are formed not only by metals; they may also be formed by other components, e. g.: *metal—metal oxide* (Cu-CuO), *salt—salt* (KCl-LiCl), *salt—water* (KCl-H_2O), and organic compounds (*naphthalene—phenol*). If one of the components is water, the most fusible mixture of crystals of ice and crystals of the second component is called a *cryohydric mixture*. Since ice melts at 0°, all cryohydric mixtures melt below 0°.

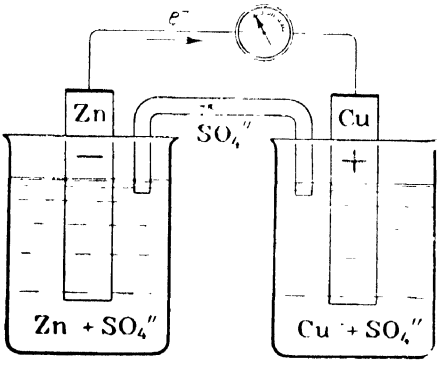


Fig. 60. Galvanic cell

When the components of a system form chemical compounds or solid solutions, the fusibility diagrams differ from those for systems with a eutectic mixture.

2. Galvanic Cell. In a galvanic cell the energy of a chemical process is transformed into the energy of an electric current. What type of chemical reactions arising in galvanic cells may be ascertained by considering the operation of a cell consisting of two galvanic couples, for instance, $Zn^0/Zn^{\cdot\cdot}$ and $Cu^0/Cu^{\cdot\cdot}$ (Fig. 60).

This type of galvanic cell was first proposed by the Russian physicist B. Yakobi.

The neutral atoms of zinc give up electrons, which travel along the outer circuit (metal wire) to the $Cu^0/Cu^{\cdot\cdot}$ couple, while SO_4'' ions move along the inner circuit (tube with electrolyte solution) in the opposite direction. In this process the zinc plate gradually dissolves, whereas the copper one grows thicker at the expense of copper from the solution. The overall chemical process can be expressed by the equation:

$$Zn \overset{2e^-}{\longrightarrow} + Cu^{\cdot\cdot} + SO_4'' = Cu + Zn^{\cdot\cdot} + SO_4''$$

From this equation it is evident that the reaction involves the transfer of electrons, i. e., it is a *redox* reaction. In this galvanic cell the

$Zn^0/Zn^{\cdot\cdot}$ couple is the reducing agent, while the $Cu^0/Cu^{\cdot\cdot}$ is the oxidising agent. At the *metal—solution of metal salt* interface in every couple there arises a definite potential, which depends (at a given concentration and temperature) upon the nature of the metal. By means of a voltmeter inserted in the outer circuit it is possible to measure the difference of potentials, or *electromotive force* (e. m. f.), of a cell. The electromotive force is a measure of the impulse of the redox reaction and is expressed by the oxidant-reductant potential difference. The e. m. f. of a reaction is equal to the E^0 of the oxidant minus the E^0 of the reductant.

The E^0 symbol denotes the electrode potential of a particular couple with respect to the couple $2H^{\cdot}/H_2$, whose potential is assumed to be equal to zero.

Example. In the case of the galvanic cell considered above E^0 for the $Zn/Zn^{\cdot\cdot}$ couple is equal to — 0.76 V; for the $Cu/Cu^{\cdot\cdot}$ couple, to 0.34 V. Accordingly, the e. m. f.=0.34—(—0.76)=+1.10 V.

A galvanic cell operates if the potential difference is a positive value. This means that a redox reaction proceeds in a chosen direction only provided the potential difference is positive.

The value of E^0 is usually determined at a temperature of 25° for unimolar concentrations * of the salt solutions.

If the electrode potentials are measured for various couples Me/Me^{+n} and arranged in a series of rising values, this will be the *electromotive series of metals* (Table 15).

A study of the electromotive series leads us to several conclusions:

(1) An element situated in the series before another is a reducing agent with respect to it.

(2) All metals with negative potentials dissolve (oxidise) in acids with the evolution of hydrogen, while the metals that follow hydrogen do not displace it from acids.

(3) Any metal of the series displaces (reduces) from a salt solution a metal of a higher potential, but does not displace a metal of a lower potential.

The reducing activity of metals mounts—and the oxidising activity of their ions diminishes—in the series from the positive potential value to the negative.

3. Electrolysis. The passage of an electric current through an electrolyte solution causes the positively charged ions to move towards the negatively charged electrode (cathode) and the negatively charged ions towards the positive pole (anode). The positive ions acquire electrons (reduction) from the cathode, while the negative ions give up electrons (oxidation) to the anode. For example, the process of

* Or, to be more exact, when the activity of the ions of that particular metal in the solution is equal to 1.

Table 15

Electromotive Series of Metals

(C = 1M; $t°$ = 25°)

Me/Me^{+n}	$E°$ in V	Me/Me^{+n}	$E°$ in V
Cs/Cs^{+}	−3.02	Co/Co^{++}	−0.28
Li/Li^{+}	−3.02	Ni/Ni^{++}	−0.25
Rb/Rb^{+}	−2.99	Sn/Sn^{++}	−0.14
K/K^{+}	−2.92	Pb/Pb^{++}	−0.13
Ba/Ba^{++}	−2.90	Fe/Fe^{+++}	−0.04
Sr/Sr^{++}	−2.89	$H_2/2H^{+}$	∓0.00
Ca/Ca^{++}	−2.87		
Na/Na^{+}	−2.71	Sn/Sn^{++++}	0.01
Mg/Mg^{++}	−2.34	Sb/Sb^{+++}	0.21
Be/Be^{++}	−1.70	Bi/Bi^{+++}	0.23
Al/Al^{+++}	−1.67	As/As^{+++}	0.30
Mn/Mn^{++}	−1.05	Cu/Cu^{++}	0.34
Zn/Zn^{++}	−0.76	Co/Co^{+++}	0.43
Cr/Cr^{+++}	−0.71	Cu/Cu^{+}	0.52
Ga/Ga^{+++}	−0.52	Ag/Ag^{+}	0.80
Fe/Fe^{++}	−0.44	Pd/Pd^{++}	0.83
Cd/Cd^{++}	−0.40	Hg/Hg^{++}	0.85
Tl/Tl^{+}	−0.34	Au/Au^{+++}	1.42
		Au/Au^{+}	1.68

electrolysis for hydrochloric acid (Fig. 61) may be written down as follows:

cathode process $2H^{+} + 2e^{-} = H_2$ (reduction)

anode process $2Cl' - 2e^{-} = Cl_2$ (oxidation)

Ions will be neutralised at electrodes only provided there is a current of sufficient voltage. Under the action of the electric current there takes place a chemical process of decomposition:

$$2HCl = H_2 + Cl_2$$

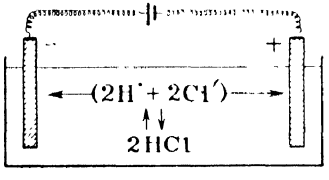


Fig. 61. Electrolysis of HCl

Electrolysis is a process of chemical decomposition of substances by an electric current; the process comprises reduction at the cathode and oxidation at the anode.

The direct decomposition of a substance at the electrodes by means of an electric current is called the primary electrolysis process. But

the electrolysis products can also interact with one another (to prevent them from coming into contact it is customary to use an electrolytic cell * with a diaphragm), with the molecules of the solvent (this can be avoided by conducting electrolysis of the molten substance), and with the material of the electrodes (this can be avoided by the use of inert electrodes made of graphite or platinum). Such processes are called secondary electrolysis processes. Some secondary products of electrolysis (NaOH, $KClO_3$, etc.) are manufactured on an industrial scale.

The quantitative study of electrolysis led to the establishment of the following laws:

1. *The amount of substance deposited on the electrodes in electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.*

2. *The passage of equal quantities of electricity through different electrolytes causes amounts of substances proportional to their chemical equivalents to be deposited on the electrodes* (Faraday's Laws).

Let us denote as Q the weight in grams of the substance deposited in electrolysis, as A the atomic weight of the element, as n the charge of the element in the compound subjected to electrolysis, and as $I \cdot t$ the number of coulombs (coulomb = ampere × second) of electricity passed through the electrolyte solution. In that case:

$$Q = \frac{A \cdot I \cdot t}{n \cdot 96{,}496}$$

Theoretically, 96,496 (or, approximately, 96,500) coulombs of electricity have to be expended to deposit 1 gram-equivalent of a substance. But actually, owing to a number of reasons, the amount of electricity expended is larger. The ratio of the theoretical amount to that actually used up is equal to the ratio of the amount of actually deposited substance to the theoretical amount and is called the *current efficiency.*

Electrolysis is used extensively in industry to prepare hydrogen, oxygen, chlorine, fluorine, and alkalis, to prepare and refine metals, to effect the anodic coating of metals with oxides, and of some metals with others.

4. General Methods of Preparing Metals. Since metals occur naturally either in the form of nuggets (gold, silver, etc.) or in the form of compounds (oxides, sulphide ores, salts), their preparation consists basically in either separating them from the gangue or in reducing them from their compounds.

(a) *The separation of noble metals from gangue* involves two processes: the oxidation of the metal by oxygen in the presence of potassium

* The bath in which electrolysis is conducted.

cyanide and the subsequent reduction of the cyan complex:

$$4Au + O_2 + 8KCN + 2H_2O = 4K[\overset{+1}{Au}(CN)_2] + 4KOH$$

$$2Zn^0 + 4K[\overset{+1}{Au}(CN)_2] = 4Au + 2K_2[\overset{+2}{Zn}(CN)_4]$$

(b) *Cathodic reduction* is the electrolysis of molten hydroxides or salts and the electrolysis of salt solutions with a mercury cathode and subsequent vacuum distillation of the amalgams obtained. The method is employed to prepare alkali metals, alkaline earth metals, and metals of the third group of the Periodic Table (including the rare earths). Cathodic reduction is also used to refine metals prepared by other techniques.

(c) *Chemical reduction* is in most cases conducted by the following reducing agents:

carbon

$$C + \overset{+4}{Sn}O_2 = Sn + \overset{+4}{C}O_2$$

hydrogen

$$7H_2 + 2K\overset{+7}{Re}O_4 = 2Re + 2KOH + 6H_2O$$

aluminium

$$2\overset{+3}{Al} + \overset{+3}{Cr}_2O_3 = 2Cr + \overset{+3}{Al}_2O_3$$

Reduction by means of aluminium has come to be known as *aluminothermics*. Other reducing agents used are sodium, magnesium, calcium carbide.

(*d*) *Intramolecular reduction* is employed to prepare noble metals from their oxides or nitrates, pyrophorous metals by the decomposition of oxalates and formiates (salts of oxalic acid and formic acid), and several other metals (Cr, Fe, Co, and Ni) by decomposing carbonyls by heating them. The following are examples of the preparation of metals from:

an oxide

$$2HgO = 2Hg + O_2$$

a nitrate

$$2AgNO_3 = 2Ag + 2NO_2 + O_2$$

an oxalate

$$FeC_2O_4 = Fe + 2CO_2$$

a formiate

$$Co(HCOO)_2 = Co + CO + CO_2 + H_2O$$

a carbonyl

$$Ni(CO)_4 = Ni + 4CO$$

(e) *Preparation of metals from sulphides.* Most of the heavy metals are prepared from sulphide ores (pyrites, glances, blendes, etc.). The process is conducted in two stages: (1) ore roasting and (2) reduction.

Ore roasting involves the oxidation of the ore by oxygen (air) at high temperatures:

$$2\overset{\overset{-2}{\longrightarrow}}{Bi_2S_3} + 9O_2 = 2Bi_2O_3 + 6SO_2$$

In this reaction it is only S^{-2} (which gives up 6 electrons) that is oxidised; in some cases the metal ion too undergoes oxidation. The resulting oxide is reduced by carbon in the second stage of the process.

QUESTIONS

1. Pure tin melts at 232°; pure lead, at 327°. The eutectic point of their alloy is 181° at a composition of 64% by weight of tin and 36% of lead. On the basis of these data draw a fusibility diagram (depicting the branches of the curve as straight lines). In the diagram draw an isotherm * for 216° and describe the system at the points of intersection of the isotherm with the branches of the curve. Through the point with the coordinates 300° and 50% of Pb draw a line parallel to the ordinate and describe all the changes in the system from the given temperature to the eutectic.
2. Give examples of the use of eutectic mixtures in industry.
3. What special point characterises the fusibility diagrams of systems whose components form chemical compounds?
4. What properties has the crystal lattice of solid solutions?
5. What galvanic couples of metals should be chosen (Table 15 on p. 164) for a galvanic cell to produce a maximum e. m. f.?
6. Draw schemes illustrating the electrolysis of $CuSO_4$ and NaBr solutions and indicate all the processes that take place at inert electrodes.
7. What chemical reactions can be used to obtain free antimony from antimony glance Sb_2S_3? Write the equations of the reactions that take place.

* An isotherm is a line of equal temperatures.

Problems

1. Draw a scheme of a cell consisting of the couples Ni/Ni$^{\cdot\cdot}$ and Cu/Cu$^{\cdot\cdot}$. Indicate the direction of the current in the inner and the outer circuit, determine the e. m. f. of the cell, and write the equation of the reaction on the basis of which the cell operates (solutions of M concentration are used; the temperature is 25°).

2. During the operation of a galvanic cell consisting of the couples Zn/Zn$^{\cdot\cdot}$ and Cu/Cu$^{\cdot\cdot}$ the weight of the cathode diminished by 0.1634 g. Calculate the amount of electricity produced.

3. The passage of a current through a dilute solution of H_2SO_4 for 10 minutes produces 652.2 ml of detonating gas (at a temperature of 18° and pressure of 746 mm). Calculate the current intensity.

4. A solution prepared by dissolving 0.45 g of brass (an alloy of zinc and copper) is subjected to electrolysis. The amount of electricity required to deposit all the copper from the solution is 482.5 coulombs. Calculate the percentage composition of copper in the brass.

5. Prove by adducing figures that nickel displaces copper, but does not displace aluminium, from solutions of their salts.

6. How many grams of a molal solution of HCl are needed to dissolve the amount of metallic zinc deposited in electrolysis on the cathode as a result of the expenditure of 4,825 coulombs of electricity?

7. Make up a galvanic cell of the couples Mg/Mg$^{\cdot\cdot}$ and Hg/Hg$^{\cdot\cdot}$, indicate the direction of the current in the circuit, write the equation of the reaction that takes place in the cell, and determine the e. m. f. if the concentration is M and the temperature is 25°.

8. How much iron will be deposited in two galvanic baths connected in series, one containing a $FeSO_4$ solution and the other a $FeCl_3$ solution, if a 2 ampere current is passed through them for 1 hour?

9. The electrolysis of molten LiCl for $2^1/_2$ hours yeilds 1.2 g of lithium at the cathode. Determine the current intensity and the volume of chlorine (reduced to N. T. P.) evolved at the anode.

10. The weight of a nickel plate immersed in a solution of silver nitrate increases by 0.73 g. How much silver is deposited on the plate?

LABORATORY WORK

Apparatus and materials: the apparatus shown in Figs. 62 and 63 (or 60 and 64); 5 ampere ammeter; 6-8 volt storage battery; 5 volt voltmeter; slide rheostat; electric key; copper electrode; zinc electrode; porous vessel; sand bath; iron crucible; thermometer for 100°; porcelain mortar; test tubes and rack; 300-400 ml beaker; 200 ml beaker; two 100 ml beakers; weighing bottle or watch glass; slides; glass tubing 5 mm in diameter; knife for cutting glass tubing; dovetail nozzle; electrolytic bridges with agar; rubber bands for attaching capillaries; steel nibs; bismuth; tin; lead; cadmium; zinc plate; copper plate; magnesium turnings; granulated zinc; copper turnings; powdered antimony; powdered iron; ferric oxalate; cupric oxide; dry crystalline phenol; crystalline naphthalene; M solution of cupric sulphate; M solution of zinc sulphate; 0.5 N solution of potassium ferricyanide; N solution of magnesium chloride; N solution of cupric chloride; 2 N solution of sodium chloride contaning phenolphthalein; 0.5 N solution of mercuric nitrate; N solution of hydrochloric acid; 2 N solution of sulphuric acid; 1:1 nitric acid; platinum or silver wire; iron wire; paraffin wax; charcoal; squared paper; thick paper, and clean rags.

Note. The phenol should be colourless and dry. If the product is coloured, it ought to be distilled and dried over potassium hydroxide for 10 days.

1. Fusibility Diagram of Naphthalene-phenol System. This is a collective job for the whole group of students, each determining one

point on the fusibility curve of the system. Ten points in all should be determined for the system (see table below). The students who receive the assignments 1 and 10 should determine the melting points of pure naphthalene and phenol, conducting the experiment as described in Exercise 7. The students receiving the assignments 2-9 determine the melting point and the crystallisation point of naphthalene-phenol mixtures.

By means of a chemical balance weigh to 0.01 g the amounts of the initial substances indicated in the table (do the weighing in weighing bottles or watch glasses). The work with phenol requires caution, as it is poisonous; besides that, upon coming into contact with the skin, it produces burns.

Place the weighed amounts into a special test tube with a glass jacket to prevent overcooling or overheating. Close the test tube with a stopper through which a thermometer and a stirrer (careful!) have been passed (Fig. 62). Place the apparatus into a beaker with water, fastening it in a clamp.

Heat the water in the beaker slowly. When the crystals begin to melt, reduce the flame of the burner so that the rise in temperature continues at a rate of 0.5° a minute.

As soon as the solid phase begins to melt, it is necessary to start stirring the contents of the test tube with the stirrer (be careful not to break the stirrer!). Note the temperature at which the last crystals melt. Then discontinue the heating and, while stirring the melt with the stirrer, begin cooling the beaker with water. Note the temperature at which the first crystals appear.

Make three determinations of the melting point and the crystallisation point, and record the results.

Fig. 62. Set-up for melting point and crystallisation point measurements

On the basis of the data in the table, plot a fusibility diagram (a convenient scale for the abscissa is 10% by weight = 1 cm; for the ordinate, 10° = 1 cm). Find the point of intersection of the branches in the diagram and determine the coordinates of the eutectic point.

2. Preparation of Wood's Metal. This experiment should be conducted in a ventilated hood. Weigh 5.3 g of Bi (m. p. 271°), 2 g of Sn (m. p. 232°), 1.5 g of Pb (m. p. 327°), and 1.2 g of Cd (m. p. 321°). Melt about 10 g of paraffin wax in an iron crucible and place the tin in it. Heat the crucible, mixing the contents with an iron wire, until the melting point is reached; then add the lead, the cadmium, and the bismuth in that order. When all the metals have melted, cool the alloy, first pouring off the molten paraffin wax. Wipe the alloy with a rag, melt it again, and pour it into a cigarette-wrapper, which serves as a mould. When the rod of alloy has cooled, lower it into a

No. of assign-ment	Composition of mixture				Determination of melting point (a) and crystallisation point (b)						Mean tempera-ture in °C	Name of student perform-ing ex-periment
	naph-thalene in g	phenol in g	naphtha-lene in % by weight	phenol in % by weight	a	b	a	b	a	b		
1	—	—	100	0								
2	1.29	0.11										
3	1.02	0.38										
4	0.81	0.59										
5	0.65	0.75										
6	0.52	0.88										
7	0.36	1.04										
8	0.29	1.11										
9	0.24	1.16										
10	—	—	0	100								

glass of water heated to 55°; slowly, at the rate of 1° a minute, continue heating the water and note the melting point. Record the result in your notebook and hand the alloy over to the laboratory assistant. Why does the alloy melt at a temperature lower than the m. p. of any one of the four constituent metals?

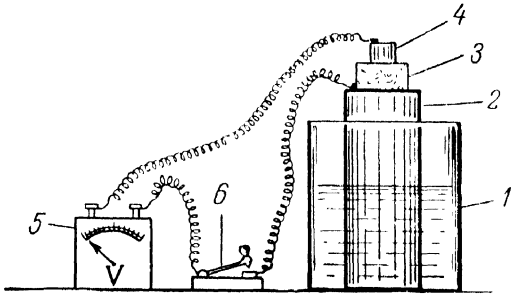


Fig. 63. Galvanic cell

1 — thick-walled jar; 2 — cylindrical copper electrode; 3 — vessel of clay; 4 — zinc electrode; 5 — voltmeter; 6 — key.

3. Galvanic Cell. Assemble the cell shown in Fig. 63 (or in Fig. 60 on p.162, in which case an electrolytic bridge filled with a solution of KCl with agar serves as the "key"). Into a thick-walled jar (1) containing an M solution of cupric sulphate lower a cylindrical electrode (2) made of sheet copper. Inside the electrode place a porous vessel of clay (3) with an M solution of zinc sulphate. Into the clay vessel lower a zinc electrode (4). Connect up the voltmeter (5) and key (6). Close the circuit by pressing the key and determine the e. m. f. by

means of the voltmeter. Disconnect the wires from the voltmeter and apply them to a slide on which is a strip of filter paper moistened with a solution of NaCl with phenolphthalein. Note which of the wires produces a crimson colouration (negative pole!). Make a drawing of the apparatus and a scheme of the cell, indicating the direction of the current in the inner and the outer circuit. Calculate the e. m. f. of the cell. Is there a discrepancy between the calculated and the experimental value? Write the equation of the chemical reaction that produces the electric current in the circuit.

4. Electromotive Series. (a) Pour 4 ml of an N solution of hydrochloric acid into each of 4 test tubes; add a piece of magnesium, zinc, copper, and antimony respectively. Do all the metals displace hydrogen from acids? Give an explanation.

(b) Select two lumps of zinc with surface areas as near equal as possible. Place one of them for 3-4 minutes into a test tube containing 1 ml of a cupric sulphate solution. Pour the solution from the test tube and wash the copper-plated zinc with water several times. Pour 3-4 ml of a hydrochloric acid solution into each of 2 test tubes; put the lump of ordinary zinc into one of them; the lump of copper-plated zinc, into the other.

In which of the test tubes is the evolution of hydrogen more vigorous?

On the surface of which metal is hydrogen evolved? Give an explanation.

(c) Into the slit of a steel nib insert a small plate of zinc; into the slit of another nib, a plate of copper of the same size. Pour 5-6 ml of a sulphuric acid solution into each of 2 test tubes and add 3-4 drops of a solution of potassium ferricyanide to each (the salt is a reagent for the ion of bivalent iron, with which it forms Turnbull's Blue). Immerse the nibs with the plates in the test tubes. Observe the appearance of a blue colouration in one of them (which?) in a few minutes. Give an explanation of this.

(d) Pour 2 N H_2SO_4 into a small beaker and lower a plate of zinc into it. Is there evolution of hydrogen on the surface of the zinc?

Touch the plate with the bent end of a platinum or silver wire. On which of the metals is hydrogen evolved and why?

(e) Pour 3-4 ml of a $MgCl_2$ solution into one test tube and an equal amount of a $HgCl_2$ solution into another; lower copper plates into the test tubes. After a period of time examine the surface of the plates, explain the phenomenon observed, and write an equation of the reaction.

5. Electrolysis. Pour a solution of $CuCl_2$ into a U-tube (Fig. 64) in such a way that 3 cm lengths of the carbon electrodes are immersed in the solution. Connect wires from a storage battery to the carbon electrodes. After 5-10 minutes observe what has been deposited on the cathode. By its odour identify the gas evolved at the anode. Remove

the copper from the cathode by dissolving it in nitric acid and wash the apparatus with water. Draw a scheme of the electrolysis process.

6. Preparation of Metals. (a) Mix 1 g of mercuric sulphide (cinnabar) in a small mortar with 1 g of powdered iron and put the mixture in a dry test tube. Heat the test tube over the flame of a burner in a ventilated hood and, after a time, observe the formation of a "mercury" belt on the cold walls of the test tube. Write the equation of the reaction that takes place.

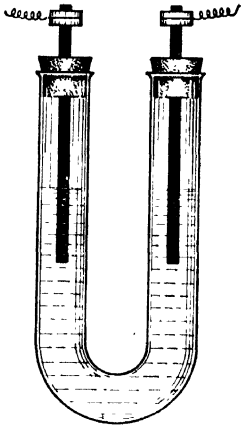


Fig. 64. Apparatus for electrolysis

(b) Mix 1 g of cupric oxide with 1 g of coal in a mortar. Place the mixture in a dry test tube and, after warming it over the flame of a burner, heat it for 7-10 minutes. After cooling, empty the test tube on a sheet of paper; ascertain (from the colour) that metallic copper has been formed. Write the equation of the reaction that has taken place.

(c) Place about 1 g of powdered ferric oxalate into a dry test tube. Fasten the test tube in a wooden clamp and heat it over the flame of a burner, holding the test tube so that the upper part is slightly below the bottom. The yellow powder is decomposed by heating, and greyish-black metallic iron is formed. After the oxalate has been completely decomposed, remove the powdered iron from the test tube, exposing it to the air. What happens? Note the colour of the oxide formed! What is the term used for metals that in the powdered state ignite spontaneously in the air? Write the equations for the reactions of the decomposition of the oxalate and the burning of the iron in the air.

Exercise 20

ALKALI METALS

SUBJECTS FOR STUDY

Alkali metals; atomic structure of these elements; their reductant properties; atomic radii and relative activity of alkali metals; attitude to oxygen, hydrogen, water, and acids; oxides and hydroxides of akali metals and their properties; salts of alkali metals, and distinctive features of lithium among the alkali metals.

The alkali metals are: Li, Na, K, Rb, Cs, and Fr. The atoms of all these elements have only one electron each in their outermost shells. In chemical reactions they part with this electron readily according to the equation $Me - 1e^- = Me^+$, thereby exhibiting highly

pronounced reductant properties. The atomic radii increase with the rise in atomic numbers, and reductant activity mounts in the same order:

	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Radius (Å)	1.56	1.86	2.23	2.43	2.62

The alkali metals are kept under a layer of kerosene, since exposure to the air causes them to undergo rapid oxidation:

$$4Me + O_2 = 2Me_2O$$

All the alkali metals come before hydrogen in the electromotive series; they are readily oxidised by water and by acids, interacting, for instance, as follows:

$$2Na + 2\overset{+1}{H}OH = H_2 + 2\overset{+1}{N}aOH$$

$$2Li + 2HCl = H_2 + 2\overset{+1}{L}iCl$$

The oxides of these metals can be prepared by reducing their peroxides by an excess of the metal:

$$2Na + Na_2\overset{-2}{[O_2]} = 2Na_2O$$

The oxides of the alkali metals are solid, highly hygroscopic substances that combine readily with water to form hydroxides, solid substances that dissolve well in water.

The aqueous solutions of the hydroxides exhibit pronounced alkaline properties, due to dissociation into ions:

$$MeOH \rightleftarrows Me^{\cdot} + OH'$$

The most important of the hydroxides are sodium hydroxide NaOH and potassium hydroxide KOH, which are prepared primarily by the electrolysis of aqueous solutions of NaCl and KCl (with subsequent evaporation).

The salts of the alkali metals are, with a few exceptions, soluble and belong to the strong electrolyte group. The salts of weak acids undergo hydrolysis in aqueous solutions, and their solutions are for this reason alkaline. The volatile salts impart characteristic colours to the colourless flame of a burner: in the case of sodium compounds the colour is yellow; lithium, carmine; potassium, violet; rubidium, reddish-violet, and caesium, violet.

QUESTIONS

1. Which metal, sodium or potassium, is oxidised more readily? Why?
2. Write the equations for the reactions of the oxidation of potassium by oxygen at room temperature and in combustion.
3. How can sodium hydroxide be prepared from Na_2CO_3 and from NaCl? Write the equations for the respective reactions.
4. Given solutions of the salts:

$$K_2CO_3 \quad NaNO_3 \quad K_2SO_4 \quad K_2S \quad KHCO_3$$

Write the equations for their interaction with water and explain why some of these solutions are alkaline.
5. Explain why CsOH is a stronger alkali than KOH.
6. Draw diagrams for the electrolysis of molten KCl and of a KCl solution, indicating the processes that take place at inert electrodes. Can the K^+ ion be reduced without resorting to electrolysis?

Problems

1. Demonstrate whether it is possible for potassium to form compounds with oxygen in which there would be 17% of oxygen and 45.1% of oxygen.
2. It is known that 0.43 g of a certain metal reacts with water to displace 123.2 ml of a gas (measured at N. T. P.). It is known too that 1.56 g of the same metal reacts with 1.415 g of chlorine. What is the metal?
3. Raising the temperature of 1 g of metallic sodium by 12° requires 3.48 Cal. Calculate the atomic weight of sodium and the relative error of the determination, the exact atomic weight being 22.997.
4. On the assumption that rubidium consists of the isotopes Rb^{85} (72.8%) and Rb^{87} (27.2%) determine the atomic weight of the element.
5. Calculate the titre and the normality of 8% KOH, the relative density of the solution being 1.065.
6. What volumes of 52% NaOH (relative density 1.56) and water should be mixed to prepare 1 ton of 16% NaOH?
7. The interaction of 1 g of sodium amalgam with water produces an alkali solution whose neutralisation requires 50 ml of a hydrochloric acid solution with a titre of 0.00365. Calculate the sodium content of the amalgam.
8. What will be the boiling point of a solution of 25 g of KOH in 800 g of water if the apparent degree of ionisation is 86%?
9. Calculate the osmotic pressure of a 6% solution of KOH (relative density 1.05 at 20°) if the apparent degree of ionisation is 84%?
10. What will be the yield of the products in the electrolysis of molten NaOH by an 0.2 a current for 5 hours?

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 33; 100 ml Erlenmeyer flask; 10 ml measuring cylinder; 25 ml burette; funnel for burette; 10 ml pipette; two porcelain casseroles; two watch glasses 7-9 cm in diameter; 100 ml measuring flask; test tubes and rack; forceps; scalpel; two glass rods; platinum wire; room thermometer; barometer; indigo or cobalt prism; sodium; potassium; 0.04-0.05 g weighed amounts of sodium; potassium chloride; sodium sulphide; sodium nitrate; potassium carbonate;

titrated solution of 0.02 N HCl; 0.5 N NaCl; 0.5 N KCl; saturated solution of potassium antimonate; 0.4 N solution of sodium bitartrate; solution of sodium cobaltinitrate; ethyl alcohol; solutions of phenolphthalein, methyl-orange, and neutral litmus; set of test tubes with saturated solutions of lithium, potassium, and sodium chlorides and concentrated hydrochloric acid; boiled distilled water, and filter paper.

Note. The preparation of sodium cobaltinitrate is described in Exercise 22.

1. Interaction of Alkali Metals with Air and with Water. (a) By means of forceps take a lump of metallic sodium from a jar in which it is kept in kerosene, place the sodium on filter paper, and make a cut in the lump with a knife or scalpel. Note how the freshly exposed lustrous metal surface tarnishes. Cut off a tiny bit of the metal the size of a match-head and throw it into a porcelain casserole with water. Cover the casserole with a piece of glass. Observe the vigorous reaction that takes place.

(b) Carry out a similar experiment with metallic potassium. Add a drop of phenolphthalein to the solutions obtained in each of the casseroles. What happens? Why?

Write the equations for the interaction of potassium and sodium with water. What accounts for the greater activity of potassium?

2. Experimental Verification of the Equivalent of Sodium. The equivalent of sodium is determined by the procedure described in Exercise 6 (experiment 2). Before conducting the experiment make certain that the apparatus is airtight.

For the acid substitute alcohol (why not water?), with which alkali metals react thus:

$$2Na + 2C_2H_5OH = H_2 + 2C_2H_5ONa$$

Take 5-6 ml of ethyl (methyl) alcohol for the experiment. After pouring the alcohol into a test tube, carefully dry the inner walls of the test tube with strips of filter paper.

By means of forceps take a lump of metallic sodium weighing about 0.04-0.05 g from a jar with kerosene, dry it quickly on a piece of filter paper, and place it in the bulb (broken line in Fig. 33) of an inclined test tube.

Close the test tube tightly with the stopper of the apparatus and lower the test tube in a vertical position, so that the sodium slips into the alcohol and reacts with it.

After the reaction has ended and the apparatus has been allowed to cool, measure the volume of the hydrogen evolved (don't forget to equalise the levels of the liquid in the burettes!) and record the barometric pressure and the temperature.

From the weight of the metal and the volume of the hydrogen evolved calculate the equivalent of the sodium. To determine the exact weight of the metal sodium taken, pour the solution of sodium ethylate formed in the test tube into a measuring flask. Rinse the

Level in burette		Hydrogen volume in ml	Barometric pressure *p* in mm Hg	Temperature in °C	Vapour tension *h* in mm Hg
before reaction	after reaction				

test tube 3-4 times with small portions (4-5 ml) of distilled water, pouring the solution each time into the measuring flask.

The hydrolysis reaction produces sodium hydroxide:

$$C_2H_5ONa + HOH = C_2H_5OH + NaOH$$

From the amount of the sodium hydroxide it is possible to calculate the amount of metal originally taken.

Bring the level of the solution in the measuring flask up to the mark so that the bottom meniscus rests on the level of the mark on the neck of the flask (Fig. 65). Close the flask with a stopper and mix the solution in it thoroughly.

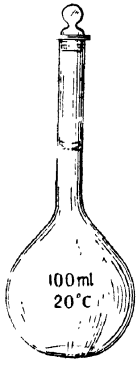


Fig. 65. Measuring flask

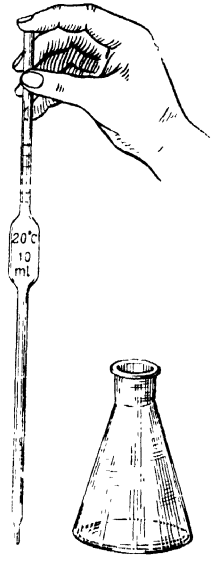


Fig. 66. Pipette and Erlenmeyer flask

Lower a dry 10 ml pipette into the flask, suck the solution into the pipette above the mark, and cover the upper end of the pipette with the index finger (Fig. 66). By reducing the pressure of the finger bring the level of the liquid down to the mark (according to the bottom meniscus) and then close the upper end of the pipette tigthly with the index finger again. Now lower the tip of the pipette into a clean Erlenmeyer flask (Fig. 66) and release the measured amount of alkali solution into it (the tip of the pipette should touch the inner wall of the neck of the flask at an angle of 45-50°). Add 2-3 drops of methyl-orange indicator to the solution; the solution turns yellow.

Pour a *titrated* solution of hydrochloric acid into a burette (Fig. 67), making sure that the *tip of the burette is filled* and the bottom meniscus touches the zero line. The glass ball (3) fitted snugly inside the rubber

tubing (2) prevents any acid from issuing from the burette. But by pressing the rubber tubing next to the ball it is possible to form a channel (*C*), through which acid passes. If any bubbles of air remain inside the burette tip, these should be removed as shown in Fig. 67*D*.

Place an Erlenmeyer flask with an alkali solution and an indicator underneath the burette and pour 1 ml of acid from the burette at a time, shaking the flask after each addition of the acid, until the yellow colour of the solution changes to orange * (normal titration) or to a pinkish-red (overtitrated solution!). Let us assume that the addition of 9 ml of acid leaves the solution yellow, while 10 ml makes it pinkish-red. In that case the exact volume of the acid is greater than 9, but less than 10 ml.

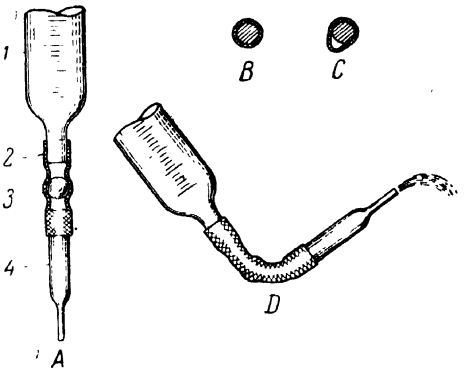


Fig. 67. Burette with pinch-cock clamp

A — burette; 1 — calibrated part; 2 — rubber tubing; 3 — pinch-cock clamp; 4 — drawn-out tip; *B* — position of ball when burette is closed; *C* — position of ball when liquid issues from burette; *D* — filling the burette tip.

Empty the Erlenmeyer flask, rinse it thoroughly with water, measure another 10 ml of the alkali solution with a pipette, and add the same amount of indicator. Titrate the solution again, at first adding several millilitres at a time (up to 9 ml in the above example), then adding the solution by drops until the colour changes to orange. Record the amount of acid solution used (with an accuracy of up to 0.05 ml). Repeat the titration two more times. Take the average of the three titrations.

Volume in ml		Amount of HCl solution used for titration in ml					Concentration of HCl solution (N)
flask	pipette	approx	exact			average of 3 exact titrations	
			1	2	3		

From the data obtained calculate the equivalent of the metallic sodium that reacted with the alcohol.

* To be able to observe the change of colour clearly, place a sheet of white paper under the Erlenmeyer flask

To do this, determine the concentration of the alkali from the concentration and volume of the acid used for the titration and the volume of the alkali. From the concentration of the alkali calculate the amount of it (in g) contained in the flask. From the formula (NaOH) calculate the amount of the metal corresponding to the found amount of the alkali. Finally, calculate the equivalent of the metal.

3. Detecting Alkali Metals by Flame Colourations. Receive from the laboratory assistant a set consisting of 4 test tubes, a rack, and a glass rod with a platinum wire protruding from it. One of the test tubes contains concentrated hydrochloric acid, while the other three contain solutions of lithium, sodium, and potassium chlorides. Introduce the platinum wire into the *outer* cone of the flame. The clean wire glows without altering the colour of the flame. Should the flame become coloured, immerse the wire in hydrochloric acid and then heat it again. Next, immerse the wire in the lithium salt solution and heat it, observing the characteristic colouration of the flame. Before testing the next salt solution in the flame, keep the wire in the flame for a time. The flame colouration produced by potassium salts should be observed through an indigo or cobalt prism (Fig. 68).

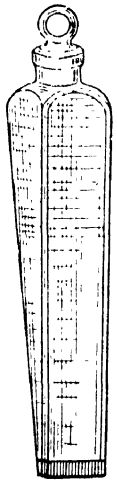


Fig. 68. Indigo or cobalt prism

4. Hydrolysis of Salts. Place a few crystals of $NaNO_3$, Na_2S, KCl, and K_2CO_3 into four test tubes respectively and add 2-3 ml of boiled distilled water to each. Then add 1 ml of neutral litmus solution to each, observing the change in colour against a background of white paper. Write the equations of the hydrolysis reactions that have taken place. Which of the four salts undergo hydrolysis?

5. Preparation of Slightly Soluble Salts. (a) To a neutral solution of a sodium salt add an equal volume of a solution of potassium hydroxoantimonate $K[Sb(OH)_6]$; to the potassium salt solution, a solution of sodium hydrogen tartrate $NaHC_4H_4O_6$. If no precipitates appear at once (owing to the formation of supersaturated solutions), rub the test tubes inside with a glass rod. To speed the formation of the potassium hydrogen tartrate crystals, it is advisable to add 2-3 ml of ethyl alcohol. How do the precipitates differ by appearance? Write the equations of the reactions that have taken place.

(b) To a neutral potassium salt solution or one acidified with acetic acid add an equal volume of a solution of sodium cobaltinitrate $Na_3[Co(NO_2)_6]$. A yellow crystalline precipitate of $K_2Na[Co(NO_2)_6]$ is formed. Write the equation of the reaction that has taken place.

6. Analysis of Solid Salt. Receive from the instructor a salt sample for analysis (NaCl, KCl, Na_2SO_4, or K_2SO_4). Write a brief plan of

how to detect the cation and anion of the salt and submit the plan to the instructor. Carry out the analysis, write it up, and submit the report to the instructor.

Exercise 21

COPPER SUBGROUP ELEMENTS

SUBJECTS FOR STUDY

The copper subgroup: copper, silver, and gold; their atomic structure and a comparison of the electron shells of their atoms and those of the alkali metals; points of similarity and difference in the properties of these metals; the position of copper, silver, and gold in the electromotive series; the attitude of these metals to oxygen, water, and acids; gold dissolved in *aqua regia*; oxides and hydroxides; major salts; oxidant properties of the ions of the noble metals, and complex compounds.

The atoms of copper, silver, and gold have one electron in their outermost shell and are in this respect structurally similar to the atoms of the alkali metals. The atoms of the alkali metals, however, have 8 electrons in the next to last shell, whereas in the case of copper, silver, and gold this shell has 18 electrons. This accounts for the marked difference between the properties of these elements and the properties of the alkali metals.

For example, let us compare the properties of potassium and copper:

	K	Cu
Atomic number	19	29
Erectron arrangement	)2)8)8)1	)2)8)18)1
Atomic radius (Å units)	2.23	1.28
Ionisation potential (ev)	4.30	7.69
Melting point (°C)	63.5	1083
Boiling point (°C)	776	2360
Density	0.86	8.95
Hardness	0.5	3.0
Conductivity	14	57
Electrode potential (V)	—2.92	0.52

With the change in electron structure from potassium (with its 8-electron structure) to copper (with its 18-electron structure), the relative density, melting point, and boiling point rise, while the atomic radius and the reductant activity diminish.

Silver and gold are noble metals and are difficult to oxidise; their positive ions, unlike the ions of the alkali metals, can act as oxidants and have a marked polarising effect, which accounts for the colouration of most of their compounds, the low thermal stability of the oxides and hydroxides, and the ability to form complexes.

The 18-electron shell of the Cu, Ag, and Au atoms is not particularly stable: in chemical reactions the atoms of these elements give up not only their outer electrons, but also electrons from the $18e^-$ shell, turning into uni- to tripositive ions.

Copper, silver, and gold rank below hydrogen in the electromotive series; since their normal potentials are positive, they are not oxidised by hydrogen ions, but can be oxidised (except gold) by acids whose radicals have a high oxidising ability (concentrated and dilute nitric acid, concentrated sulphuric acid, etc.). In these reactions the acids act both as oxidant and as the medium.

As we know from earlier work (Exercise 19, paragraph 2), the normal electrode potential values can be used to find the e.m.f. of redox reactions and to predict their direction. By using a hydrogen electrode, it is possible to determine the E^0 not only of metal couples (Table 15), but also of couples consisting of more complicated oxidising agents and their reduced forms or of complicated reducing agents and their oxidised forms. For instance, the nitric acid ion can by reduction be converted to nitrogen peroxide; the potential of the $NO_3^- + 2H^+/NO_2 + H_2O$ couple, measured by means of a platinum electrode, proved equal to 0.81 V. The normal redox potentials of other couples (Table XV on p. 336) can be measured in the same way.

Example. Can metallic copper be oxidised by concentrated nitric acid that is reduced to nitrogen peroxide?

(a) Write the equation of the reaction (see Exercise 16, experiment 6):

$$\underset{\longrightarrow}{\overset{2e^-}{}}\quad \overset{+5}{}\qquad\qquad \overset{+2}{}\qquad\qquad \overset{+4}{}$$
$$\underline{Cu} + \underline{\underline{2HNO_3}} + 2HNO_3 = \underline{Cu}(NO_3)_2 + \underline{\underline{2NO_2}} + 2H_2O$$

(b) In the equation underline the reductant and its oxidised form once; the oxidant and its reduced form, twice. The galvanic cell corresponding to this reaction is the cell:

$$Cu/Cu^{2+}//NO_3^- + 2H^+/NO_2 + H_2O$$

Consequently, the Cu/Cu^{2+} couple is the reductant, while the $NO_3^- + 2H^+/NO_2 + H_2O$ couple is the oxidant.

(c) From the potentials of the couples $E^0_{Cu/Cu^{2+}} = 0.34$ V (Table 15) and $E^0_{NO_3^- + 2H^+/NO_2 + H_2O} = 0.81$ V (Table XV, p. 336) determine the e. m. f.

$$\text{e. m. f.} = E^0_{NO_3^- + 2H^+/NO_2 + H_2O} - E^0_{Cu/Cu^{2+}} = 0.81 - 0.34 = 0.47 \text{ V}.$$

The e. m. f. being positive, the reaction between these substances is possible.

Metallic gold, which is insoluble in hydrochloric, sulphuric, or nitric acid, dissolves in *aqua regia* (a mixture of three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid):

$$Au + 4HCl + HNO_3 = H[AuCl_4] + NO + 2H_2O$$

The reaction can be explained as consisting of the following stages:
(1) the interaction of the two acids to form monoatomic chlorine and nitrosyl chloride NOCl:

$$2\overset{-1}{H}Cl + H\overset{+5}{N}O_3 + HCl = 2Cl + \overset{+3}{N}OCl + 2H_2O$$

(2) the oxidation of the gold by the monoatomic chlorine and nitrosyl chloride:

$$Au + 2Cl + \overset{+3}{N}OCl = \overset{+3\ -1}{AuCl_3} + \overset{+2}{N}O$$

(3) the combination of the auric chloride with excess hydrochloric acid to form chloroauric acid:

$$AuCl_3 + HCl = H\,[AuCl_4]$$

At ordinary temperatures the oxygen of the air has no effect on copper, silver, or gold. But when copper is heated, it is oxidised to cupric oxide or, when the access of air is limited, to cuprous oxide. Dissolved oxygen, in the presence of substances that form complex compounds with $Cu^{\cdot\cdot}$, $Ag^{\cdot}$, and $Au^{\cdot}$, oxidises these metals, e. g.:

$$2Cu + O_2 + 8NH_4OH = 2[Cu\,(NH_3)_4]\,(OH)_2 + 6H_2O \qquad (1)$$

$$4Au + O_2 + 8KCN + 2H_2O = 4K\,[Au\,(CN)_2] + 4KOH \qquad (2)$$

Reaction (2) is used to extract gold from quartz sand.
The treatment of copper, silver, and gold salt solutions with alkalis produces hydroxides, e. g.:

$$Cu^{\cdot\cdot} + 2OH' = Cu\,(OH)_2$$

$$2Ag^{\cdot} + 2OH' \rightleftarrows 2AgOH \rightleftarrows Ag_2O + H_2O$$

Silver hydroxide at ordinary temperatures decomposes reversibly to water and the oxide; cupric hydroxide decomposes irreversibly, moreover only when heated. The oxides of these metals do not dissolve in water, except silver oxide, whose saturated solution exhibits alkaline properties perceptibly. Upon being heated, the oxides of silver and gold decompose to the metal and oxygen.

The salts of the univalent cations are mostly colourless and insoluble. The compounds of bivalent copper are blue-green or green, while the salts of trivalent gold are golden yellow. The salts of copper, silver, and gold undergo hydrolysis.

The positive ions $Cu^{\cdot\cdot}$, $Ag^{\cdot}$, $Au^{\cdot}$, $Cu^{\cdot}$, and $Au^{\cdot\cdot\cdot}$ may, in reactions, exhibit oxidant properties, e. g.:

$$3\overset{+2}{Sn}Cl_2 + 2\overset{+3}{Au}Cl_3 + 6HCl = 3H_2\,[\overset{+4}{Sn}Cl_6] + 2Au \quad (6e^-)$$

$$2\overset{+2}{Fe}SO_4 + \overset{+2}{Ag}_2SO_4 = \overset{+3}{Fe}_2(SO_4)_3 + 2Ag \quad (2e^-)$$

Characteristic of these ions are complex compounds, the most important being ammoniates, such as $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]Cl$, and cyanides, such as $K[Ag(CN)_2]$ and $K[Au(CN)_2]$.

QUESTIONS

1. What are the points of similarity and difference between the metals of the copper series and the alkali metals? Explain this.
2. Copper objects are often covered with a green coating of basic copper carbonate $Cu_2(OH)_2CO_3$. Write the equation for the reaction of the formation of this salt, bearing in mind that it is formed in the presence of copper, water, oxygen, and carbon dioxide.
3. Write the equations for the reactions that take place when metallic copper is dissolved (with heating) in concentrated sulphuric acid and when silver is dissolved in concentrated nitric acid.
4. Why is silver oxide decomposed by heating, while potassium oxide is not?
5. By writing the equations of relevant reactions, demonstrate that $Au(OH)_3$ is an amphoteric compound.
6. What is the effect of aqueous solutions of $CuSO_4$ and $AuCl_3$ on litmus, and why is this so?
7. Write the equations of two reactions illustrating how the $Ag^{\cdot}$ ion is precipitated and reduced.

Problems

1. The heating of 20 g of metallic copper from 97 to 100° requires 5.71 cal. Calculate the atomic weight of copper and express in percentages the discrepancy between the value found and the exact value of 63.54.
2. What amount of 20% HCl is needed for the complete precipitation of the silver from a solution obtained by dissolving 50 g of a silver alloy of the 875 standard in nitric acid?

3. How many litres of nitric oxide (at 18° and 750 mm Hg) will be produced when 1 kg of copper is dissolved in an excess of dilute nitric acid?
4. Twenty grams of 8.5% ammonia solution is used to dissolve 7.17 g of silver chloride. Determine the composition of the complex compound formed.
5. Calculate the amounts of substances needed to extract 1 kg of gold from quartz sand by the cyanide method.
6. Calculate the percentage and molar concentrations of a solution prepared by mixing 18 lit of a 4% solution of $CuCl_2$ (relative density 1.036) with 4 lit of a 22% solution of $CuCl_2$ (relative density 1.23).
7. The heat of formation of cuprous oxide from its elements is 42.5 Cal.; of cupric oxide, 38.5 Cal. Calculate the heat of the reaction of the oxidation of cuprous oxide to cupric oxide.
8. The surface of a cylinder 16 cm high and 6 cm in diameter is to be coated galvanically by a layer of gold 0.005 mm thick. How much electricity and $K[Au(CN)_2]$ salt will this require, if the density of the gold is 19.3 g/cu cm?
9. Draw a diagram of a galvanic cell consisting of the couples $Al/Al^{\cdots}$ and $Au/Au^{\cdots}$. Explain the operation of the cell in terms of E^0 values.
10. Calculate the solubility product for AgCl, knowing that $5.15 \cdot 10^{-4}$ g of AgCl dissolves in 100 ml of the solution at 50°.

LABORATORY WORK

Apparatus and materials: 6-8 V storage battery; 5 A ammeter; 5 V voltmeter; stop watch; slide rheostat; electric key; two 2 mm copper plates; electric wires; test tubes and rack; funnel; 300 ml beaker; crucible tongs; copper turnings; copper wire; copper gauze turned into a cylinder; litmus paper; starch paper; sandpaper; filter paper; Fehling's solution (in two solutions); concentrated nitric acid; 2 N H_2SO_4; 1 : 1 and 15% nitric acid; concentrated, 2 N, and 6% HCl; 1% and 0.1 N $AgNO_3$; 10% ammonia solution; 1% and 2 N NaOH; 0.5 N KI; 0.5 N KBr; 0.5 N KCl; 0.5 N $CuSO_4$; N Na_2CO_3; N solution of sodium thiosulphate; 2% solution of glucose; ethyl alcohol; hydrogen sulphide water, and copper plating solution.

Preparation of Fehling's Solution. Two solutions are prepared: I—34.64 g of cupric sulphate in 500 ml of water, and II—52 g of sodium hydroxide and 173 g of potassium sodium tartrate $NaKC_4H_4O_6$ in 500 ml of water.

Preparation of Electrolysis Solution. Dissolve 150 g of cupric sulphate in 1 litre of water containing 50 g of sulphuric acid (relative density 1.84) and 50 ml of ethyl alcohol.

Precaution! All the spent solutions of silver salts should be collected in special bottles!

1. Reductant Properties of Copper. (a) *This experiment should be conducted in a ventilated hood.* Test the action of dilute and concentrated H_2SO_4 on metallic copper with and without heating.

(b) *This experiment too should be conducted in a ventilated hood.* Test the action of dilute and concentrated nitric acid on metallic copper with heating. Note the colour of the gases evolved. Determine the e.m.f. of the first reaction from redox potential values (Table XV on p. 336).

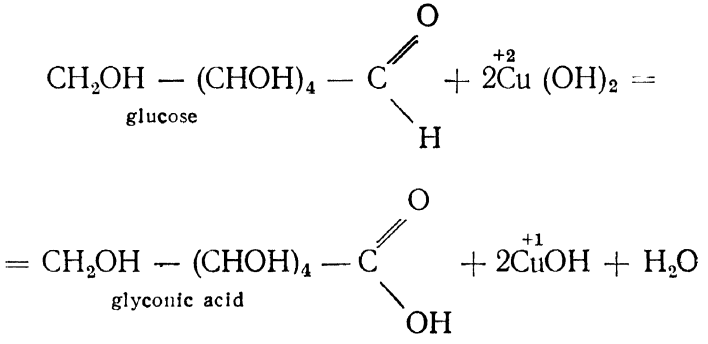
(c) Take some bits of copper wire with forceps and heat the wire in the outer cone of a nonluminous flame of a burner. What changes are observed? Write the equation of the reaction that takes place.

2. Action of Alkalis on Cupric and Silver Salts. Study the action of an alkali solution on solutions of cupric and silver salts. Record the external changes that take place and write the relevant equations. Shake the solution with the cupric hydroxide precipitate and pour it into four test tubes. Heat one of the test tubes and describe the changes observed. Treat the precipitate in another test tube with an acid solution. Write the equations of the reactions that take place.

Pour 2-3 ml of concentrated sodium hydroxide solution into the third test tube and shake it vigorously. Let the precipitate settle. What is now the colour of the solution? Write the equation of the reaction between cupric hydroxide and sodium hydroxide. What are the properties of cupric hydroxide? What is cuprite? Leave the fourth test tube with the cupric hydroxide precipitate for experiment 10.

3. Preparation of Cuprous Oxide. Mix 1.5 ml each of the two solutions used to make Fehling's solution in a test tube with an equal volume of a 1% solution of glucose and boil the contents of the test tube. A yellow precipitate of CuOH is formed at first; further boiling converts this to red Cu_2O.

The reaction may be set down as follows:



$$2CuOH = H_2O + Cu_2O$$

4. Preparation of Cupric Oxide and Its Oxidant Properties. Heat a cylinder of copper gauze in the oxidising flame of a burner. Observe the formation of black cupric oxide. Immerse the heated "sausage" in a test tube with 3-4 ml of ethyl alcohol. What happens? Write the equation of the reaction that takes place on the assumption that the alcohol is oxidised to acetaldehyde.

5. Hydrolysis of Salts. (a) Test solutions of some cupric and silver salts with litmus paper. Observe the changes in its colour and write the equations of the hydrolysis reactions involved.

(b) Add a saturated soda solution to a concentrated solution of cupric sulphate. Observe the formation of the precipitate $[Cu_2(OH)_2CO_3]$

and the evolution of a gas. Write the equation of the reaction that takes place.

6. Oxidant Properties of $Cu^{\cdot\cdot}$ Ion. Add a solution of potassium iodide to a solution of cupric sulphate. A white precipitate is formed (Cu_2I_2), while the solution turns yellow, owing to the formation of free iodine (test with starch paper). Write the equation of the reaction that takes place. What is the role of the iodine ion?

7. Silver Plating of Glass. In a test tube mix 1 ml of 10% $AgNO_3$ with 1 ml of 1% NaOH and dissolve the brown precipitate formed in 2 ml of a 10% ammonia solution. Add 2 ml of a 2% solution of glucose and place the test tube in a beaker with water heated to 60°. After a time a silver mirror forms on the walls of the test tube. What properties of the silver ion does this reaction illustrate?

8. Silver Halides. By means of exchange reactions prepare precipitates of silver chloride, bromide, and iodide. Note the colours of the precipitates and write the equations for the reactions by which they were prepared. Filter off the bromide and iodide precipitates, unfold the filter papers with the precipitates, and expose them to the light. After a time note how they have darkened (photochemical reactions). Leave the silver chloride precipitate for experiment 10.

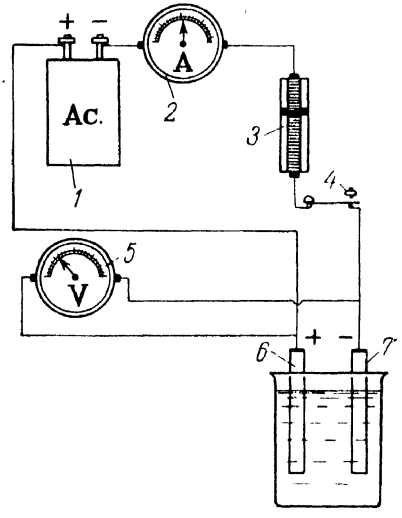


Fig. 69. Diagram of arrangement for electrolysis of copper

1 — storage battery; 2 — ammeter; 3 — rheostat; 4 — key; 5 — voltmeter; 6 — copper anode; 7 — iron cathode.

9. Cupric and Silver Sulphides. By means of exchange reactions prepare cupric and silver sulphides. Note the colours of the precipitates. Test the action of concentrated HCl and HNO_3 solutions on them. Write the equations of the reactions that take place. Why do not these sulphides dissolve in hydrochloric acid?

10. Complex Compounds of Copper and Silver. (a) Add ammonia solution to a cupric hydroxide precipitate. What happens to the precipitate? Note the colour of the resulting solution and write the equation of the reaction that takes place, the formula of the product being $[Cu(NH_3)_4](OH)_2$.

(b) Shake the silver chloride precipitate with the solution and pour it into two test tubes. Add ammonia solution to one of them. What happens to the precipitate? Write the equation of the reaction that takes place, the formula of the product being $[Ag(NH_3)_2]Cl$. Add sodium

thiosulphate solution to the other test tube. Note the changes that occur and write the equation of the reaction. What is the practical significance of this last reaction?

11. Detection of the Cupric and the Silver Ion. Receive from the instructor a test solution containing one of these ions. By means of the maximum number of the reactions you have studied, prove the presence of one of these ions in the solution.

12. Electrolysis. Clean the surface of a copper plate with sandpaper until it shines, immerse it for 3-4 minutes in a 15% solution of nitric acid, rinsing it afterwards thoroughly with water under the tap. Assemble the apparatus shown in Fig. 69. Into the electrolytic cell pour an amount of the solution sufficient to cover three-quarters of the plates. Lower the electrodes into the solution and adjust the rheostat to maximum resistance. Close the circuit by means of the key, note the time of the beginning of the experiment (start the stop watch), and reduce the resistance so as to bring the voltage up to 1.2-1.4 V. Read the current intensity on the ammeter. Exactly 15 minutes later break the circuit and rinse the iron plate with water. The copper coating is a compact reddish layer without lustre. Measure the surface area of the plate. Knowing the current intensity and the duration of electrolysis, calculate the thickness of the coating (the density of copper is 8.9 g/cu cm).

Exercise 22

COMPLEX COMPOUNDS

SUBJECTS FOR STUDY

Basic principles of the Coordination Theory; central atom; coordination number; ligands; the inner and the outer coordination sphere.

Electrolytic properties of complex compounds and their conductivity; dissociation of a complex ion and the instability constant of complex compounds; complex ions in exchange reactions, and complex ions in redox reactions.

The so-called complex compounds contain more elaborate groups of ions, with properties differing from those of elementary ions, e. g.:

$$Na_3[\overset{+3}{Co}(NO_2)_6] \qquad K[\overset{+3}{Co}(NH_3)_2Cl_4] \qquad [\overset{+2}{Zn}(NH_3)_6](OH)_2$$

$$[\overset{+4}{Pt}(NH_3)_4Cl_2]Cl_2$$

A complex compound has a *central atom*, or *complex-forming ion*, with a characteristic valence (charge) and a coordination number, which indicates how many groups, atoms, ions, or molecules are linked to the complex former in the inner sphere. With these ligands*

* This term has superseded the earlier term *addend*.

the complex former constitutes what is known as a complex ion, whose charge is the algebraic sum of the charges of the complex former and the ligands.

If the complex ion has a negative charge, the outer sphere consists of positive ions, and *vice versa*. For example:

$$\underset{\text{complex anion}}{K^{\cdot}\,[Au\,(CN)_2]'} \qquad \underset{\text{complex cation}}{[Cu\,(NH_3)_4]\,\ddot{Cl}_2}$$

To write the formula of a complex compound, it is necessary to know the valence (charge) of the complex former and the ligands, as well as the coordination number. The following are the coordination numbers of the most important complex formers:

2		4		6			
^{+1}Ag,	^{+1}Au	^{+2}Cu,	^{+2}Hg	^{+2}Co,	^{+3}Co,	^{+2}Ni,	^{+2}Fe
		^{+2}Pt,	^{+3}Au	^{+3}Fe,	^{+4}Pt,	^{+3}Cr,	^{+2}Mn
		^{+2}Pb,	^{+3}B	^{+2}Zn,	^{+2}Cd,	^{+4}Sn,	^{+3}Al

These are the most widespread coordination numbers of central atoms. Less frequent coordination numbers are 3, 8, and 12.

One and the same complex former may have several different coordination numbers: for instance, Al^{+3}, Co^{+2}, and Zn^{+2} are known to have the coordination numbers 4 and 6.

Both electrically neutral molecules (H_2O, NH_3, NO, etc.) and negative ions (O^{--}, OH^-, NO_2^-, CN^-, Cl^-, Br^-, I^-, CO_3^{--}, etc.) can be ligands.

Example in Writing the Formula of a Complex Compound. Write the formula of a complex compound consisting of the ions Fe^{+3}, CN^-, and K^+. Since the positive ions K^+ cannot be part of the inner sphere, the CN^- ions form the inner coordination sphere around the Fe^{+3} ion. The latter ion has the coordination number 6; the formula is therefore $K_3[Fe(CN)_6]$.

The most important complex compounds with neutral ligands are the *ammoniates*, e. g., $[Co(NH_3)_6]Cl_3$, and *aquocomplexes*, e. g., $[Cr(H_2O)_6]Cl_3$; the latter group includes the so-called crystalline hydrates. Complex compounds in which negatively charged acid radicals are grouped around the central atom are known as *acid complexes*, e. g., $K_3[Co(NO_2)_6]$.

In an aqueous solution complex compounds dissociate into a complex ion and the ions that make up the outer sphere. For example:

$$[Cu\,(NH_3)_4]\,SO_4 \rightleftarrows [Cu\,(NH_3)_4]'' + SO_4''$$

$$Na_3\,[Co\,(NO_2)_6] \rightleftarrows 3Na^{\cdot} + [Co\,(NO_2)_6]'''$$

In exchange reactions complex ions pass from one compound to another without any change in their composition:

$$2Cu^{\cdot\cdot} + 2SO_4'' + 4K^{\cdot} + [Fe(CN)_6]''' = Cu_2[Fe(CN)_6] + 4K^{\cdot} + 2SO_4''$$

In solution complex ions dissociate to a certain degree:

$$[Cu(NH_3)_4]^{\cdot\cdot} \rightleftarrows Cu^{\cdot\cdot} + 4NH_3$$

For this case of equilibrium we may write:

$$\frac{[Cu^{\cdot\cdot}][NH_3]^4}{[[Cu(NH_3)_4]^{\cdot\cdot}]} = K$$

The quantity K (the ratio of the product of the concentrations of the particles into which the complex ion dissociates to the concentration of the complex ion) is called the *instability constant of the complex ion*. The greater this constant, the less stable the complex.

$$[Ag(NH_3)_2]^{\cdot} \rightleftarrows Ag^{\cdot} + 2NH_3$$
$$K = 6.8 \cdot 10^{-8}$$
$$[Ag(CN)_2]' \rightleftarrows Ag^{\cdot} + 2CN'$$
$$K = 1 \cdot 10^{-21}$$

It is evident from these figures that the ammoniate of silver is less stable a complex than the cyanide.

The instability constants of some complex ions are listed in Table XIV (p. 335).

A decrease in the concentration of one of the components of a complex can cause its destruction. Let us take solutions of two nickel salts: $NiSO_4$ and $[Ni(NH_3)_6]SO_4$. Both solutions are in a state of equilibrium:

$$NiSO_4 \rightleftarrows Ni^{\cdot\cdot} + SO_4''$$
$$[Ni(NH_3)_6]SO_4 \rightleftarrows [Ni(NH_3)_6]^{\cdot\cdot} + SO_4''$$
$$\downarrow\uparrow$$
$$Ni^{\cdot\cdot} + 6NH_3$$

The addition of a solution of NaOH causes the precipitation of $Ni(OH)_2$ in the first solution, but no precipitation in the second.

For a precipitate to be formed, it is necessary that the product of the concentrations $[Ni^{\cdot\cdot}] \cdot [OH']^2$ be greater than the solubility product $SP_{Ni(OH)_2}$. Although the complex ion $[Ni(NH_3)_6]^{\cdot\cdot}$ does dissociate into $Ni^{\cdot\cdot}$ ions and NH_3 molecules, the extent to which it does this is so small that the concentration $[Ni^{\cdot\cdot}]$ is insufficient for the SP value to be reached and no precipitate is therefore formed.

The addition of ammonium sulphide to the $NiSO_4$ and $[Ni(NH_3)_6]SO_4$ solutions causes a precipitate of NiS to be formed in both cases. Nickel sulphide is much less soluble ($SP_{NiS} = 1.4 \cdot 10^{-24}$) than is nickel hyd-

roxide ($SP_{Ni(OH)_2} = 1.6 \cdot 10^{-14}$). The concentration of $Ni^{\cdot\cdot}$ ions even in the complex salt solution is sufficient for the SP_{NiS} value to be reached.

As the S'' ions bind the $Ni^{\cdot\cdot}$ ions, there is a shift in the equilibrium in the system $[Ni(NH_3)_6]^{\cdot\cdot} \rightleftarrows Ni^{\cdot\cdot} + 6NH_3$ towards the dissociation of the complex ion, which leads to the complete destruction of the complex ion.

Redox reactions of complex compounds involve either a change in the charge of the complex former without any substantial disturbance in the composition of the complex (example 1) or the complete destruction of the complex with the formation of oxidation products of simpler composition (example 2):

$$(1)\ 2K_4\overset{2e^-}{\overset{+2}{[Fe}}(CN)_6] + Cl_2 = 2K_3\overset{+3}{[Fe}(CN)_6] + 2K\overset{-1}{Cl}$$

$$(2)\ 2K_2\overset{1e^-}{\overset{8e^-}{\overset{+2}{[Ni}}}(CN)_4] + 9Br_2 + 6KOH = 2\overset{+3}{Ni}(OH)_3 + 8\overset{+1}{CNBr} + 10KBr.$$

If a complex contains positive ions, which are oxidising agents, as complex formers, they can be extracted as neutral atoms by the method of reduction:

$$Zn + 2K\overset{2e^-}{\overset{+1}{[Au}}(CN)_2] = 2Au + K_2\overset{+2}{[Zn}(CN)_4]$$

The positive ions can be reduced by means of an electric current (in galvanisation, for gold- and silver-plating, etc.).

The process whereby amphoteric hydroxides dissolve in solutions of alkalis is now regarded as a process of the formation of specific complex compounds called *hydroxysalts*, in which the complex ion consists of a central atom and hydroxyl ions in its coordination sphere. For example, when stannous hydroxide is dissolved, the process may be represented by the following equation:

$$Sn(OH)_2 + 2K^{\cdot} + 2OH' = K_2[Sn(OH)_4]$$

This compound is called potassium hydroxystannite.

QUESTIONS

1. Is there a difference between double and complex salts?
2. Write the coordinate formulae for the ammoniates $CoCl_3 \cdot 6NH_3$ and $CoCl_3 \cdot 5NH_3$. Why does the precipitation of the chloride ions from 1 mol of the former compound require 3 mols of silver nitrate, whereas the precipitation of the chloride ions from 1 mol of the latter requires only 2 mols?

3. For the system in equilibrium

$$[Ag(NH_3)_2]Cl \rightleftarrows [Ag(NH_3)_2]^{\cdot} + Cl'$$

write the equations of the ionisation constant and the instability constant. Why is no AgCl precipitate formed despite the presence of $Ag^{\cdot}$ and Cl' ions in the solution? Why does the addition of nitric acid to the solution cause the precipitation of AgCl?

4. Why does the treatment of a $CdCl_2$ solution with an alkali produce a $Cd(OH)_2$ precipitate, while the treatment of a $[Cd(NH_3)_6]Cl_2$ solution does not?

5. Write the equations for the oxidation of yellow prussiate of potash $K_4[Fe(CN)_6]$ by hydrogen peroxide in an acid solution and for the oxidation of the complex compound $K_4[Co(CN)_6]$ by the oxygen of the air in a neutral solution.

6. Write the equation for the reaction of the formation of potassium hydroxyaluminate from aluminium hydroxide.

Problems

1. A certain amount of metallic zinc reacts with a solution of $K[Au(CN)_2]$ to yield 7.89 g of metallic gold. The amount of 10% HCl needed to dissolve the same amount of metallic zinc is 14.6 g. Calculate the equivalent of the gold.

2. A complex compound contains $Co^{\cdot\cdot\cdot}$, NH_3, and Cl'. The precipitation of the Cl' from 11.67 g of this salt requires 8.5 g of silver nitrate. When the same amount of the complex salt was broken down, the yield of ammonia was 4.48 litres (reduced to N. T. P.). The molecular weight of the salt is 233.3. Write the coordinate formula of the complex compound.

3. What amount of a 5% solution of $(NH_4)_2S$ is needed for the complete precipitation of the copper as sulphide from 120 ml of an 0.1 M solution of $[Cu(NH_3)_4]SO_4$?

4. The oxidation of a 3% solution of H_2O_2 in an alkaline medium by potassium ferricyanide $K_3[Fe(CN)_6]$ yields 560 ml of O_2, measured at N. T. P. Calculate the amounts of 3% H_2O_2, solid $K_3[Fe(CN)_6]$, and 20% KOH that were used up.

5. It is necessary to prepare 80 litres of an 8% solution (relative density 1.043) of $K_3[Fe(CN)_6]$ by diluting an 18% solution (relative density 1.10). Calculate the amounts of water and of the initial solution that have to be mixed.

6. Determine the molarity of a solution of $[Ag(NH_3)_2]Cl$ if 4.4 ml of HNO_3 (titre 0.063) is used to bind the ammonia contained in 20 ml of the solution.

7. What will be the boiling point of 0.1 M $K_3[Fe(CN)_6]$, its relative density being 1.02 and its degree of ionisation 65%?

8. Calculate the osmotic pressure at 0° of 8% $K_3[Fe(CN)_6]$, its relative density being 1.043 and α being 62%.

9. For how long is it necessary to pass a 2-ampere electric current through a $K[Ag(CN)_2]$ solution to deposit 0.24 g of metallic silver?

10. A 5-ampere current is passed for 20 minutes through a $[Ni(NH_3)_6]SO_4$ solution. Calculate by how many grams the weight of the cathode increases.

LABORATORY WORK

Apparatus and materials: test tubes and rack; funnel; 2 watch glasses; filter paper; wash bottle; litmus paper; splints; 2 N KOH; N $BaCl_2$; N $FeCl_3$; 2 N $(NH_4)_2S$; 0.5 N KSCN. 2 N HNO_3; 0.5 N solution of aluminium potassium sulphate; 2 N KOH;

0.4 N solution of sodium bitartrate; solution of sodium cobaltinitrate; saturated and 0.1 N solutions of silver nitrate; saturated solution of $CoCl_2$; saturated solution of ammonium rhodanate; saturated solution of potassium iodide; 0.5 N $ZnCl_2$; 0.5 N KCl; 0.5 N $CuSO_4$; 10% ammonia solution; 3% H_2O_2; N solutions of potassium ferro- and ferricyanide; N $FeSO_4$, and chlorine water.

Preparation of Sodium Cobaltinitrate. Dissolve 50 g of $CoCl_2 \cdot 6H_2O$, with gentle heating, in 50 ml of water, cool the solution, and mix it with a solution of 150 g of sodium nitrite in 500 ml of water. Add 50 ml of 5% CH_3COOH, while stirring. When the precipitate has settled, pour off the liquid into reagent bottles.

1. Ions of a Double Salt. Pour 2 ml of a $KAl(SO_4)_2$ solution into each of three test tubes; add a sodium bitartrate solution (see Exercise 20, experiment 5) to the first, a few drops of an NaOH solution to the second, and a barium salt solution to the third. Write ionic equations for all three reactions. What ions may be assumed to be present in the initial solution on the basis of these reactions? Write the equation for the electrolytic dissociation of $KAl(SO_4)_2$.

2. Ions of a Complex Salt. (a) Pour 2 ml of a $FeCl_3$ solution into each of two test tubes; add a solution of $(NH_4)_2S$ to one and a KSCN solution to the other. What is formed? Write ionic equations of the reactions. What ion may be assumed to be present in the $FeCl_3$ solution on the basis of the reactions with the S'' and SCN' ions?

(b) Carry out analogous reactions, substituting a $K_3[Fe(CN)_6]$ solution for the $FeCl_3$ solution. Is a black precipitate * formed? Does a red colouration appear? Are there Fe''' ions in the $K_3[Fe(CN)_6]$ solution?

Write the equation for the electrolytic dissociation of $K_3[Fe(CN)_6]$. Prove experimentally that the solution of this salt contains potassium ions (see Exercise 20, experiment 5). What are complex salts? Can a sharp dividing line be drawn between double and complex salts? Write equations of electrolytic dissociation for the salts:

$$NH_4Cr(SO_4)_2 \qquad [Cu(NH_3)_4]Cl_2 \qquad K_2[PtCl_6]$$

3. Compounds with a Complex Negative Ion. (a) Place a drop of a saturated solution of silver nitrate on a watch glass and add a saturated solution of potassium iodide to it by drops until the precipitate formed dissolves. Write the equations of the reactions that have taken place. Keep the solution for experiment 6.

(b) Place 3-4 drops of concentrated solutions of $CoCl_2$ and NH_4SCN on a watch glass. The solution acquires the blue colour typical of $[Co(SCN)_4]''$ ions. Write the equation of the reaction. Keep the solution for experiment 6.

(c) Add an alkali solution by drops to a zinc salt solution until a white precipitate is formed. Write the equation of the reaction. Add

* The yellow precipitate formed is sulphur produced by a side reaction of oxidation.

excess alkali to the precipitate. The precipitate dissolves owing to the formation of hydroxyzincate. Write the equation of the reaction.

4. Compounds with a Complex Positive Ion. Prepare the precipitates of AgCl and $Cu(OH)_2$ by exchange reactions, pour off the liquid from the precipitates when they have settled, and add excess ammonia solution to the precipitates. Write the equations of the reactions whereby the precipitates are dissolved. Note the colour of the solutions of the complex compounds. Keep the ammonia solutions for experiment 6.

5. Complex Compounds in Exchange Reactions. (a) Add a solution of yellow prussiate of potash to an equal volume of a dilute, acidified solution of $FeCl_3$. What is formed? Write the equation of the reaction that takes place.

(b) Add a $Na_3[Co(NO_2)_6]$ solution to a KCl solution. A yellow crystalline precipitate of $K_2Na[Co(NO_2)_6]$ is formed. Write the equation of the reaction.

6. Destruction of Complex Ions. (a) Dilute with water (by drops) the complex compound solutions on watch glasses left over from experiment 3. Observe the changes that take place. Write the equations for the electrolytic dissociation of the complex ions. How is the balance shifted by the addition of water? How does the concentration of the solution affect the stability of complex compounds?

(b) Add nitric acid to the solution of silver diamminochloride $[Ag(NH_3)_2]Cl$ from experiment 4 until the solution changes the colour of litmus paper. A white precipitate of silver chloride is formed. Write the equation of the electrolytic dissociation of the complex compound and explain the role of nitric acid.

(c) Divide the blue solution of cupric tetramminohydroxide left over from experiment 4 into two parts. Add a sodium hydroxide solution to one part and an ammonium sulphide solution to the other. Explain why a precipitate is formed in one case only.

7. Complex Compounds in Redox Reactions. (a) Mix 2 ml of a hydrogen peroxide solution in a test tube with an equal volume of a potassium hydroxide solution; add 2 ml of a $K_3[Fe(CN)_6]$ solution. Confirm by a glowing splint that oxygen is evolved. Write the equation of the reaction that has taken place.

(b) Test the effect of a newly prepared $FeSO_4$ solution on potassium ferrocyanide and ferricyanide. Which of these salts produces a blue colouration? Add a few drops of potassium ferrocyanide to 3-4 ml of chlorine water and boil the solution thoroughly (to remove the excess chlorine). Add $FeSO_4$ to the resulting solution. What is observed? Write the equation for the oxidation of potassium ferrocyanide by chlorine.

Exercise 23

BERYLLIUM, MAGNESIUM, AND THE ALKALINE EARTH METALS

SUBJECTS FOR STUDY

Atomic structure of beryllium, magnesium, and the alkaline earth metals; position in the electromotive series; attitude to water, acids, oxygen, and oxidants; oxides and hydroxides, their preparation and chemical properties; principal soluble and insoluble salts; magnesium and calcium salts in natural waters; the hardness of water and the methods of its removal.

In their compounds Be, Mg, Ca, Sr, Ba, and Ra are bipositive. This is because the outer electron shells of their atoms contain two electrons each, which are easily given up under the action of oxidising agents:

$$Me - 2e^- = Me^{+2}$$

The atomic radii increase from Be to Ra; reductant activity rises in the same direction:

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number . . .	4	12	20	38	56	88
Radius in Ångström units	1.05	1.62	1.97	2.13	2.17	—

Barium and strontium are usually kept under a layer of kerosene or, like radium, in sealed glass tubes, while the other metals of this series, which are weaker reducing agents, may be kept simply in closed jars.

Heated in oxygen or air, the metals burn with a bright flame. In the electromotive series all of them rank above hydrogen and are, accordingly, easily oxidised by water with (Be and Mg) or without (Ca-Ra) heating:

$$\overset{\overset{2e^-}{\rightarrow}}{Me} + 2HOH = H_2 + \overset{+2}{Me}(OH)_2$$

Oxidation proceeds even better in acid solutions:

$$\overset{\overset{2e^-}{\rightarrow}}{Me} + 2HCl = H_2 + \overset{+2}{Me}Cl_2$$

Beryllium, because it is amphoteric, also dissolves in alkali solutions, forming hydroxyberyllates: $Me_2[Be(OH)_4]$.

The oxides of the metals are for practical purposes prepared by the thermal decomposition of the carbonates (Mg and Ca) or the nitrates (Sr and Ba):

$$CaCO_3 \rightleftarrows CaO + CO_2$$

$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$$

The hydroxides of the group may be prepared by treating the oxides with water; the hydroxides of magnesium and beryllium may also be prepared by exchange reactions of salts with alkalis, thanks to the poor solubility of these hydroxides in water.

The oxides and hydroxides become increasingly alkaline with the rise in the radius of the Me^{+2} ion; the hydroxide corresponding to Be^{+2}, the ion with the smallest radius, is amphoteric.

In the laboratory it is customary in most cases to use a solution of $Ca(OH)_2$, known as lime water, or a suspension of solid calcium hydroxide in a saturated solution, known as lime milk, and a solution of $Ba(OH)_2$, known as baryta water.

The volatile salts of calcium, strontium, and barium impart a brick red, carmine, and yellowish green colour respectively to a nonluminous flame of the Bunsen burner.

Among the insoluble salts, mention should be made of the carbonates $MeCO_3$ and the ortho-phosphates $Me_3(PO_4)_2$. The solubility of the sulphates $MeSO_4$ decreases from Be to Ra: the sulphates of Sr, Ba, and Ra are practically insoluble, $CaSO_4$ is somewhat soluble, and the sulphates of Be and Mg are highly soluble.

Barium chromate $BaCrO_4$, unlike strontium chromate, which dissolves in acetic acid, dissolves in hydrochloric acid. The chromates have a yellow colour.

Treatment of the carbonates with an aqueous solution of carbon dioxide causes them to dissolve with the formation of bicarbonates:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

Natural water with large amounts of calcium and magnesium salts in solution is known as *hard water*. Soft water contains relatively small amounts of dissolved salts. According to the Standards in operation in the U.S.S.R., the hardness of water is expressed in the *number of milligram-equivalents of* $Ca^{\cdot\cdot}$ *or* $Mg^{\cdot\cdot}$ *ions in 1 litre of water*. Water with a hardness of less than 4 mg-equiv./lit is called soft; water with a hardness of from 4 to 8 mg-equiv./lit is called medium; from 8 to 12, hard, and above 12, very hard.

One mg-equiv. of $Ca^{\cdot\cdot}$ corresponds to 20.04 mg; 1 mg-equiv. of $Mg^{\cdot\cdot}$, to 12.16 mg.

The presence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in natural water is responsible for what is known as *temporary* (or removable) hardness. The chlorides and sulphides of calcium and magnesium are the cause of what is termed the *permanent hardness* of water. Together, the tempo-

rary and the permanent hardness of water add up to the *total hardness*. This is easily calculated from the number of mg of $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ in 1 litre of the water:

$$\text{total hardness} = \frac{mg_{Ca^{\cdot\cdot}}}{20.04} + \frac{mg_{Mg^{\cdot\cdot}}}{12.16} \text{ mg-equiv./lit}$$

Temporary hardness can be determined by titrating a definite volume of water with a hydrochloric acid solution of known concentration in the presence of the indicator methyl-orange. The reaction that takes place is expressed by the equation:

$$Ca(HCO_3)_2 + 2HCl = 2H_2O + 2CO_2 + CaCl_2$$

In this reaction two mols of HCl are used up to one mol of $Ca(HCO_3)_2$. Since a mol of $Ca(HCO_3)_2$ is equivalent to a gram-ion of $Ca^{\cdot\cdot}$, we can, knowing the amount of acid used up, calculate the number of mg-equiv. of $Ca^{\cdot\cdot}$ in 1 litre of water and in this way determine the temporary hardness.

Example. The titration of 100 ml of tap water requires the expenditure of 2.65 ml of an HCl solution whose titre is equal to 0.0032. Determine the temporary hardness of the water.

First, it is necessary to determine the number of mg of HCl used up for the titration:

$$2.65 \cdot 0.0032 = 0.00848 \text{ g} = 8.48 \text{ mg}$$

From the ratio $Ca^{\cdot\cdot} : 2HCl$, bearing in mind ionic and molecular weights, find the number of mg of $Ca^{\cdot\cdot}$ corresponding to the quantity of the acid used up:

$$\begin{array}{c} 40.08 \text{ — } 2 \cdot 36.46 \\ x \text{ — } 8.48 \end{array}$$

Accordingly,

$$x = \frac{40.08 \cdot 8.48}{2 \cdot 36.46} = 4.66 \text{ mg}$$

Hence, 100 ml of water contains 4.66 mg of $Ca^{\cdot\cdot}$; 1 litre, consequently, contains 46.6 mg. To establish the hardness of the water, this number should be divided by 20.04, i. e., by the equivalent of calcium. The hardness of the water will therefore be equal to

$$\frac{46.6}{20.04} = 2.3 \text{ mg-equiv./litre}$$

The total hardness can be determined by precipitating the calcium and magnesium salts by an alkaline mixture consisting of equal volumes of 0.1 N NaOH and 0.1 N Na_2CO_3. Part of the mixture is used up for the precipitation, e. g.:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O$$

The unreacted part of the mixture is titrated (after the precipitate has been filtered off) by 0.1 N HCl with methyl-orange. The difference between the titration of the initial mixture and the titration of the mixture with water gives the number of ml of 0.1 N NaOH used up to precipitate the hardness-causing salts.

Example. Fifteen ml of alkaline mixture is added to 100 ml of tap water. After the precipitate has been filtered off, the titration of the surplus mixture requires 9.90 ml of 0.1 N HCl. Determine the total hardness.

Equinormal solutions react in equal volumes. Accordingly, 9.90 ml of 0.1 N HCl is equivalent to 9.90 ml of 0.1 N NaOH, which is the remainder of the alkali after precipitation. The amount used up for the precipitation of the salts from 10 ml of water is therefore:

$$15.00 - 9.90 = 5.10 \text{ ml of } 0.1 \text{ N NaON}$$

Precipitating all the salts from 1 litre of water would require 51 ml of 0.1 N NaOH. This volume is equivalent to the same volume of an 0.1 N solution of the $Ca^{\cdot\cdot}$ ion.

Now determine the amount of the $Ca^{\cdot\cdot}$ ion contained in 51 ml of its 0.1 N solution, knowing that the equivalent of $Ca^{\cdot\cdot}$ is 20.04:

$$\begin{array}{c} 1{,}000 - \dfrac{20.04}{10} \\ 51 - x \end{array}$$

Therefore

$$x = \frac{51 \cdot 20.04}{10 \cdot 1{,}000} = 0.1022 \text{ g} = 102.2 \text{ mg}$$

The number of mg-equiv. of $Ca^{\cdot\cdot}$ in 1 litre of water (or its hardness) equals

$$\frac{102.2}{20.04} = 5.1$$

QUESTIONS

1. Why are the alkaline earth metals less potent reducing agents than the alkali metals?
2. Draw a diagram of a galvanic cell consisting of the couples $Mg/Mg^{\cdot\cdot}$ and $H_2/2H^{\cdot}$; determine its e. m. f. Will metallic magnesium dissolve in M HCl?
3. How would you distinguish lime water from baryta water?
4. By means of what chemical reactions is it possible to effect the following processes:

(a) $BaSO_4 \rightarrow BaS \rightarrow BaCO_3 \rightarrow BaCl_2$

(b) $Ca(NO_3)_2 \rightarrow CaO \rightarrow Ca_3(PO_4)_2$

Write the equations for these reactions. Which of the reactions that you have proposed are redox reactions?

5. Write the equations for the electrolytic dissociation of beryllium hydroxide and for dissolving it in acid and alkali solutions.

6. A potassium chromate solution is added to solutions of $CaCl_2$ and $BaCl_2$ having the same concentration. Why does a precipitate form only in the barium salt solution?

7. How is the temporary and the permanent hardness of water removed?

Problems

1. How many grams of a unimolal solution of sodium hydroxide are needed to convert to beryllate the beryllium chloride contained in 600 g of a 6% solution of it?

2. What volume of 35.38% HCl (relative density 1.18) will be needed to dissolve 1 kg of an alloy consisting of 24% of magnesium and 76% of aluminium?

3. What will be the yield of $CaSO_4$ from 1 cu m of its saturated solution if the solution is heated from 40 to 100°? The solubility of $CaSO_4$ is given in Table II at the end of the book.

4. What is the hardness of water if 7 g of calcium hydroxide per 100 litres is required to soften it?

5. Fifty litres of water contain 4.5 g of magnesium bicarbonate. Express the temporary hardness of the water in mg-equiv./lit.

6. It is required to reduce the temporary hardness of water from 14 to 6 mg-equiv./lit. How much calcium hydroxide will be needed to soften 1,000 cu m of the water?

7. One mol of anhydrous calcium chloride dissolves with the evolution of 17.41 Cal. The hexahydrate dissolves with a thermal effect of —4.31 Cal. What is the thermal effect of the hydration of the salt?

8. The thermal effects of the formation of barium peroxide and aluminium oxide are 144.2 and 378 Cal., respectively. Determine the thermal effect of the reaction of the aluminothermic reduction of barium peroxide.

9. How many faradays of electricity should be passed through molten carnallite ($KCl \cdot MgCl_2$) to obtain 1 kg of metallic magnesium?

10. Draw a diagram of a galvanic cell consisting of the couples $Mg/Mg^{\cdot\cdot}$ and $Cd/Cd^{\cdot\cdot}$, indicate the direction of the current in the inner and the outer circuit, determine the e. m. f., and write the equation of the reaction by virtue of which hte cell operates.

LABORATORY WORK

Apparatus and materials: Kipp gas generator for preparing carbon dioxide; blowpipes; test tubes and rack; crucible tongs; file; four 200 ml Erlenmeyer flasks; 25 ml burette; funnel for the burette; 100 ml pipette; 20-25 ml pipette; 50 ml beaker; funnel; sandpaper; filter paper; platinum wire; chalk or marble; magnesium shavings; calcium shavings; 10% ammonia solution; 5% calcium chloride solution; 5% strontium chloride solution; 5% barium chloride solution; 2 N and 0.1 N titrated HCl; 2 N and concentrated H_2SO_4; 2 N CH_3COOH; 2 N NaOH; N NH_4Cl; saturated solution of ammonium sulphate; N K_2CrO_4; N $MgCl_2$; N Na_2HPO_4; 0.5 N $BeCl_2$; N Na_2SO_4; saturated solution of strontium sulphate; alkaline mixture; methyl-orange and phenolphthalein solutions; lime water.

Preparation of Alkaline Mixture. Mix equal volumes of 0.1 N NaOH and 0.1 N Na_2CO_3.

1. Reductant Properties of Magnesium and Calcium. (a) Test the action of small lumps of these metals on water (if necessary, heat the

water) and on dilute hydrochloric acid. Record the changes observed and write the equations of the reactions that take place.

(b) Carefully examine the surface of metallic magnesium and calcium, then by means of a file or sandpaper remove the top layer of the metal. How has the surface of the metal changed? Take the cleaned lumps of the metals by means of tongs and heat each, in turn, in the flame of a burner. Write up the experiment, giving the equations of the reactions. Collect the product of the oxidation of magnesium for the next experiment.

2. Oxides of the Metals. (a) Take a small lump of chalk or marble by means of tongs and heat it in the flame of a blowpipe for 3-5 min. After the lump has cooled, wet it with such an amount of water (adding it by drops from a dropper or pipette) that all the water is absorbed by the calcium oxide and none remains. What do you observe? Write the equations of the reactions that take place. What is the name used in industry for the reaction of calcium oxide with water?

Mix the powder obtained with a small quantity of water in a porcelain casserole and add a drop of an alcoholic solution of phenolphthalein. Explain the appearance of the colouration.

(b) Treat with water (in a test tube) the white powder of magnesium oxide obtained in experiment 1. Test the solution with phenolphthalein. Note the shade of colour and heat the solution. Does the colour become deeper? Explain the experiment.

3. Beryllium and Magnesium Hydroxides. By what methods can the hydroxides of these metals be prepared? Perform the necessary experiments and write the equations of the reactions that take place. Prove experimentally that beryllium hydroxide is amphoteric.

4. Temporary Hardness of Water. Pour 100 ml of tap water into an Erlenmeyer flask by means of a pipette and add 5-6 drops of a methyl-orange solution; titrate from a burette with 0.1 N HCl until a single drop of the HCl changes the colour of the water from yellow to orange. Record the volume of the acid used up with an accuracy of up to 0.05 ml. Repeat the titration with another portion of water. The second result should not differ from the first by more than $\pm$ 0.05 ml of HCl. Calculate the temporary hardness of the water.

5. Permanent and Total Hardness of Water. Pour 100 ml of tap water by means of a pipette into each of two Erlenmeyer flasks, add 20 ml of alkaline mixture (also by means of a pipette) to each flask, and boil each for 5 min. Then filter the solutions through folded filters into two other Erlenmeyer flasks. After filtration wash the precipitates twice with 10-15 ml of distilled water, adding the wash water to the filtrate. Add 5-6 drops of methyl-orange solution to each of the flasks and titrate the filtered solutions with 0.1 N HCl until the colour of the solution changes from yellow to orange.

From the titration results calculate the total hardness of tap water. From the data of experiments 4 and 5 calculate the permanent hardness.

6. Calcium Carbonate and Bicarbonate. Pour 3 ml of lime water and 7 ml of distilled water into a beaker and pass a current of CO_2 from the Kipp gas generator through it. The carbon dioxide should be passed through the water at a rate making it possible to count the bubbles of the gas. A precipitate is formed, which dissolves when an excess of CO_2 has been passed through the water (write the equations). How can calcium carbonate be precipitated by two different methods from the calcium bicarbonate formed in the solution? Perform these experiments, dividing the solution into two portions. Write the equations of the reactions that take place.

7. Sulphates of the Metals. (a) Test the solutions of beryllium, magnesium, calcium, strontium, and barium chlorides with a dilute solution of sulphuric acid. In which cases are precipitates formed?

(b) To a calcium salt solution add an equal volume of concentrated sulphuric acid. Why does a precipitate form in this case?

(c) Pour 1 ml of $SrCl_2$ solution into one test tube, and 1 ml of $CaCl_2$ solution, into another. Add first a small amount and then an excess of a saturated solution of ammonium sulphate to each of them. The $CaSO_4$ precipitate dissolves because of the formation of the soluble complex compound $(NH_4)_2[Ca(SO_4)_2]$. Write the equations of the reactions that take place.

(d) To a solution of barium salt add a saturated solution of strontium sulphate. What happens? Is a precipitate formed if a saturated solution of barium sulphate is added to a strontium salt solution?

8. Chromates of the Metals. Pour 1 ml of a calcium salt solution into one test tube; 1 ml of a strontium salt solution, into a second, and 1 ml of a barium salt solution, into a third test tube. Add 1 ml of a potassium chromate solution to each of them. In which cases do precipitates form and what are their colours? Add 3-4 ml of an acetic acid solution to each of the precipitates. Do all the precipitates dissolve? Can strontium ions be precipitated by the chromate ion in the presence of acetic acid?

9. Precipitation of Magnesium Ammonium Phosphate. To 1 ml of a magnesium salt solution add an equal volume of NH_4OH and 3-4 ml of an NH_4Cl solution (the magnesium hydroxide precipitated at first should dissolve).

Add 2-3 ml of Na_2HPO_4 solution to the solution obtained; large crystals of $MgNH_4PO_4$ are precipitated. Why do hydroxyl ions have to be introduced into this reaction?

10. "Dry Reactions". By means of a platinum wire introduce volatile salts of beryllium, magnesium, calcium, strontium, and barium into the flame of a burner (as described in experiment 3, Exercise 20), observing the changes in the colour of the flame. Which are the metals whose salts change the colour of the flame? What colours do they impart to the flame?

11. Cation Detection. Receive from the instructor a test solution that may contain one of the following cations: $Ba^{..}$, $Sr^{..}$, $Ca^{..}$, $Mg^{..}$, or $Be^{..}$.

Take part of the solution and add to it half as much (by volume) of a sulphuric acid solution. The formation of a white precipitate points to the presence of the $Ba^{..}$ or $Sr^{..}$ ion in the solution; if no white precipitate is formed, the solution may contain one of the three other cations. By means of the reactions studied in this Exercise (3, 7, 8, 9, and 10) establish the presence of a definite cation. Write up the analysis briefly and submit your report to the instructor.

Exercise 24

ZINC, CADMIUM, AND MERCURY

SUBJECTS FOR STUDY

The metals of the zinc subgroup; their atomic structure, reductant properties, and position in the electromotive series; features distinguishing mercury from zin; and cadmium; attitude of zinc, cadmium, and mercury to various oxidising agentsc oxides and hydroxides of these metals; their simple and complex salts; amalgams.

The neutral atoms of zinc, cadmium, and mercury have two electrons each in their outermost shells; in chemical reactions they give them up

$$Me - 2e^- = Me^{+2}$$

forming the bipositive ions Zn^{+2}, Cd^{+2}, and Hg^{+2}.

Apart from the compounds of bivalent mercury, called mercuric compounds, there is a series of compounds containing the — Hg — Hg — group and called mercurous.

The similarity between the elements of the zinc subgroup and the alkaline earth metals is due to their having the same number of electrons in the outermost shell. But in the next to last shell the atoms of the zinc subgroup elements have 18 electrons, which gives rise to certain distinct properties: a weaker reductant activity, a more pronounced tendency to form complex compounds, etc.

Zinc and cadmium, at ordinary conditions, are oxidised by oxygen and the air only at the surface (their tarnishing is caused by the formation of an oxide film), but, when heated, they burn up, e. g.:

$$2Zn + O_2 = 2ZnO$$

Mercury, at ordinary conditions, is not oxidised either by oxygen or by the air.

The reductant activities of the elements in the row zinc-cadmium-mercury are reflected in the position of these metals in the electromotive series:

. . . . $Zn/Zn^{\cdot\cdot}$	$Cd/Cd^{\cdot\cdot}$	$H_2/2H^{\cdot}$	.$Hg/Hg^{\cdot\cdot}$ . . .
-0.76 V	-0.4 V	± 0.00 V	$+0.85$ V

Zinc and cadmium dissolve in dilute hydrochloric acid and sulphuric acid with the evolution of hydrogen, but scarcely react at all with water, since when they are immersed in water the reaction commences on the surface according to the equation

$$Zn + 2HOH = H_2 + Zn(OH)_2$$

but is at once halted by the formation of a hydroxide film. Unlike cadmium and mercury, metallic zinc also dissolves in alkali solutions (it is amphoteric).

Mercury can be oxidised by concentrated nitric and sulphuric acids. It dissolves many other metals, forming alloys that are known as amalgams; with some metals mercury forms chemical (intermetallic) compounds.

The following oxides are known: ZnO, CdO, HgO, and Hg_2O. The oxides of mercury are prepared by exchange reactions of its salts with alkalis. The corresponding hydroxides $Hg(OH)_2$ and $Hg_2(OH)_2$ are unstable; no sooner are they formed than they break up, e. g.:

$$Hg(OH)_2 = HgO + H_2O$$

The red modification of mercuric oxide is prepared by heating the nitrates of mercury. ZnO and CdO can be prepared either by oxidising the metals or, best of all, by the thermal decomposition of the hydroxides, carbonates, nitrates, etc. The oxides of the metals of the zinc subgroup do not react with water.

The hydroxides $Zn(OH)_2$ and $Cd(OH)_2$ are prepared by the interaction of salts and alkalis; the former is an amphoteric hydroxide, the latter, a base.

Some of the mercurous salts are unstable compounds and decompose the moment they are formed, yielding mercury and mercuric compounds, e. g.:

$$Hg_2S = HgS + Hg$$

The salts of mercury that have practical applications are: mercurous chloride Hg_2Cl_2, known as calomel, which is insoluble in water; mercurous nitrate $Hg_2(NO_3)_2$; mercuric nitrate $Hg(NO_3)_2$, and mercuric chloride $HgCl_2$, known as corrosive sublimate. All the soluble compounds of mercury are very poisonous.

The nitrates and sulphates of zinc, cadmium, and mercury are soluble in water and undergo hydrolysis. Among the insoluble salts, mention should be made of the sulphides. These have characteristic colours: ZnS is white, CdS is yellow or orange, and HgS is black or red.

Some salts, such as mercuric iodide HgI_2, are polymorphic, i. e., they can exist in several forms, each of which has a distinct colour of its own. For instance, the α-form of mercuric iodide is bright red and stable to a temperature of 127°, while the β-form is yellow and unstable at ordinary conditions. At 127° one modification is converted to the other. This temperature is called the *transition point*.

Mercuric salts possess oxidant properties, the reduction of the $Hg^{\cdot\cdot}$ proceeding either to mercurous salts or to free mercury, e. g.:

$$\overset{+2}{Sn}Cl_2 + 2\overset{+2}{Hg}Cl_2 + 2HCl = H_2[\overset{+4}{Sn}Cl_6] + \overset{+1}{Hg_2}Cl_2 \ *$$

($2e^-$: $\overset{+2}{Sn} \rightarrow \overset{+4}{Sn}$)

$$\overset{+2}{Sn}Cl_2 + \overset{+1}{Hg_2}Cl_2 + 2HCl = H_2[\overset{+4}{Sn}Cl_6] + 2Hg$$

($2e^-$: $\overset{+2}{Sn} \rightarrow \overset{+4}{Sn}$)

In complex compounds the ions of this series usually have the following coordination numbers: Zn^{+2}, 4 and 6; Cd^{+2}, 4 and 6; Hg^{+}, 2 and 4.

Typical of the Hg^{+2} ion is the formation of what are called ammono compounds of mercury (such as $HgNH_2Cl$ or $Hg_2NH_2ONO_3$), which should be regarded as products of the substitution of $Hg^{\cdot\cdot}$ for hydrogen ions in the ammonia group.

Among the complex compounds with halogens, mention should be made of the soluble colourless compound $K_2[HgI_4]$; its alkaline solution (Nessler's solution) is a sensitive reagent for free ammonia, with which it forms the reddish brown iodide precipitate $[OHg_2 \cdot NH_2]I$.

QUESTIONS

1. What are the points of similarity and difference between the elements of the zinc subgroup and the alkaline earth metals?
2. Write the equations for the treatment of metallic mercury (upon heating) with concentrated nitric and sulphuric acids.
3. Why does metallic zinc dissolve in an ammonium chloride solution? Write the relevant equations.
4. How can potassium hydroxyzincate be prepared from zinc sulphate?

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* To prevent hydrolysis, hydrochloric acid is added to the stannous chloride solution; the resulting stannic chloride combines with the acid to form a complex compound, chlorostannic acid.

5. Write the equations of the reactions in the consecutive preparation of the following substances:

$$Cd(NO_3)_2 \rightarrow CdO \rightarrow Cd \rightarrow CdCl_2 \rightarrow [Cd(NH_3)_6](OH)_2$$

6. How can metallic zinc be prepared from zinc blende and cadmium sulphate from cadmium nitrate? Write the equations of the reactions that take place.

7. By means of what reactions is it possible to distinguish a solution containing the $Ba^{\cdot\cdot}$ ion from a solution containing the $Cd^{\cdot\cdot}$ ion?

8. Why does the $Ca^{\cdot\cdot}$ ion have a less pronounced complex-forming tendency than the $Zn^{\cdot\cdot}$ ion? Why is the coordination number of $Ca^{\cdot\cdot}$ greater than of $Zn^{\cdot\cdot}$?

Problems

1. A compound of mercury and oxygen consists of 96.23% of Hg and 3.77% of O. When 43.32 g of another compound of the same two elements is heated, the yield of oxygen is 2,345 ml, measured at 1.05 atm and 27°. Are these figures in keeping with the Law of Multiple Proportions?

2. The heating of 10 g of metallic mercury from —77.2° to —41.8° requires 11.65 cal. Determine the atomic weight of mercury from these data and the discrepancy between the found value and the exact value equal to 200.61.

3. How many atoms make up a molecule of cadmium (atomic weight 112.4) vapour, if 1.686 g of the vapour, obtained at boiling point and reduced to N. T. P., occupies a volume of 336 ml?

4. At boiling point 6.02 g of a metal produces a vapour whose volume, after reduction to N. T. P., equals 672 ml. Determine the number of atoms in the molecule of the metal, knowing that its specific heat is 0.0319.

5. A zinc ore contains 30% of ZnS. What is the volume of sulphur dioxide that can be obtained by burning a ton of the ore?

6. Determine the titre, molarity, and normality of a 25% solution of $CdSO_4$, which has a relative density of 1.294.

7. What are the volumes of a 45% solution of $ZnCl_2$ (relative density 1.489) and of water that have to be mixed to prepare 1 cu m of an 8% solution with a relative density of 1.084?

8. The solubility of corrosive sublimate at 100° is 35.1 g, whereas at 0° it is 4.1 g. How much corrosive sublimate and water should be taken to obtain 1 kg of the salt by recrystallisation in that temperature range?

9. From the value of the solubility product determine the number of grams of CdS contained in 500 ml of a saturated solution.

10. How many 200 ml jars can be filled with the metallic mercury (density 13.55 g/cu cm) prepared by reducing 314.4 kg of pure cinnabar?

LABORATORY WORK

Apparatus and materials: conical test tube with stopper and thermometer; refractory test tube; test tubes and rack; crucible tongs; tray or pans; porcelain crucible with lid; pipestem triangle; 200 ml and 1 litre beakers; asbestos cone; glass stirrer; glass rod; indigo or cobalt prism; splints; filter paper; platinum wire; mercury (in a special dropper); zinc; sodium amalgam; zinc oxide; cadmium oxide; mercuric oxide; mercuric iodide; concentrated nitric acid; concentrated and 2 N H_2SO_4; 0.05 N $KMnO_4$; 2 N HCl; 30% and 2 N NaOH; 10% ammonia solution; 20% KOH; saturated solution of strontium sulphate; 2 N Na_2CO_3; 0.5 N $ZnCl_2$; 0.5 N $CdCl_2$;

0.2 N $Hg(NO_3)_2$; N $HgNO_3$; N solution of sodium dihydrogen phosphate; N $SnCl_2$; 2N $(NH_4)_2S$; 2 N NH_4Cl; 2 N NH_4NO_3; saturated solution of ammonium sulphate; 0.5 N KI; 0.4 N solution of sodium bitartrate; saturated solution of potassium antimonate; Nessler's solution, and vaseline oil.

Preparation of Nessler's Solution. Dissolve 32 g of HgI_2 and 20 g of KI in 50 ml of water and dilute the solution with distilled water to 200 ml. Mix the solution with 300 ml of 20% KOH.

Special bottles with ground-in stoppers should be on the laboratory tables for left-over solutions containing metallic mercury that has not reacted.

1. Granulating of Zinc. Place several lumps of zinc in a porcelain crucible, put it on a pipestem triangle, and heat it in a burner flame until the metal melts. Fill a 1 litre beaker with water almost to the brim, insert an asbestos cone with a 2 mm orifice in a ringstand ring over the beaker, and pour the molten metal from the crucible (picking it up with tongs) into the cone. Store away the zinc granules for future work.

2. Reductant Properties of Metals. (a) By means of three separate tests, study the action of water, hydrochloric acid, and a concentrated alkali solution on metallic zinc. Write the equations of the reactions that have taken place. How will cadmium react to the same solvents?

(b) From a special dropper pour* 1-2 drops of metallic mercury into each of three test tubes (mercury should be poured over a tray without spilling any of it on the table or the floor!). Test the action on it of water, hydrochloric acid, and concentrated nitric acid (with and without heating). Write the equations of the reactions that have taken place. *Precaution! Pour the remains of the metallic mercury into the special bottles! Conduct the experiment in a ventilated hood!*

3. Reductant Properties of Amalgam. Pour 4 ml of a dilute solution of sulphuric acid and 2 drops of a potassium permanganate solution into a test tube, shake the contents, and pour the solution into two test tubes. Immerse a lump of sodium amalgam into one of the test tubes and, when the reaction has ended, compare the colour of the solution with that of the solution in the other test tube. Write the equation of the reaction that has taken place.

4. Preparation of Hydroxides. Add a few drops of an alkali solution to solutions of the salts $ZnCl_2$, $CdCl_2$, $Hg(NO_3)_2$, and $Hg_2(NO_3)_2$. What is formed? Write the equations of the reactions that have taken place. Add excess alkali to all the precipitates. What happens to the zinc hydroxide precipitate? Write the equation of the reaction that has taken place. In what way do the hydroxides of zinc, cadmium, and mercury differ?

5. Calcination of Oxides. (a) Place a pinch of zinc oxide on the lid of a porcelain crucible; handling the lid with tongs, heat it in the flame of a burner until it is red-hot. Does the colour of the zinc oxide change when it is heated and after cooling?

* This experiment should be conducted only in those laboratories that are equipped for work with mercury!

(b) Carry out a similar experiment with cadmium oxide. Do these oxides undergo chemical decomposition upon heating?

(c) Carry out a similar experiment with mercuric oxide in a refractory test tube held in the clamp of a ringstand. Establish the presence of oxygen in the test tube and of drops of mercury on its walls. Write the equation of the reaction that has taken place.

Why is it that mercuric oxide, unlike zinc oxide or cadmium oxide, decomposes upon heating?

6. Preparation and Properties of Sulphides. By treating solutions of the salts of the zinc subgroup metals with an ammonium sulphide solution prepare sulphide precipitates. Note their colours and the action of hydrochloric acid upon them. By referring to the *SP* values, explain why the sulphides of these metals react differently with hydrochloric acid.

7. Determining the Transition Point of Mercuric Iodide. Put 2-3 g of mercuric iodide into a conical test tube and close it with a stopper through which a thermometer has been passed. The bulb of the thermometer should be submerged in the powdered salt. Fasten the test tube in a ringstand clamp and lower it into a beaker filled with vaseline oil and fitted with a stirrer (an oil bath). Heat the beaker over the flame of a burner, stirring the oil in the beaker gently. When the temperature reaches 105-110°, reduce the flame so that the temperature does not rise by more than 1° per minute (continue the stirring). Note the temperature at which the colour of the salt changes from red to yellow.

Remove the test tube from the oil and allow it to cool. Does the colour of the salt revert to red? Open the test tube and rub the yellow powder with a glass rod against the wall of the test tube. What happens? Give a definition of the transition point. Why is the reconversion of the yellow modification to the red delayed?

8. Oxidant Properties of Mercury Salts. (a) Place a drop of a mercury salt solution on a copper or bronze coin. Two or three minutes later wash the solution off and rub the grey stain on the coin with a piece of filter paper. Write the equation of the reaction that has taken place.

(b) Test the action of stannous chloride on mercuric salts (for both an excess and a shortage of $SnCl_2$). Write the relevant equations.

9. Zinc, Cadmium, and Mercury Complexes. (a) Test the action of an ammonia solution (shortage and excess) on solutions of salts of these metals. Write the equations of the reactions that take place.

(b) Add a KI solution by drops to 1 ml of 0.2 N $Hg(NO_3)_2$ until the red precipitate formed is fully dissolved. Write the equation of the reaction that has taken place. Add to the resulting solution an equal volume of 20% KOH. The solution prepared in this way, which is very close to what is known as Nessler's solution, can be used for the qualitative detection of ammonia and ammonium salts. Carry out

such a reaction and write its equation. What is the reddish brown precipitate formed?

10. Analysis of a Solution. A test solution should contain only one of the following cations:

Na^{+} K^{+} Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+} Zn^{2+} Cd^{2+} Cu^{2+} Ag^{+} Hg^{2+}

Detect this cation by qualitative reactions.

One cation can be detected in a solution by the combined use of group precipitants and identifying reagents. The group precipitants separate several cations from the solution simultaneously. The given mixture of cations can be tentatively divided into three groups:

(1) Zn^{2+}, Cd^{2+}, Cu^{2+}, Ag^{+}, and Hg^{2+}, which are precipitated by a solution of $(NH_4)_2S$;
(2) Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, which are precipitated by a solution of Na_2CO_3, and
(3) Na^{+} and K^{+}, which have no group precipitant.

Receive your test solution from the instructor.

(a) Add 3 ml of an ammonium nitrate solution and 1-2 ml of a solution of $(NH_4)_2S$ to 1 ml of the test solution. If *a precipitate is formed*, the solution contains one of the cations of the first group (note the colour of the precipitate). In this case by testing the solution separately by specific reactions establish the presence of a definite cation:

Ag^{+} is detected as in experiment 8, Exercise 21;
Cu^{2+} is detected as in experiment 10a, Exercise 21;
Zn^{2+} and Cd^{2+} are detected as in experiments 4 and 6 of the present Exercise, and
Hg^{2+} is detected as in experiment 8 of the present Exercise.

If no precipitate is formed with $(NH_4)_2S$, the solution is analysed by the procedure described in "b".

(b) Add 1-2 ml of a Na_2CO_3 solution to the rest of the test solution. If *a precipitate is formed*, the solution contains one of the cations of the second group. In this case by testing the solution separately by specific reactions establish the presence of a definite cation:

Ca^{2+}, Sr^{2+}, and Ba^{2+} are detected as in experiments 7, 8, and 10, Exercise 23, and
Mg^{2+} is detected as in experiment 9, Exercise 23.

If the addition of soda produces no precipitate, the solution contains no cations of the second group and can contain only the cation Na^{+} or K^{+} (see below).

(c) Since the cations K^{+} and Na^{+} have no group precipitant, they are detected separately by specific reactions (experiments 3 and 5, Exercise 20).

Write up the analysis carried out, giving the equations of the reactions by which the cation in the solution was detected. Submit your report to the instructor.

Exercise 25

THE ELEMENTS OF THE THIRD GROUP OF THE PERIODIC SYSTEM

SUBJECTS FOR STUDY

The elements boron, aluminium, gallium, indium, and thallium; the structure of their atoms and outermost electron shells; features distinguishing boron from the rest of the group.

Boron; boric anhydride; boric acids and their salts; borax; reductant activity in the Al-Tl series; attitude of aluminium to oxygen, water, acids, and alkalis; aluminium oxide and hydroxide; comparison of hydroxides; aluminium salts and the alums.

The atoms of the boron group elements have three electrons each in their outermost shells. All of them, with the exception of boron, exhibit the chemical properties of metals and, upon oxidation, give up three electrons: $Me - 3e^- = Me^{+3}$. The valence +1 occurs in the compounds of aluminium and its analogues, but is most common in the case of thallium.

Amorphous boron is best dissolved by concentrated nitric acid, which is reduced to nitrogen dioxide:

$$\overset{\overset{3e^-}{\rightarrow}}{B} + 3\overset{+5}{H}\overset{+5}{N}O_3 = \overset{+3}{H_3}\overset{+3}{B}O_3 + 3\overset{+4}{N}O_2$$

The electrode potential of the $Al/Al^{\cdot\cdot\cdot}$ couple is −1.67 V. Aluminium is oxidised by $H^{\cdot}$ ions, but the reaction comes to a standstill quickly because of the formation of a protective film of hydroxide, which is insoluble in water:

$$\overset{\overset{6e^-}{\rightarrow}}{2Al} + 6\overset{+1}{H}OH = \overset{0}{3H_2} + 2\overset{+3}{Al}(OH)_3$$

In hydrochloric acid and dilute sulphuric acid, aluminium dissolves with the evolution of hydrogen.

Because of its amphoteric properties, aluminium dissolves in alkalis. Concentrated nitric acid without heating renders the surface of metallic aluminium passive, owing to the formation of a film of oxide *.

* The termination of the reaction between a metal and a medium (acid, alkali, etc.), owing to the formation of a surface oxide film, constitutes the essence of the "film" theory of metal corrosion formulated by the late Academician V. A. Kistyakovsky.

In oxygen, boron and aluminium burn up to form B_2O_3 and Al_2O_3 respectively.

Elementary boron is a nonmetal; it possesses oxidant, as well as reductant, properties. Upon heating, it interacts vigorously with some metals to form *borides*, e. g.:

$$3\overset{6e^-}{\overbrace{\overset{\rightarrow}{Mg}}} + 2B = \overset{+2\ -3}{Mg_3B_2}$$

The chemical character of the hydroxides corresponding to the tripositive ions changes with their radius:

Ion radius . . . . . (in Ångström units)	0.20	0.50	0.62	0.81	0.95
Hydroxide	H_3BO_3	$Al(OH)_3$	$Ga(OH)_3$	$In(OH)_3$	$Tl(OH)_3$
Its character	acidic	amphoteric			basic

With a decrease in radius, the acidic properties of the hydroxide become more pronounced, while with an increase in radius, basic properties come to the fore.

Boric anhydride forms several acids: orthoboric acid H_3BO_3, metaboric acid HBO_2, and the polyboric acids that have the general formula $(B_2O_3)_x \cdot (H_2O)_y$. The simplest of the polyboric acids ($x = 2$ and $y = 1$) is tetraboric acid $H_2B_4O_7$. All the boric acids are weak electrolytes. The stablest in aqueous solution is H_3BO_3; the others combine with water to form orthoboric acid:

$$HBO_2 + H_2O = H_3BO_3$$
$$H_2B_4O_7 + 5H_2O = 4H_3BO_3$$

The stablest boric acid salt is sodium tetraborate, which is commonly known as borax. It is prepared by crystallisation from an aqueous solution at a temperature not higher than 50-60° in the form of the hydrate $Na_2B_4O_7 \cdot 10H_2O$.

Borax interacts with strong acids to form orthoboric, or simply boric, acid:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl$$

When borax is heated, the crystals swell and give up the water of crystallisation:

$$Na_2B_4O_7 \cdot 10H_2O = 10H_2O + Na_2B_4O_7$$

Molten borax dissolves metal oxides to form metaborates, salts that rank among the most stable thermally, e. g.:

$$CoO + Na_2B_4O_7 = 2NaBO_2 + Co(BO_2)_2$$

Boric anhydride, upon being fused with metal oxides, likewise dissolves them readily to form metaborates, e. g.:

$$CoO + B_2O_3 = Co(BO_2)_2$$

Many of the metaborates have distinctive colours, a property that is used in preparing coloured glasses or the borax beads employed in analytical chemistry.

As the salt of a weak acid, borax undergoes hydrolysis:

$$Na_2B_4O_7 + 2HOH + 5H_2O \rightleftarrows 4H_3BO_3 + 2NaOH$$

Borax can therefore be used as an alkali for titrating acids.

All the volatile compounds of boron impart a bright green colour to the flame of a burner. A drop of boric acid solution produces a red stain on a yellow curcuma test paper; moistened with an alkali solution, the stain becomes greenish black.

Aluminium hydroxide is amphoteric.

Two aluminium acids are known: orthoaluminic acid H_3AlO_3 and metaaluminic acid $HAlO_2$. The process that takes place when $Al(OH)_3$ dissolves in alkalis may be represented by the equations:

$$H_3AlO_3 + 3NaOH = 3H_2O + Na_3AlO_3$$
$$H_3AlO_3 + NaOH = 2H_2O + NaAlO_2$$

Aluminium hydroxide possesses highly pronounced adsorption properties and is used in the purification of water and as a mordant in dyeing.

Among the soluble salts of aluminium uses have been found for the sulphate $Al_2(SO_4)_3$, the chloride $AlCl_3$, the nitrate $Al(NO_3)_3$, and potassium, or potash, alum $KAl(SO_4)_2 \cdot 12H_2O$. All of these salts experience hydrolysis in aqueous solutions and give acid reactions. Some aluminium salts, such as Al_2S_3 or $Al_2(CO_3)_3$, are completely hydrolysed in aqueous solutions:

$$Al_2S_3 + 6HOH = 3H_2S + 2Al(OH)_3$$

These salts cannot therefore be prepared by exchange reactions in solutions.

QUESTIONS

1. In what ways does boron differ in chemical properties from the other elements of its group?
2. Why cannot the reaction of reduction by charcoal be used to prepare boron from B_2O_3? When B_2O_3 is reduced by magnesium, why is it inadvisable to have the magnesium in excess?
3. Write the equation for the reaction between Al and an alkali solution.

4. How can orthoboric acid be converted to metaboric and to tetraboric acid, and *vice versa*? Write the structural formulae of those three acids.

5. Write the equation for the neutralisation of H_3BO_3 by a sodium hydroxide solution.

6. The boiling of an aqueous solution of ammonium aluminate precipitates aluminium hydroxide, whereas the boiling of a sodium aluminate solution causes no precipitate to be formed. Explain why this is so.

7. Which base is the stronger: $Tl(OH)_3$ or TlOH? Why?

Problems

1. The heating of 8 g of aluminium from 273° to 283° requires 19.13 cal. Determine the atomic weight of aluminium and the discrepancy (in per cent) between this value and the exact value (26.98).

2. What amount of boric acid can be prepared from amorphous boron upon its oxidation by 65.3% nitric acid if the amount of acid used is 1 litre (relative density 1.4)?

3. What is the titre and normality of a borax solution if 20 ml of that solution is neutralised by 16 ml of 0.1 N HCl?

4. What volume of M NaOH is required to neutralise 200 g of 3% H_3BO_3?

5. The heat of decomposition of MnO_2 is —123 Cal., while the heat of formation of Al_2O_3 is 399 Cal. Determine the thermal effect of the reaction of the aluminothermic reduction of manganese dioxide.

6. Determine the $[H^+]$, pH, and α% of 0.001 M H_3BO_3, taking into consideration only the first step in its dissociation.

7. For how long should a 20,000 A current be passed through an electrolyte to deposit 10 kg of metallic aluminium on the cathode?

8. A galvanic cell consisting of the couples $Al/Al^{...}$ and $Cu/Cu^{..}$ is operated for 1 hour, with the weight of the cathode diminishing by 1.12 g. Determine the intensity of the current in the circuit.

9. Draw the diagram of galvanic cell consisting of the couples $Al/Al^{...}$ and $Bi/Bi^{...}$, indicate the direction of the current, and determine the e. m. f. (the salt solutions are of molar concentration).

10. What amounts of aluminium trifluoride and 40% HF are needed to prepare 39.6 g of hexafluoroaluminic acid $H_3[AlF_6]\cdot 3H_2O$?

LABORATORY WORK

Apparatus and materials: hot-water funnel; suction filter; 50 ml beaker; 100 ml beaker; 50 ml measuring cylinder; funnel; porcelain casserole; porcelain mortar; test tubes and rack; glass bath; watch glass; two glass rods; platinum wire; scissors; aluminium plate; sandpaper; litmus paper; curcuma paper; lead paper; filter paper; pieces of white fabric; asbestos millboard; aluminium turnings; aluminium dust; magnesium ribbon; powdered sulphur; anhydrous borax; concentrated nitric acid; concentrated sulphuric acid; concentrated hydrochloric acid; 30% and 2 N NaOH; 10% ammonia solution; 0.2 N $Hg(NO_3)_2$; 0.5 N $Al_2(SO_4)_3$; 10% solution of potassium alum; crystalline copper nitrate or sulphate; saturated solution of ammonium chloride; 0.05% solution of methyl-violet; ethyl alcohol; alkaline solution of alizarin; snow or ice.

1. Preparation of Boric Acid. Weigh about 4 g of anhydrous borax to 0.01 g. Transfer the weighed amount of borax to a beaker, add 20 ml of distilled water to it, and heat it over a small flame until all of the borax dissolves (do not allow the solution to boil). If the solution is turbid after the borax has been dissolved, it should be filtered through an ordinary filter, using a hot-water funnel. Test a clear borax solution with litmus paper; what change does the litmus paper undergo and why? Write the equation for the reaction of the hydrolysis of borax.

Heat the solution to 80-90° and add to it a hydrochloric acid solution prepared by mixing 6 ml of concentrated HCl with an equal volume of water. Make sure that the amount of acid taken is sufficient (how?).

Cool the beaker with the solution to room temperature and then place it into a casserole with ice or snow. Filter off the crystals formed, using a Buchner filter, and dry them between filter paper until they are as dry as possible.

By means of a glass rod spread the crystals on a piece of filter paper in a thin layer and dry them in the air for 20-30 min., stirring them from time to time. Weigh the dried crystals and calculate the percentage yield of the product. Submit the crystals to the instructor. Keep the filtrate for experiment 2.

2. Reaction for Detecting Boric Acid. (a) By means of a glass rod place a drop of the boric acid solution prepared in the previous experiment and a drop of an HCl solution on a piece of curcuma paper and dry it over the flame of a burner. What is the colour of the stain? Moisten the stain with a drop of sodium hydroxide solution. How does the colour change?

(b) Evaporate 3-4 ml of the boric acid solution in a porcelain casserole, cool the casserole, moisten the crystals with 3-4 drops of concentrated sulphuric acid, add 2-3 ml of methyl or ethyl alcohol, and stir the mixture well. Put the casserole in a ventilating hood, ignite the alcoholic solution, and observe the colour of the flame. Write the equations for the reactions of the formation of methyl-borate (ethyl-borate) and its combustion.

3. Preparation of Borax Beads. Heat the end of a platinum wire in an oxidising flame until it is red-hot and touch some borax crystals with it. Carry the clinging crystals into the flame. The borax first swells and then fuses to become a clear glass; this is known as a colourless bead. The bead should best be 1.5 mm in diameter. Wet the bead on the wire loop with water; then touch some copper nitrate or sulphate crystals with the moist bead and heat it in an oxidising flame until it becomes transparent. Note the colour of the bead when it cools. Then place the bead into the central zone of a reducing flame and heat it for 5-7 min. Cool the bead first in the lower part of the flame, near the end of the nozzle, and then in the air; determine its colour. Salts of the other metals listed in Table 16 may be used instead of the copper salt.

Table 16

Colour of Borax Beads

Metal	Oxidising flame	Reducing flame
Vanadium	Greyish yellow	Pale green
Tungsten	Colourless	Yellow
Iron	Yellow	Pale green
Cobalt	Blue	Blue
Manganese	Pale violet	Colourless
Copper	Blue	Reddish brown
Molybdenum	Light yellow	Dark brown
Nickel	Reddish brown	Grey
Titanium	Colourless	Yellow
Uranium	Yellow	Green
Chromium	Green	Green

4. Attitude of Aluminium to Air and to Water. (a) Clean an 80 mm length of aluminium wire with sandpaper, bend it to form an angle of 30°, and immerse one end in a beaker with water. Is there any evolution of hydrogen from the water?

(b) Immerse the aluminium wire from the previous experiment in a mercuric nitrate solution for 2 min, wipe it with a piece of filter paper, and immerse one end of the wire in a beaker with water. Observe the evolution of hydrogen from the water and the oxidation of the aluminium surface exposed to the air. Write the equation of the reaction that takes place.

5. Passivation of Aluminium. Immerse an aluminium shaving for 3-4 min in a test tube containing 2-3 ml of concentrated nitric acid. Are any changes noticeable? Pour the solution off and, carefully, without shaking (!), wash the metal with water.

6. Attitude of Aluminium to Acids and to Alkalis.

(a) Pour 2-3 ml of concentrated nitric acid into each of two test tubes. Place an ordinary aluminium shaving into one of them, and a shaving with a passivated surface (from the previous experiment) into the other.

What happens? Give an explanation.

(b) Test the action of concentrated nitric acid upon aluminium with boiling (ventilated hood!). Note the colour of the gas evolved. Write the equation of the reaction that takes place.

(c) Test the action of a 30% solution of alkali upon aluminium with slight (!) heating. Demonstrate that hydrogen is evolved (be careful!) in the reaction. Write the equation of the reaction.

7. Amphoteric Character of Aluminium Hydroxide. Prepare aluminium hydroxide and test its effect on an acid and on an excess of alkali. Write the equations of all the reactions that have taken place.

8. Hydrolysis of Aluminium Salts. (a) To 1-2 ml of an alkaline solution of an aluminate add an equal volume of a saturated solution of ammonium chloride and a triple volume of water. Boil the solution, observing the formation of a precipitate. Write the equations of the reactions that have taken place. Why does the precipitation of $Al(OH)_3$ require the addition of NH_4Cl and water?

(b) Mix 0.54 g of aluminium dust and 0.96 g of sulphur in a mortar and then transfer the mixture to a sheet of asbestos to form a small heap. Insert a small strip of magnesium ribbon into the mixture. In a ventilated hood ignite the magnesium by the flame of a burner. After the reaction has taken place, cool the product, transfer it to a test tube, add 3-4 ml of water to it, and cover it with a moist lead paper. What colour does the lead paper acquire? Write the equations of the reactions of the formation of aluminium sulphide, of its hydrolysis by water, and of the interaction of hydrogen sulphide with a lead salt.

9. Adsorption of Dyes by Aluminium Hydroxide.

(a) Prepare a precipitate of aluminium hydroxide and filter it off. Wash the precipitate on the filter once with water. Pour a faintly coloured solution of methyl-violet on the filter and observe that the filtrate is a colourless solution.

(b) Moisten a strip of white cotton fabric on a watch glass with a 10% solution of potassium alum. Pour off the excess alum solution and pour a few drops of a 10% ammonia solution on the fabric.

What is deposited in the fibres of the fabric? Five minutes later wash the treated fabric with water and place it in a beaker with an alkaline solution of alizarin together with a strip of fabric not treated with an alum solution. After 5-7 min wash both strips thoroughly in water and compare their colours.

Exercise 26

CARBON, SILICON, AND THEIR COMPOUNDS

SUBJECTS FOR STUDY

The elements of the fourth group of the Periodic System; atomic structure; carbon and silicon; attitude of these elements to oxygen and to acids; hydrogen compounds of carbon and silicon; carbides and silicides.

Carbon monoxide and silicon oxide; carbon dioxide and silicon dioxide; carbonic acid and silicic acids; carbonates, bicarbonates, and silicates; hydrolysis of salts; glass.

The atoms of the elements of the carbon—lead series have 4 electrons each in their outermost shells. In chemical reactions they exhibit reductant (in reactions with oxidising agents) and oxidant (in reactions with reducing agents) properties:

$$R - 4e^- = \overset{+4}{R} \qquad R - 2e^- = \overset{+2}{R} \qquad R + 4e^- = \overset{-4}{R}$$

Owing to this equally pronounced tendency to give up and to gain electrons, the atoms of these elements combine with the atoms of other elements primarily by means of covalent bonds, forming nonpolar compounds.

Carbon, silicon, and their compounds are dealt with in this Exercise, while the elements of the germanium and titanium series and their compounds are examined in the next Exercise.

At ordinary temperatures oxygen has practically no effect on either carbon or silicon. At higher temperatures the elements undergo more or less vigorous oxidation with the formation of the oxides RO_2 and RO.

Upon heating with concentrated nitric and sulphuric acids, carbon is oxidised to carbon dioxide. Acids, except hydrofluoric, have no effect on silicon.

In the presence of alkalis, silicon displaces hydrogen from water:

$$Si + 2NaOH + H_2O = 2H_2 + Na_2SiO_3$$

The compounds of carbon with metals are called carbides (e. g., calcium carbide CaC_2), while the compounds of silicon with metals are called silicides (e. g., magnesium silicide Mg_2Si).

Some of these compounds may be prepared synthetically, for instance:

$$2Mg + Si = Mg_2Si$$

The carbides and silicides of the alkaline and alkaline earth metals and of aluminium are easily decomposed by water (hydrolysis) and by acids to form gaseous hydrogen compounds:

$$CaC_2 + 2HOH = C_2H_2 + Ca(OH)_2$$
$$Mg_2Si + 4HCl = SiH_4 + 2MgCl_2$$

The simplest hydrogen compounds, in which the number of hydrogen atoms corresponds to the maximum valency of the element, may be represented by the general formula RH_4. These compounds (CH_4 and SiH_4), with covalent bonds between the atoms, are gaseous and nonpolar; they exhibit reductant properties.

Methane CH_4, when ignited, burns according to the equation:

$$CH_4 + 2O_2 = 2H_2O + CO_2$$

Mixtures of methane with air or oxygen are explosive, like detonating gas.

The hydrogen compounds of silicon, called *silanes* (SiH_4, Si_2H_6, etc.), are spontaneously inflammable in air.

Carbon monoxide CO and silicon oxide SiO are indifferent oxides, since they do not combine with water and exhibit neither acidic nor basic properties. Carbon monoxide may be prepared by heating a mixture of formic acid and concentrated sulphuric acid. Carbon monoxide is poisonous and exhibits reductant properties.

Carbon dioxide is prepared by burning coal or by decomposing carbonates or bicarbonates by heating them or by treating them with acids.

At N. T. P. one volume of water dissolves 1.7 volumes of CO_2. The resulting carbonic acid is a very weak acid. The solution is, in fact, a system in equilibrium:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^{\cdot} + \underbrace{HCO_3'}_{\downarrow\uparrow}$$
$$\underbrace{H^{\cdot} + CO_3''}$$

Heating tilts the balance towards the evolution of CO_2.

Among the silicic acids mention should be made of metasilicic acid H_2SiO_3 and orthosilicic acid H_4SiO_4, which are formed as gels in the exchange reactions between silicic acid salts and mineral acids. Many so-called polysilicic acids are known, their general formula being $(SiO_2)_x \cdot (H_2O)_y$. The simplest of these ($x = 2$; $y = 1$) is disilicic acid $H_2Si_2O_5$. The silicic acids are very weak acids.

Carbonic acid gives rise to two series of salts: carbonates (with the CO_3'' ion) and bicarbonates (with the HCO_3' ion). The carbonates of the alkaline metals (with the exception of lithium) and of ammonium are soluble in water; the most important of these are sodium carbonate, or soda ash, Na_2CO_3, hydrated sodium carbonate, or washing soda, $Na_2CO_3 \cdot 10H_2O$, anhydrous and hydrated potash, K_2CO_3 and $K_2CO_3 \cdot 2H_2O$, and ammonium carbonate $(NH_4)_2CO_3$. The most important of the bicarbonates is sodium bicarbonate, or baking soda, $NaHCO_3$.

The silicic acid salts are called silicates, and the only water-soluble ones among them are Na_2SiO_3 and K_2SiO_3 (soluble glass).

The average composition of ordinary window glass is expressed by the formula $Na_2O \cdot CaO \cdot 6SiO_2$; water partly dissolves glass.

The soluble salts of the above acids undergo hydrolysis; their solutions are alkaline. The hydrolysis of soda ash, for instance, follows the equation:

$$2Na^{\cdot} + CO_3'' + HOH \rightleftarrows Na^{\cdot} + HCO_3' + Na^{\cdot} + OH'$$

The other salts behave similarly, except for Na_2SiO_3 and K_2SiO_3, which are converted by hydrolysis to salts of disilicic acid:

$$4Na^{\cdot} + 2SiO_3'' + HOH \rightleftarrows 2Na^{\cdot} + Si_2O_5'' + 2Na^{\cdot} + 2OH'$$

Strong reducing agents (such as Mg and P) are oxidised at combustion temperature by carbon dioxide or silicon dioxide:

$$2Mg + CO_2 = 2MgO + C$$

QUESTIONS

1. What is activated charcoal made from and how?
2. Briefly explain the uses of the radioisotope C^{14} in science and engineering.
3. How can pure carbon monoxide be prepared from oxalic acid?
4. List the main constituents of water gas, producer gas, and illuminating gas. Which of these gases has the highest calorific value? Why is this so?
5. How can pure carbon dioxide be prepared from exhaust gases?
6. What are the processes that have to be carried out to obtain silicic acid gel from silica?
7. By means of what chemical reactions can a carbonate be turned into a bicarbonate, and *vice versa*?
8. Why is it that in one of the stages of the ammonia-soda process

$$NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl$$

the balance is shifted to the right?

Problems

1. Calculate the "mean molecular weight" of a mixture consisting of 42% of carbon dioxide and 58% of nitrogen.
2. A compound consists of 42.86% of carbon and 57.14% of oxygen. The density of this gas in terms of chlorine is 0.396. Determine the formula of the substance and its density in terms of air.
3. A mixture of 100 ml of methane and 100 ml of oxygen is ignited. Determine the volume of the gas that has not reacted.
4. Determine the atomic weight of silicon from the following data:

	Mol. weight	Content of Si (%)
Silicon tetrafluoride . . .	104.06	26.96
Disilane	62.17	90.27
Silicochloroform	135.45	20.72

5. What are the amounts (by weight) of each of the initial products needed to prepare 1 ton of soda ash by the Le Blanc process, the yield of soda ash being 35%?
6. One hundred and eighty grams of washing soda is dissolved in 1,300 g of water. Determine the titre and the percentage, molar, and normal concentrations of the solution in terms of the anhydrous salt, the relative density of the solution being 1.16.
7. According to the data of O. Alekin, 100 ml of the water of the Belaya River contains 11.4 mg of $Ca^{\cdot\cdot}$ and 2.5 mg of $Mg^{\cdot\cdot}$, while 2 litres of the water of the Ishim River contains 163 mg of $Ca^{\cdot\cdot}$ and 154.6 mg of $Mg^{\cdot\cdot}$. Which of the rivers has the harder water?

8. The gas from the oil wells of Soviet Azerbaijan contains 85% (by volume) of CH_4, 2.8% of C_2H_6, and 1.2% of C_4H_{10}, the rest of the gases being noncombustible. The combustion heats of these gases are 212.8, 372.8, and 687,9 Cal. respectively. Determine the calorific value of 1 cu m of the gas. Express in percentage the discrepancy between this result and the practical figure of the calorific value, which is equal to 8,014 Cal./cu m.

9. The heat of formation of SiH_4 is —8.7 Cal. Determine the combustion heat of SiH_4, knowing that the heat of formation of water is 68.35 Cal. and the heat of formation of SiO_2 is 203.34 Cal.

10. Determine the pH and the α % of 0.001 M H_2CO_3, taking into account only the first step in its electrolytic dissociation.

LABORATORY WORK

Apparatus and materials: apparatus shown in Figs. 35 and 70; Kipp gas generator; barometer; room thermometer; metal ruler; two porcelain crucibles; pipestem triangle; porcelain mortar; jar; burette and funnel for it; two funnels; gas-delivery tube with stopper; refractory test tube; test tubes; test tube with a hole in the bottom and a gas-delivery tube; two Erlenmeyer flasks; 100 ml flask with stopper and cooling pipe; glass rod; two cylinders with glass covers; 250 ml measuring cylinder; cane sugar; activated charcoal; 4 : 5 and 8 : 5 mixtures of magnesium and quartz sand; ferrosilicon; fused sodium acetate; soda lime; calcium carbide; bismuth oxide; powdered glass; powdered (0.25-0.5 mm) silica gel; sodium carbonate; sodium carbonate in tablets; potassium carbonate; calcium carbonate; sodium bicarbonate; concentrated sulphuric acid; concentrated, 2 N, 3 M, and 0.01 N titrated hydrochloric acid; formic acid; 2 N NaOH; 25% Na_2SiO_3; 0.1 N $AgNO_3$; saturated solution of ammonium chloride; 10% solution of sodium carbonate; 10% solution of commercial sodium chloride; 10% ammonia solution; 0.5 N $Al_2(SO_4)_3$; 10% $CuSO_4$; hydrogen sulphide water; lime water; indigo solution, neutral litmus solution; phenolphthalein solution; palladium paper, and filter paper.

Preparation of Palladium Paper. Impregnate a piece of filter paper with an 0.01% solution of $PdCl_2$, 100 ml of which contains 15 drops of N HCl. Dry the paper in the absence of CO. Keep the paper in a jar with a ground-in lid. It is advisable to prepare it every time it is needed.

Preparation of Powdered Glass. Bottle, window, or chemical-ware glass should be ground thoroughly in a mortar. Approximately 1 g quantities of the powder should then be weighed on a technical balance, wrapped in paper, and marked, indicating the type of glass.

1. Preparation of Charcoal from Sugar. Put about 3 g of pure cane sugar (powdered) in a porcelain crucible, place the crucible on a pipestem triangle, and heat it. The sugar at first melts and is charred, a froth rising on account of the burning of the volatile products. Stir the mass with a glass rod and heat it for several minutes over a blowpipe until a large porous mass is obtained. Write the equation of the reaction that has taken place. Keep the product for experiment 4.

2. The Adsorption Properties of Charcoal. Pour some hydrogen sulphide water into one Erlenmeyer flask and some indigo solution into another. Add 1 g of finely ground charcoal to each and shake the contents of the flasks vigorously. Ten or 15 minutes later filter off the charcoal and establish the absence (by odour and colour) of hydrogen sulphide or indigo in the solutions.

What distinctive property does activated charcoal exhibit?

3. Preparation of Silicon. Conduct this experiment in a ventilated hood. Place 2 g of a mixture of metallic magnesium and quartz sand (4 : 5 by weight) in a dry crucible and heat the crucible *carefully* over the flame of a burner until the mixture catches fire. If the quartz sand is very fine, the reaction may even be accompanied by an explosion. When the mixture has cooled, transfer it to a beaker with a hydrochloric acid solution. The magnesium oxide and silicide dissolve, leaving a dark brown precipitate of amorphous silicon in the beaker (the decomposition of the magnesium silicide by the acid produces silanes, which upon contact with the air ignite!).

Filter off the precipitate and keep it for experiment 4. Write the equations of the reactions whereby Si is prepared and Mg_2Si is formed.

4. Reductant Properties of Charcoal and of Silicon. (a) Test the action of concentrated sulphuric acid, when heated, upon the charcoal prepared in experiment 1. Identify (with caution!) the gas evolved by its odour. Write the equation of the reaction that has taken place.

(b) Test the action of a concentrated alkali solution on the amorphous silicon prepared in experiment 3 or on a lump of ferrosilicon. Write the equation of the reaction that takes place.

5. Preparation and Properties of Methane. Mix 3 g of fused sodium acetate and the same amount of soda lime in a mortar, and transfer the mixture to a dry test tube. Close the test tube with a stopper through which a gas-delivery tube has been passed; fasten the test tube horizontally in the clamp of a ringstand, and immerse the end of the gas-delivery tube in a large jar with water (crystalliser tank). Place two cylinders in the beaker, one of them full of water and the other half-full. Warm the test tube with the flame of a burner and then heat it from the bottom up. Fill both cylinders with the gas that is evolved, cover them under water with lids, remove them from the jar, and bring them up to the flame of the burner. The pure methane burns quietly, whereas the mixture with air *explodes (careful!)*. Write the equations for the reactions of the preparation and burning of methane. Does the mixture explode whatever the proportion of the volumes in which CH_4 and O_2 are mixed?

6. Preparation and Properties of Acetylene. Conduct this experiment in a ventilated hood. Place 2-3 small lumps of calcium carbide in a dry test tube with a hole in its bottom, close the test tube with a stopper through which a straight gas-delivery tube has been passed, and lower it into a beaker with water. After a minute or two ignite the gas and note the type of flame. Blow at the acetylene flame carefully and observe whether it changes. Write the equations for the reactions of the preparation and burning of acetylene. Why, unlike methane, does acetylene burn in the air with a smoking flame?

7. Preparation of Hydrogen Compounds of Silicon. Conduct this experiment in a ventilated hood. Place 1.5-2 g of a mixture of metallic magnesium and quartz sand (8 : 5 by weight) in a dry test tube and

fasten the test tube vertically in the clamp of a ringstand. Warm the test tube and then heat it until the mixture ignites (careful!). When the test tube has cooled, break it, transfer the mixture into a hydrochloric acid solution, and observe the spontaneous combustion of the hydrogen compounds of silicon in the air. Write the equations of the reactions that have taken place.

8. Carbon Monoxide and Its Reductant Properties. Conduct the experiment in a ventilated hood. Prepare the apparatus shown in Fig. 70. Pour 10-15 ml of concentrated sulphuric acid into the flask and an

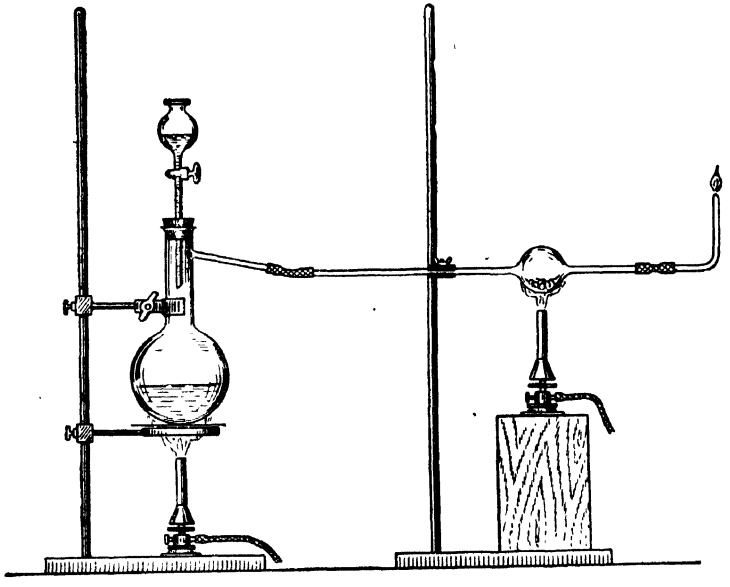


Fig. 70. Apparatus for preparing carbon monoxide

equal volume of formic acid into the dropping funnel. Place about 1 g of bismuth oxide into the bulb of the refractory tube. Add the acid from the funnel to the flask and heat the flask gently. When the carbon monoxide begins to flow evenly, ignite the gas at the outlet of the gas-delivery tube. Heat the bulb with a burner until a drop of molten metal forms in it. Then stop heating the bulb and hold a palladium paper, moistened with a drop of water, over the outlet of the tube. What happens to the paper? Turn the tip of the gas-delivery tube downwards and immerse it in a test tube with a heated solution of silver diamminochloride. What happens? Write the equations for the reactions of the preparation of CO, its burning, and its action upon Bi_2O_3, $PdCl_2$ and $[Ag(NH_3)_2]Cl$.

9. Dissolving Co_2 in Water. Pour 5 ml of a neutral litmus solution into a test tube and pass a stream of carbon dioxide from the Kipp gas

generator through it slowly, washing the CO_2 with water in a wash bottle for gases. How does the colour of the litmus change? Why is this? Write the equation of the reaction that has taken place. Pour half of the solution into another test tube, and heat it carefully for some time. How does the colour change? Why?

10. Preparation of Silicic Acid Gel. Add 4 ml of concentrated hydrochloric acid to an equal volume of a 25-30% solution of sodium silicate. Observe the formation of silicic acid gel 20 min later. The contents of the test tube, it should be noted, remain in it even when the test tube is turned over. Write the equation of the reaction that has taken place.

11. The Adsorption Properties of Silica Gel. Add an ammonia solution by drops to 15-20 drops of a cupric sulphate solution until the solution becomes dark blue owing to the formation of a cuprammonium complex. Now add 2 g of ground silica gel (0.25-0.5 mm grain diameter) to the solution and shake the mixture for some time. The colourless powder of silica gel acquires a dark blue colour, whereas the solution becomes pale. Pour off the solution, wash the silica gel 3-4 times by decantation, add 2 ml of hydrochloric acid, and shake the solution. The silica gel loses its blue colour because the cuprammonium complex is washed away by the acid.

12. Calcination of Carbonates and Their Treatment with Acids. (a) Place 0.5 g of the salts $CaCO_3$, $NaHCO_3$, Na_2CO_3, and K_2CO_3 into four dry test tubes respectively. Close each test tube in turn with a stopper through which a gas-delivery tube has been passed, the tube being bent at a right angle and immersed in a test tube with lime water. Heat the test tube with the substance over the flame of a burner, noting that the lime water becomes cloudy. Which carbonic acid salts are not decomposed by heating? Write the equations for all the reactions carried out.

(b) Treat 0.5 g of the same salts in test tubes with 2 N HCl. Do all the salts dissolve in the acid? What characteristic phenomenon is observed when carbonates dissolve in acids? Write the equations for the reactions carried out. Explain why sodium bicarbonate, rather than carbonate, is used in fire extinguishers.

13. Hydrolysis of Salts. (a) Test a solution of sodium carbonate and a solution of sodium silicate with red litmus paper. Write the equations for the reactions of hydrolysis that take place. Which of the salts undergoes hydrolysis more readily? Why is this so?

(b) Add a sodium carbonate solution to an aluminium sulphate solution. A voluminous white precipitate of aluminium hydroxide is formed, with the simultaneous evolution of bubbles of CO_2. Write the relevant equations.

(c) Mix a solution of sodium silicate (1-2 ml) with a double volume of ammonium chloride solution. Heat the mixture slightly, observing the formation of a precipitate. Identify the gas evolved (by its odour).

Write the equations of the reactions that take place. In which case is hydrolysis plactically irreversible?

14. Determining the Percentage Content of Bound Carbon Dioxide in Sodium Carbonate. The experiment is conducted in the apparatus shown in Fig. 35. Fill one-third of the beaker with a 10% solution of sodium chloride. Fill a 250 ml measuring cylinder with the same solution, cover it with a glass lid, and turn it over into the beaker. Fasten the cylinder with a clamp attached to a ringstand.

Pour 30-40 ml of 3 M HCl into the flask and dry the inner wall of the neck of the flask with some rolled-up filter paper. Weigh about 0.8-0.85 g of sodium carbonate pressed into tablets. Place the weighed sodium carbonate into the neck of the flask, which is in a horizontal position (shown by broken line in Fig. 35); close the flask tightly with the stopper through which a delivery tube has been passed. Place the end of the delivery tube under the cylinder, and let the sodium carbonate tablets slip into the acid. The carbon dioxide collects in the cylinder. When all the sodium carbonate has dissolved, measure the volume of the gas evolved and the height of the column of the liquid in the cylinder over the level of the liquid in the beaker; note the room temperature and the barometric pressure.

Experimental Results

Weight of Na_2CO_3 in g	Volume of gas in ml	Temperature in °C	Barometric pressure in mm Hg	Height P_w in mm	Vapour tension h in mm Hg

From the data obtained calculate the percentage content of bound CO_2 in the sodium carbonate. Calculate the percentage content of CO_2 from the formula of sodium carbonate; compare this figure with the experimental result.

15. Determining the Resistance of Glass to the Action of Water. Receive from the instructor a glass sample for testing (weighing 1 g). Place the weighed sample in a flask, add 25 ml of distilled water, and close the flask with a stopper through which a long tube has been passed to act as a cooling pipe *. Attach the flask to a ringstand and heat it on a wire gauze with an asbestos centre to boiling point. Boil the water for 20 min in such a way that all the vapour should be condensed in the cooling pipe. After cooling the flask, add 2-3 drops of a

* The flask and the tube should first be treated with live steam.

phenolphthalein solution: the solution will acquire a pink colour. Fill a burette with 0.01 N HCl and titrate the extract carefully until the addition of one drop of extra acid causes the solution to become colourless. From the data of the following table determine the grade of the glass:

Grade of glass	Number of ml of 0.01 N HCl used up to titrate 25 ml of the extract
Unaffected	0-0.32
Resistant	0.32-0.65
Hard for chemical ware	0.65-2.8
Soft for chemical ware	2.8-6.5
Ordinary (window glass, bottle glass)	over 6.5

Write the equation for the hydrolysis of the soluble part of the glass.

Exercise 27

THE ELEMENTS OF THE GERMANIUM AND TITANIUM SERIES AND THEIR COMPOUNDS

SUBJECTS FOR STUDY

The elements of the germanium series: germanium, tin and lead; simple substances, their preparation and properties; valence in compounds; oxides and hydroxides of the bivalent elements, and their amphoteric nature; the most important salts and their chemical properties; stannic oxide and lead dioxide.

The elements of the fourth subgroup: titanium, zirconium, and hafnium; their atomic structure and chemical properties; the nature of their oxides; titanium dioxide and its hydroxide; pertitanic acid.

The elements germanium, tin, and lead belong to the fourth main group and are chemical analogues of carbon and silicon. In compounds they are bi- and tetrapositive, and they form gaseous compounds with hydrogen.

As to physical properties, tin and lead are metals with low melting points.

Water at ordinary temperatures has practically no effect on either tin of lead: it oxidises them, a protective coating appearing on their surface and preventing a continuation of the reaction.

Hydrochloric acid acts only on Sn and Pb, turning them into bivalent ions:

$$Sn + 2HCl = H_2 + SnCl_2$$

With lead the reaction requires heating, since $PbCl_2$ is almost insoluble in cold water.

Nitric acid oxidises lead to $Pb^{\cdot\cdot}$. Tin is oxidised by concentrated nitric acid to SnO_2 or β-stannic acid, which probably has the composition $(SnO_2)_x.(H_2O)_y$:

$$\overset{4e^-}{\rightarrow}$$
$$Sn + 4\overset{+5}{H}NO_3 = \overset{+4}{Sn}O_2 + 4\overset{+4}{N}O_2 + 2H_2O$$

Dilute nitric acid oxidises tin to form $Sn(NO_3)_2$, while at the same time undergoing reduction to NO; very dilute acid is reduced to ammonium nitrate:

$$\overset{8e^-}{\rightarrow}$$
$$4Sn + 10\overset{+5}{H}NO_3 = 4\overset{+2}{Sn}(NO_3)_2 + \overset{-3}{N}H_4NO_3 + 3H_2O$$

Dilute sulphuric acid has no effect on lead (owing to the formation of a protective $PbSO_4$ film, which is insoluble in acid); concentrated sulphuric acid (80% and higher concentration) dissolves the protective film:

$$PbSO_4 + H_2SO_4 = Pb(HSO_4)_2$$

The oxides of lead and tin dissolve in acids and alkalis.

The hydroxides $Sn(OH)_2$ and $Pb(OH)_2$ are prepared by exchange reactions between salts and alkalis. Water scarcely dissolves them at all, but they do dissolve in acids and alkalis, in the latter case forming hydroxystannites $Me_2[Sn(OH)_4]$ or hydroxyplumbites $Me_2[Pb(OH)_4]$.

The most soluble salt of bivalent tin is stannous chloride $SnCl_2$.

The soluble salts of lead are the nitrate $Pb(NO_3)_2$ and the acetate $Pb(CH_3COO)_2$; the chloride $PbCl_2$ and the iodide PbI_2 are soluble in hot water. The salts of bivalent tin are used as good reducing agents in diverse media, e. g.:

$$\overset{2e^-}{\rightarrow}$$
$$\overset{+2}{Sn}Cl_2 + 2\overset{+3}{Fe}Cl_3 + 2HCl = H_2[SnCl_6] + 2\overset{+2}{Fe}Cl_2$$

The salts of bivalent lead can also undergo oxidation to tetravalent lead compounds

$$\overset{2e^-}{\rightarrow}$$
$$\overset{+2}{Pb}(CH_3COO)_2 + \overset{+1}{NaO}Cl + H_2O = \overset{+4}{Pb}O_2 + \overset{-1}{NaCl} + 2CH_3COOH$$

but they are very weak reducing agents and are therefore not used for reduction reactions.

The sulphides SnS (brown) and PbS (black) are insoluble in water. The formation of the black precipitate of PbS serves as a reaction for detecting the S'' ion; the precipitate dissolves in nitric acid.

Stannous sulphide dissolves in a solution of ammonium polysulphide, undergoing oxidation from the bivalent to the tetravalent state:

$$\overset{+2}{Sn}S + (NH_4)_2\,[\overset{-2}{S_2}] = (NH_4)_2\,\overset{+4}{Sn}S_3$$

(the $2e^-$ arrow connects Sn and S)

The resulting salt, ammonium thiostannate, is a salt of thiostannic acid H_2SnS_3, which is extremely unstable and decomposes the moment it is formed:

$$H_2SnS_3 = H_2S + SnS_2$$

The insoluble salts of lead that deserve mention are the sulphate $PbSO_4$, the basic carbonate $Pb_3(OH)_2(CO_3)_2$, also known as white lead, and the chromate $PbCrO_4$.

Stannic oxide SnO_2 and lead dioxide PbO_2 are insoluble in water and do not react with it chemically; they are amphoteric.

Two acids correspond to stannic oxide: α-stannic acid H_2SnO_3 and β-stannic acid H_4SnO_4; similar acids correspond to lead dioxide. In the $H_2CO_3 - H_2PbO_3$ series acidity declines from carbonic to metaplumbic acid. The hydroxides of tetravalent germanium, tin, and lead exhibit amphoteric properties.

The salts of the stannic acids are called α- and β-stannates; the salts of the plumbic acids, meta- and orthoplumbates. The plumbates include minium (or red lead) Pb_3O_4 and the trioxide Pb_2O_3, which are lead salts of orthoplumbic and metaplumbic acid respectively:

$$\overset{+2}{Pb}_2\overset{+4}{Pb}O_4 \text{ and } \overset{+2}{Pb}\overset{+4}{Pb}O_3$$

The salts of tetravalent lead are extremely unstable in aqueous solution and experience complete hydrolysation to the more stable compound PbO_2.

The compounds PbO_2 and Pb_3O_4 are often used for oxidation reactions, e. g.:

$$2K\overset{-1}{I} + \overset{+4}{Pb}O_2 + 2H_2SO_4 = I_2 + \overset{+2}{Pb}SO_4 + K_2SO_4 + 2H_2O$$

($2e^-$ arrow connects I and Pb)

$$2K\overset{-1}{I} + Pb_2\overset{+4}{Pb}O_4 + 4H_2SO_4 = I_2 + 3\overset{+2}{Pb}SO_4 + K_2SO_4 + 4H_2O$$

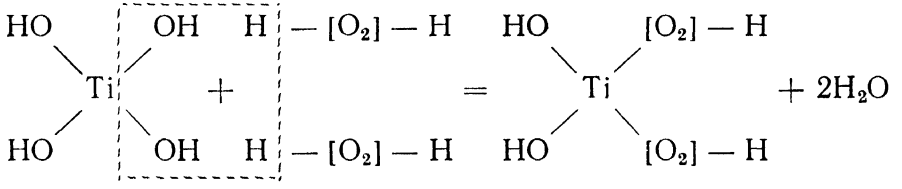
($2e^-$ arrow connects I and Pb)

The elements of the titanium series are titanium, zirconium, and hafnium. The atoms of these elements have two electrons in their outermost shells, with 8 + 2 electrons in the next shell.

In chemical reactions the atoms of these elements can give up 4 electrons (2 from the outermost shell and 2 from the next). The maximum valence of these elements in compounds is 4 (a point of analogy with the elements of the carbon series). However, these elements, as reducing agents, do not, unlike the carbon elements, form negative ions and do not produce gaseous hydrides with hydrogen.

Although titanium, zirconium, and hafnium may be bivalent, trivalent, and tetravalent in compounds, the latter valence is the most characteristic and the one typical of their stable compounds. Some of the compounds of titanium—TiO_2, $TiCl_4$, etc.—are used in the laboratory.

The colourless compounds of Ti^{+4}, upon interacting with strong reducing agents, turn into pale violet compounds of Ti^{+3}. Exposure to air causes the violet colour to disappear because of the oxidation of Ti^{+3} to Ti^{+4}. When Ti^{+4} salts react with an alkali solution, a white gelatinous precipitate of hydroxide is formed, which dissolves only in acids. With hydrogen peroxide in water, Ti^{+4} compounds form the yellow-orange pertitanic acid. The reaction follows the equation



and is used for the qualitative detection of titanium.

QUESTIONS

1. Write the equations for the reactions whereby tin is dissolved in dilute—and lead, in concentrated—nitric acid.
2. Why is hydrochloric acid added to water in preparing an aqueous solution of $SnCl_2$? Write the equations of the reactions that take place.
3. Write the equations for the reactions of the decomposition of ammonium thiostannate by hydrochloric acid.
4. Write the equations for the reactions of the preparation of sodium zirconate and its hydrolysis.
5. What can be used to dissolve metallic zirconium? Write the equations for the reactions whereby it is dissolved.
6. Write the equations for the reactions whereby the following consecutive transformations are effected:

$$TiCl_4 \rightarrow Ti \rightarrow TiO_2 \rightarrow TiCl_4 \rightarrow Ti(OH)_4$$

7. Write the structural formulae for Na_2SnS_3 and Pb_3O_4.

8. Draw the diagram of a lead storage battery. What chemical reactions take place at the cathode and at the anode when the battery is charged and when it is discharged?

Problems

1. The interaction of 23.7 g of metallic tin with excess hydrochloric acid produces an amount of hydrogen sufficient to obtain 12.7 g of metallic copper by reducing cupric oxide. Determine the equivalent of tin.

2. What volume of nitrogen dioxide will be produced when 1 kg of lead is dissolved in concentrated nitric acid? The gas is collected at 20° and 750 mm Hg.

3. What will be the volume (at N. T. P.) of nitrogen dioxide produced if 50 g of an alloy containing 70% of copper and 30% of tin is treated with concentrated nitric acid in excess?

4. Assuming lead to consist of the isotopes Pb^{204} (1.37%), Pb^{206} (25.15%), Pb^{207} (21.11%), and Pb^{208} (52.38%), determine the atomic weight of lead.

5. Determine the percentage concentration and the normality of a $SnCl_2$ solution prepared by mixing 2.5 litres of a 22% solution (relative density 1.19) and 1.5 litres of a 4% solution (relative density 1.03).

6. What volume of 2 N KOH should be added to 200 g of a 5% solution of $SnCl_2$ to convert all of the latter to stannite?

7. One hundred grams of minium was treated with excess nitric acid; after the reaction the solution was filtered and evaporated; the dry residue was then dissolved, the solution filtered and diluted to 2 litres. Determine the molar concentration and normality of the solution prepared.

8. One gram of a chemically resistant zirconium alloy yielded 0.88 g of zirconium dioxide, 0.37 g of ferric oxide, and 0.145 g of aluminium oxide. Determine the proportion (%) in which these metals are contained in the alloy.

9. The burning of a gram-molecule of titanium carbide generates 202.45 Cal. of heat. The heats of formation of titanium dioxide and carbon dioxide are 218 and 94.45 Cal. respectively. Determine the heat of formation of titanium carbide.

10. The reduction of the complex compound $K_2[HfF_6]$ by metallic potassium involves the expenditure of 3.13 g of the metal. What is the yield of hafnium?

LABORATORY WORK

Apparatus and materials: apparatus shown in Fig. 69; felt or cloth polishing wheel; blowpipe; funnel; test tubes and rack; coal in lumps; lead dioxide; 1 : 1 mixture of coal and lead oxide; 1 : 1 mixture of coal and stannic oxide; zinc in granules; stannic chloride; concentrated and 2 N HNO_3; 2 N H_2SO_4; concentrated and 2 N HCl; 2 N NaOH; 2 N KOH; 0.5 N $SnCl_2$; 0.5 N $Pb(NO_3)_2$; 0.5 N $Pb(CH_3COO)_2$; 0.5 N $Bi(NO_3)_2$; 0.5 N KI; N solution of ammonium polysulphide; 0.5 N K_2CrO_4; 3 N Na_2CO_3; 2% solution of titanium sulphate; 0.3 N $SnCl_4$; 3% H_2O_2; saturated solution of lime chloride; electrolysis solution; hydrogen sulphide water; filter paper, litmus paper, and sandpaper.

Preparation of Titanium Sulphate Solution. Boil titanium dioxide slowly with concentrated sulphuric acid; then either dissolve it in water or fuse the titanium dioxide with potassium pyrosulphate (1 : 7); dissolve the melt in 0.2 N H_2SO_4.

Preparation of Solution for Electrolysis. Dissolve 6 g of crystalline $SnCl_2$ and 2 g of NH_4Cl in 300 ml of water containing 2 ml of concentrated hydrochloric acid.

1. Preparation of Lead and Tin. (a) Make a hollow 1 cm in diameter in a lump of coal (or coke) and fill it with a 1 : 1 mixture of lead oxide and powdered coal. Moisten the mixture with 2-3 drops of water. Hold a blowpipe at the fringe of the reducing flame of a burner and, blowing

air into it carefully by mouth, direct the elongated flame at the mixture (Fig. 71). Carry on reduction in this way until a drop of molten metal is formed. Write the equation of the reaction that has taken place.

(b) Conduct a similar experiment with stannic oxide, mixing it with an equal amount of coal (or coke). Write the equation of the reaction. Keep the resulting beads of lead and tin for the next experiment.

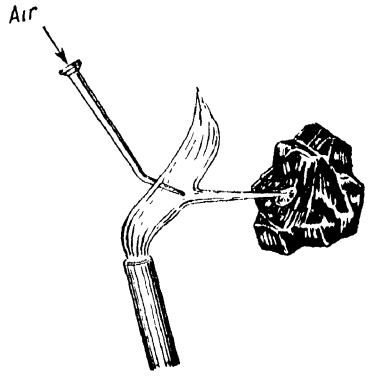


Fig. 71. Reduction on a lump of coal

2. Dissolving Lead and Tin in Acids. (a) Test the action of hot concentrated nitric acid on the bead of lead. What is the gas evolved? Write the relevant equations.

(b) Dissolve the bead of tin in concentrated hydrochloric acid, heating it gently. Write the equation of the reaction that takes place. How is stannic chloride prepared?

3. Electrolytic Tinning. Assemble the apparatus shown in Fig. 69. Clean 40×80 mm copper electrodes thoroughly with fine sandpaper, wash them with water, and wipe them with filter paper. Pour 300 ml of the electrolysis solution into the jar. Immerse 55 mm of the electrodes in the solution and fasten them at a distance of 50 mm from each other. Switch on the current (the voltage should be about 2.2 V, the current intensity 0.2-0.25 A) and conduct electrolysis for 10 min. Then switch off the current, remove the cathode from the solution, wash it in water, and wipe it dry with filter paper.

Polish the dry plate on a felt or cloth polishing wheel. Note the outward appearance of the tin coating. How can this layer be removed from the copper electrode? Dismantle the apparatus.

4. Amphoteric Nature of Stannous and Plumbous Hydroxides. Prepare precipitates of hydroxides from salt solutions containing the Sn^{++} and Pb^{++} ions and prove by experiment that they are amphoteric. Write the equations of all the reactions carried out. Why is plumbous hydroxide usually dissolved in nitric rather than hydrochloric or sulphuric acid? Keep the hydroxystannite solution for the next experiment.

5. Reductant Properties of Sn^{+2} and Pb^{+2}. (a) Prepare a precipitate of bismuth hydroxide by an exchange reaction and add to it the alkaline solution of hydroxystannite prepared in the previous experiment. The white precipitate turns black, owing to the reduction of Bi^{+3} to metallic bismuth. Write the equations of the reactions that have taken place.

(b) Pour 2 ml of a $Pb(CH_3COO)_2$ solution and 3-4 ml of a saturated solution of lime chloride* (CaClOCl) into a test tube and boil the solution. A brown precipitate of lead dioxide is thrown down. Write the equation of the reaction that has taken place. Filter off the precipitate, wash it with hot water several times, and keep it for experiment 10. Why are the salts of bivalent lead not used in practice as reducing agents?

6. Insoluble Compounds of Pb^{+2} and Sn^{+2}. (a) Test solutions of $SnCl_2$ and $Pb(NO_3)_2$ in separate test tubes with the following reagents: sulphuric acid, hydrogen sulphide, and potassium iodide. Do precipitates form in all the test tubes? Note the colours of the precipitates formed. Write the equations of the reactions that have taken place.

(b) Divide the solution with the PbI_2 precipitate into two parts; let the precipitate settle in each test tube and pour off the solution. Add an excess of KI solution to one of them. Observe that the precipitate dissolves. Explain this. Write the equation of the reaction that has taken place. Add 5-10 ml of 2 N CH_3COOH to the precipitate in the other test tube and heat it to boiling point. When it cools, lustrous golden crystals of PbI_2 are precipitated.

(c) Pour off the solution from the SnS precipitate (colour?) and add ammonium polysulphide solution to the precipitate. What happens to the precipitate? Write the equation of the reaction that has taken place. Add 2 N HCl to the solution until litmus paper dipped in the solution exhibits an acid reaction and heat the solution slightly. Observe the formation of a precipitate (colour?). Write the equation of the reaction that has taken place.

(d) Add a solution of potassium chromate and sodium carbonate to the lead salt solution in two test tubes. Note the colours of the precipitates formed in each of them. Write the equations of the reactions that have taken place, bearing in mind that the reaction with sodium carbonate produces a basic lead salt. What are the commercial uses of these products?

7. Preparation and Burning of Stannic Hydride. (This experiment should be conducted in a ventilated hood!) Pour 5-6 ml of concenrtated HCl and10-15 drops of a stannic chloride solution into a crucible; add 2-3 granules of metallic zinc. Stir the contents of the crucible with a test tube half full of cold water. Quickly place the test tube in the flame of a burner: the stannic hydride ignites, producing bright blue scintillations. Write the equations of the reactions that have taken place.

8. Preparation and Properties of Stannic Acid. Add a NaOH solution by drops to a stannic salt solution. Divide the white amor-

* In lime chloride, which has the structural formula $Ca\begin{matrix}O-\overset{+1}{Cl}\\Cl\end{matrix}$, the unipositive chlorine, as a strong oxidising agent, can receive two electrons.

phous precipitate formed, together with the solution, into two parts. Add excess alkali to the part in one test tube, excess acid, to the part in the other. What happens? Write the equations of the reactions that have taken place.

9. Hydrolysis of Stannic Chloride. Inside a ventilated hood open a jar containing liquid stannic chloride. What do you observe? Write the equation of the reaction that takes place. What practical application has the reaction?

10. Oxidant Properties of PbO_2. Pour 5-6 drops of a KI solution and 4 ml of H_2SO_4 into a test tube; add some of the lead dioxide prepared in experiment 5b, introducing it on a glass spatula. Heat the test tube, allow the precipitate to settle, and determine the colour of the solution.

11. Titanium Hydroxide and Its Properties. Add 2 ml of an alkali solution to an equal volume of titanium sulphate solution. What is formed? Write the equation of the reaction that has taken place. Shake the solution with the precipitate and divide it into two parts. Add excess alkali to the part in one test tube; a sulphuric acid solution, to the part in the other. What conclusions may be drawn from these experiments?

12. Reduction of Tetravalent Titanium. Dilute 2 ml of a titanium salt solution with an equal volume of 2 N HCl and lower a bit of zinc into the solution. After a time the solution acquires a violet colour. Write the equation of the reaction that has taken place. Pour off the violet solution into another test tube and note that it loses its colour. Explain this.

13. Preparation of Pertitanic Acid. Add a hydrogen peroxide solution to a slightly acidified solution of a titanium salt and observe the appearance of a yellow-orange colour. Write the equation of the reaction that has taken place.

14. Analysis of a Test Solution. Receive from the instructor a test solution that may contain one of the following ions: $Pb^{\cdot\cdot}$, $Sn^{\cdot\cdot}$, or $Ti^{\cdot\cdot\cdot\cdot}$. Establish by means of the reactions studied which of these ions is present in the solution. Write up the results of the experiment and submit the report to the instructor.

Exercise 28

COLLOIDAL SOLUTIONS

SUBJECTS FOR STUDY

Dispersed systems; colloidal solutions; preparation of colloidal solutions and their distinctive properties; degrees of dispersion; micelles; sols; lyophilic and lyophobic colloids; coagulation, sedimentation, and the causes of the formation of

a precipitate in colloidal systems; gels; mutual coagulation of colloids; reversible and irreversible colloids.

Colloidal solutions occupy an intermediate position among the dispersed systems somewhere between the suspensions and the true solutions: the diameter of the dispersed particles in the liquid phase of a colloidal solution ranges from 1 to 100 mμ*. These solutions can be prepared by two different methods: the *dispersion method* (reducing the size of the particles of coarser dispersed systems, suspensions) and the *condensation method* (increasing the size of the particles of true solutions, in which there is molecular or ionic dispersion of the substance). Colloidal solutions are also called sols. Unlike true solutions, colloidal solutions are *optically inhomogeneous* systems, since a beam of light experiences scattering in them. This accounts for the opalescence of colloidal solutions (their different colours in reflected and transmitted light), which is a distinguishing feature of such systems. The particle size of colloidal solutions of one and the same substance ranging within broad limits, their colour too may differ. Owing to their extremely high degree of dispersion, colloidal solutions exhibit all the phenomena that occur at the interface of two phases, especially the surface absorption of various substances (*adsorption*). One of the products of adsorption from solutions may be molecules of the solvent, specifically water. Colloidal systems in which the particles are subjected to surface hydration by a thin layer of water molecules are called *hydrophobic* (e. g., colloidal metals, sulphides, etc.). *Hydrophilic* colloids are distinguished by the fact that, in addition to surface hydration, their particles bind a large number of water molecules by a "loose" internal structure (e. g., silicic acid, glue, etc.). The particles of a colloidal solution can, in addition to the molecules of water, adsorb ions on their surface. They adsorb from a solution the ions that are part of their composition and that are present in the solution in excess.

Colloids that adsorb positive ions are called *positive* (e. g., the hydroxides of metals), while those that adsorb negative ions are called *negative* (e. g., sulphides and colloidal metals). The colloidal particles with the adsorbed ions are termed *granules*, while with the ions of opposite charge ("counter-ions") linked to the granules they are called *micelles*. The qualitative composition of micelles is illustrated by the following two formulae:

$$\overbrace{\{\underbrace{m\,(As_2S_3)}_{\text{nucleus}}\, n HS' \cdot (n - x)\, H^{\cdot}\}^{-} + x H^{\cdot}}^{\text{micelle of arsenic trisulphide}}$$

$$\underbrace{\qquad\qquad}_{\text{granule}}$$

* mμ is the designation for millimicron, which is a millionth of a millimetre.

micelle of ferric hydroxide

$$\{\underbrace{m\,[Fe(OH)_3]}_{\text{nucleus}}\,n\,FeO^{\cdot}\cdot(n-x)\,Cl'\}^{+}+x\,Cl'$$

granule

An electric current sends the granules moving towards one electrode and the counter-ions towards the other. This migration of colloidal particles under the influence of an electric current is called *cataphoresis*. Through cataphoresis it is possible to determine whether the granules in micelles are positively or negatively charged.

Colloidal solutions are rather stable systems and can be kept for some time without undergoing any change. The relative stability of colloidal systems is governed by the relationship between the forces of attraction, which tend to cause particle growth, and the forces of repulsion preventing this. The repulsion effect is caused by the electrostatic forces arising between the grains, since they carry like charges. In lyophilic colloids, aggregation to larger particles is also prevented by the solvate envelope around the solvent molecules.

When the electric charges of the granules are neutralised, this produces particle aggregation, and the process is known as *coagulation*. The larger particles are precipitated (*sedimentation*). The precipitates formed in the coagulation of colloidal solutions are called *gels*. Lyophilic colloids, when precipitated, retain a relatively large amount of the solvent, forming *jellies*. Substances producing coagulation are referred to as coagulants; these include various electrolytes. When an electrolyte is added, the granule adsorbs oppositely charged ions, which neutralises its charge. The smaller the charge of the coagulating ion, the greater the number of ions required to coagulate the colloid. When two colloidal solutions whose granules are oppositely charged are mixed, *mutual coagulation* of the colloids takes place. To coagulate hydrophilic colloids it is necessary not only to neutralise the charge of the granules, but also to break up the hydrate envelope by dehydrating means (alcohol, concentrated salt solutions). Lyophilic colloids coagulate with much greater difficulty: their addition to hydrophobic colloids increases the stability of these; in other words, the former have a "protective" influence on the latter. Colloids are considered *reversible* if the precipitate formed upon the addition of a solvent can be transferred back into the liquid phase, with the formation of a sol. *Irreversible* colloids are not transferred into the liquid phase upon the addition of a solvent, but can form a sol in the presence of minute amounts of an electrolyte; this phenomenon has come to be known as *peptisation*.

Adsorption processes have numerous technical applications. By means of various adsorbents it is possible to extract dissolved substances

from solutions. In 1903 M. Tsvet established that when a solution containing several substances of different colours is passed through a column with a colourless adsorbent, each substance is adsorbed in a definite part of the column, which produces several zones of different colours. Tsvet named this the *chromatographic method*. Organic resins are today used extensively as adsorbents. Resins that adsorb positive ions (cations) from solutions are called *cationites*, while resins adsorbing negative ions (anions) from solutions are called *anionites*.

QUESTIONS

1. By what methods can a colloidal solution be distinguished from a true solution?
2. What is behind the kinetic and aggregate stability of colloidal solutions?
3. Draw a diagram of the structure of a silver iodide micelle, the colloidal solution having been prepared by the addition of a silver nitrate solution to an excess of a potassium iodide solution. The granule in this case carries a negative charge.
4. A colloidal solution of a certain substance does not coagulate upon the addition of an electrolyte. The addition of alcohol, following the addition of the electrolyte, does cause coagulation. To which type does the colloid belong and what role does alcohol play?
5. The peptisation of stannic acid by hydrochloric acid involves the following process:

$$H_2SnO_3 + 2HCl = 2H_2O + SnOCl_2$$

The resulting stannic oxychloride breaks up into ions:

$$SnOCl_2 \rightleftarrows SnO^{\cdot\cdot} + 2Cl'$$

By means of cataphoresis it has been established that the granules of the stannic acid sol migrate to the negative pole. Draw a diagram of the structure of the stannic acid micelle.
6. What is flotation and what is the mechanism by which it operates?

LABORATORY WORK

Apparatus and materials: adsorption columns shown in Fig. 72; Kipp gas generator for preparing hydrogen sulphide; test tubes and rack; 200 ml Erlenmeyer flask; three 100 ml Erlenmeyer flasks; 50 and 200 ml measuring cylinders; wash bottle; three 100 ml beakers; 100-200 ml flask; 100 ml cylinder with stopper; dropping funnel; porcelain mortar; set of meshes; fluroscein; sulphur sifted aluminium oxide aluminate; 0.25-0.5 mm grain diameter anionite in OH-form; 0.25-0.5 mm grain diameter cationite in H-form; saturated alcoholic solution of sulphur or 2% alcoholic solution of colophony; 8% $SnCl_4$; N HCl; 2 N HNO_3; 1.33% H_3PO_4; 2 N H_2SO_4; 3 N Na_2CO_3; N NaCl; N solution of sodium phosphate; 1% Na_2SO_4; 1% $BaCl_2$; 2% $NiCl_2$; 2% $FeCl_3$; 0.1 M KCl; N $AlCl_3$; 0.05 N $Na_2S_2O_3$; 0.1 N $AgNO_3$;

1.5% $FeCl_3$; 0.5% solution of arsenous oxide; 1% solution of dimethylglyoxime; 6% butyl alcohol solution, and 0.5% gelatin solution.

Preparation of Cationites and Anionites. (a) To prepare a cationite in H-form, the cationite is ground, sifted, and treated with 6-8% HCl until the $Fe^{...}$ and $Fe^{..}$ ions are removed (test with potassium ferri- and ferrocyanide). The cationite is then washed with distilled water to remove acid until it exhibits a neutral reaction in the methyl-orange test.

(b) To prepare an anionite in OH-form, the anionite is ground, sifted, and treated with 6% NaOH (100 ml of solution to 50 g of the anionite); it is then washed with distilled water until its reaction is neutral in the phenolphthalein test.

1. Dispersion Method of Preparing Sols. Add 2-3 drops of a soda solution to half a test tube of distilled water; drop a *tiny* grain of fluorescein into the test tube. Shake the solution and determine its colour in reflected and transmitted light.

2. Condensation Method of Preparing Sols. (a) Add a 2% alcoholic solution of colophony or a saturated alcoholic solution of sulphur by drops to 100 ml of water. This produces an opalescent colloidal solution of colophony or sulphur. What is the colour of the resulting hydrosol?

(b) Pass hydrogen sulphide from the Kipp gas generator slowly, at the rate of one bubble a second, into a beaker containing 50 ml of an 0.5% solution of arsenous oxide diluted by an equal volume of distilled water. After two minutes discontinue the passage of hydrogen sulphide and determine the colour of the sol in reflected and in transmitted light. Write the equation of the reaction between arsenous oxide and hydrogen sulphide. What type of colloid is arsenous sulphide? Draw a diagram of the structure of its micelle.

(c) Heat 50 ml of distilled water to boiling point and add 4-5 ml of 1.5% $FeCl_3$ in three parts, shaking the flask. How does the colour change? Boil the solution for 3-5 min. Write the equation for the hydrolysis of ferric chloride. Draw a diagram of the structure of the micelle of ferric hydroxide sol. What ions does ferric hydroxide adsorb?

Keep the arsenous sulphide and ferric hydroxide sols for further experiments.

3. Change in the Colour of Sulphur Sol. Pour 5 ml each of 1.33% H_3PO_4 and 0.05 N $Na_2S_2O_3$ into a test tube and mix the solution thoroughly. A few minutes later note that the solution acquires a yellow colour in transmitted light (blue in reflected light). Note further changes in the colour of the sol. Why does its colour change? As a result of what reaction was the sulphur formed?

4. Mutual Coagulation of Colloids. Pour equal volumes of the colloidal solutions of arsenous sulphide and ferric hydroxide, prepared in experiment 2, into a test tube. After a time observe the coagulation of the colloidal solutions. What are the substances that form the solid phase?

5. Coagulation of Colloidal Solutions by Electrolytes. (a) Add a sodium phosphate solution by drops from a burette to a colloidal solu-

tion of ferric hydroxide and observe how the solution grows turbid following the addition of each drop. Repeat the experiment, using sodium chloride solution instead of the sodium phosphate. In which case does coagulation take place faster? Why is this?

(b) Carry out a similar experiment with a colloidal solution of arsenous sulphide, adding aluminium trichloride solution to one test tube and sodium chloride to another. In which test tube does coagulation take place faster? Why?

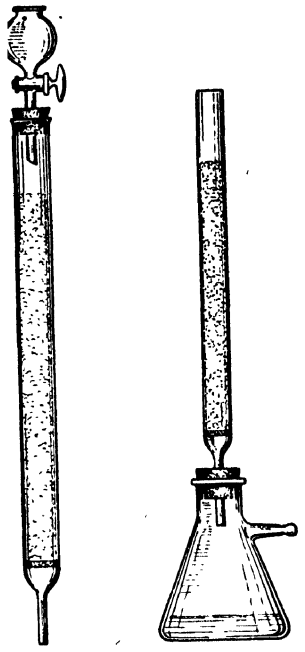


Fig. 72. Adsorption towers

6. Protective Colloids. Add two drops of 0.1 N $AgNO_3$ and four drops of 2 N HNO_3 to 10 ml of distilled water. Stir the solution and divide it into two equal parts, pouring them into test tubes. Add 1 ml of 0.5% gelatin solution to one test tube; and 1 ml of water, to the other. Shake both test tubes thoroughly. Add three drops of 0.1 N KCl to each. Describe the changes observed in the two test tubes and explain why the results differ.

7. Adsorption on Solid Adsorbents in Columns. (a) Adsorption on a cationite. Fill a column 200 mm high and 7-8 mm in diameter with an organic cationite in H-form. Mix 10 ml of 1% $BaCl_2$ and 40 ml of water in a beaker. Add a small amount of a sulphuric acid solution to 2 ml of this solution. What is formed? Pour the rest of the solution into a dropping funnel (Fig. 72) and slowly, by drops, pass it through the column, collecting the solution issuing from the column in a test tube. Test the issuing solution with sulpuric acid: is barium sulphate precipitated? Explain the process that takes place in the column.

(b) Adsorption on an anionite. Fill the column with an organic anionite in OH-form. Mix 10 ml of 1% Na_2SO_4 with 40 ml of water and demonstrate that the sulphate ion is present in the solution. Pass the rest of the solution slowly, by drops, through the column with the anionite. Does the solution issuing from the column contain the SO_4'' ion?

Explain the process that takes place in the column.

(c) Chromatographic separation of ions. Fill the column with aluminium oxide aluminate (see p. 316), first sifted through a sieve with 0.25-0.50 mm diameter orifices. Pass 15 ml of a solution containing 0.2 g each of ferric chloride, cupric sulphate, and cobaltic chloride

through the column, the solution entering the column slowly from a dropping funnel. After a time distinct zones of the adsorbed substances will appear on the aluminium oxide.

According to the colour of the zones determine the order in which the cations chosen have been adsorbed.

8. Flotation. Mix 2 g of powdered sulphur (particle diameter less than 0.25 mm) with 2 g of pure, fine sand. Pour the mixture into a 200 ml cylinder containing 100 ml of water and shake it thoroughly. The whole of the sand and part of the sulphur (oxidised at the surface) sinks. Add 10-12 drops of 5% butyl alcohol to the cylinder and shake it thoroughly. What rises to the surface of the liquid? What are the applications of flotation?

9. Peptisation of Stannic Acid Gel. Heat 50 ml of distilled water to boiling point. Add an 8% solution of $SnCl_4$ by drops to the boiling water until appreciable amounts of a white precipitate have formed. Let the precipitate settle, pour off the solution, and wash the precipitate by decantation with hot distilled water four times. Add 15 drops of N HCl and 100 ml of water to the precipitate; close the flask with a stopper and shake it well. What happens? What is the difference between dissolving a substance and peptisation?

Exercise 29

THE ELEMENTS OF THE FIFTH GROUP OF THE PERIODIC SYSTEM AND THEIR HYDRIDES

SUBJECTS FOR STUDY

The elements of the nitrogen group; their atomic structure and chemical characteristics; nitrogen, phosphorus, arsenic, antimony, and bismuth as simple substances; their preparation.

The hydrides; their electrolytic and reductant characteristics; methods of preparation; ammonia; nitrides and phosphides; ammonium as a complex ion; ammonium salts and their chemical properties; ammoniates.

The elements of the vanadium subgroup: vanadium, niobium, and tantalum; their atomic structure and properties.

The elements of the nitrogen group are nitrogen, phosphorus, arsenic, antimony, and bismuth. In their outermost electron shells the atoms of these elements have five electrons each. Accordingly, they exhibit both reductant and oxidant properties. Their atoms can give up a maximum of five electrons: $R - 5e^- = R^{+5}$. They can also give up fewer electrons, their positive valence in compounds in this case ranging from one to five.

The neutral atoms of the nitrogen group elements can also add three electrons, turning into R^{-3} ions; in this case they act as oxidising agents.

The nitrogen molecule consists of two atoms. The presence of three linking electron pairs :N⁝⁝N: accounts for a certain inertness of molecular nitrogen: at ordinary temperatures it does not react at all. At the expense of external energy the nitrogen molecule may be broken down: $N_2 = N + N - 170$ Cal. Atomic nitrogen is highly reactive. With a rise in temperature, nitrogen begins to combine with certain metals, with hydrogen, and certain other elements.

Phosphorus exists in several modifications. White phosphorus, unlike the other modifications (red, violet, and black), is soluble in carbon disulphide.

Most oxidising agents convert elementary phosphorus to the pentavalent state; oxidation to the trivalent state is rarer.

Arsenic, antimony, and bismuth are readily oxidised by oxygen, upon heating, to form R_2O_3 oxides. The normal potentials of As, Sb, and Bi are positive; in the electromotive series these elements are situated between hydrogen and copper; they do not displace hydrogen from acids, but are oxidised by concentrated nitric acid (As and Bi) and by *aqua regia* (Sb).

The simplest hydrogen compounds of the nitrogen group elements have the general formula RH_3. Ammonia NH_3 is produced commercially primarily by synthesis:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 22 \text{ Cal.}$$

In the laboratory NH_3 is prepared by heating some ammonium salt with an alkali, e. g.:

$$NH_4Cl + NaOH = H_2O + NH_3 + NaCl$$

Phosphine is prepared by the hydrolysis of phosphides or by heating white phosphorus with an alkali solution:

$$Ca_3P_2 + 6HOH = 2PH_3 + 3Ca(OH)_2$$

$$4P + 3H_2O + 3KOH = \overset{-3}{P}H_3 + 3K\overset{+1}{H_2}PO_2$$

In the latter case the other reaction product is potassium hypophosphite, a normal salt of the monobasic phosphinous acid. This is an auto-redox reaction.

AsH_3 and SbH_3 may be prepared by reducing various compounds of arsenic and antimony respectively by nascent hydrogen, e.g.:

$$12H + \overset{+3}{As_2}O_3 = 2\overset{-3\ +1}{As}H_3 + 3H_2O \quad (12e^-)$$

The hydrides of the nitrogen group elements, corresponding to the general formula RH_3, are gases.

These hydrides may be represented by the following formula:

$$\begin{matrix} & & \cdot\cdot & & \\ & H & :\dot{R}: & H & \\ & & \cdot\cdot & & \\ & & H & & \end{matrix}$$

The RH_3 compounds exhibit an insignificant polarity, diminishing from NH_3 to BiH_3. They have a low solubility in water, with the exception of ammonia (1,176 volumes of which dissolve in a single volume of water at N.T.P.). When ammonia dissolves in water, there is a process of interaction between them:

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows [NH_4]^{\cdot} + OH'$$

The resulting solution is faintly alkaline. NH_4OH is sometimes referred to as "ammonium hydroxide". An aqueous solution of ammonia is also commonly known as "ammonia spirit". Its neutralisation by acids produces salts known as ammonium salts.

All ammonium salts are volatile; when heated, they are decomposed in one of the following ways:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

(the gaseous reaction products, upon cooling, recombine, and the reaction is thus reversible)

$$NH_4PO_3 = NH_3 + HPO_3$$

(the acid resulting from the decomposition is nonvolatile)

$$NH_4NO_2 = N_2 + 2H_2O$$

(irreversible decomposition, no ammonia is formed).

Ammonium salts have several properties similar to those of potassium salts, this being due to the approximately equal radii of the $NH_4^{\cdot}$ and $K^{\cdot}$ ions.

Among the other hydrides of the nitrogen group elements only PH_3 forms the complex ion phosphonium $[PH_4]^{\cdot}$. Phosphonium compounds are extremely unstable.

Apart from the $H^{\cdot}$ ion, the positive ions of metals can unite with the NH_3 molecule, forming the complex ions $[\overset{+n}{Me}(NH_3)_x]^{+n}$. Compounds containing this complex ion are called *ammoniates*.

In the general series of hydrides from NH_3 to BiH_3 we observe a rise in reducing power and a decrease in the stability of the compounds and the tendency to form complex compounds (AsH_3, SbH_3, and BiH_3 do not form them at all).

Among the other hydrogen compounds used in the laboratory mention should be made of hydrazine N_2H_4 and hydroxylamine NH_2OH. Both have highly pronounced reductant properties and are ordinarily

used in the form of salts: as the chlorides $N_2H_4 \cdot HCl$ or $NH_2OH \cdot HCl$, or the sulphates $N_2H_4 \cdot H_2SO_4$ or $(NH_2OH)_2 \cdot H_2SO_4$.

In the vanadium—niobium—tantalum subgroup, it is vanadium and its compounds that are most important in practice. The maximum positive valence of these elements, equal to five, is due to the loss of five valence-electrons by their atoms. The atoms of vanadium and tantalum have two electrons in their outermost shells and (8 + 3) electrons in the next shell, while the niobium atom has 1 electron in its outermost shell and (8 + 4) in the next.

The elements of this subgroup, unlike the nitrogen group elements, do not form gaseous hydrides.

Vanadium dissolves in concentrated nitric acid; niobium and tantalum, in a mixture of nitric and hydrofluoric acids.

QUESTIONS

1. By what method was the number of atoms in the molecule of white phosphorus established? Why cannot this method be used for the other modifications of phosphorus?
2. Write the equations for the reactions in which arsenic and bismuth are treated with concentrated nitric acid, and antimony, with *aqua regia*.
3. Air consists of nitrogen, oxygen, and inert gases, containing as admixtures carbon dioxide and water vapour. Give a sequence of reactions for the consecutive chemical separation of all the constituents for isolation of the inert gases.
4. Why is the synthesis of ammonia $N_2 + 3H_2 \rightleftarrows 2NH_3 + 2 \times$ $\times$ 11 Cal. at a pressure of 200 atm conducted at 450° and not at a low temperature?
5. Gaseous ammonia may be prepared by heating a 25% ammonia solution. Draw a diagram of the apparatus required to obtain dry ammonia.
6. Write equations for the following reactions: (a) the preparation of stibine SbH_3, the initial material being $Na[Sb(OH)_6]$, and (b) the decomposition of NH_4NO_2 and NH_4NO_3 by heating.
7. What chemical properties distinguish vanadium from phosphorus?
8. Write the equations for the reactions needed to effect the sequence of transformations:

$$As \rightarrow As_2O_3 \rightarrow AsH_3 \rightarrow As \rightarrow H_3AsO_4$$

Problems

1. What volume of air (at N. T. P.) will be needed for the roasting of 1 ton of bismuthinite, which contains 82% of Bi_2S_3?
2. What volume of ammonia (at N. T. P.) can be obtained by boiling 100 ml of its 25% solution (relative density 0.91)?

3. Determine the titre and molarity of an ammonia solution, knowing that 20 ml of it was needed to neutralise 15 ml of HCl (titre 0.049).

4. Determine the percentage concentration of ammonia in a solution prepared by mixing 20 litres of a 25% ammonia solution (relative density 0.91) with 10 litres of a 5% solution (relative density 0.98).

5. What amount of hydrochloric acid (T = 0.073) is required to neutralise 50 ml of an 8% ammonia solution (relative density 0.967)?

6. What will be the boiling point of a solution containing 4.5 g of NH_4Cl in 75 g of water (degree of ionisation 0.86)?

7. The molar concentrations of hydrogen and ammonia in the system $N_2 + 3H_2 \rightleftarrows 2NH_3$ at equilibrium are 2.56 and 0.84 respectively. Determine the nitrogen concentration, the equilibrium constant being equal to 2.

8. Determine the heat of reaction of the roasting of Sb_2S_3, the heat of formation of Sb_2S_3 being 35.7 Cal., and the heats of formation of Sb_2O_4 and SO_2, 208.9 and 70.9 Cal. respectively.

9. Determine the heat of combustion of PH_3, its heat of decomposition being 2.3 Cal. The heats of formation of P_2O_5 and H_2O are 360 and 68.35 Cal. respectively.

10. A complex compound consists of a calcium ion, ammonia molecules, and chlorine ions. From 2.47 g of this compound it is possible to prepare 1 g of $CaCO_3$; upon heating, it yields 1,792 ml of ammonia. Silver nitrate precipitates 2.868 g of AgCl from the same amount of the compound. Determine the formula of the compound.

LABORATORY WORK

Apparatus and materials: the apparatus shown in Figs. 73 and 74; test tubes and rack; crucible tongs; lid of a porcelain crucible; large crystalliser; 100 or 150 ml beaker; 250 ml beaker; 50 ml measuring cylinder; cylinder with glass cover; four 100 ml flasks; 100 ml measuring bottle; three 100 ml Erlenmeyer flasks; 10 ml pipette; glass spatula; gas-delivery tube with stopper for collecting gases under water; glass vessel; 7 × 7 cm sheets of paper; splints; cotton wool; ammonium chloride; $Ca(OH)_2$; zinc in granules; red phosphorus; concentrated hydrochloric acid; concentrated nitric acid; 1 : 5 H_2SO_4; saturated solution of NH_4Cl; 0.4 N titrated HCl; 2 N KOH; saturated solution of $NaNO_2$; 25% ammonia solution; 0.5 N solution of sodium arsenate; 0.5 N $ZnSO_4$; 0.5 N $NiSO_4$; methyl-orange and phenolphthalein solutions.

1. Preparation of Nitrogen and Its Properties. Pour 5 ml amounts of saturated solutions of ammonium chloride and sodium nitrite into a flask, and close it with a stopper through which a gas-delivery tube has been passed. Immerse the bent end of the tube in a vessel with water (large crystalliser). Fill a cylinder with water, turn it over, and lower it into the vessel. Heat the flask, with a wire gauze under it, and collect the gas in the cylinder (do not collect the first portions of the gas, which contain air!). Remove the cylinder with the gas from the vessel, and introduce a burning splint into it. How can nitrogen be distinguished from carbon dioxide? Write the equations for the reactions by which nitrogen has been prepared.

2. Conversion of Red Phosphorus to White Phosphorus. Place several grains of red phosphorus in a dry test tube, close it with cotton wool, and heat it gently over a small flame, so that the phosphorus is gradually vaporised. What is formed on the cooler parts of the tube?

3. Preparation of Ammonia. The apparatus for preparing ammonia (Fig. 73) consists of a refractory test tube (1), with a stopper and gas-delivery tube connected to an absorption tower (2) filled with glass beads or short lengths of glass tubing. The tower is connected by rubber tubing with a glass tube which is immersed not more than 1 mm deep in the water in a beaker (3).

Pour 10-15 ml of distilled water into the absorption tower (d = 35 mm), moistening the surface of the beads. The level of the water in the tower should be several millimetres below the side tube,

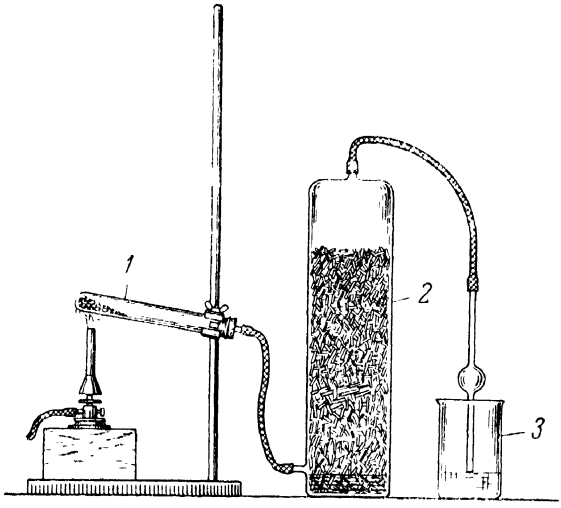


Fig. 73. Apparatus for ammonia preparation
1 — refractory test tube; 2 — absorption tower; 3 — beaker with water.

which is 20 mm above the bottom of the tower. Pour 20 ml of water into the beaker and immerse the delivery tube in it, so that *it barely touches the surface of the water*. Weigh 2 g of NH_4Cl and an equal amount of slaked lime, and mix them on a piece of paper, using a spatula.

Transfer the mixture into the test tube and connect it (in an inclined position) to the apparatus in such a way that the bottom of the test tube is 1-2 cm above its mouth.

Warm the whole of the test tube carefully and then heat it for 20-25 min. When the apparatus has cooled, pour the contents of the absorption tower into a 100 ml measuring bottle. Transfer the solution from the beaker to the absorption tower, washing the beads with it, and collecting it in the measuring bottle. Then wash the absorption tower thrice with 10 ml of water, adding it each time to the solution in the measuring bottle. Bring the level of the solution in the bottle up to the mark and mix it thoroughly.

By means of a pipette transfer 10 ml portions of the solution from the measuring bottle to Erlenmeyer flasks and titrate them with a hydrochloric acid solution of known concentration (0.4-0.5 N). Repeat the titration several times until the results do not differ by more than ± 0.05 ml.

From the titration results determine the weight of the NH_3 contained in the bottle. On the basis of the equation of the reaction calculate the weight of the NH_3 that should be formed from the amount of NH_4Cl taken. Calculate the yield (in %).

Amount of NH_4Cl taken (in g)	NH_3 solution		Amount of HCl solution used up (in ml)				Concentration of HCl (N)
	bottle volume (in ml)	pipette volume (in ml)	I	II	III	average	

4. Equilibrium in Ammonia Solution. Take 10 ml of ammonia solution from the bottle, measuring it in a cylinder, dilute it with a double amount of water, and add 3-4 drops of phenolphthalein to it. Pour the coloured solution into three flasks. Place one flask on a ring with a wire gauze and boil it; add a pinch of solid NH_4Cl to the second flask and shake it. Compare the colour of the solution in all three flasks. Explain the effect of temperature and of the addition of NH_4Cl on the balance of the following reactions:

$$NH_{3\,gas} + aq \rightleftarrows NH_{3\,sol} + 8.35\ Cal.$$

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows [NH_4]^{\cdot} + OH'$$

5. Preparation of Arsine and Its Decomposition. Set up the apparatus shown in Fig. 74. Place 10-15 granules of zinc (containing no arsenic!) in a small flask and close it with a stopper through which a funnel and a gas-delivery tube have been passed. Connect the end of the tube to a special tube with a bent capillary tip. Place the apparatus in a ventilated hood and conduct the rest of the experiment there, since *arsine is an extremely poisonous gas.* Pour sufficient 1 : 5 sulphuric acid into the flask for the tip of the funnel to be immersed in acid (liquid seal). When all the air has been driven out of the apparatus (take a test!), light the hydrogen at the tip of the capillary tube. Now pour 3-4 ml of an arsenic salt solution into the flask through the funnel. How does the colour of the flame change after the addition of the salt? Why is this so? Heat the glass tube, as shown in Fig. 74, and observe

the formation of an "arsenic mirror" on the interior of the tube. What is the practical significance of this reaction?

After the experiment, pour the contents of the flask down *a drain fitted with a ventilated hood.* Dissolve the "arsenic mirror" in a drop of concentrated nitric acid; wash the tube with water. Write the equations for the preparation of arsine, its burning, its decomposition, and for the reaction whereby arsenic dissolves in concentrated nitric acid.

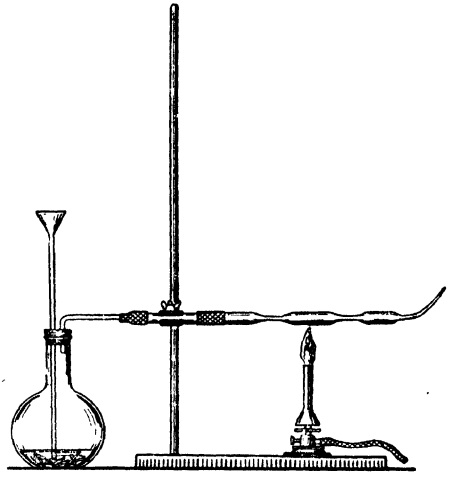


Fig. 74. Apparatus for detecting arsenic

6. Formation of Ammonium Salts. Moisten a glass rod with concentrated hydrochloric acid and bring it close to a jar containing a concentrated ammonia solution. Observe the formation of "smoke". Write the equation of the reaction that has taken place.

7. Decomposition of Ammonium Salts. (a) Place a few grains of ammonium chloride on the lid of a porcelain crucible, pick up the lid with tongs, and heat it in the flame of a burner (in a ventilated hood). Does anything remain on the lid? Write the equation for the reaction of ammonium chloride decomposition. Which two ammonium salts, upon decomposition, yield nitrogen instead of ammonium? Write the equations of these reactions.

(b) Heat a small crucible containing some impure ammonium chloride over a small flame. When white fumes appear over the crucible, place a small funnel over it and continue heating it. After a time a layer of white sublimed ammonium chloride condenses on the inner surface of the funnel. Give a definition of sublimation.

(c) Dissolve a few crystals of ammonium chloride in 2 ml of water, add 2 ml of alkali solution, and heat to boiling point. Identify the gas evolved by its odour.

8. Preparation of Ammoniates. Prepare precipitates of $Zn(OH)_2$ and $Ni(OH)_2$ in two test tubes and add ammonia solution to them. The precipitates dissolve because of the formation of ammoniates. Write the equations of the reactions that have taken place, noting the colours of the precipitates and of the complex compound solutions.

Exercise 30

OXYGEN COMPOUNDS OF THE ELEMENTS OF THE FIFTH GROUP

SUBJECTS FOR STUDY

Positive valence of the nitrogen group elements; oxides of nitrogen, their preparation and chemical properties.

Oxygen compounds of phosphorus, arsenic, antimony, and bismuth; comparison of the oxides of tri- and pentavalent elements; nitric and nitrous acids, their preparation and properties; acids of phosphorus, arsenic, antimony, and bismuth: oxygen compounds of the vanadium subgroup elements.

The elements of the nitrogen group exhibit positive valences equal to 5, 4, 3, 2, and 1 in their oxygen compounds. The most general oxide formulae are R_2O_3 and R_2O_5. The oxides corresponding to the maximum valence of the element are acid anhydrides. The oxides N_2O_5 and Bi_2O_5 form only meta-acids of the composition HNO_3 and $HBiO_3$. Three types of acids correspond to the pentoxides of phosphorus, arsenic, and antimony: the meta-acid HRO_3, the pyro-acid $H_4R_2O_7$, and the ortho-acid H_3RO_4.

In the series HNO_3-HPO_3-$HAsO_3$-$HSbO_3$-$HBiO_3$ acidity decreases.

The most important acids practically are nitric acid HNO_3 and orthophosphoric acid H_3PO_4.

Other acids that have practical applications are fuming nitric acid (relative density 1.55), concentrated nitric acid (relative density 1.41) with a 67.5% HNO_3 content, and 1 : 1 dilute nitric acid (relative density 1.2) with a 32.36% HNO_3 content.

Nitric acid is one of the strongest acids: an 0.1 N solution has a 93% degree of ionisation.

The pentapositive nitrogen in the NO_3' radical possesses highly pronounced oxidant properties and can add from 1 to 8 electrons, depending upon the concentration of the acid and the nature of the reducing agent:

$$\overset{+5}{N}O_3' + 1e^- + 2H^+ = \overset{+4}{N}O_2 + H_2O \quad (1)$$

$$\overset{+5}{N}O_3' + 3e^- + 4H^+ = \overset{+2}{N}O + 2H_2O \quad (2)$$

$$2\overset{+5}{N}O_3' + 8e^- + 10H^+ = \overset{+1}{N}_2O\,^* + 5H_2O \quad (3)$$

$$2\overset{+5}{N}O_3' + 10e^- + 12H^+ = \overset{0}{N}_2 + 6H_2O \quad (4)$$

$$\overset{+5}{N}O_3' + 8e^- + 10H^+ = \overset{-3}{N}H_4^+ + 3H_2O \quad (5)$$

* Nitrogen is in this compound tentatively assumed to be univalent.

The more water the nitric acid contains, the further its reduction proceeds. Some metals, situated below hydrogen in the electromotive series, react with concentrated nitric acid according to (1); with dilute acid, according to (2). More active metals, such as zinc, magnesium, and calcium, reduce nitric acid according to (3); very dilute acid is reduced by them to ammonia, which reacts with the excess acid to form ammonium salts. Metals of medium activity, such as iron, nickel, cobalt, and tin, react according to (2), or according to (5) if the acid is very dilute; cobalt in these conditions reacts according to (4). Most nonmetals reduce nitric acid according to (2).

The reduction of HNO_3 is usually accompanied by parallel reactions yielding a mixture of reduction products: NO_2, NO, etc. The above five reactions illustrate only some reduction processes.

Nitric acid does not react with gold, platinum, iridium, or rhodium. Pure iron, aluminium, and chromium do not dissolve in concentrated nitric acid without heating because they are made "passive" by the formation of an oxide film on the surface of the metal.

All *nitrates*, i. e., salts of nitric acid, are soluble in water.

The acids of pentavalent phosphorus are derivatives of the anhydride P_2O_5, which is a white powder with an extraordinary avidity for water. Its interaction with cold water at first produces metaphosphoric acid, which upon lengthy storage or heating turns into orthophosphoric acid:

$$HPO_3 + H_2O = H_3PO_4$$

Orthophosphoric acid is produced either by the action of concentrated sulphuric acid upon calcium phosphate

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

or by the oxidation of phosphorus by concentrated nitric acid when boiled

$$3P + 5HNO_3 + 2H_2O = 3\overset{+5}{H_3PO_4} + 5\overset{+2}{NO}$$

(P → $\overset{+5}{H_3PO_4}$: $15e^-$; $\overset{+5}{N}$ → $\overset{+2}{N}$)

Orthophosphoric acid is an acid of medium strength. The R_2O_3 oxides are solid substances, except for N_2O_3, which is a liquid. Their chemical nature differs: N_2O_3 and P_2O_3 are acidic, As_2O_3 and Sb_2O_3 are amphoteric, and Bi_2O_3 is basic.

The hydroxides exhibit the following properties: HNO_2 and H_3PO_3 are acids, the hydroxides of arsenic and antimony are amphoteric, and $Bi(OH)_3$ is a typical base.

Nitrous acid is a weak acid; it is known only in dilute solutions. The acid displays both oxidant and reductant properties (undergoing reduction to NO or oxidation to HNO_3).

At high concentrations, owing to the reaction of disproportionation, nitrous acid decomposes according to the equation:

$$3\overset{+3}{H}NO_2 = \overset{+5}{H}NO_3 + 2\overset{+2}{N}O + H_2O$$

Because of the instability of HNO_2, its salts, *nitrites*, are used in practice.

Orthophosphorous acid H_3PO_3 (or H_2HPO_3) is dibasic, and only two of its hydrogen atoms are replaceable. It is a strong reducing agent.

As pointed out above, both $As(OH)_3$ and $Sb(OH)_3$ are amphoteric hydroxides; in the former case, however, acidic properties are more pronounced, while in the latter case basic properties predominate. The electrolytic dissociation of $Sb(OH)_3$ follows the equations:

$$Sb''' + 3OH' \rightleftarrows Sb(OH)_3 \rightleftarrows 3H^{\cdot} + SbO_3'''$$
$$\downarrow\uparrow$$
$$H_2O$$
$$SbO^{\cdot} + OH' \rightleftarrows \overset{+}{H}SbO_2 \rightleftarrows H^{\cdot} + SbO_2'$$

Antimonous acid H_3SbO_3, upon dehydration, gives up a molecule of water to become metaantimonous acid $HSbO_2$, which, apart from dissociating according to the acidic pattern, can ionise like a base, with the formation of the compound cation $SbO^{\cdot}$, called antimonyl.

Bismuth hydroxide $Bi(OH)_3$ is a base that can, in the process of ionisation, give up a molecule of water to form the ion $BiO^{\cdot}$, bismuthyl.

Nitric oxide NO is a colourless gas with neither acidic nor basic properties. In the laboratory it is prepared by treating copper with dilute nitric acid. Nitric oxide is a vigorous reducing agent and when exposed to the air is oxidised to NO_2, which is a brown gas. The NO molecule is polar, and nitric oxide is encountered as an addendum in a number of complex compounds.

Nitrogen dioxide NO_2 is prepared by the oxidation of nitric oxide or by the action of concentrated nitric acid on copper. When cooled, NO_2 is converted to the colourless tetroxide:

$$2NO_2 \rightleftarrows N_2O_4 + 13.6 \text{ Cal.}$$

From the standpoint of its chemical properties, the dioxide is acidic (a mixed anhydride of nitrous and nitric acids) and dissolves in water to form those acids:

$$2\overset{+4}{N}O_2 + H_2O = \overset{+5}{H}NO_3 + \overset{+3}{H}NO_2$$

Nitrous oxide N_2O is a colourless gas formed in the thermal decomposition of ammonium nitrate.

The most typical compounds of vanadium, niobium, and tantalum are those in which they are pentavalent. Their pentoxides are anhydrides, whose acidic character becomes less pronounced from vanadium to tantalum.

Vanadic anhydride reacts with alkali solutions, like the pentoxide of phosphorus, to form three types of salts: ortho-, pyro-, and meta-vanadates. The meta-vanadates are the most stable of these. When a colourless solution of ammonium meta-vanadate NH_4VO_3 is reduced by nascent hydrogen, a change in the colour of the solution makes it possible to observe the consecutive reduction of V^{+5} to compounds of lower valence.

The vanadium compounds of the intermediate valences V^{+4}, V^{+3}, and V^{+2} have definite colours: blue, green, and violet.

Meta-vanadic acid (or its salts in acid solution) react with hydrogen peroxide to form pervanadic acids, which have the composition $H_4V_2O_x$ ($x > 7$). They are orange or reddish brown and decompose gradually, with the evolution of oxygen.

QUESTIONS

1. Write the equations for the reactions whereby nitric acid is prepared from the nitrogen of the air.
2. Write one equation for each of the reactions of the oxidation of various reducing agents by nitric acid given schematically on p. 243.
3. Write the structural formulae of the acids formed by phosphoric anhydride and water.
4. Explain the difference in the properties of $P(OH)_3$ and $Bi(OH)_3$ in terms of ion radii.
5. On the assumption that the valence of nitrogen in NO_2 is $+4$, explain the process of its interaction with H_2O.
6. Write the equations for reactions effecting the following consecutive transformations:

$$V \rightarrow V_2O_5 \rightarrow NH_4VO_3 \rightarrow NaVO_3 \rightarrow HVO_3$$

7. In the reduction of vanadic acid by hydrogen iodide the solution, after boiling (to remove the iodine formed), acquires a green colour. Write the equation of the reaction that takes place.

Problems

1. A 120 ml mixture of the two gases NO and NO_2 is mixed with 100 ml of oxygen. Following the reaction, the mixture is found to contain 60 ml of oxygen. Determine the percentage composition of the initial mixture in terms of volume and weight.
2. The weight of 550 ml of an oxide of nitrogen, measured at 27.3° and $p = 770$ mm, is 1.04 g. Determine its molecular weight and its density in terms of air.

3. The heating of a certain amount of sodium nitrite with a 20% solution of ammonium chloride produces 5.57 litres of nitrogen, measured at 27° and $p = 750$ mm. Determine the amounts of sodium nitrite and of the 20% NH_4Cl that were involved in the reaction.

4. What volume of nitric acid (relative density 1.2) can be prepared from 1,000 cu m of air by the ammonia method if the ammonia synthesis process has a yield of 15.8%, while the other stages of the process follow the equations of corresponding reactions?

5. Red phosphorus contains 2.6% of moisture. What amount (by weight) of nitric acid (relative density 1.41) will be needed to oxidise 100 g of the phosphorus and how many litres of nitric oxide will be evolved?

6. How many grams of KNO_2 are needed for the complete reduction of 400 ml of 0.1 M $K_2Cr_2O_7$ in an acid solution?

7. It is necessary to prepare 1 kg of $NaNO_3$ by recrystallisation from an unpurified product containing 2.7% of KCl. What amounts of the initial product and of water have to be taken, considering that at 100° the solubility of $NaNO_3$ is 63.5%, while at 10° it is 44.6%? The solution saturated at 100° is cooled to 10°.

8. The absorption coefficient of ammonia at 20° is 702. Determine the percentage concentration of an NH_3 solution saturated at 20° and the amount of nitric acid solution (relative density 1.2) needed to neutralise 500 g of the ammonia solution.

9. What will be the freezing point of a solution containing 2.2 g of K_3PO_4 in 100 g of water if $\alpha = 62\%$ for the salt?

10. What products, and in what amounts, are needed to prepare 50 g of tantalic fluoride TaF_5?

LABORATORY WORK

Apparatus and materials: a П-shaped glass apparatus filled with nitrogen dioxide; test tubes and rack; gas-delivery tube with stopper; crucible tongs; wash bottle; porcelain casserole; 25 ml measuring cylinder; two cylinders with glass covers; 100 ml flask; 250 ml measuring bottle; two 400 ml beakers; three 100 ml Erlenmeyer flasks; 20-25 ml pipette; large crystalliser; glass rod; zinc in granules; copper turnings; red phosphorus; recrystallised ferrous sulphate; coal in lumps; fuming nitric acid; nitric acid of relative density 1.41; 1 : 1 nitric acid; concentrated and 2 N sulphuric acid; 2 N hydrochloric acid; 0.5 N $Bi(NO_3)_3$; 0.1 N $AgNO_3$; 0.1 N titrated and 2 N NaOH; saturated solution of sodium nitrite; saturated solution of ferrous sulphate; 0.5 N solution of antimonic chloride; N H_3PO_4; N HPO_3; N $H_4P_2O_7$; 0.5 N solution of ammonium meta-vanadate; N KSCN; 3% H_2O_2; 0.5 N Na_3PO_4; 0.5 N $Na_4P_2O_7$; 0.5 N $NaPO_3$; albumen solution; diphenylamine solution; litmus and methyl-orange solutions; table salt, and ice.

Preparation of Albumen Solution. Shake the white of a raw egg with 200-250 ml of distilled water.

Preparation of Diphenylamine Solution. Shake 0.5 g of diphenylamine with 20 ml of water and gradually add 100 ml of concentrated chemically pure sulphuric acid.

1. Preparation of Phosphoric Acid. Weigh about 0.2 g of red phosphorus to 0.01 g in a porcelain casserole. Measure 10-12 ml of concentrated nitric acid in a cylinder. Moisten the red phosphorus in the casserole with a few drops of water and add the acid in 2-3 ml portions (in a ventilated hood), mixing thoroughly with a glass rod. Heat the casserole with the mixture over a weak flame. Add each new portion of acid only when the evolution of the brown fumes of nitrogen dioxide has ceased.

When all the nitric acid has been added, heat the casserole for 10-15 minutes on a gauze with an asbestos centre over a small flame

(in a ventilated hood). The reaction is considered complete when the evolution of the brown fumes of nitrogen dioxide has ceased and all the phosphorus has dissolved. Pour the resulting solution into a 250 ml measuring bottle, washing the remains of the solution from the casserole into the bottle with the help of a wash bottle. Add water, bringing the level of the solution up to the bottle mark; mix the solution well.

2. Determination of the Phosphoric Acid Yield. Transfer full pipettes of the resulting solution to three Erlenmeyer flasks and titrate at least three times with 0.1 N NaOH solution in the presence of methyl-orange. Record the titration results as follows:

Pipette volume in ml	Amount of NaOH used (in ml)				Concentration of NaOH solution (N)
	I	II	III	average	

From the average volume of sodium hydroxide solution used for the titration, calculate the amount of the acid contained in the measuring bottle, it being assumed that the reaction follows the equation:

$$H_3PO_4 + NaOH = H_2O + NaH_2PO_4$$

Calculate the amount of phosphoric acid that should be formed by the oxidation of the amount of phosphorus taken initially. On the basis of these data determine the yield in per cent.

3. Oxidant Properties of Nitric Acid. (a) Fasten a test tube containing 2-3 ml of fuming nitric acid in a vertical position and heat it carefully in a ventilated hood. Drop a bit of smouldering coal into the hot acid carefully. Observe the burning of the coal and the evolution of brown fumes of NO_2. Write the equation of the reaction that has taken place.

(b) Dissolve 3-4 crystals of a freshly recrystallised ferrous salt in 5 ml of distilled water. Divide the solution in half, pouring the two halves into two test tubes. Add 5 drops of concentrated nitric acid to one of them and boil the solution for 2-3 min. When it has cooled, add a few drops of potassium thiocyanate solution to both test tubes. In which test tube does the solution turn dark red? Write equations of all the reactions that have taken place. What part does nitric acid play?

4. Reaction for Detecting Nitric Acid. (a) Pour 1 ml of a saturated solution of ferrous sulphate and 3 ml of concentrated sulphuric acid into a test tube, stir the mixture, and cool it. Incline the test tube

with the cooled mixture and carefully add 1-2 ml of 1 : 1 nitric acid, allowing the acid to trickle down the wall of the test tube.

Where the two liquids come into contact there forms a brown ring of the complex compound $[Fe(NO)]SO_4$. Write the equation of the reaction in two stages: the reduction of HNO_3 to NO and the formation of the complex. The reaction serves to detect HNO_3 in the absence of HNO_2.

(b) Add a few drops of a nitric acid solution to 2-3 ml of a diphenylamine solution in concentrated sulphuric acid. Note that the solution acquires a blue colouration (reaction to detect HNO_3 in the absence of other oxidising agents).

5. Phosphoric Acids. Pour 2 ml of an orthophosphoric acid solution into each of two test tubes; 2 ml of a metaphosphoric acid solution, into each of two others, and 2 ml of a pyrophosphoric acid solution, into each of still another pair.

To each of three test tubes containing solutions of different acids, add an equal volume of albumen solution. Which of the acids coagulates the albumen, and why is this so?

To each of the other three test tubes, add 1 ml of $AgNO_3$ solution. Do precipitates form? Instead of the acids, pour solutions of their salts into three test tubes and test them with an $AgNO_3$ solution. Note the colour of the precipitates formed. Why does $AgNO_3$ produce no precipitates with the prosphoric acids, while it does produce precipitates with their salts?

6. Formation of Nitrous Acid and Its Decomposition. Add dilute sulphuric acid to 3-4 ml of a concentrated $NaNO_2$ solution. The solution acquires a bluish green colour, which can be observed against the background of a sheet of white paper. A mixture of nitrogen oxide and dioxide forms over the solution. Write the equations of the reactions that have taken place.

7. Preparation of Hydroxides of Antimony and Bismuth. By means of exchange reactions prepare precipitates of the hydroxides of antimony and bismuth (write corresponding equations). Establish by experiments which of these hydroxides is amphoteric. Write the equations of the reactions carried out.

8. Preparation of Nitrogen Oxide and Dioxide. (a) (Conduct the experiment in a ventilated hood!). Place some copper turnings in a flask, pour 20 ml of 1 : 1 HNO_3 into the flask, and close it with a stopper, through which a gas-delivery tube, immersed in a vessel with water, has been passed. Place the end of the gas-delivery tube under a cylinder filled with water. Fill two cylinders with the gas.

(b) Cover one of the cylinders with a glass, remove it from the vessel, and, lifting the cover slightly, observe the formation of brown fumes. Explain what takes place. Cover the cylinder again, turn it over, and immerse it in the vessel. Once the cylinder is under water, remove the cover; after a time observe water being "drawn" into the

cylinder. Why does this happen? Test the solution in the cylinder with litmus. Write the equations of the reactions that have taken place: the preparation of nitrogen oxide, its oxidation, and the interaction of nitrogen dioxide with water.

(c) Pour half a test tube of ferrous sulphate solution swiftly into the second cylinder, lifting its cover, then cover it again, and shake the solution with the gas. Why does the solution grow darker? Write the equation of the reaction that has taken place.

9. Polymerisation of Nitrogen Dioxide. Receive from the laboratory assistant an apparatus consisting of two glass bulbs connected by a glass tube and filled with nitrogen dioxide, the brown gas. Place one of the bulbs in a beaker with a cooling mixture (ice and table salt); the other, in a beaker with hot water. After 4-5 minutes remove the apparatus from the beakers and compare the intensity of the colouration of the gas in the two bulbs. Put the apparatus in the beakers again, but this time lower the heated bulb into the cooling mixture, while the cooled bulb goes into the hot water. Observe the changes that take place and explain them.

10. Reduction of Pentavalent Vanadium. Add 2 ml of 2 N HCl to an equal volume of an ammonium meta-vanadate solution; drop 2-3 small granules of zinc into the solution. Observe the change in the colour of the solution first to blue, then to green, and finally to violet. Write the equations of the reactions that have taken place.

11. Formation of Pervanadic Acid. Add dilute sulphuric acid to an ammonium meta-vanadate solution; then add a hydrogen peroxide solution by drops. The solution acquires an orange-red colour, typical of pervanadic acid. Write the equation for the reaction by which $H_4V_2O_8$ is formed.

12. Anion Detection. Receive from the instructor a test solution containing one of the following anions: NO_2', NO_3', PO_4''', or VO_3'. By means of the reactions studied earlier establish the presence of a definite anion in the solution. Submit your results to the instructor.

Exercise 31

OXYGEN COMPOUNDS OF ELEMENTS OF THE FIFTH GROUP (continued)

SUBJECTS FOR STUDY

Compounds corresponding to the general formulae RX_3 and RX_5; their properties; hydrolysis of salts of antimony and bismuth; antimonyl and bismuthyl ions; sulphides and thiosalts.

Nitrites, phosphites, and arsenites; their preparation; nitrous acid salts as reducing and oxidising agents; sodium arsenite; its reductant properties.

Nitrates; their preparation and properties; nitres; phosphates and hydrophosphates; heteropolyacids of phosphorus and arsenic; their salts; bismuthates.

The most important of the compounds corresponding to the general formulae RX_3 and RX_5 are the halides, such as PCl_3, PI_3, PCl_5, $SbCl_3$, $AsCl_3$, PBr_3, and $BiCl_3$, as well as bismuth nitrate $Bi(NO_3)_3$. All these compounds readily undergo hydrolysis, e. g.:

$$SbCl_3 + 2HOH \rightleftarrows Sb(OH)_2Cl + 2HCl$$
$$\downarrow\uparrow$$
$$H_2O + SbOCl$$
$$PCl_3 + 3HOH \rightarrow 3HCl + H_3PO_3$$
$$PCl_5 + HOH \rightarrow 2HCl + POCl_3$$
$$PCl_5 + 4HOH \rightarrow 5HCl + H_3PO_4$$

The compounds $SbCl_3$ and $BiCl_3$ are typical salts; they undergo reversible hydrolysis, forming a basic chloride and an acid. The halogen compounds of phosphorus belong to a special class of compounds called acid halides and undergo hydrolysis practically irreversibly, forming two acids.

Two types of salts of bismuth and antimony should be distinguished: normal salts, such as $Bi(NO_3)_3$ and $SbCl_3$, and basic salts containing the radicals bismuthyl and antimonyl (e. g., $BiONO_3$ and SbOCl). The compounds of antimonyl and bismuthyl dissolve in water poorly.

The reactions of $AsCl_3$, $SbCl_3$, and $BiCl_3$ with hydrogen sulphide produce sulphides that are insoluble in water or dilute acids and are yellow, orange, and brown respectively. The sulphides As_2S_3 and Sb_2S_3 dissolve in ammonium sulphide and ammonium polysulphide solutions to form thiosalts (unlike Bi_2S_3).

The salts of nitrous acid, *nitrites*, exhibit both oxidant and reductant properties in chemical reactions (see Exercise 16). Similar properties, but less pronounced, are exhibited by phosphites and arsenites. A reducing agent used in the laboratory is sodium metaarsenite $NaAsO_2$:

$$\overset{+3}{NaAsO_2} + I_2 + Na_2CO_3 + H_2O = \overset{+5}{NaH_2AsO_4} + 2\overset{-1}{NaI} + CO_2 \quad (-2e^-)$$

The salts of nitric acid, *nitrates*, are soluble in water. The most important nitrates are a group known as nitres: sodium nitre, or Chile saltpetre, $NaNO_3$; potassium nitre, or saltpetre, KNO_3; ammonium nitre NH_4NO_3, and calcium nitre $Ca(NO_3)_2$.

When heated (in dry reactions) and in alkaline solutions all nitrates act as oxidising agents. According to the manner in which they

decompose upon heating, nitrates may be divided into three groups.

(1) those that decompose to form oxygen and nitrites (the nitrates of the alkali metals):

$$2KNO_3 = O_2 + 2KNO_2$$

(2) those that decompose to form oxygen, an oxide of the metal and nitrogen dioxide (nitrates of metals other than the alkali and the noble metals):

$$2Pb(NO_3)_2 = O_2 + 2PbO + 4NO_2$$

(3) those that decompose to form oxygen, nitrogen dioxide, and a metal (nitrates of noble metals):

$$2AgNO_3 = O_2 + 2NO_2 + 2Ag$$

Nitrates are reduced to ammonia by some metals (Na, Ca, Mg, Al, Zn, and others) in an alkaline solution:

$$4Zn + \overset{+5}{K}NO_3 + 7KOH = \overset{-3}{N}H_3 + 4K_2\overset{+2}{Z}nO_2 + 2H_2O$$

Three types of salts — orthosalts Me_3RO_4, metasalts $MeRO_3$, and pyrosalts $Me_4R_2O_7$— correspond to the three forms of phosphoric, arsenic, and antimonic acids. Among the normal salts the salts of the alkali metals and ammonium are soluble. Calcium orthophosphate $Ca_3(PO_4)_2$ has a poor solubility in water, but treatment with strong acids converts it to the acid water-soluble salts $CaHPO_4$ and $Ca(H_2PO_4)_2$. The heating of primary sodium phosphate (or mono-sodium phosphate) NaH_2PO_4 and of secondary sodium phosphate (or di-sodium phosphate) Na_2HPO_4 yields meta- and pyrophosphates. Sodium metabismuthate $NaBiO_3$ can be prepared by fusing bismuth oxide with sodium peroxide or by oxidising bismuth oxide by chlorine in an alkaline solution. The salt is used in an acid solution as a strong oxidising agent.

Heteropoly acids are acids whose anion is a complex group in which the positive central atom R^{+n} is surrounded in the coordination sphere by acid radicals of the $Me_2O_7^{--}$ and MeO_4^{--} type; their composition is expressed by the general formula

$$H^+_{12-n}[R^{+n}(Me_2O_7)_6^{--}]^{-(12-n)}$$

or

$$H^+_{12-n}[R^{+n}(MeO_4)_6^{--}]^{-(12-n)}$$

$$\overset{+3}{B},\ \overset{+4}{Si},\ \overset{+5}{P},\ \overset{+5}{As}$$

The central atoms R^{+n} may be B, Si, P, As, etc. The $Me_2O_7^{--}$ ions may be the acid radicals $W_2O_7^{--}$, $Mo_2O_7^{--}$, etc., and the MeO_4^{--} ions may be the acid radicals WO_4^{--} and MoO_4^{--}. For instance, the acid $H_7[P(Mo_2O_7)_6]$ is called phospho-molybdic acid, while $H_7[As(Mo_2O_7)_6]$ is known as arseno-molybdic acid. The ammonium salts of these acids

are of yellow colour and are insoluble in water; they can be prepared by treating phosphates (in the cold) and arsenates (upon boiling) with "molybdenum liquor", which is a solution consisting of ammonium molybdate and nitric acid. The reaction of precipitation follows the equation:

$$Na_2HPO_4 + 12\,(NH_4)_2\,MoO_4 + 23HNO_3 = (NH_4)_3H_4\,[P(Mo_2O_7)_6] + \\ + 21NH_4NO_3 + 2NaNO_3 + 10H_2O$$

QUESTIONS

1. When $BiCl_3$ is dissolved in water, hydrolysis produces a white precipitate: bismuthyl chloride. Write the equation of the hydrolysis reaction. What should be added to the water to prevent the formation of BiOCl?
2. What processes take place when NaCl, $CaCl_2$, $AlCl_3$, and PCl_3 are dissolved in water? To what class does each of these compounds belong?
3. Write the equations for the reactions that take place when Sb_2S_3 is dissolved in a $(NH_4)_2S$ solution and in a $(NH_4)_2S_2$ solution.
4. Write the equation for the reaction whereby $NaNO_3$ is reduced by metallic aluminium in an alkaline solution, taking into account the amphoteric nature of $Al(OH)_3$.
5. How can meta- and pyrophosphates be prepared from orthophosphates?
6. Write the structural formulae of the primary, secondary, and tertiary calcium salts of orthophosphoric acid.
7. Write the formulae of two heteropoly acids: silico-molybdic acid and boro-tungstic acid.

Problems

1. How much sodium peroxide is needed to oxidise 23.2 g of bismuth oxide to sodium bismuthate?
2. The burning of gunpowder follows the approximate equation:

$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2$$

How many litres of gas, reduced to N. T. P., will be evolved by the burning of 100 g of gunpowder?

3. Determine the percentage and the molar concentration of a solution prepared by mixing 24 litres of 16% KNO_2 (relative density 1.102) and 16 litres of 6% KNO_2 (relative density 1.036).
4. How much water has to be evaporated from 50 litres of 9% KNO_3 (relative density 1.056) to prepare a solution saturated at 20°, the solubility of KNO_3 at that temperature being 24.1%?
5. The solubility of $Na_4P_2O_7 \cdot 10H_2O$ at 80° is 23.1%, while at 0° it is 3.1%. What amount of the salt (in terms of the anhydrous product) will be precipitated when 10 kg of a solution saturated at 80° is cooled with snow?

6. Determine the percentage content of As_2O_3 in a saturated aqueous solution, knowing that 10 g of the solution requires 15.76 ml of 0.1 N iodine solution for oxidation in a slightly alkaline solution.

7. Determine the vapour tension at 100° of a solution prepared by dissolving 10.1 g of KNO_3 in 180 g of water, the apparent degree of ionisation of the salt being 0.86.

8. Determine α% for an 0.001 M solution of arsenous acid, taking into account the first step in its electrolytic dissociation ($K = 5.8 \cdot 10^{-10}$).

9. Plates of corresponding metals are immersed in unimolar solutions of zinc nitrate and lead nitrate; a voltaic cell is made up of these couples. Determine the e. m. f. of the cell and the number of coulombs of electricity that will have passed through the circuit if the weight of the zinc plate has diminished by 4.2 g.

10. The side of a match-box contains 30.8% of red phosphorus. The phosphorus from 0.5 of g the match-box side was converted to the phosphate ion and precipitated fully by "molybdenum liquor" as an ammonium salt of phospho-molybdic acid. What amount of the salt was obtained in the dry state?

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 75; test tubes and rack; crucible tongs; funnels; porcelain casserole; three porcelain crucible lids; asbestos millboard; spatula; paper; litmus paper; filter paper; chromic oxide; powdered aluminium; powdered zinc; potassium permanganate; primary sodium phosphate; secondary sodium phosphate; phosphorus trichloride; phosphorus pentachloride; powdered sulphur; powdered coal; powdered potassium nitrate; crystalline potassium nitrate; 1 : 1 mixture of crystalline potassium nitrate and potassium carbonate; 30% KOH; concentrated and 2 N HCl; 2 N H_2SO_4; 0.5 N KI; saturated solution KNO_3; N Na_3PO_4; N solution of primary sodium orthophosphate; N solution of secondary orthophosphate; 2 N solution of ammonium sulphide; 0.5 N $BiCl_3$; 0.5 N $Bi(NO_3)_3$; 0.5 N $MnSO_4$; N $K_2Cr_2O_7$; N KNO_3; saturated solution of sodium bicarbonate; 1% iodine solution; 0.5 N solution of sodium arsenite; 0.5 N solution of sodium arsenate; neutral litmus solution; hydrogen sulphide water, and "molybdenum liquor".

Preparation of "Molybdenum Liquor". Dissolve 42 g of ammonium molybdate in a mixture of 70 ml of 25% ammonia solution and 140 ml of water; pour the resulting solution carefully into a mixture of 250 ml of nitric acid (relative density 1.4) and 500 ml of water and dilute with water to 1 litre.

1. Hydrolysis of Phosphorus Trichloride and Pentachloride. Pour 5 ml of water into each of two test tubes. Add 2-3 drops of phosphorus trichloride from a dropping bottle to one of them; drop some solid phosphorus pentachloride into the other, using a glass spatula. By means of an indicator test the acidity of the solutions. Write the equations of the reactions that have taken place.

2. Hydrolysis of Antimony and Bismuth Salts. Pour 15-20 drops each of $SbCl_3$ and $BiCl_3$ respectively into two test tubes and add water until precipitates form. Write the equations of the reactions that have taken place. Add a few drops of concentrated hydrochloric acid. What happens to the precipitates? Give an explanation, using the equation for the equilibrium constant.

3. Hydrolysis of Orthophosphates. Pour 3 ml of 0.5 N solutions of Na_3PO_4, Na_2HPO_4, and NaH_2PO_4 respectively into three test tubes and add 2 ml of a neutral litmus solution to each of them. Write the

equations of the reactions that have taken place and explain why the colour of the litmus changes differently in the three solutions. Which salt undergoes hydrolysis to a greater extent: Na_2HPO_4 or Na_2HAsO_4? Why is this so?

4. Preparation of Sulphides. By treating solutions of the salts of trivalent arsenic, antimony, and bismuth, acidified with hydrochloric acid, with hydrogen sulphide water, prepare sulphide precipitates. Write the equations of the reactions that have taken place and note the colours of the precipitates formed. Why do the solutions have to be acidified?

5. Preparation of Thiosalts. Carefully pour the solutions off from the precipitates prepared in the previous experiment and add an ammonium sulphide solution to each of the the precipitates. Write the equations of the reactions whereby As_2S_3 and Sb_2S_3 are dissolved. Treat the thiosalt solutions with hydrochloric acid and heat them slightly. Observe the formation of precipitates and write the equations of the reactions that have taken place. Why does Bi_2S_3 form no thiosalts?

6. Reductant Properties of Nitrites. Add 3-4 ml of a potassium nitrite solution and 3 ml of a sulphuric acid solution to 1 ml of a $K_2Cr_2O_7$ solution and heat it slightly. Observe a change in the colour from orange to green. Write the equation of the reaction that has taken place.

7. Oxidant Properties of Nitrites. Establish by experiment that potassium nitrite is an oxidising agent with respect to an acidified potassium iodide solution. What changes are observed in conducting this reaction? Write the equation of the reaction. By making use of the table of redox potentials, determine the e. m. f. of the reaction (the solutions are of M concentration).

8. Reduction of Nitrates in an Alkaline Solution. Add 3 ml of 30% KOH and a pinch of powdered aluminium (or zinc) to 1 ml of a potassium nitrate solution. Heat the solution and identify the gas evolved by its odour. Write the equation of the reaction that has taken place.

9. Nitrates as Oxidising Agents in Dry Reactions. (a) Weigh 1.54 g of potassium nitre, 0.22 g of sulphur, and 0.24 g of coal (all in powders) and mix them thoroughly on a piece of paper with a spatula. Transfer the resulting gunpowder mixture to some asbestos millboard and ignite it with a long splint in a ventilated hood (do this with caution!). Write the equation for the reaction of the burning of the mixture. Why is potassium nitre, rather than sodium nitre, used in the manufacture of gunpowder?

(b) Heat about 0.2 g of potassium nitrate in a dry test tube. When the residue has been cooled, dissolve it in water and test it, as in experiment 7. What are the calcination products? Write the equation of the reaction that has taken place.

(c) Melt a small amount of a 1 : 1 mixture of saltpetre and potash on the lid of a porcelain crucible, introduce a few grains of chromic

oxide into the melt, and calcine it well. What is the colour of the product? Write the equation of the reaction that has taken place.

10. Reductant Properties of Arsenite. To a sodium arsenite solution add an equal volume of a saturated solution of sodium bicarbonate and then add an iodine solution by drops. What causes the iodine solution to lose its colour? Write the equation of the reaction that takes place.

11. Preparation of Meta- and Pyrophosphate. Calcine a pinch of di-sodium phosphate for 5-7 minutes on a crucible lid. When the residue has cooled, dissolve it in 4-5 ml of water. By means of the reactions described in experiment 5, Exercise 30, establish of which acid the product is a salt. Conduct a similar experiment with mono-sodium phosphate. Write the equations for the reactions of calcination carried out.

12. Action of "Molybdenum Liquor". (a) Add an excess of "molybdenum liquor" to a solution of di-sodium phosphate. A yellow precipitate of a complex salt is formed. Write the equation of the reaction that has taken place.

(b) Conduct a similar reaction with a sodium arsenate solution. A yellow precipitate is formed only upon heating.

13. Preparation of Sodium Bismuthate and Its Properties. (a) Pour 1 ml of a $Bi(NO_3)_3$ solution and 3 ml of 30% NaOH into a test tube, and heat it to boiling point. Into the hot solution pass chlorine prepared from concentrated hydrochloric acid as a result of its interaction with potassium permanganate (see p. 283). A dark brown precipitate of sodium bismuthate is formed. Filter off the precipitate and wash it twice with water.

(b) Pour 3-4 ml of dilute nitric acid and 2-3 drops of a $MnSO_4$ solution into a porcelain casserole. Now, using a glass spatula, add a small amount of the precipitate prepared in the previous experiment. The solution acquires a pink colour, as the bivalent manganese is oxidised to MnO_4^- ion. Write the equations of the reactions of the preparation of the bismuthate and the oxidation of the bivalent manganese salt by it.

Exercise 32

THE ELEMENTS OF THE SIXTH GROUP OF THE PERIODIC SYSTEM AND THEIR HYDROGEN COMPOUNDS

SUBJECTS FOR STUDY

Sulphur, selenium, tellurium, and polonium as analogues of oxygen; sulphur and its allotropic modifications; changes in the properties of sulphur with heating; selenium and tellurium, and their redox characteristics.

The hydrogen compounds of sulphur, selenium, and tellurium; their preparation and chemical characteristics; sulphides and hydrosulphides; polysulphides.

Several allotropic modifications of sulphur are known, of which rhombic sulphur (density 2.06 g/cu cm and m. p. 112.8°) and monoclinic sulphur (density 1.96 g/cu cm and m. p. 119°) have been studied most. When rhombic sulphur is heated to 95.6°, it is transformed, without melting, to the monoclinic variety. If the latter, on the other hand, is cooled, the reverse transformation takes place. Consequently, at 95.6° (called the transition temperature) there is a state of equilibrium:

$$S_{rh} \rightleftarrows S_{mon}$$

If sulphur is carefully heated further, without exceeding the melting point, at 119° it turns into a mobile liquid of amber colour, which consists of the molecules S_8. A still further rise in temperature makes the liquid more viscous and darker, changes connected with the decomposition of the S_8 molecules.

Maximum viscosity is reached at 200°; if at this temperature the containing vessel is inverted, the sulphur does not run out. With still further heating the viscosity declines; above 200° the sulphur becomes fluid again and turns brown. Sulphur boils at 444.5°.

When liquid sulphur, heated to the boiling point, is cooled slowly, all the above-described changes take place in reverse. Drastic cooling to low temperatures (as when boiling sulphur is poured into cold water) produces so-called plastic, or amorphous, sulphur, which gradually reverts to the crystalline state.

Selenium is known in two modifications: grey with a metallic lustre and glassy reddish brown.

The atoms of the elements S, Se, and Te have different numbers of internal electron shells, but all have six electrons in their outermost shells. From the standpoint of chemical properties, the elements are nonmetals and act both as oxidising agents ($R + 2e^- = R^{-2}$) and as reducing agents ($R - 6e^- = R^{+6}$). Apart from the positive valence of six, they also exhibit a valence of four ($R - 4e^- = R^{+4}$) and a valence of two ($R - 2e^- = R^{+2}$).

With the increase in atomic radii in the oxygen—polonium group, reductant activity rises, while oxidant activity drops:

	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Radius (in Å units) . . .	0.66	1.04	1.17	1.37	—

The hydrogen compounds of the elements — hydrogen sulphide H_2S, hydrogen selenide H_2Se, and hydrogen telluride H_2Te — are poisonous gases with unpleasant odours. They are prepared either

by synthesis or by exchange reactions, such as:

$$MeS + H_2SO_4 = H_2S + MeSO_4$$

The gases are but slightly soluble in water. For instance, one volume of water at N. T. P. dissolves 4.7 volumes of H_2S. Such a solution is called hydrogen sulphide water and is faintly acidic, since part of the hydrogen sulphide molecules dissociate:

$$H_2S \rightleftarrows \underbrace{H^{\cdot} + HS'}_{\updownarrow} \quad \underbrace{\qquad\qquad}_{H^{\cdot} + S''}$$

With the rise in ionic radius from S^{-2} to Te^{-2}, the acidity of the hydrogen compounds increases.

The reducing power of these compounds is associated with the ability of the R^{-2} ion to give up varying numbers of electrons:

$$R^{-2} - 2e^- = R \qquad (1)$$

$$R^{-2} - 6e^- = R^{+4} * \qquad (2)$$

$$R^{-2} - 8e^- = R^{+6} \qquad (3)$$

For example:

(1) Treatment with weak oxidising agents

$$2\overset{-2}{H_2S} + H_2\overset{+4}{S}O_3 = 3S + 3H_2O \quad (4e^-)$$

(2) Reaction of calcination

$$2\overset{-2}{Z}nS + 3O_2 = 2\overset{+2}{Z}nO + 2\overset{+4}{S}O_2 \quad (12e^-)$$

(3) Treatment with strong oxidising agents

$$\overset{-2}{H_2S} + 4Br_2 + 4H_2O = \overset{+6}{H_2S}O_4 + 8\overset{-1}{H}Br \quad (8e^-)$$

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* It is in accordance with this scheme that hydrogen sulphide burns:

$$2\overset{-2}{H_2S} + 3O_2 = 2H_2O + 2\overset{+4}{S}O_2$$

If some cold object is introduced into the hydrogen sulphide flame, the reaction on its surface proceeds according to the equation:

$$2\overset{-2}{H_2S} + O_2 = 2H_2O + 2\overset{0}{S}$$

Reductant properties in the H_2S, H_2Se, H_2Te series increase with the rise in ionic radii, while the stability of the compounds decreases.

Two types of salts correspond to the H_2S, H_2Se, and H_2Te acids: normal salts containing the R^{-2} ion and called *sulphides*, *selenides*, and *tellurides* respectively, and acid salts containing the HR^{-1} ion and called *hydrosulphides* and *hydroselenides* respectively (no hydrotellurides are known). In practice the most important salts are the sulphides. The sulphides of the alkaline and alkaline-earth metals, as well as of ammonium, are water-soluble, while the rest are not. Most sulphides are coloured (yellow, red, brown, or black). Sulphides are prepared by synthesis, by reducing sulphates with coal at a high temperature, or by precipitation with hydrogen sulphide from aqueous salt solutions.

Several cations, e. g., $Zn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Co^{\cdot\cdot}$, are not precipitated by the S'' ion in acidic solutions, but only in weakly alkaline solutions; the cations of other metals produce precipitates in acidic solutions. This serves as the basis of the classic method of cation separation in qualitative analysis.

When H_2S is passed into an alkali solution, hydrosulphides are formed:

$$NaOH + H_2S = H_2O + NaHS$$

Excess alkali turns the hydrosulphides into sulphides:

$$NaHS + NaOH = H_2O + Na_2S$$

All the soluble sulphides and hydrosulphides undergo hydrolysis in aqueous solutions, which are, accordingly, alkaline.

The R^{-2} negative ion is capable of coordinating neutral atoms of the same element around itself. The smaller the radius of the R^{-2} ion, the more pronounced this complex-forming ability.

The S^{-2} ion can coordinate from 1 to 8 neutral sulphur atoms around itself, forming the complexes:

$$[\overset{-2}{S}\cdot S]^{-2} \qquad [\overset{-2}{S}\cdot S_2]^{-2} \qquad [\overset{-2}{S}\cdot S_8]^{-2}$$

The compounds of these complex ions with the $H^{\cdot}$ ion, as well as the salts of these acids, are known as polysulphides. Polysulphides are prepared by heating solutions of alkaline sulphides with sulphur:

$$Na_2S + S = Na_2[S_2] \qquad Na_2S + 2S = Na_2[S_3]$$

The polysulphides of practical importance are the disulphides of ammonium $(NH_4)_2[S_2]$ and iron $Fe[S_2]$, the latter being known as iron pyrites. They are oxidising, as well as reducing, agents. In the former case $[S_2]^{-2}$ gains two electrons, turning into $2S^{-2}$.

QUESTIONS

1. The transformation of monoclinic into rhombic sulphur at the transition temperature is accompanied by the evolution of 0.075 Cal. The molecules of both modifications having the same composition (S_8), explain what accounts for the evolution of heat in this transformation.
2. Why does plastic sulphur after a time become brittle? Is this transformation accompanied by the absorption or evolution of heat?
3. Hydrogen sulphide can be prepared by passing hydrogen over molten sulphur. Can hydrogen telluride be prepared in the same way?
4. Why cannot hydrogen sulphide be dried by passing it through concentrated sulphuric acid? What substance may be used to dry it?
5. Why is H_2Te a more vigorous reducing agent than H_2S?
6. Write the equations for the reactions of the oxidation of H_2S by potassium bichromate in an acidic solution and of selenium by concentrated nitric acid.

Problems

1. Determine the percentage composition (in terms of volume) of a mixture of hydrogen sulphide and oxygen, knowing that the mixture, when ignited, yields 200 ml of sulphur dioxide, while 40 ml of oxygen does not react.
2. Determine the molecular weight of hydrogen selenide, knowing that 375 ml of the gas, measured at 27° and 750 mm Hg, weighs 1.215 g. How many times heavier than H_2S is the gas?
3. Determine the density in terms of air and the molecular weight of hydrogen sulphide, knowing that 750 ml of it at 27° and 750 mm Hg weighs 1.024 g.
4. The following are reactions for the preparation of sulphur according to one of the known methods:

$$CaS + H_2O + CO_2 = H_2S + CaCO_3$$
$$2H_2S + O_2 = 2H_2O + 2S$$

How much sulphur can be prepared from 1 ton of soda waste containing 86.4% CaS, and how much air will be needed to oxidise the hydrogen sulphide produced in the first stage of the process?
5. What is the weight of the hydrogen sulphide contained in 1 litre of the water of the Black Sea taken at a depth of 2,970 m, if the oxidation of this H_2S requires 37.9 ml of 0.01 N iodine solution?
6. The absorption coefficient of hydrogen sulphide at 15° is 2.913. What is the weight of the H_2S that can dissolve in 100 litres of water at a gas pressure of 1.6 atm?
7. A solution containing 1 g of sulphur in 50 g of carbon disulphide boils at 46.38° With the knowledge that the ebullioscopic constant of CS_2 is 2.3° and that the b. p. of pure CS_2 is 46.2°, determine how many atoms there are in the sulphur molecule.
8. The thermal effect of the formation of H_2S from H_2 and S_{rh} is 4.8 Cal. The transformation of monoclinic sulphur into the rhombic variety is accompanied by the evolution of 0.075 Cal. Determine the thermal effect of the formation of H_2S from hydrogen and from monoclinic sulphur.
9. From the first-step ionisation constant of hydrogen sulphide acid determine the pH and α% of an 0.01 M solution.
10. How many times greater is the solubility of zinc sulphide in pure water than in an 0.01 M solution of Na_2S?

LABORATORY WORK

Apparatus and materials: 50 ml flask with stopper, funnel, and gas-delivery tube; Kipp gas generator for preparing hydrogen sulphide; test tubes and rack; 500 ml beaker; 100 ml beaker; 60 cm glass tube with stopper; porcelain mortar; porcelain crucible with cover; crucible tongs; 100 ml measuring cylinder; funnel; knife; blowpipe; test tube holder; asbestos millboard; filter paper; lead paper; anhydrous sodium sulphate; powdered coal; coal (coke) in lumps; sulphur in lumps; powdered sulphur; iron plates; iron sulphide; zinc dust and sulphur mixture; concentrated nitric acid; 2 N and 4 N H_2SO_4; 10% ammonia solution; 2 N HCl; 2 N ammonium sulphide solution; 2 N Na_2S solution; 0.5 N $SbCl_3$; 0.5 N $CuCl_2$; zinc chloride; 0.5 N $MnCl_2$; 2 N $BaCl_2$; saturated solution of sulphurous acid; 10% solution of H_2SeO_3; neutral litmus solution; ethyl alcohol; xylene, and hydrogen sulphide water.

Preparation of Lead Paper. Impregnate some filter paper with a 10% solution of lead acetate and dry it in premises free of hydrogen sulphide; cut the dry paper into strips and keep it in jars with ground-in stoppers.

1. Melting of Sulphur. By means of a wooden holder, slowly heat a dry test tube one-third of which is filled with lumps of sulphur until the sulphur melts. Shake the test tube continually while heating it (because of the poor heat conductivity of the sulphur, the process of melting is very slow). When the sulphur melts, incline the test tube slightly and observe how the mobile amber liquid flows along the wall of the tube. Continue heating and observe how the liquid changes colour and becomes more viscous: invert the test tube and note that the sulphur does not run out (temperature about 200°). Continue heating to boiling point and note that the sulphur turns dark and becomes mobile again. Pour the boiling sulphur in a thin stream into a beaker with cold water. A minute or two later remove the sulphur from the water and note its plastic condition.

Keep a lump of plastic sulphur until the end of the day's work in the laboratory. Does it preserve its properties?

Explain all the changes observed in the course of the experiment.

2. Preparation of Monoclinic Sulphur. (a) In a small crucible melt some sulphur over a weak (why?) flame and let it cool. When the surface of the sulphur has become covered with a crystalline crust, pierce a hole about 1 cm in diameter in the middle with the tip of a knife blade and pour the molten sulphur out of the crucible quickly. When the crucible cools, transparent needles of monoclinic sulphur form on its interior; after a time they cease to be transparent, owing to conversion to the rhombic modification.

(b) Pour 8-10 ml of xylene into a dry test tube, add 0.5 g of powdered sulphur, and close the test tube with a stopper, which has a 60 cm long glass tube passed through it. Fasten the test tube in the clamp of a ringstand and heat it until all the sulphur has dissolved (the tube serves to cool the xylene vapour). When the solution cools, observe the precipitation of long prismatic crystals of monoclinic sulphur. Examine the crystals under a magnifying glass.

3. Preparation of Selenium. Pour 8-10 drops of a saturated aqueous solution of sulphur dioxide into 3 ml of a concentrated solution of

selenious acid. At first the solution turns yellow, then red, and, finally, after a time, a fine precipitate of the reddish brown modification of selenium is formed. Filter off the precipitate and keep it for the next experiment. Write the equation of the reaction that has taken place.

4. Reductant Properties of Sulphur and Selenium. (a) Pour 2-3 ml of concentrated HNO_3 into a test tube, add a small amount of powdered sulphur, and heat the mixture to boiling point. When the solution has cooled, add a solution of $BaCl_2$. Observe the formation of a white precipitate. What ion is present in the solution? Write the equation of the reaction of the oxidation of sulphur by nitric acid.

(b) Transfer the selenium precipitate filtered off in experiment 3 to an iron plate and dry it carefully, placing the plate over the flame of a burner. Ignite the dry selenium in the flame of the burner (in a ventilated hood) and watch it burn. Write the equation of the reaction taking place.

5. Oxidant Properties of Sulphur. Place a small amount of a 1 : 2 mixture (by weight) of sulphur and zinc on a sheet of asbestos millboard and ignite it carefully (in a ventilated hood) with a burning splint. Demonstrate experimentally that the resulting white powder contains the S^{-2} ion. Write the equations of the reactions that have taken place.

6. Preparation of Hydrogen Sulphide and Its Properties. (Conduct this experiment in a ventilated hood!) (a) Place a few lumps of iron sulphide in a small flask and close the flask with a stopper fitted with a funnel reaching almost the bottom of the flask and with a gas-delivery tube. Through the funnel pour enough 4 N H_2SO_4 to submerge the tip of the funnel. If the reaction is not vigorous enough, heat the flask slightly.

(b) Lift the end of the delivery tube and, after testing the purity of the issuing gas (how?), light the gas. Write the equation of the reaction that has taken place. Introduce the cover of a porcelain crucible into the flame and, after a time, observe the appearance of a yellow stain on it. Write the equation of the reaction that has taken place.

(c) Hold a piece of lead paper over the tip of the delivery tube. In the presence of hydrogen sulphide it becomes black. Write the equation of the reaction that has taken place.

(d) Immerse the outlet of the tube for 3-4 minutes in a beaker with water. Keep the hydrogen sulphide water prepared in this way for the next experiments. Test a small amount of the solution with neutral litmus. What happens when H_2S dissolves in water? Write the equation of the reaction that takes place.

(e) Pass hydrogen sulphide from the Kipp gas generator for 7-10 minutes into a beaker with 10 ml of ammonia solution. What is formed in the beaker? Add another 10 ml of ammonia solution to the contents of the beaker. What is formed? Write the equations of the reactions

that have taken place. Keep the ammonia solution for the next experiment.

7. Preparation of Sulphides. (a) Pour 3 ml portions of solutions of the chlorides of barium, manganese, zinc, copper, and antimony respectively into five test tubes. Add to each of them 1 ml of a solution of HCl and 3 ml of the hydrogen sulphide water prepared in the previous experiment. In which of the test tubes do precipitates form? Note the colours of the precipitates and write the equations of the reactions by which they were prepared.

(b) Pour 3 ml each of solutions of the chlorides of manganese and zinc respectively into two test tubes and add equal volumes of ammonium sulphide solution. Note the colours of the precipitates formed. Why are the $Zn^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$ ions not precipitated by hydrogen sulphide in an acid solution, but do form precipitates with ammonium sulphide? Explain this by referring to the *SP* figures for these precipitates (Table XIII on p. 335).

(c) Mix 0.5 g amounts of anhydrous sodium sulphate and coal (or coke); add water by drops and prepare a paste. Spread some of the paste on the surface of a lump of coal (Fig. 71) and, by means of a blow-pipe, heat it in a reducing flame until there has clearly been fusion. Transfer the "melt" to a test tube, dissolve it in 5 ml of water, and filter the solution. Add a solution of lead salt to the filtrate. What is the colour of the precipitate formed? Write the equations of all the reactions that have taken place.

8. Preparation of Sodium Polysulphide. Pour 4-5 ml of a colourless solution of sodium sulphide into a test tube, add a pinch of powdered sulphur moistened with alcohol, and boil the solution for 3-5 minutes, observing the change in the colour of the solution. Write the equation of the reaction that has taken place. Filter the hot solution and add HCl until it becomes acidic. A fine precipitate of highly dispersed sulphur is now formed (although a colloidal condition may be observed at first).

Exercise 33

OXYGEN COMPOUNDS OF THE ELEMENTS OF THE SIXTH GROUP

SUBJECTS FOR STUDY

The dioxides of sulphur, selenium, and tellurium, and their preparation; solubility in water; sulphurous, selenious, and tellurous acids; their properties; sulphites, hydrosulphites, and pyrosulphites; selenites and tellurites; redox characteristics of the quadrivalent compounds of sulphur, selenium, and tellurium; hyposulphurous acid and its salts; their reductant properties; halogen compounds; thionyl chloride and its hydrolysis.

The dioxides of sulphur, selenium, and tellurium (SO_2, SeO_2, and TeO_2) can be prepared by burning the respective element in air or in oxygen.

In the laboratory SO_2 is usually prepared by reducing concentrated sulphuric acid by metallic copper or by an exchange reaction between a strong acid and a salt of sulphurous acid.

Sulphur dioxide is condensed to a liquid at ordinary pressure at a mere —10°. The dioxides of selenium and tellurium are, at ordinary conditions, colourless crystalline substances. SO_2 and SeO_2 are highly soluble in water, whereas TeO_2 has a comparatively poor solubility. When the dioxides dissolve in water, this is accompanied by interaction with it, e. g.:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows \underbrace{H^+ + HSO_3^-}_{\downarrow\uparrow} \quad \underbrace{\qquad\qquad}_{H^+ + SO_3^{2-}}$$

The aqueous solutions are acidic. H_2SO_3 is an acid of medium strength; selenious and tellurous acids are weaker, but only selenious acid has been isolated in the free state. It is usually prepared by heating selenium with dilute nitric acid:

$$3\overset{0}{Se} + 4H\overset{+5}{N}O_3 + H_2O = 3H_2\overset{+4}{Se}O_3 + 4\overset{+2}{N}O \qquad (12e^- \rightarrow)$$

Two types of salts should correspond to these acids: normal salts (Me_2RO_3) and acid salts ($MeHRO_3$), but an acid salt is known only in the case of sulphurous acid. The sulphites and hydrosulphites are prepared by passing SO_2 through an alkali solution.

In the quadrivalent state sulphur, selenium, and tellurium can act both as reductants ($R^{+4} - 2e^- = R^{+6}$) and as oxidants ($R^{+4} + 4e^- = R$). Their reductant properties are used more frequently, sulphur dioxide or sodium sulphite being employed in most cases.

Sulphur dioxide and sulphurous acid are used as bleaching agents. The molecules of sulphur dioxide or sulphurous acid can combine with certain organic compounds, such as the molecules of dyes, forming colourless products with them. At high temperatures these addition products are unstable.

Among the halogen compounds of quadrivalent sulphur, mention should be made of thionyl chloride $SOCl_2$, a colourless liquid that readily undergoes hydrolysis:

$$SOCl_2 + 2HOH \rightarrow 2HCl + H_2SO_3$$

QUESTIONS

1. Write the equations of four different reactions by which sulphur dioxide can be prepared.
2. By what methods can free sulphur be prepared from sulphur dioxide?
3. Write the equations for the reactions by which potassium sulphite and potassium hydrosulphite can be prepared.
4. Write the equations for the reactions whereby SO_2, $NaHSO_3$, and $Na_2S_2O_5$ are oxidised by potassium permanganate in acid solutions.
5. Write the structural formulae of the salts: potassium hydrosulphite, potassium pyrosulphite, and potassium tellurite.
6. Determine the reduction equivalents of $NaHSO_3$, $K_2S_2O_5$, and $Na_2S_2O_4$.

Problems

1. Determine the percentage composition (by volume) of a mixture of SO_2 and O_2, knowing that 200 ml of it reacts to form 0.438 g of sulphur trioxide.
2. What amount of thionyl chloride has reacted with water if 68 g of 10% $AgNO_3$ is needed to precipitate the chloride ion from the resulting hydrochloric acid?
3. Determine the volume of sulphur dioxide that can be prepared by the reaction of 200 ml of 16% K_2SO_3 (relative density 1.14) with an acid upon heating.
4. Determine the normality of a solution of K_2SO_3 if the oxidation of 20 ml of it in an acid solution requires 16 ml of 0.05 N $KMnO_4$.
5. The heating of a tin containing 800 g of sulphited fruit preserves releases an amount of sulphur dioxide that reacts with 2.54 g of iodine. Determine the percentage content of sulphur dioxide in the fruit preserves.
6. How many grams of sodium sulphite are contained in 1 litre of a solution if 25 ml of that solution bleaches 20 ml of an 0.04 N iodine solution?
7. How much water should be evaporated from 6 litres of an 8% solution of K_2SO_3 (relative density 1.067) to prepare a 51.6% solution?
8. Ten cubic metres of the waste gas of an iron and steel works is passed through a vessel containing 100 kg of 10% $NaSO_3$, reducing the concentration of the $NaSO_3$ to 7.41%. Determine the percentage content (by volume) of the SO_2 in the waste gas.
9. Determine whether an M solution of K_2SO_3 can be oxidised in an acid solution by a potassium bichromate solution of the same concentration.
10. The solubility of $BaSO_3$ in 100 ml of a solution at 20° is $1.97 \cdot 10^{-1}$ g Determine the *SP* value for $BaSO_3$.

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 75; Kipp gas generator for preparing hydrogen sulphide; 100 ml measuring cylinder; 100 ml beaker; porcelain casserole; Na_2SO_3; powdered selenium; 40% and 2N H_2SO_4; concentrated and 2 N HCl; 1 : 1 dilute nitric acid; saturated solution of sulphurous acid; 1% $AgNO_3$; N $BaCl_2$; N $K_2Cr_2O_7$; N Na_2SO_4; N Na_2SO_4; N $NaHSO_3$; 0.2% fuchsine solution; 0.002% malachite green solution; neutral litmus solution, and iodine water.

1. Preparation of Sulphur Dioxide. (Conduct the experiment in a ventilated hood!) Weigh 6.30 g of crystalline sodium sulphite and place

it in the flask (1) shown in Fig. 75. Into the funnel (2) pour a volume of 40% H_2SO_4 that is double the theoretically required volume. Immerse the gas-delivery tube (3) with the bulb in the beaker (4) containing 75 ml of distilled water. From the dropping funnel add sulphuric acid by drops to the contents of the flask; the gas evolved in the reaction saturates the water. When all the acid has been added, close the cock of the funnel and heat the flask slightly until no more bubbles of gas are formed.

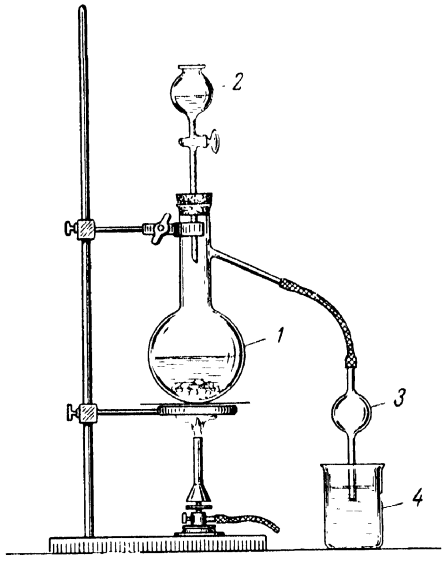

Fig. 75. Apparatus for preparing sulphur dioxide

1 — flask with sodium sulphite; 2 — dropping funnel; 3 — gas-delivery tube; 4 — beaker.

Keep the resulting solution of sulphurous acid for subsequent experiments.

2. Equilibrium in Sulphurous Acid Solution. Pour about 5 ml of sulphurous acid solution into a test tube and add 3 ml of neutral litmus solution. What causes the litmus to turn red? What is a solution of sulphur dioxide in water? Divide the solution in half, pouring the two halves into two test tubes. Boil one of them for a lengthy period of time. Why does the colour change?

3. Reductant Properties of Sulphurous Acid. (a) Establish experimentally what happens to an acidified solution of $K_2Cr_2O_7$ when a solution of sulphurous acid is added to it. Write the equation of the reaction that takes place.

(b) Add an iodine solution by drops to a sulphurous acid solution and observe the changes that take place. Write the equation of the reaction.

(c) Conduct the same experiment, using a sodium hydrosulphite solution instead of the sulphurous acid solution. Write the equation of the reaction that takes place.

4. Oxidant Properties of Sulphurous Acid. To 3-4 ml of a sulphurous acid solution add an equal volume of a transparent solution of hydrogen sulphide water or pass hydrogen sulphide from the Kipp gas generator through the solution. Why does the solution become turbid? Write the equation of the reaction that takes place.

5. Bleaching of Dyes by Sulphurous Acid. (a) Add a fuchsine solution by drops to 5-6 ml of a sulphurous acid solution and shake it vigorously. Add the fuchsine until a single drop of excess fuchsine causes

the solution to acquire a pale pink colour. The excess fuchsine is then bleached by the addition of 1 ml of sulphurous acid solution. Divide the resulting colourless solution of fuchsine-sulphurous acid into two parts, pouring them into two test tubes. Boil the solution in one of them and observe the changes that take place, comparing the solutions in the two test tubes. Explain the changes.

(b) Add a drop of sulphurous acid solution to a drop of malachite green solution on a glazed porcelain surface (a cup or plate). What happens?

6. Formation of Sulphito-Complexes. Add a sodium sulphite solution by drops to 2 ml of an $AgNO_3$ solution. A white precipitate of Ag_2SO_3 is formed at first, which then dissolves in excess Na_2SO_3 with the formation of a complex salt. Write the equations of the reactions that take place on the assumption that the coordination number of the sulphite ion is two.

7. Difference between Sulphite Ion and Sulphate Ion. Pour 2 ml of a $BaCl_2$ solution into each of two test tubes. Add freshly prepared sodium sulphite solution to one of them; sodium sulphate solution, to the other.

Can the resulting precipitates be distinguished by their appearance? Add 2 ml of concentrated HCl to each of the test tubes. What happens to the precipitates? *

8. Preparation of Selenious Acid. (Conduct the experiment in a ventilated hood!) Pour about 10 ml of 1 : 1 dilute nitric acid into a porcelain casserole and add some powdered selenium on the tip of a knife-blade. Put the casserole on a wire gauze and heat it until the volume of the solution is reduced to about half. Allow the solution to settle and pour it off into a test tube. Write the equation of the reaction whereby H_2SeO_3 is prepared.

9. Reduction of Selenious Acid. Add a few drops of concentrated HCl and 3-4 ml of a sulphurous acid solution to the selenious acid solution prepared in the previous experiment. Observe the formation of a reddish brown precipitate of selenium. Pour the solution with the precipitate into a special bottle. Write the equation of the reaction that has taken place.

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* If some white slime remains in the test tube when the $BaSO_3$ is dissolved, this indicates that the initial sulphite was partly oxidised.

Exercise 34

OXYGEN COMPOUNDS OF THE ELEMENTS OF THE SIXTH GROUP

(continued)

SUBJECTS FOR STUDY

The oxides of hexavalent sulphur, selenium, and tellurium; sulphuric acid; its electrolytic and redox characteristics; the hydrates of sulphuric acid and the thermal effect of hydration; a comparison of the properties of sulphuric, selenic, and telluric acids.

Soluble and insoluble sulphates; their attitude to heating; hydrogen sulphates and pyrosulphates; selenates and tellurates; persulphuric acid and persulphates; thiosulphuric acid and thiosulphates; polythionic acids; sulphuryl chloride and other halides of sulphur.

The oxides of the hexavalent elements under consideration have the composition SO_3, SeO_3, and TeO_3 and are anhydrides of sulphuric acid H_2SO_4, selenic acid H_2SeO_4, and telluric acid H_2TeO_4 respectively.

Sulphuric acid is manufactured by the "contact process" and the lead-chamber process. According to the relevant U.S.S.R. Standard, sulphuric acid should have a 1.830-1.835 relative density and contain 93.56-95.60% H_2SO_4. Another extensively used product is oleum, which is a solution of SO_3 in 100% sulphuric acid.

When sulphuric acid is poured into water, much heat is liberated, this being related to the hydration of the acid. This vigorous reaction of the acid with water accounts for the use of H_2SO_4 as a dehydrating agent. When sulphuric acid dissolves in water, ionisation proceeds in two steps:

$$H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4^{\prime}$$
$$\downarrow\uparrow$$
$$H^{\cdot} + SO_4^{''}$$

Sulphuric acid is a strong acid; the apparent degree of the ionisation of its 0.1 N solution is 58%. It is necessary to distinguish the dilute and the concentrated acid. In the dilute acid the oxidising agent is the $H^{\cdot}$ ion. When it reacts with reducing agents (metals situated before hydrogen in the electromotive series), it is reduced to gaseous hydrogen, e. g.:

$$Zn + \overset{+1}{H_2}SO_4 = H_2 + \overset{+2}{Zn}SO_4 \quad (2e^-)$$

In concentrated sulphuric acid the oxidising agent is the hexavalent sulphur of the acid radical, which is reduced in one of the following two ways:

$$\overset{+6}{S}O_4'' + 2e^- + 4H^+ = \overset{+4}{S}O_2 + 2H_2O$$

$$\overset{+6}{S}O_4'' + 8e^- + 10H^+ = \overset{-2}{H_2S} + 4H_2O$$

It is the second pattern that is followed in reactions with vigorous reducing agents, e. g.:

$$4Zn + 5H_2\overset{+6}{S}O_4 = \overset{-2}{H_2S} + 4H_2O + 4\overset{+2}{Z}nSO_4 \quad (8e^-)$$

Selenic and telluric acids are prepared by oxidising H_2SeO_3 and H_2TeO_3 with strong oxidising agents. Selenic acid is similar to sulphuric acid in strength; it is just as hygroscopic and chars organic substances easily. Telluric acid is a very weak acid.

The normal salts of sulphuric acid are called *sulphates*; the insoluble sulphates are $BaSO_4$, $PbSO_4$, and $SrSO_4$, while $CaSO_4$ is very slightly soluble. The acid salts are called *hydrogen sulphates* and are all soluble. The salts corresponding to the general formula* $MeSO_4 \cdot 7H_2O$ are called *vitriols*, and it is customary to list $CuSO_4 \cdot 5H_2O$ among them. Salts of the composition $\overset{+1}{M}e_2SO_4 \cdot \overset{+3}{M}e_2(SO_4)_3 \cdot 24H_2O$ are called *alums*.

The sulphates of the heavy metals, when heated vigorously, decompose with the evolution of SO_3 and the formation of metal oxides. Aqueous solutions of these sulphates are acidic, owing to hydrolysis.

The salts of selenic acid, called *selenates*, have properties similar to those of sulphates, but the salts of telluric acid, called *tellurates*, are markedly different.

When concentrated solutions of hydrogen sulphates or sulphuric acid are subjected to electrolysis, the HSO_4' ions are oxidised at the anode, forming molecules of persulphuric acid:

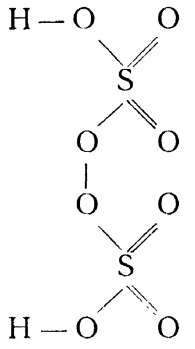
$$HSO_4' - 1e^- \rightarrow HSO_4$$

$$HSO_4' - 1e^- \rightarrow HSO_4$$

$$HSO_4 + HSO_4 \rightarrow H_2S_2O_8$$

* The symbol Me here designates the atom of a heavy metal.

From the structural formula of persulphuric acid



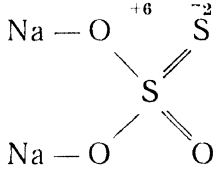
it follows that the compound contains the peroxide group $[O_2]^{-2}$, which accounts for its oxidant properties. In practice use is made of its salts, called *persulphates*, such as $K_2S_2O_8$ or $(NH_4)_2S_2O_8$. The persulphate ion is transformed in redox reactions into two SO_4'' ions, gaining two electrons in the process, e. g.:

$$2Mn(NO_3)_2 + 5K_2S_2O_8 + 8H_2O = 2HMnO_4 + 4HNO_3 + 10KHSO_4 *$$

One of the methods of preparing thiosulphates is by oxidising sulphites with elementary sulphur:

$$\overset{+4}{Na_2SO_3} + S = Na_2S_2O_3 \quad (2e^- \rightarrow)$$

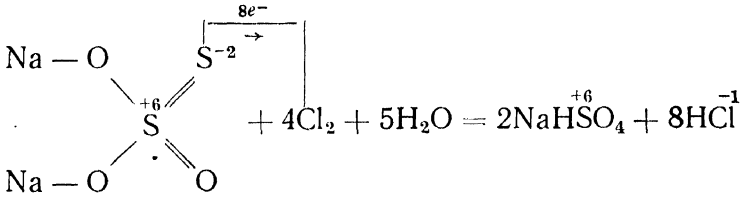
The most important of the thiosulphates in practice is sodium thiosulphate, sometimes wrongly called hyposulphite. It has the structural formula:



The reductant properties of thiosulphate may be traced to the binegative sulphur S^{-2} in its molecule. When thiosulphate is oxidised by chlorine, the binegative sulphur S^{-2} gives up eight electrons and is

* The reaction proceeds slowly and is accelerated by heating or by the presence of a catalyst (silver salts).

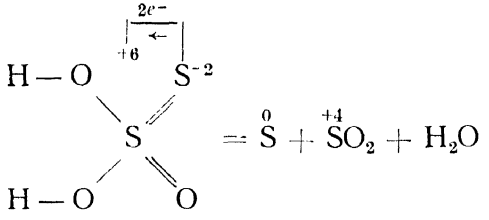
transformed into an SO_4^{-2} ion:



If a sodium thiosulphate solution is acidified, thiosulphuric acid is formed:

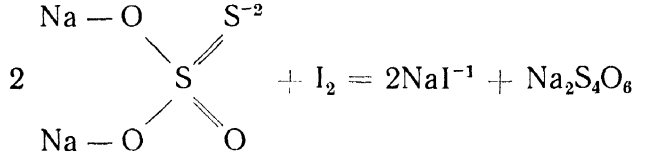
$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2S_2O_3$$

The acid has not been isolated in the free state; in solution it undergoes decomposition by virtue of an intramolecular redox reaction:



The thiosulphate ion serves as an addendum in complex ions, forming so-called metallo-thiosulphate complexes, such as $Na_3[Ag(S_2O_3)_2]$. It is on this property that the use of thiosulphate as a fixing agent in photography is based.

The polythionic acids are compounds corresponding to the general formula $H_2S_xO_6$, where $x = 2, 3...6$. One such compound is tetrathionic acid $H_2S_4O_6$, whose sodium salt is a product of the reaction between sodium thiosulphate and iodine. The structural formula of tetrathionic acid is that of persulphuric acid in which the $[O_2]$ group has been replaced by the similar group $[S_2]$. Tetrathionate is formed from thiosulphate upon oxidation by iodine according to the equation:



QUESTIONS

1. Why is it that in the production of sulphuric acid by the "contact process" the sulphur trioxide is dissolved in concentrated sulphuric acid rather than in water?

2. Why, in preparing sulphuric acid solutions, must the concentrated acid be poured into the water, and not *vice versa*?

3. Why is it that in the reaction

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$

the weaker acid displaces the stronger acid?

4. The following dry gases have to be prepared: NH_3, CO_2, CH_4, and H_2Se. Which of them cannot be dried by passage through concentrated sulphuric acid? Why is this so? Write the equations of the relevant reactions.

5. Why is it that lead sulphate, which is insoluble in dilute sulphuric acid, dissolves appreciably in hot concentrated solutions of that acid?

6. Determine the value of the reduction equivalent of thiosulphate from its reactions with chlorine and iodine.

7. Write the equation for the reaction whereby AgBr is dissolved in a sodium thiosulphate solution.

8. Write the structural formula of pentathionic acid.

9. What happens when a $FeSO_4$ solution interacts with an acidic solution of $Na_2S_2O_8$?

Problems

1. The initial mixture of gases for the production of sulphuric acid consists of sulphur dioxide, oxygen, and nitrogen. The oxidation of the sulphur dioxide contained n 100 ml of the mixture requires 6.2 ml of 0.1 N $KMnO_4$ in an acid solution. Determine the percentage content (by volume) of the SO_2 in the mixture.

2. The action of excess sulphuric acid on an 0.1 N solution of sodium thiosulphate yields 4.8 g of sulphur. What was the volume of the thiosulphate solution subjected to decomposition?

3. What volume of 60% H_2SO_4 (relative density 1.504) can be prepared from 1 ton of iron pyrite, assuming that there are no losses in the process of production?

4. What amount of metallic silver can be dissolved upon heating in 600 ml of 92.1% sulphuric acid (relative density 1.83) if the final concentration of the acid is 20%?

5. The absorption of the entire chlorine contained in 2 litres of its mixture with nitrogen at N. T. P. requires the expenditure of 3.16 g of sodium thiosulphate Determine the percentage composition of the gas mixture (by volume).

6. Telluric acid is prepared from powdered tellurous oxide, 30% KOH (relative density 1.29), and 15% H_2O_2 (relative density 1.054), the resulting potassium tellurate being decomposed by 65.3% HNO_3 (relative density 1.4). Calculate the weight of the TeO_2 and the volumes of the KOH, H_2O_2, and HNO_3 solutions that will be needed to prepare 1 kg of telluric acid, having the composition $H_2TeO_4 \cdot 2H_2O$.

7. Determine the molarity of sulphuric acid prepared by the "contact process", knowing that the acid contains 74.66% H_2SO_4 and has a relative density of 1.67.

8. One litre of water from the Luga river, according to O. Alekin's data, contains 42.3 mg of $Ca^{\cdot\cdot}$, 9.5 mg of $Mg^{\cdot\cdot}$, 175 mg of HCO'_3, 5.6 mg of SO''_4, 5 mg of Cl', and certain amounts of $K^{\cdot}$ and $Na^{\cdot}$. Determine the sum of the mg-equiv. $K^{\cdot} + Na^{\cdot}$, assuming that the sum of the mg-equiv. of all the cations is equal to the sum of the mg-equiv. of all the anions.

9. From the *SP* value of $PbSO_4$, given in Table XIII, derive the amount of lead in g-ions contained in 250 ml of a saturated solution.

10. What is the weight of the persulphuric acid formed in the anode chamber of an electrolytic cell if a 5A current is passed for 32 min 10 sec through a concentrated sulphuric acid solution in the cell?

LABORATORY WORK

Apparatus and Materials: the apparatus shown in Fig. 76; test tubes and rack; suction filter; glass bath; porcelain casserole; 50 ml measuring cylinder; 50 ml beaker; funnel; thermometer to 100°; two glass rods; piece of cloth; filter paper; copper turnings; zinc; powdered sulphur; crystalline sodium sulphite; freshly recrystallised ferrous sulphate; sodium sulphate; concentrated and 2 N H_2SO_4; 2 N NaOH; 0.5 N KI; N solution of sodium thiosulphate; 2 N HCl; N $BaCl_2$; N solution of potassium persulphate; N solution of strontium chloride; N $CaCl_2$; N solution of lead nitrate; 0.1 N $AgNO_3$; 0.5 N NaCl; 0.5 N Na_2S; fuchsine solution; starch solution; ethyl alcohol; chlorine water; iodine water; snow or ice.

1. Preparation of Sodium Thiosulphate. Weigh 10 g of crystalline sodium sulphite and 1.5 g of powdered sulphur. Transfer the sulphite to a 100 ml flask, add 20 ml of distilled water, and heat the flask until the sulphite dissolves. Then add the weighed sulphur, first moistened with a few drops of alcohol (without this treatment sulphur will not be wetted by the aqueous solution).

Attach to the flask a condenser held vertically by the clamps of a ringstand (Fig. 76) and allow a stream of water from the tap to pass through the condenser (instead of the condenser, the flask may be closed with a stopper through which a 70-80 cm long glass tube has been passed).

Boil the solution in the flask until nearly all the sulphur has reacted. Write the equation of the reaction that has taken place. Filter the solution, using a small filter and collecting the filtrate in a porcelain casserole. Evaporate the filtrate until crystallisation begins. Then cool the casserole with snow or ice and filter the solution (with the crystals formed), using a suction filter, unti drops of the solution cease dripping from the tip of the funnel. Disconnect the rubber tube of the suction pump from the filter flask and only then turn off the water.

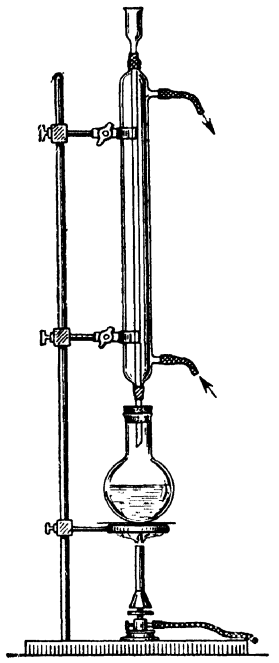


Fig. 76. Apparatus for preparing sodium thiosulphate

Now turn the funnel upside down over a piece of clean filter paper. By tapping lightly on the funnel remove the crystals with the round filter. Cover the crystals with a dry piece of filter paper and, by pressing it down with

the palm of your hand, remove the last traces of the solution. Leave the crystals exposed to air for about 20 minutes, stirring them from time to time with a glass rod.

The dry crystals should not cling to the rod. Weigh the dry crystals and determine the yield in per cent. Submit the salt prepared to the instructor.

2. Reductant Properties of Thiosulphate. (a) Add 1 ml of starch solution to 2-3 ml of a sodium thiosulphate solution. Now add an iodine solution by drops. Why is there no blue colouration? Write the equation of the reaction between the thiosulphate and the iodine. Add iodine until all the thiosulphate has been oxidised and the solution turns blue.

(b) Add chlorine water to 2 ml of thiosulphate solution. What happens? Write the equation of the reaction that has taken place. Demonstrate that the solution contains $SO_4^{''}$ ions resulting from the oxidation of the $S_2O_3^{''}$ ions.

3. Instability of Thiosulphuric Acid. Add 2 ml of an HCl solution to an equal volume of thiosulphate and watch the solution grow turbid after a time. What accounts for this? Write the equation of the reaction that has taken place.

4. Formation of Thiosulphato-Complex and Its Stability. Add a concentrated solution of sodium thiosulphate by drops to 3 ml of 0.1 N $AgNO_3$ until the precipitate formed dissolves. Write the equations of the reactions that have taken place. Divide the solution into four parts, pouring them into four test tubes. Add equal volumes of NaOH to the first, NaCl to the second, KI to the third, and Na_2S to the fourth. In which of the test tubes do precipitates form? Explain this.

5. Thermal Effect Observed When Sulphuric Acid Dissolves. Pour water into a test tube until it is half-full and measure its temperature. Pour 3 ml of concentrated H_2SO_4 from another test tube into the first. Stir the water carefully with a thermometer, noting the temperature. What happens? Write the equation of the hydration reaction that has taken place.

6. Charring of Organic Matter by Sulphuric Acid. (a) With a glass rod moistened with concentrated H_2SO_4 write something on a piece of paper. Heat the paper slightly, holding it high above the flame of a burner. Watch the paper darken after a time. Explain this.

(b) By means of a glass rod place a drop of concentrated H_2SO_4 on a piece of cloth. After a time test the strength of the material.

7. Oxidant Properties of Sulphuric Acid. Test the action of dilute H_2SO_4 on metallic zinc and of concentrated H_2SO_4 on metallic copper with heating. How can the products of the reduction of H_2SO_4 be identified? Write the equations of the reactions that have taken place.

8. Insoluble Sulphates. Prepare the known insoluble sulphates and write the relevant equations.

9. Thermal Effect Observed When Sodium Sulphate Dissolves. Weigh two 5 g amounts of $Na_2SO_4 \cdot 10H_2O$. Place one of them in a porcelain casserole and heat it, stirring the contents from time to time, until the evolution of water vapour ceases. Then cool the casserole and transfer the resulting anhydrous salt to a piece of paper. Pour 10 ml of water into a beaker, measure its temperature, and quickly throw the weighed amount of $Na_2SO_4 \cdot 10H_2O$ into it. Stir the water carefully with a thermometer, observing the change in the temperature it registers. Note the initial and the final temperature. Repeat the same experiment with the anhydrous salt. Explain the difference in the results obtained.

10. Oxidation with Persulphate. (a) Test the action of an acidic solution of persulphate on a KI solution. Demonstrate that the oxidation product is free iodine. Write the equation of the reaction that has taken place.

(b) Dissolve a few crystals of recrystallised ferrous sulphate in 5-6 ml of water and divide the solution into two parts, pouring them into two test tubes. Add a persulphate solution to one of them. Then add NaOH to both of them. Are the precipitates formed in the two test tubes of the same colour? Write the equations of the reactions that have taken place.

11. Anion Detection. Receive a solution or solid salt for analysis from the instructor. It should contain one of the following anions: S'', SO_3'', SO_4'', S_2O_3'', or S_2O_8''. By means of the reactions studied in Exercises 32, 33, and 34, establish which of the above anions is present. Write up the results of the analysis and submit them to the instructor.

Exercise 35

THE ELEMENTS OF THE CHROMIUM SUBGROUP

SUBJECTS FOR STUDY

The elements of the chromium subgroup; structure of the electron shells of the atoms of these elements.

Chromium oxide and hydroxide, and their chemical character; chromic salts, and the oxidation of trivalent chromium to hexavalent.

The trioxides of chromium, molybdenum, and tungsten; the chemical character of their hydroxides; chromic and bichromic acids; chromates and bichromates; oxidant properties of hexavalent chromium compounds.

The elements of the chromium series make up the sixth subgroup in Mendeleyev's Table of Elements.

The atoms of the chromium subgroup elements have the following electron distributions in their two outer shells: Cr and Mo)8 + 5)1,

W)8 + 4)2 All these elements are metals and exhibit reductant properties in chemical reactions. They do not form negative ions. Unlike the elements of the sulphur subgroup, they do not form gaseous compounds with hydrogen. They display different valences according to the number of electrons they give up.

In the case of chromium the most stable are those compounds in which it is trivalent or hexavalent.

Chromic oxide and hydroxide possess amphoteric properties. Trivalent chromium forms two series of salts: those in which it is the cation, such as chromic chloride $CrCl_3$ and chromic sulphate $Cr_2(SO_4)_3$, and those in which the chromium is in the anion, such as the salts of chromous acid $HCrO_2$ and of orthochromic acid H_3CrO_3. Trivalent chromium salts are either green, or blue-green, or bluish violet.

The conversion of Cr^{+3} to Cr^{+6} is usually effected in an alkaline solution by means of a strong oxidising agent. This is accompanied by a change in the green colour of Cr^{+3} to the yellow typical of CrO_4^{-2} ions.

Chromic anhydride CrO_3 is known in the free state in the form of dark red crystals, but the corresponding chromic acids are known only in the form of salts. The simplest acid is chromic acid H_2CrO_4; however, a series of chromic isopolyacids are also known, conforming to the general formula $H_2CrO_4 \cdot nCrO_3$. The simplest of these ($n = 1$) is bichromic acid $H_2Cr_2O_7$.

Salts containing the CrO_4^{-2} ion are known as chromates and are yellow, while those containing the $Cr_2O_7^{-2}$ ion are called bichromates and are orange. The conversion of chromates to bichromates, and *vice versa*, is accompanied by a change of colour. This conversion depends upon the acidity of the solution:

$$CrO_4'' \underset{OH'}{\overset{H'}{\rightleftarrows}} Cr_2O_7''$$

The soluble chromic acid salts are the salts of the alkaline metals, ammonium, and calcium. The insoluble salts are $BaCrO_4$, $PbCrO_4$, $SrCrO_4$, Ag_2CrO_4, $Ag_2Cr_2O_7$, and Hg_2CrO_4. The last three salts are brown or brown-red.

The compounds of hexavalent chromium in acid solution act as strong oxidants, undergoing reduction to Cr^{+3} compounds (with a change of the orange colour to green). A solution of $K_2Cr_2O_7$ containing sulphuric acid is called a chromic acid mixture and is a potent oxidising agent. The action of hydrogen peroxide or the peroxides of metals upon hexavalent chromium compounds in an acid solution produces the blue chromium peroxide, which is unstable in aqueous solution, but stable when dissolved in ether. The formation of chromium peroxide may be expressed by the following equation:

$$K_2Cr_2O_7 + 4H_2O_2 + H_2SO_4 = 2CrO_5 + K_2SO_4 + 5H_2O$$

As for molybdenum and tungsten, it is the compounds of the hexavalent elements that have been studied most. The anhydrides WO_3 and MoO_3 are insoluble in water, but dissolve in alkali solutions to form salts of molybdic acid H_2MoO_4 and tungstic acid H_2WO_4 respectively.

The acids H_2CrO_4, H_2MoO_4, and H_2WO_4 decrease in strength in that order. Laboratories are usually stocked with ammonium molybdate $(NH_4)_2MoO_4$ and sodium tungstate Na_2WO_4, both of which are colourless soluble salts. Salts of the type $Me_2Mo_2O_7$ and $Me_2W_2O_7$, similar to dichromates, are likewise known.

Unlike hexavalent chromium compounds, hexavalent molybdenum and tungsten compounds are very weak oxidising agents and can be reduced by strong reducing agents, such as nascent hydrogen. Molybdenum and tungsten compounds of lower valences have definite colours: blue, green, brown, etc.

QUESTIONS

1. Which of the metals of the chromium subgroup is the most vigorous reducing agent? Why is this so?
2. Write the equations of the reactions whereby $CrCl_3$ can be converted to salts of chromous and orthochromic acids.
3. Write the equation for the reaction of the oxidation of sodium chromite in an alkaline solution by lead dioxide.
4. Write the structural and coordination formulae of chromic and bichromic acids.
5. How does the colour of the solution change when Cr^{+3} is oxidised to CrO_4'' in an alkaline medium?
6. Write the equation of the reaction that takes place when excess sodium hydroxide is added to a potassium bichromate solution.
7. Write the equations for the following sequence of transformations:

$$Na_2MoO_4 \rightarrow H_2MoO_4 \rightarrow MoO_3 \rightarrow K_2MoO_4$$

Problems

1. The heating of 15 g of metallic tungsten from 16 to 20°calls for the expenditure of 2.142 cal. Calculate the atomic weight of the metal and the discrepancy (%) between the value found and the exact value.
2. The element tungsten consists of five stable isotopes: W^{180} (0.126%), W^{182} (26.31%), W^{183} (14.29%), W^{184} (30.67%), and W^{186} (28.6%). Calculate the atomic weight of the element.
3. The fusing of 3.04 g of chromic oxide with an oxidising agent in the presence of sodium hydroxide yields 6.37 g of sodium chromate. Determine the yield of the product in per cent.
4. What amount of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) can be prepared from 100 g of tungstic anhydride by dissolving it in 40% NaOH and what is the volume of alkali that will be needed for this (see Table VII)?

5. Determine the percentage content of $Na_2Cr_2O_7$ in the commercial product, knowing that 1.0 g of that product oxidises 3.38 g of KI in an acid solution.

6. How many millilitres of 0.5 N $K_2Cr_2O_7$ will be needed for the complete oxidation of 22 g of KI in an acid solution?

7. Commercial sodium bichromate contains 90% of $Na_2Cr_2O_7$. What amount of this product will be needed to prepare 1 kg of pure $Na_2Cr_2O_7$ by recrystallisation if the solubility of the salt at 98° is 81.24% and at 10° it is 63.0%, crystallisation being conducted in that temperature range.

8. The heat of formation of molybdic anhydride is 176.5 Cal. For aluminium oxide the figure is 380 Cal. Determine the thermal effect of the reaction $2Al + MoO_3 = Mo + Al_2O_3$.

9. What amount of metallic chromium will be deposited from a CrO_3 solution in 40 min at a current intensity of 4 A, the current efficiency being 13%?

10. A voltaic cell is made up of the couples $Cr/Cr^{\cdots}$ and $Bi/Bi^{\cdots}$. Draw a diagram of the cell, determine its e. m. f., and write the equation of the reaction which produces the current, the concentration of the salts being M.

LABORATORY WORK

Apparatus and materials: Kipp gas generator for producing hydrogen sulphide; two porcelain crucibles with covers; test tubes and rack; refractory test tube; two glass rods; filter paper; splints; 20 × 20 cm asbestos millboard with hole for crucible; tungstic anhydride; molybdic anhydride; chromic anhydride; 1 : 2 mixture of potassium nitrate and potassium carbonate; zinc in granules; ammonium bichromate; methyl alcohol; ethyl alcohol; ethyl ether; concentrated sulphuric acid; concentrated hydrochloric acid; 2 N sulphuric acid; 2 N hydrochloric acid; 2 N KOH; 2 N NaOH; 3% H_2O_2; 2 N CH_3COOH; 2 N HNO_3; N K_2CrO_4; N $K_2Cr_2O_7$; 0.1 N $AgNO_3$; 0.5 N $Pb(CH_3COO)_2$; N solution of strontium chloride; N $BaCl_2$; saturated solution of lime chloride; 0.5 N $Cr_2(SO_4)_3$; 0.5 N $CrCl_3$; N solution of sodium carbonate; 2 N $(NH_4)_2S$; litmus paper.

1. Preparation of Chromic Oxide. Weigh 2-3 g of ammonium bichromate ground to a powder and pour it into a large crucible (with a cover), placed into a round hole in a sheet of asbestos millboard on the ring of a ringstand. Lift the cover so that there is a small opening and then heat the crucible; discontinue the heating as soon as the reaction of the decomposition of the salt begins.

When the reaction ends, open the crucible and heat it for 5-10 min (removal of water). Cool the crucible and transfer the powder to a piece of filter paper. Weigh the powder and calculate the yield of chromic oxide.

2. Amphoteric Properties of Chromic Hydroxide. By means of an exchange reaction prepare a precipitate of chromic hydroxide and treat it first with HCl and then with NaOH. What happens? What is the colour of the resulting solutions?

3. Oxidation of Compounds of Trivalent Chromium. (a) Add an equal volume of lime chloride to the alkaline solution of chromite from the previous experiment. Heat the solution to boiling point. What happens? Write the equation of the reaction that has taken place.

(b) Place 1-2 g of a 1 : 2 mixture of potassium nitrate and potassium carbonate in a crucible and heat it until the mixture melts. Introduce a few grains of chromic oxide into the molten mixture and continue

heating until the oxide "dissolves". What is the colour of the cooled melt? Write the equation of the reaction that has taken place.

4. Hydrolysis of Salts of Trivalent Chromium. (a) Test a solution of chromic chloride or nitrate with blue litmus paper. What happens? Write the equation of the hydrolysis reaction.

(b) Pour 2 ml of chromic chloride solution into each of two test tubes. Add an equal volume of ammonium sulphide solution to one of them; an equal volume of sodium carbonate solution, to the other. Do the precipitates in the two test tubes differ in colour? Write the equations of the reactions that have taken place, bearing in mind that in the case of salts of weak acids and weak polyacidic bases hydrolysis is practically irreversible.

5. Conversion of Chromate to Bichromate and Vice Versa. Add a sulphuric acid solution to 3-4 ml of a K_2CrO_4 solution and observe the change of colour. Now add a KOH solution. What happens? Write the equations of the reactions that have taken place.

6. Oxidant Properties of Hexavalent Chromium. (a) Using a glass rod, mix a few crystals of chromic anhydride with 5-6 drops of concentrated H_2SO_4 in a porcelain crucible. Now add a drop of methyl or ethyl alcohol. What happens?

(b) Place a pinch of chromic anhydride crystals in a dry refractory test tube and heat it carefully in the flame of a burner. From time to time introduce a glowing splint into the test tube and watch it flare up. Write the equation of the reaction of the decomposition of chromic anhydride. What type of reaction is it?

(c) Add 3 ml of an H_2SO_4 solution to 1 ml of a bichromate solution and pass a slow stream of hydrogen sulphide from the Kipp gas generator into it. Note the colour of the resulting solution. Write the equation of the reaction that has taken place.

7. Insoluble Chromates and Bichromates. In separate test tubes treat solutions of salts containing the ions $Ba^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, and $Ag^{\cdot}$ with potassium chromate and potassium bichromate. Note the colours of the precipitates and write the equations of the reactions of their formation. How do the precipitates react to acetic acid? Explain the changes observed.

8. Preparation of Chromium Peroxide. Pour 2 ml each of solutions of hydrogen peroxide, sulphuric acid, and ethyl ether into a test tube. Dip a clean glass rod into a $K_2Cr_2O_7$ solution and then immerse it in the test tube below the ether layer. What changes can be observed in the solution? Shake the solution carefully. Does the ether layer remain colourless? What is the substance formed in the reaction?

9. Preparation of Molybdic and Tungstic Acids. Pour 3 ml of an alkali solution into each of two test tubes. Add a small amount (on the tip of a penknife) of powdered molybdic anhydride to one of them; tungstic anhydride, to the other. The anhydrides dissolve, forming salts. Write the equations of the reactions that have taken place. Now

add concentrated HCl to the salts until molybdic and tungstic acids respectively are precipitated. Note the colours of the acids. Write the equations of the reactions that have taken place.

10. Reduction of Molybdenum and Tungsten Compounds. Add 2-3 ml of concentrated HCl and a granule of zinc to the precipitates prepared in the previous experiment. Observe the appearance of a blue colouration, which turns first to green and then to brown, depending upon the degree of reduction. Write the equations of the reactions that have taken place.

Exercise 36

THE HALOGENS

SUBJECTS FOR STUDY

Fluorine, chlorine, bromine, and iodine; atomic structure and chemical characteristics; oxidant power; physical properties, and attitude to water and other solvents.

The atoms of the halogens, while differing in their number of inner electron shells, all have 7 electrons in their outermost shell.

In chemical reactions the halogens display oxidant properties, adding one electron to the outer shell. Their reductant properties are not at all pronounced and are totally absent in the case of fluorine, whose atoms defy all attempts to wrest electrons from them in chemical reactions.

The oxidising power of the halogens rises with the decrease in atomic radii, so that fluorine is the strongest oxidising agent among them. Iodine is a more active reductant than the others:

	F	Cl	Br	I
Atomic number	9	17	35	53
Radius in Å units	0.68	0.97	1.13	1.35
Electron affinity in Cal . . .	92	85	77	72

As oxidants, the halogens react vigorously with most elements, but do not combine directly with oxygen or nitrogen. The halogen molecules consist of two atoms linked by a covalent type of bond and are therefore nonpolar.

At ordinary conditions fluorine is a yellowish gas, chlorine is a yellow-green gas, bromine is a reddish brown liquid that is easily vaporised, and iodine is a dark violet solid with a metallic lustre.

Solid iodine forms a vapour even at ordinary temperature and should therefore be kept in a jar with a ground-in lid; the process, called *sublimation*, can be accelerated markedly by gentle heating.

It is used to rid iodine of impurities. Iodine vapour is violet, this colour being typical of the I_2 molecules.

Iodine is poorly soluble in water. The solution, called iodine water, contains only 0.3 g of iodine to 1 litre of water. Iodine dissolves better in a solution of potassium iodide; this is accompanied by interaction between the I^- ion and I_2 molecules, with the formation of a complex ion:

$$KI + I_2 \rightleftarrows K[I_3]$$

Aqueous solutions of iodine have a brown colour, this evidently being the colour of the solvated molecules; in alcohol, in which iodine dissolves readily, it has the same colour. On the other hand, in solvents of no or low polarity iodine dissolves exhibiting the violet colour characteristic of I_2 molecules.

Bromine solutions in water range in colour from a golden yellow to reddish brown, depending upon concentration. The solubility of bromine in water is 3.5%, and the solution is called bromine water.

Similarly, chlorine dissolves in water to form chlorine water, in which the chlorine interacts slowly with the water:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$

The reaction produces hypochloric and hydrochloric acids.

A similar state of equilibrium, but shifted far more towards the halogen molecules, exists in aqueous solutions of bromine and iodine.

Fluorine oxidises water, forming ozone, oxygen, and hydrogen fluoride.

In nature the halogens are encountered chiefly as negative ions, and their preparation in the free state therefore boils down to oxidation, e. g.:

$$2\overset{-1}{Cl} - 2e^- = Cl_2$$

The F^{-1} ion does not yield to oxidation by chemical methods, and free fluorine is therefore prepared by oxidising the F^- ion at the anode by an electric current. Free iodine can also be prepared from sodium iodate $NaIO_3$ by treating it with reducing agents.

QUESTIONS

1. Which of the following reactions can be effected:

$KCl + F_2 =$ $\quad H_2S + Cl_2 =$ $\quad MgBr_2 + I_2 =$ $\quad HBr + S =$

Explain why this is so.

2. List three reactions for preparing elementary iodine from KI.

3. Upon oxidation, a colourless aqueous solution containing the Br^- or I^- ion acquires a yellow colour. What is the simplest

experiment for establishing whether the colour is due to bromine or iodine?

4. The thermal effect of the reaction $\frac{1}{2}H_2 + \frac{1}{2}F_2 = HF$ is 64 Cal; the thermal effect of the reaction $\frac{1}{2}H_2 + \frac{1}{2}I_2 = HI$ is —5.91 Cal. Are these values in agreement with the positions of these elements among their analogues?

5. Why can a $K[I_3]$ solution be used in reactions as free iodine?

6. How can bromine be prepared from sodium bromide, using manganese dioxide as an oxidising agent?

Problems

1. The element chlorine consists of the two stable isotopes Cl^{35} (75.43%) and Cl^{37} (24.57%). Determine its atomic weight.

2. The atomic weight of bromine is 79.92. The element consists of the two stable isotopes Br^{79} and Br^{81}. Determine the percent content of each.

3. What is the volume of gaseous chlorine at N. T. P. that can be obtained from a 20 litre tank of liquid chlorine if the density of the liquid chlorine is 1.5 g/cu cm?

4. What is the volume of chlorine at 15° and 760 mm Hg that will be needed to oxidise to free iodine the NaI from the ash produced by the burning of 10 tons of marine algae containing 0.64% NaI?

5. Tincture of iodine is a 5% solution of iodine in alcohol. What is the volume of 0.5 N $Na_2S_2O_3$ that will be needed to bleach 6 g of tincture of iodine?

6. A gas mask canister contains 40 g of activated charcoal. Determine the weight of the chlorine that can be adsorbed by the gas mask if 1 g of the charcoal adsorbs 235 ml of chlorine (reduced to N. T. P.).

7. A solution of 3.8 g of iodine in 100 g of chloroform boils at 61.78°. Determine the composition of the iodine molecule, knowing that the atomic weight of iodine is 126.9. For additional data see Table XI on p. 333.

8. The equilibrium constant for the reversible system $H_2 + I_2 \rightleftarrows 2HI$ at 443° is 50. Determine the concentration of the hydrogen at equilibrium, knowing that the concentrations of I_2 and HI at that same moment are 0.0114 and 0.0315 mols/litre respectively.

9. The heat of decomposition of a gram-molecule of chlorine to atoms is 58 Cal. The formation of a bromine molecule from atoms releases 46 Cal. The decomposition of two gram-molecules of NaBr requires 173.4 Cal, while the reaction $2Na + 2Cl = 2NaCl$ is accompanied by the evolution of 196 Cal. Determine the thermal effect of the reaction

$$2NaBr + Cl_2 = Br_2 + 2NaCl + x \text{ Cal.}$$

10. Draw a diagram of the electrolysis of an aqueous solution of NaCl in a graphite vessel which serves as the anode and which is separated by a diaphragm from an iron cathode. What will be the products obtained at the electrodes (and in what amounts) if a 0.5 A current is passed through the solution for 1 hour?

LABORATORY WORK

Apparatus and materials: the apparatus shown in Figs. 77 and 78; test tubes and rack; porcelain mortar; three cylinders with glass covers; 100 ml measuring cylinder; 100 ml beakers; 250 ml beaker; iron deflagrating spoon; glass spatula; 10 ml pipette; porcelain casserole; scalpel or knife; crucible tongs; filter paper; powdered aluminium; powdered magnesium; zinc dust; copper foil; powdered metallic anti-

mony; metallic sodium; crystalline iodine; potassium permanganate; manganese dioxide; KI; NaBr; concentrated HCl; concentrated H_2SO_4; chloroform; 0.5 N KI; 1% solution of iodine in KI; indigo solution; starch solution; hydrogen sulphide water; bromine water and chlorine water.

1. Preparation of Chlorine and Chlorine Water. (Conduct the experiment in a ventilated hood!) Place 4 g of $KMnO_4$ in a test tube (or flask) with a side tube, as shown in Fig. 77, and close the test tube with a stopper, through which a dropping funnel has been passed. Calculate the volume of hydrochloric acid (relative density 1.19) that will be needed to react with the amount of permanganate taken. Take 20% more than the calculated amount of HCl. Measure the required volume of concentrated HCl and pour it into the dropping funnel. Lower the end of the gas-delivery tube into the dry cylinder and start the acid dripping from the funnel into the flask. Fill three cylinders with the gas evolved (watch the cylinders fill by observing the yellow-green colour of the gas against the background of a sheet of white paper, held behind the cylinder). Then immerse the delivery tube in a beaker with 50 ml of water and saturate the water with chlorine. Towards the end of the reaction the flask may be heated gently. In the absence of permanganate, 5 g of manganese dioxide in grains may be taken. Since the latter reacts poorly with HCl without heating, the process should be conducted with heating, but not above 90°.

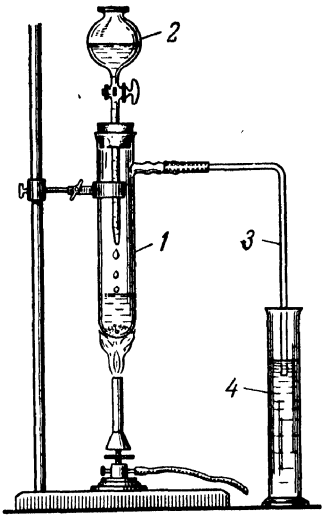


Fig. 77. Apparatus for preparing gases (chlorine)

1 — test tube with $KMnO_4$; 2 — dropping funnel; 3 — gas-delivery tube; 4 — cylinder.

2. Oxidant Properties of Chlorine. (Conduct these experiments in a ventilated hood!) (a) Into one of the cylinders drop a strip of copper foil that has been heated slightly over the flame of a burner (in the absence of foil it is possible to use stranded wire the strands of which have been taken apart). What happens?

(b) By means of a glass scoop take a small amount of powdered antimony (freshly ground) and transfer it to another cylinder with chlorine. What happens?

(c) Into the third cylinder lower a deflagrating spoon with a piece of metallic sodium on it. What happens? Write the equations of the reactions that have taken place.

3. Oxidant Properties of Chlorine Water. (a) Add some chlorine water to hydrogen sulphide water. What happens? Write the equation of the reaction that has taken place.

(b) Add some chlorine water to an equal volume of blue litmus solution; observe the blue colour first change to red and then disappear. Explain these changes. In what way does bleaching with chlorine differ from bleaching with sulphur dioxide?

4. Extraction of Bromine by Solvents. Pour 3-4 ml of bromine water and 1 ml of chloroform into a test tube; shake the mixture vigorously. What colour does the chloroform acquire?

5. Preparation of Bromine. (Conduct the experiment in a ventilated hood!) (a) Mix small amounts of NaBr and MnO_2 in a test tube. Pour 2-3 ml of concentrated H_2SO_4 over the mixture. Heat the test tube carefully and observe the evolution of brown bromine vapour.

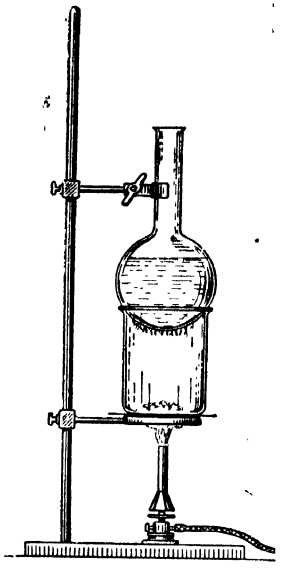


Fig. 78. Apparatus for sublimation of iodine

(b) Add 2 ml of chlorine water to an equal volume of KBr solution. What colour does the solution acquire? Add 1 ml of chloroform and shake the solution. Write the equation of the reaction that has taken place, according to the observed results. Does chlorine or bromine have the greater electron affinity? Why is this so?

6. Oxidant Properties of Bromine. (a) Add a pinch of powdered metallic magnesium, zinc, or aluminium to some bromine water and watch the solution lose its colour. Write the equation of the reaction that has taken place.

(b) Add bromine water by drops to hydrogen sulphide water and shake the solution vigorously. What happens? Write the equation of the reaction that has taken place.

7. Solubility of Iodine. Drop a crystal of iodine into a test tube with 2-3 ml of water and shake the contents of the test tube vigorously. Does the iodine dissolve in the water at all appreciably? Add a small crystal of KI and shake the test tube again a minute later. What accounts for the increased solubility of iodine in the KI solution? Add 1 ml of chloroform to the solution and note the colour of the chloroform after shaking the test tube.

8. Detection of Free Iodine. Conduct a reaction between solutions of iodine and starch. How does the blue colouration of the adsorption product change upon heating and cooling?

9. Preparation of Iodine. (a) Grind a few crystals of KI in a mortar with a pinch of MnO_2. Transfer the mixture to a test tube, add 1 ml of concentrated H_2SO_4, and heat the test tube slightly. Observe what happens. Write the equation of the reaction that has taken place.

(b) Prepare iodine in the same way that bromine was prepared

in experiment 5b. From the two experiments draw a conclusion about the relative oxidising power of the halogens.

10. Oxidant Properties of Iodine. (a) Conduct experiment 6b, substituting for bromine water an iodine solution in the presence of KI.

(b) (Conduct this experiment in a ventilated hood!) Grind a few crystals of iodine in a mortar and mix in a pinch of zinc dust.

Transfer the mixture to a porcelain casserole and add a drop of water from a pipette. Observe the appearance of violet iodine vapour. What accounts for the conversion of solid iodine to vapour? What role does water play in this reaction?

11. Sublimation of Iodine. Drop 5-10 crystals of iodine into a dry spoutless beaker and put it on a wire gauze with an asbestos centre, placed on a ringstand. Above the beaker fasten a round-bottom flask filled with water (Fig. 78). Heat the beaker *carefully* by means of a small flame. The entire beaker will soon be filled with violet iodine vapour, and small crystals of sublimed iodine condense on the walls of the flask, aggregating with time into clusters of crystals. Detach the iodine crystals from the flask bottom, collecting them in a jar with a ground-in lid.

Exercise 37

HYDROGEN COMPOUNDS OF THE HALOGENS

SUBJECTS FOR STUDY

Hydrogen fluoride, hydrogen chloride, hydrogen bromide, and hydrogen iodide; their physical properties; the solubility of these gases in water; the aqueous solutions as acids; electrolytic characteristics of the hydrogen halide compounds; relative strength of the acids; hydrochloric and hydrofluoric acids; salts of the hydrogen halide acids; soluble and insoluble halides; reductant characteristics of the negatively charged halide ions, and methods of preparing the hydrogen halide compounds.

The hydrogen compounds of the halogens are colourless gaseous substances, whose molecules are slightly polar. They dissolve readily in water, and the solutions are distinctly acidic.

At definite concentrations the aqueous solutions of the hydrogen halides are so-called "solutions of constant boiling point", which distill off at a quite definite temperature without any change of composition. The constant boiling mixture of hydrochloric acid contains 20.24% of HCl and boils at 110°. When hydrochloric acid solutions of a concentration lower than 20.24% are boiled, practically only water evaporates, whereas when a concentrated solution is boiled, the vapour contains chiefly hydrogen chloride.

Hydrochloric (muriatic), hydrobromic, and hydroiodic acids are strong acids, their apparent degrees of ionisation in 0.1 N solutions exceeding 90%. The degree of ionisation of hydrofluoric acid * is about 8%, this markedly lower strength being due to HF polymerisation to form H_2F_2 molecules.

The salts of the hydrogen halide acids are called *fluorides, chlorides, bromides, and iodides* respectively. Among the latter three the insoluble salts are AgCl, AgBr, AgI, Hg_2Cl_2, and Hg_2Br_2; the slightly soluble salts are those of lead. The silver salt of hydrofluoric acid has a high solubility in water, whereas the fluorides of calcium and magnesium, unlike the salts of the other hydrogen halide acids, have a low solubility.

The halide negative ions are reducing agents (with the exception of F^{-1}) and can be oxidised by various oxidants, e. g.: $2Br^{-1} - 2e^- = Br_2$. With the rise in ionic radii from Cl^{-1} to I^{-1}, there is an increase in reducing power and a decline in compound stability.

Hydrofluoric and hydrochloric acids are prepared by decomposing their salts by means of exchange reactions with a nonvolatile acid, such as concentrated H_2SO_4. Since H_2SO_4 is a strong oxidising agent, while HBr and HI are the strongest reductants among the hydrogen halides, they are immediately upon formation oxidised by the sulphuric acid to free halogens:

$$\overset{-1}{8HI} + \overset{+6}{H_2SO_4} = 4I_2 + \overset{-2}{H_2S} + 4H_2O \qquad (8e^-)$$

The best method for preparing pure HBr and HI is the hydrolysis of phosphorus halides:

$$PI_3 + 3HOH \rightarrow 3HI + H_3PO_3$$

QUESTIONS

1. What accounts for the fuming of the hydrogen halides upon exposure to air?
2. Why does hydrogen iodide, unlike the other hydrogen halides, burn in oxygen?
3. Do the reactions of HCl preparation from NaCl and H_2SO_4 proceed the same way in laboratory and industrial conditions?
4. What will be the product of the reaction between concentrated sulphuric acid and crystalline potassium iodide?
5. Give possible reactions for detecting the Cl′ and I′ ions in solution.
6. What are the chemical properties of KI?

* The names of hydrofluoric acid and fluorine originated from the mineral fluorspar CaF_2, from which hydrogen fluoride is usually obtained.

Problems

1. A mixture of hydrogen and chlorine (269.4 ml) has reacted without any change in volume. The resulting gas mixture is passed through an iodide solution, liberating 0.254 g of iodine. Determine the percentage composition (by volume) of the initial mixture.
2. Fifty 25 litre carboys of 37% HCl (relative density 1.19) have been prepared industrially from 1 ton of common salt containing 98.5% of NaCl. Determine the HCl yield in per cent.
3. How many millilitres of M $Na_2S_2O_3$ will be needed to convert 9.39 g of AgBr to $Na_3[Ag(S_2O_3)_2]$?
4. What amount of N $KMnO_4$ can be reduced by 100 ml of 14% HBr (relative density 1.105)?
5. Determine the percentage and molar concentrations of an HCl solution prepared by mixing 120 litres of its 36% solution (relative density 1.18) with 200 litres of water.
6. A potassium bromide solution saturated at 100° is cooled by melting snow, yielding 830 g of recrystallised KBr. What was the weight of the initial solution taken, and what was the loss of KBr in the mother liquor? The solubility of the salt at 100° is 51.2%; at 0°, 34.5%.
7. Determine the normality of a KI solution if 20 ml of that solution reacts quantitatively in an acid medium with 24 ml of 0.05 N $KMnO_4$.
8. One mol each of gaseous oxygen and hydrogen chloride have been mixed in a closed vessel. Their interaction (at increased temperature and in the presence of a catalyst) produces the equilibrium:

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$$

The HCl concentration at equilibrium is found to be 0.6 mol. Find the equilibrium constant.
9. The AgBr solubility product at 25° equals $3.5 \cdot 10^{-13}$. How many times greater is its solubility in water than in 0.01 M KBr?
10. The electrolysis of concentrated HCl releases 5,600 ml of hydrogen at the cathode. Find the volume and weight of the chloride liberated at the anode.

LABORATORY WORK

Apparatus and materials: the apparatus shown in Figs. 77, 79, and 80; test tubes and rack; 100 ml measuring cylinder; 100 ml measuring bottle; three 100 ml Erlenmeyer flasks; 250 ml round-bottom flask with side arm condenser; adapter; 10 ml pipette; porcelain mortar; lead crucible; knife; glass plate; narrow cylinder for relative density measurements; hydrometer (relative density 1.2); thermometer to 200°; aluminium shavings; copper shavings; zinc shavings; common salt; calcium fluoride; paraffin wax or beeswax; benzine; concentrated H_2SO_4; 2N HCl; dry red phosphorous; bromine; powdered iodine; 2 N and 70% H_2SO_4; 0.5 N titrated NaOH; 0.1 N $AgNO_3$; N $CaCl_2$; 0.5 N NaCl; 0.5 N NaF; 0.5 N NaBr; 0.5 N NaI; N $K_2Cr_2O_7$; 0.5 N $KMnO_4$; 0.5 N KNO_2; 0.5 N KIO_3; chlorine water; bromine water; starch solution; methyl-orange and litmus solutions.

1. **Preparation of Hydrochloric Acid.** Weigh 15 g of common salt and place it in a flask (Fig. 79). Pour 40 ml of 70% H_2SO_4 in the dropping funnel. Pour 75 ml of distilled water into each of the absorption bottles and close them tightly with the stoppers. The ends of the glass tubes should almost touch the surface of the water, but should not be submerged. Pour half of the sulphuric acid in the dropping funnel into the flask, allow the salt to become impregnated

with the acid, and then heat the flask. Ten minutes later pour the rest of the acid into the flask and continue the heating for another 30 minutes.

Then discontinue the heating, disconnect the absorption bottles, pour the HCl solution into a cylinder and dilute it with water to 250 ml. Mix the solution thoroughly and determine the relative density by means of a hydrometer. Calculate the percentage concentration (by means of a table) and the yield of the product.

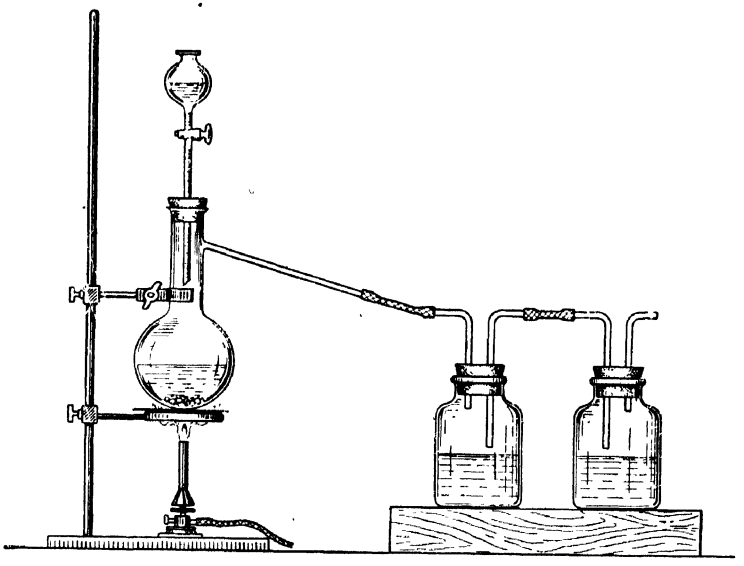


Fig. 79. Apparatus for preparing hydrochloric acid

2. Distillation of Hydrochloric Acid (Fig. 80). Pour 100 ml of 12% HCl into a flask (1), close it with a stopper through which a thermometer has been passed, and connect it with a Liebig condenser (2). Beneath the adapter (3) of the condenser place an Erlenmeyer flask (4). Now allow water to pass through the condenser and heat the flask on a wire gauze. Note the initial boiling point of the solution and continue heating the solution until the thermometer shows 110° (at normal pressure). Discontinue the heating and cool the solution in the flask. Weigh a 100 ml measuring bottle and pour 8-9 ml of the HCl solution from the flask (1) into it. Weigh the measuring bottle again, with the solution, dilute it with water to the mark, and mix the contents thoroughly. Draw off 10 ml of the solution from the measuring bottle in a pipette and titrate it with 0.5 N NaOH in the presence of phenolphthalein. Repeat the titration until the results coincide.

On the basis of the titration data calculate how many grams of anhydrous HCl were contained in the measuring bottle; from this determine the concentration of the HCl solution that boils at 110°.

3. Preparation of Hydrogen Fluoride and Its Properties. (Conduct the experiment in a ventilated hood!) Place about 1 g of calcium fluoride in a lead or porcelain crucible. Cover a glass plate with a layer of paraffin wax or beeswax and then write some letter on it, penetrating the wax to the glass with a needle or sharpened match.

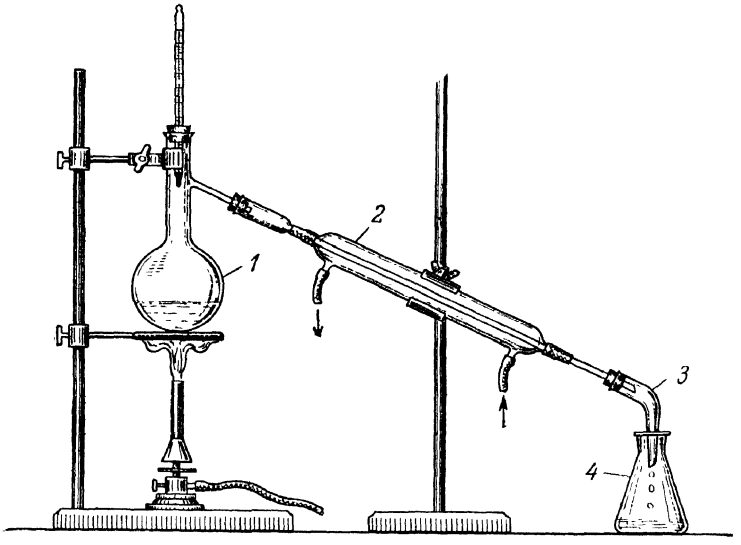


Fig. 80. Distillation apparatus

1 — distillation flask; 2 — condenser; 3 — adapter; 4 — receiver.

Now pour 2-3 ml of concentrated H_2SO_4 into the crucible and cover it quickly with the glass plate, wax layer downwards. Five or six minutes later lift the plate, remove the wax first with a knife and then with some cloth wetted in benzine, and observe the etched design on the glass. Write the equations of the reactions that have taken place.

4. Reaction of Bromides and Iodides with Concentrated Sulphuric Acid. (Conduct the experiment in a ventilated hood!) Pour 2-3 ml of concentrated H_2SO_4 into each of two test tubes. Add 0.5 g of potassium bromide to one, and the same amount of potassium iodide, to the other. Observe what is formed. Why are free bromine and iodine formed in these reactions, in addition to hydrogen bromide and hydrogen iodide?

5. Preparation of Hydrogen Bromide and Its Properties. (Conduct the experiment in a ventilated hood!) Place about 0.1 g of dry red phosphorus in the test tube (1) of the arrangement shown in Fig. 77 and add 5-6 drops of bromine. Close the test tube with a stopper fitted with a small dropping funnel (2), containing 2 ml of water. Pour water into the cylinder (4) until its level is 1-2 mm below the tip of the delivery tube (3). Pour the water from the dropping funnel into the test tube (1), close the tap of the funnel, and heat the test tube over a small flame. After 5 minutes discontinue the heating and demonstrate by two reactions that the cylinder (4) contains a solution of hydrobromic acid. Write the equations of the reactions that have taken place.

6. Preparation of Hydrogen Iodide and Its Properties. Use the same apparatus as in the previous experiment. Into the dry test tube place a thoroughly mixed mixture of 1 g of iodine and 0.1 g of dry red phosphorus. Add water from the funnel by drops. The reaction commences without heating. Five or six minutes later demonstrate by two reactions that the cylinder (4) contains a solution of hydroiodic acid. Write the equations of the reactions that have taken place.

7. Action of Hydrochloric Acid on Metals. In separate test tubes test the action of hydrochloric acid on the metals: zinc, aluminium, and copper. Which of the metals are dissolved? Write the equations of the reactions that have taken place.

8. Salts of the Hydrogen Halide Acids. Make separate tests of the action of the $Ag^{\cdot}$ and $Ca^{\cdot\cdot}$ ions on fluoride, chloride, bromide, and iodide solutions. Note the colours of the precipitates and write the equations of the reactions that have taken place.

9. Reductant Properties of Halide Negative Ions. Plan three experiments demonstrating that the Cl', Br', and I' ions are reducing agents. After consulting the instructor, carry out the experiments and write the equations of the reactions that have taken place.

10. Dry Salt Analysis. Receive from the instructor a pure salt that may contain one of the four anions F', Cl', Br', or I' and one of the three cations $K^{\cdot}$, $Na^{\cdot}$, or $NH_4^{\cdot}$.

Dissolve the salt in water ($\frac{3}{4}$ of a test tube). Since the ammonium ion hampers the detection of sodium and potassium ions, its presence or absence should be established first.

Making use of reactions studied earlier, carry out the analysis of the salt and submit to the instructor a report according to the following form:

(a) the number of the salt analysed . . . . . .
(b) analytic procedure followed . . . . . .
(c) detected cation: . . . . . .
detected anion: . . . . . .

Exercise 38

OXYGEN COMPOUNDS OF THE HALOGENS

SUBJECTS FOR STUDY

The positive valences of the halogens; their oxides and oxygen acids; the comparative strength of the acids; hypochlorites, chlorites, chlorates, bromates, iodates, and perchlorates; general methods for preparing these salts and acids; their oxidant properties and reaction to heating.

With seven electrons in their outermost shells, the halogen atoms can give up different numbers of electrons: 1, 2, 3, 4, 5, or 7. Not all of the halogens, however, exhibit all of these valences: bromine, for instance, does not form Br^{+7}, while fluorine does not assume positive valences at all.

The following table gives the composition of the oxides, acids, and salts corresponding to the halogen valences from +1 to +7. The acids whose formulae are given in bold face type are known in the free state; the rest, only in solutions.

Positive valence of halogens	+1	+3	+4	+5	+7
General formulae of oxides and their names	R_2O hypo... orous anhydride	R_2O_3 ... orous anhydride	RO_2 dioxide	R_2O_5 pentoxide	R_2O_7 heptoxide
Known compounds	Cl_2O	—	ClO_2, IO_2	I_2O_5	Cl_2O_7
General formulae of acids and their names	HRO hypo...orous acid	HRO_2 ... ous acid	—	HRO_3 ... ic acid	HRO_4 per ... ic acid
Known compounds	HClO, HBrO, HIO	$HClO_2$	—	$HClO_3$, **HIO_3**	$HClO_4$ **$HIO_4 \cdot 2H_2O$**
General formulae of salts and their names	MeRO hypo ... ite	$MeRO_2$ ... ite	—	$MeRO_3$ ... ate	$MeRO_4$ per ... ate

The salts of some of these acids have practical applications. This is true of sodium hypochlorite NaClO, whose solution is known as Javelle water; the mixed calcium salt of hydrochloric and hypochlorous acids $CaCl \cdot OCl$, which is the main constituent of bleaching powder; potassium chlorate $KClO_3$; the bromate $KBrO_3$ and the iodate

KIO_3; ammonium perchlorate NH_4ClO_4, which is used in explosive mixtures, and potassium perchlorate, which is insoluble in water and serves for the quantitative estimation of the potassium ion. All of these compounds are used primarily as oxidising agents.

All halogens of positive valences can be reduced to the negatively charged ion, e. g.:

$$\overset{+2}{2Ni}(OH)_2 + \overset{+1}{NaClO} + H_2O = \overset{+2}{2Ni}(OH)_3 + \overset{-1}{NaCl}$$

$$6FeSO_4 + \overset{+5}{KClO_3} + 3H_2SO_4 = \overset{+3}{3Fe_2}(SO_4)_3 + \overset{-1}{KCl} + 3H_2O$$

If the negatively charged ion of the same halogen is used as the reducing agent, the redox process proceeds to the neutral molecule, e. g.:

$$5\overset{-1}{KI} + \overset{+5}{KIO_3} + 3H_2SO_4 = 3I_2 + 3K_2SO_4 + 3H_2O$$

Among the acids in which clorine has different valences

$$\overset{+1}{HClO} \qquad \overset{+3}{HClO_2} \qquad \overset{+5}{HClO_3} \qquad \overset{+7}{HClO_4}$$

acidity increases from HClO to $HClO_4$.

The oxidising power of the acids decreases in the same direction, since the transition to the stablest Cl^- state is effected most readily by the unipositive Cl^{+1}, which gains only 2 electrons.

In the row of acids of different halogens with the same valence

$$\overset{+1}{HClO} \qquad \overset{+1}{HBrO} \qquad \overset{+1}{HIO}$$

the strength of the acids and their oxidising power decline from HClO to HIO.

The halogens of intermediate valence can be reducing, as well as oxidising agents. The ClO_3^- ion, for instance, gives up two electrons to become the ClO_4^- ion.

This reaction takes place when potassium chlorate is heated carefully:

$$4\overset{+5}{KClO_3} = 3\overset{+7}{KClO_4} + \overset{-1}{KCl}$$

Such disproportionation reactions are used extensively in preparing oxygen compounds of halogens of higher charge from compounds of lower charge.

The disproportionation reaction forms the basis of the processes used for preparing hypochlorites, chlorates, bromates, and iodates. The following reactions take place, for instance, when Cl_2 reacts with alkali solutions:

(1) at room temperature

$$Cl_2 + 2KOH = \overset{+1}{K}ClO + \overset{-1}{K}Cl + H_2O$$

(2) upon heating to 100°

$$3Cl_2 + 6KOH = \overset{+5}{K}ClO_3 + 5\overset{-1}{K}Cl + 3H_2O$$

QUESTIONS

1. Why is it that fluorine does not form positive ions?
2. By means of what two reactions can HIO_3 be prepared?
3. Why does an iodine solution lose its colour upon the addition of chlorine water?
4. Give examples of reactions involving KIO_3 and $KClO_3$ as oxidising agents.
5. How can oxygen be obtained from bleaching powder?
6. Explain the reaction between $KClO_3$ and concentrated H_2SO_4.

ASSIGNMENT

Carry out all the necessary calculations for experiment 1 of this Exercise: *the preparation of calcium hypochlorite from 7.4 g of calcium hydroxide.*

For this purpose:

(a) Write the equation of the reaction whereby calcium hypochlorite is prepared from calcium hydroxide and chlorine.

(b) Calculate the weight of the chlorine needed for the reaction.

(c) Write the equation of the reaction and calculate the amounts of the initial products needed to prepare the required amount of chlorine, the chlorine being obtained from common salt, manganese dioxide, and 70% H_2SO_4. Multiply the calculated amounts by 1.5 for the experiment.

(d) Calculate the volumes of 95.6% H_2SO_4 and water needed to prepare the amount of 70% H_2SO_4 found in "c".

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 81; test tubes and rack; wide-mouth test tube; suction filter; porcelain mortar; two 100 ml measuring cylinders; 100 ml beaker; thermometer to 150°; pipette; wash bottle; scissors; glass rod; splints; porcelain casserole; MnO_2; common salt; crystalline $FeSO_4$; $KClO_3$; $Ca(OH)_2$; powdered sugar or starch; concentrated H_2SO_4; concentrated HCl; 2 N NaOH; 0.5 N KI; 2N H_2SO_4; 0.5 N $MnSO_4$; 5% KIO_3; indigo solution; bromine water; litmus paper; filter paper, and ice.

1. Preparation of Calcium Hypochlorite. (Conduct the experiment in a ventilated hood!) Verify the airtightness of the apparatus shown in Fig. 81, consisting of a flask (1) fitted with a dropping funnel (2), a wash bottle (3), and a gas-delivery tube (4) immersed in a test tube (5). Weigh the calculated amounts of common salt and manganese dioxide, grind them in a mortar, and transfer them to the flask (1). Prepare the calculated amount of 70% H_2SO_4, *adding the concentrated*

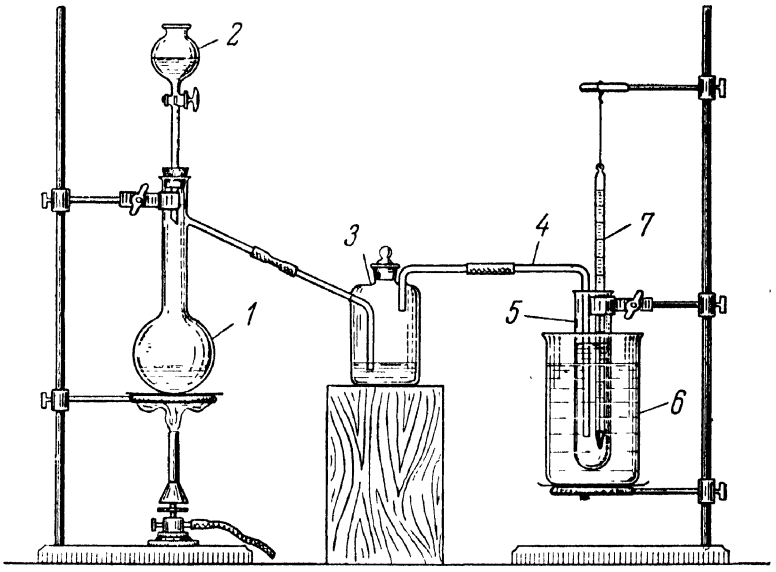


Fig. 81. Apparatus for preparing calcium hypochlorite

1 — flask with side arm; 2 — dropping funnel; 3 — wash bottle for gases; 4 — gas-delivery tube; 5 — test tube; 6 — beaker with water; 7 — thermometer.

acid in small portions to the water, but not vice versa! Pour the prepared 70% acid into the dropping funnel. Pour enough water into the wash bottle for the tip of the tube to touch the surface of the water (is it necessary to wash the gas?). Pour 15 ml of distilled water into the wide-mouth test tube, adding 7.4 g of powdered calcium hydroxide and stirring the contents of the test tube with a glass rod. Place the test tube in a beaker with water (6) put on a ring with a gauze; lower the gas-delivery tube and a thermometer (7) into the beaker.

Pour the H_2SO_4 solution from the dropping funnel into the flask and, when the mixture has become impregnated with it, heat the flask over a small flame. See that the flow of gas is even and not very intense. During the experiment the temperature of the reaction mixture should not rise above 30°; if it does, the test tube should be

cooled with cold water. When the flow of chlorine from the flask ceases, disconnect the test tube from the apparatus.

The calcium hypochlorite formed, together with the partly unreacted calcium hydroxide, should be filtered through a small funnel (see Exercise 11). Wash the precipitate on the filter twice with 3 ml of ice-cold distilled water.

Transfer part of the precipitate to a test tube, add 12-15 ml of water, and shake the contents of the test tube thoroughly. Keep the resulting saturated solution of calcium hypochlorite for the next experiment.

2. Properties of Hypochlorites. (a) Test (in a ventilated hood!) the action of concentrated sulphuric acid on solid lime chloride. Identify the product by its odour (carefully!). Write the equation of the reaction that has taken place.

(b) Dissolve a few crystals of $FeSO_4$ in 2-3 ml of water and add an equal volume of NaOH solution. Note the colour of the precipitate formed and write the equation of the reaction that has taken place. Add 3-4 ml of the saturated solution of calcium hypochlorite to the test tube. What change does the colour of the precipitate undergo? Write the equation of the reaction that has taken place.

(c) Test the action of the calcium hypochlorite solution on a $Mn(OH)_2$ precipitate prepared by treating a manganese salt with a NaOH solution. Write the equation of the reaction that has taken place.

(d) Mix an indigo solution with an equal volume of H_2SO_4 solution and add a small amount of solid lime chloride. What happens?

3. Preparation of Hypobromite and Its Properties. Add 2 ml of bromine water by drops to a test tube containing an equal volume of NaOH solution. Watch the bromine lose colour. Write the equation of the reaction that has taken place.

Add sulphuric acid to a colourless hypobromite solution until the solution becomes acidic (litmus paper test) and watch the solution become yellow. What has happened? Write the equation of the reaction that has taken place.

4. Properties of Chlorates. (Conduct experiments 4a and 4b in a ventilated hood!)

(a) Test the action of concentrated HCl on a small amount (pinch) of $KClO_3$. Record your observations and write the equation of the reaction that has taken place.

(b) Grind (*carefully!*) 0.5 g $KClO_3$ to a powder in a clean mortar. Mix the powder on a piece of paper with some powdered sugar or some starch; place the mixture in a porcelain casserole in a ventilated hood and pour 1-2 drops of concentrated H_2SO_4 from a pipette on it. What happens? Write the equation of the reaction that has taken place.

(c) Place about 1 g of $KClO_3$ in a dry test tube fastened vertically in the clamp of a ringstand and heat the test tube until the salt melts.

Insert a glowing splint into the test tube. Does it flare up? Now add a pinch of MnO_2 to the molten salt and observe the violent decomposition of the salt. Repeat the test with a glowing splint. Write the equation of the reaction that has taken place.

5. Properties of Iodates. Add a few drops of 5% KIO_3 to an acidic, colourless solution of KI. What is observed? Explain this and write the equation of the reaction that has taken place.

Exercise 39

THE ELEMENTS OF THE MANGANESE SUBGROUP

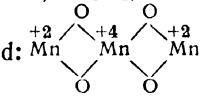
SUBJECTS FOR STUDY

The elements manganese, technetium, and rhenium; the structure of their atoms. The oxides of manganese and their chemical character; the hydroxides of manganese of different valences and their redox characteristics; the conversion of Mn^{+2} to Mn^{+7} and *vice versa*; permanganates, manganates, and manganites.

The atoms of manganese, technetium, and rhenium, although differing in number of inner electron shells, have two electrons in their outermost shell and 8 + 5 in the next one. In the course of oxidation they can give up a maximum of 7 electrons, exhibiting a positive valence of 7. Manganese, in addition to this, forms compounds in which it displays positive valences of 2, 3, 4, 5, and 6. Rhenium is known to exhibit the valences 1, 3, 4, 5, and 6 in compounds. Technetium stands closer to rhenium than to manganese in its properties.

Manganese is a non-noble metal, with the normal electrode potential $E^0 = -1.05$ V. It dissolves readily in acids, releasing hydrogen and forming salts in which it is bivalent. The normal potential of rhenium is +0.15 V. Rhenium does not dissolve in solutions of either hydrochloric or sulphuric acid, but is oxidised by concentrated nitric acid to perrhenic acid $HReO_4$. The following oxides correspond to each valence form of manganese:

MnO	Mn_2O_3	MnO_2	Mn_2O_5	MnO_3	Mn_2O_7
manganous oxide	manganic oxide	manganese dioxide	manganese pentoxide *	manganese trioxide	manganese heptoxide
basic oxides		amphoteric oxide	acid anhydrides		

* The oxides Mn_2O_5 and MnO_3 have not been isolated in the free state. An oxide with a mixed manganese valence, Mn_3O_4, is also known. It may be regarded as a manganese salt of manganic acid: 

With the increase in the valence of manganese, its oxides become more acidic.

The action of reducing agents upon MnO_2 in an acid solution produces Mn^{+2} salts, which are pink in the solid state and in concentrated solutions, while in dilute solutions they are colourless. The treatment of the solutions with alkalis precipitates manganous hydroxide $Mn(OH)_2$, which grows dark upon exposure to air or in the presence of other oxidising agents, owing to conversion to Mn^{+4} compounds according to the reactions:

$$2\overset{+2}{Mn}(OH)_2 + 2H_2O + O_2 = 2\overset{+4}{Mn}(OH)_4 \quad (4e^-)$$

$$\overset{+2}{Mn}(OH)_2 + Br_2 + 2KOH = \overset{+4}{Mn}(OH)_4 + 2K\overset{-1}{Br} \quad (2e^-)$$

$Mn(OH)_4$ is an amphoteric hydroxide called manganous acid. Its salts, manganites, undergo hydrolysis readily, producing the brown precipitate of manganous acid.

Strong oxidising agents in an alkaline medium (in solutions or upon fusing) convert Mn^{+4} compounds to salts of hexavalent manganese, the *manganates* Me_2MnO_4, which have a green colouration (the colour of the MnO_4^{-2} ion). When manganates are acidified, for example in the reaction

$$Na_2MnO_4 + H_2SO_4 = H_2MnO_4 + Na_2SO_4$$

manganic acid is formed, undergoing prompt decomposition (the disproportionation reaction) *:

$$3\,H_2\overset{+6}{Mn}O_4 = 2H\overset{+7}{Mn}O_4 + \overset{+4}{Mn}O_2 + 2H_2O$$

The MnO_2 forms a brown precipitate, while the solution acquires a violet colour. Manganic acid and its anhydride MnO_3 have not been isolated in the free state.

Permanganic acid $HMnO_4$ is known only in solutions. Its salts are called *permanganates*, and the most important of them is potassium permanganate $KMnO_4$. This is a strong oxidising agent, which, depending upon the solution, is reduced either to Mn^{+2} compounds (in acid solutions), or to Mn^{+4} compounds (in neutral or slightly alkaline solutions), or to Mn^{+6} compounds (in strongly alkaline solutions or in the presence of small quantities of the reducing agent). In all these reactions the colour of the solution changes to that of the resulting ion.

* Reactions of this type were formerly called auto-redox reactions.

The compounds of permanganic acid are usually prepared by oxidising manganates by chlorine or by oxidising the MnO_4^{-2} ion at the anode.

Some reactions of the oxidation of Mn^{+2} to MnO_4^{-1} are known involving such oxidising agents as lead dioxide PbO_2 in concentrated nitric acid or sodium bismuthate $NaBiO_3$ — or ammonium persulphate $(NH_4)_2S_2O_8$—in a slightly acidic solution.

The reaction between solid $KMnO_4$ and concentrated H_2SO_4 produces manganese heptoxide Mn_2O_7 in the form of a heavy liquid; it is a very potent oxidising agent and is highly explosive.

Particularly important (for analytical purposes) is the reaction of the oxidation of oxalic acid and its salts (oxalates) by potassium permanganate in an acidic solution. The $C_2O_4^{-2}$ ion gives up two electrons to become CO_2:

$$5Na_2C_2O_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 =$$
$$= 10CO_2 + 5Na_2SO_4 + K_2SO_4 + \overset{+2}{Mn}SO_4 + 8H_2O$$

QUESTIONS

1. Why is it that manganese forms several oxides with sharply differing chemical properties?
2. Write equations for the following oxidation reactions:

$Mn^{+2} \rightarrow Mn^{+4}$; $Mn^{+2} \rightarrow MnO_4^{-1}$; $MnO_2 \rightarrow MnO_4^{-2}$; $MnO_4^{-2} \rightarrow MnO_4^{-1}$

3. Calculate the oxidation equivalent of $KMnO_4$ depending upon the type of solution.
4. Write equations for reactions in which MnO_4^{-1} and MnO_2 are reduced to Mn^{+2}.
5. Write structural formulae for all the hydroxides of manganese.
6. Write the equation for the reaction in which metallic rhenium dissolves in concentrated HNO_3, knowing that the product of the reaction is perrhenic acid $HReO_4$.

Problems

1. In what proportion does the element rhenium (atomic weight 186.31) contain the isotopes Re^{185} and Re^{187}.
2. Ten grams of metallic manganese were heated to 82° and immersed in 40 g of water at 18.20°, raising its temperature to 20°. Determine the atomic weight of manganese.
3. The heating of MnO_2 above 530° produces Mn_3O_4. If the amount of MnO_2 heated is 240 g, what will be the product, what will be its weight, and what will be its volume (at N. T. P.)?
4. What amount of 0.3% H_2S solution is needed to reduce 120 ml of 0.5 N $KMnO_4$ in an acidic solution?

5. What amounts of pyrolusite and auxiliary materials (KNO_3, KOH, and Cl_2) will be needed to produce 100 kg of $KMnO_4$ (assuming a 100% yield)?
6. How much chlorine by weight and volume (at 15° and 770 mm) will be released when 31.6 g of $KMnO_4$ is treated with HCl?
7. The oxidation of oxalic acid in an acidic solution by 0.5 N $KMnO_4$ yields 1,120 ml of CO_2, measured at N. T. P. What was the weight of the oxalic acid that reacted, and what was the volume of the $KMnO_4$ solution used up?
8. One hundred millilitres of a solution contain 16.7 g of $KMnO_4$. What amounts of the solution and of water have to be taken to prepare 2 litres of an 0.5 N solution, required for oxidation in an acidic solution?
9. How much water has to be evaporated from 1 kg of a 4.9% solution of $KMnO_4$ to prepare a solution saturated at 60°, the solubility of $KMnO_4$ at 60° being 20%?
10. What amount of metallic manganese can be prepared from a $MnCl_2$ solution by passing a 2 A current through it for 40 minutes, the current efficiency being 68%?

LABORATORY WORK

Apparatus and materials: test tubes and rack; porcelain crucible; watch glass; pipette; glass rod; splints; hygroscopic cotton wool; litmus paper; lead dioxide; minium; $KMnO_4$; $KClO_3$; calcined MnO_2; KOH; $NaSO_3$; concentrated HNO_3; concentrated and 2 N H_2SO_4; 0.05 N $KMnO_4$; 10% NH_4Cl; 10% ammonia solution; 30% and 2 N NaOH; saturated solution of H_2SO_3; N $MnSO_4$; N $FeSO_4$; 2 N $(NH_4)_2S$; ethyl alcohol; hydrogen sulphide water; chlorine water and bromine water.

1. Heating of Potassium Permanganate. Fasten a dry test tube with a small amount (0.5 g) of potassium permanganate in it vertically in a clamp. After warming the whole test tube, start heating it. Establish that one of the decomposition products is oxygen. Continue the heating until the evolution of gas ceases. Cool the test tube to room temperature, add 3 ml of water, and shake the solution thoroughly. Note the colour of the precipitate and the colour of the solution. Write the equation for the reaction of the thermal decomposition of $KMnO_4$.

2. Reaction between Potassium Permanganate and Concentrated Sulphuric Acid. Place 5-6 crystals of $KMnO_4$ on a watch glass and add a few drops of concentrated H_2SO_4 from a pipette. Because the manganese heptoxide produced in this reaction is *highly explosive, do not increase the amounts* of $KMnO_4$ and H_2SO_4.

Stir the mixture very carefully with a glass rod. Wet a bit of cotton wool in alcohol and bring close to it a glass rod with some of the mixture of acid and $KMnO_4$ at its tip; the alcohol bursts into flame. Write the equation of the reaction that has taken place.

3. Reduction of Potassium Permanganate. (a) Place a crystal of $KMnO_4$ and 3-4 crystals (1 into the last test tube) of Na_2SO_3 into each of three test tubes. Add H_2SO_4 to the first test tube; an equal volume of water, to the second, and an equal volume of concentrated NaOH solution, to the third. Observe the change of colour in each test tube and write the equations of the reactions that have taken place.

(b) Mix 3 ml of a $KMnO_4$ solution with an equal volume of $MnSO_4$ solution in a test tube. What can be observed? What should be the effect of the solution on litmus paper? Test it. Write the equation of the reaction that has taken place.

4. Preparation of Manganate. Place 0.5 g of $KClO_3$ and 1 g of solid KOH in a porcelain crucible and melt the mixture over the flame of a burner. Add a pinch of powdered manganese dioxide to the molten mixture and continue the heating until the contents of the crucible are fused into a green-coloured product. Write the equation of the reaction that has taken place. Cool the crucible and add 5-6 ml of water. When the product has dissolved, pour the green solution into three test tubes for the next experiment.

5. Redox Properties of Manganate. Add a few drops of chlorine water to one of the test tubes from the previous experiment; a solution of H_2SO_4, to the second test tube (until the solution becomes acidic), and a solution of H_2SO_3, to the third. How does the colour change in the test tubes? Write the equations of the reactions that have taken place.

6. Manganous Hydroxide and Its Oxidation. By means of an exchange reaction prepare a precipitate of manganous hydroxide and note its colour. Divide the precipitate and solution into two equal portions. In one test tube observe the darkening of the precipitate upon exposure to air (this process can be hastened by shaking). To the portion in the other test tube add 10-15 drops of bromine water; note the changes that take place. Keep the precipitate for the next experiment. Write the equations of the reactions that have taken place.

7. Oxidant Properties of Tetravalent Manganese. (a) Add H_2SO_4 and $FeSO_4$ solution to the precipitate prepared in the previous experiment. Watch the precipitate dissolve. Write the equation of the reaction that has taken place. What is the role of $FeSO_4$ in the reaction? What properties does MnO_2 exhibit in this experiment and in experiment 4?

(b) Pour some powdered MnO_2 into a dry test tube and heat it over the flame of a burner. Establish that one of the decomposition products is oxygen. What is the type of the reaction that has taken place? Write its equation.

8. Oxidation of Bivalent Manganese. Pour 3 ml of concentrated HNO_3 over a pinch of minium or lead dioxide in a test tube, add 8-10 drops of $MnSO_4$ solution, and heat the solution carefully to boiling point. When it cools, dilute it with an equal volume of water and allow the precipitate to settle. What is the colour of the solution over the precipitate? Write the equation of the reaction that has taken place.

9. Preparation of Manganous Sulphide. Pour 3 ml of $MnSO_4$ solution into each of two test tubes. Add an equal volume of ammonium

sulphide solution to one of them; an H_2S solution, to the other. Does a precipitate form in both cases? Explain this.

10. Equilibrium in the $Mn(OH)_2 + NH_4Cl$ System. Pour 2 ml of $MnSO_4$ solution into each of two test tubes. Add 2 ml of 10% NH_4Cl to one of them and 2 ml of ammonia solution to each. Explain why no precipitate is formed in the solution containing NH_4Cl.

Exercise 40

IRON AND ITS ANALOGUES

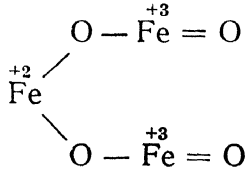
SUBJECTS FOR STUDY

The iron, ruthenium, and osmium series of elements; their atomic structure; the valences of iron in compounds; the position of iron in the electromotive series and its attitude to various oxidants; the oxides of iron and their chemical character; oxidising as a means of combating the corrosion of iron; the hydroxides of iron; ferrous and ferric salts; their redox characteristics; the complex compounds of iron.

The elements of this series are iron, ruthenium, and osmium. The atoms of iron and osmium have two electrons in their outermost shells and)8+ 6) in the next to last; ruthenium atoms have 1 and (8+ 7) electrons in those shells respectively. The ruthenium and osmium atoms can give up 8 electrons, thus displaying a maximum valence of 8. The most characteristic valences of iron are 2 and 3.

In the electromotive series iron occupies a position above hydrogen and is relatively easily oxidised by the hydrogen ions of dilute acids (HCl, H_2SO_4), with the formation of hydrogen and ferrous salts. Acids whose anions possess oxidant properties oxidise Fe^{+2} to Fe^{+3} upon heating, but high concentrations of these acids, without heating, cause a thin oxide film to form on the surface of the iron, which is thus passivated.

Iron and oxygen, depending upon conditions, produce either FeO or Fe_2O_3. The magnetic oxide of iron, Fe_3O_4, formed when iron is burned, appears to be a salt of bivalent iron and ferrous acid. The following structural formula has been proposed for this salt:



Upon exposure to air, iron undergoes oxidation (rusting) readily, due to action of water, oxygen, and carbon dioxide. The process consists of several stages:

(1) carbon dioxide dissolves in water, producing $H^{\cdot}$ ions

$$CO_2 + HOH \rightleftarrows H^{\cdot} + HCO_3^{\prime}\ .$$

(2) iron is oxidised by the hydrogen ions, with the subsequent hydrolysis of the ferrous carbonate

$$Fe + \overset{+1}{H_2}CO_3 = H_2 + \overset{+2}{Fe}CO_3$$

$$FeCO_3 + 2HOH = Fe(OH)_2 + H_2O + CO_2$$

(3) ferrous hydroxide is oxidised by the oxygen of the air to rust $Fe_2O_3 \cdot H_2O$

$$4\overset{+2}{Fe}(OH)_2 + O_2 = 2H_2O + 2(\overset{+3}{Fe_2}O_3 \cdot H_2O)$$

This reaction is one of the causes of the corrosion of iron. Substances hastening corrosion are said to stimulate it, while substances delaying corrosion are said to inhibit it. The metal is protected from corrosion by the formation of a nonporous film of oxides on its surface, a process that in engineering is known as oxidising, or blueing. The colour of oxidised iron ranges from straw yellow to blue-black.

Ferrous oxide and the corresponding hydroxide $Fe(OH)_2$ are basic in character and react with acids to form salts, which are mostly pale green in the crystalline state. The most important in the laboratory are ferrous sulphate (or green vitriol) $FeSO_4 \cdot 7H_2O$ and ferrous ammonium sulphate $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. Both in the solid state and in solution ferrous salts are readily oxidised upon exposure to air and are converted to ferric salts. In acidic solutions oxidation proceeds more slowly. In studying the properties of the Fe^{+2} ion, it is therefore necessary to use freshly prepared solutions of recrystallised salts.

The hydroxide $Fe(OH)_3$ in ordinary conditions exhibits a basic character and forms salts in which Fe^{+3} is the cation, e. g.: $FeCl_3$ and $Fe_2(SO_4)_3$*.

Ferric compounds are weak oxidising agents and, when treated with reductants, are converted to derivatives of Fe^{+2}, e. g.:

$$\overset{-2}{H_2}\overset{0}{S} + \overset{+3}{Fe_2}(SO_4)_3 = \overset{0}{S} + 2\overset{+2}{Fe}SO_4 + H_2SO_4 \qquad (2e^-)$$

The complex compounds of iron used in the laboratory are potassium ferrocyanide (or yellow prussiate of potash) $K_4[Fe(CN)_6]$, which is a reagent for detecting the Fe^{+3} ion, with which it forms a blue precipitate, Prussian blue, and potassium ferricyanide (or red prus-

* Ferric hydroxide partly dissolves in hot concentrated solutions of alkalis to form so-called *ferrites* (such as $NaFeO_2$), which are salts of ferrous acid $HFeO_2$.

siate of potash) $K_3[Fe(CN)_6]$, which can be used as a reagent to detect Fe^{+2}, with which it forms a blue precipitate known as Turndull's blue.

QUESTIONS

1. How can ferrous chloride and ferric chloride be prepared from metallic iron?
2. Explain the processes of the corrosion of zinc-plated and tinned iron when cracks are formed on their surfaces.
3. How can yellow prussiate of potash be transformed into red prussiate of potash and *vice versa*? Write the equations of the reactions involved.
4. How can solutions of ferrous salts be protected from oxidation during storage?
5. Write the equation of a reaction whereby Fe^{+2} is oxidised to Fe^{+3}, as well as the equation of the reverse reaction of reduction.
6. Give two reactions by which it is possible to distinguish Fe^{+3} from Fe^{+2}. Write their equations.
7. List all the metals that are passivated in concentrated HNO_3.

Problems

1. The heating of 10 g of iron from 90 to 97° requires 7.95 cal. Determine the metal's atomic weight.
2. What amounts of ferric chloride and potassium ferrocyanide are needed to obtain 1 kg of Prussian blue?
3. What is the volume of 10% HCl (relative density 1.05) that should be taken to dissolve 7.4 g of iron?
4. How much $Fe(OH)_2$ can be oxidised to $Fe(OH)_3$ by 2 litres of oxygen, whose volume was measured at 20° and 750 mm?
5. Two hundred and fifty millilitres of an aqueous solution are prepared from 1 g of commercial green vitriol; the amount of 0.01 N $KMnO_4$ spent to titrate 20 ml of that solution in an acidic medium is 24.6 ml. Determine the percentage content of $FeSO_4 \cdot 7H_2O$ in the sample investigated.
6. From the reduction equivalent of $FeSO_4 \cdot 7H_2O$ determine the normality of a solution containing 16.2 g of that salt in 500 ml.
7. Calculate the thermal effect of the oxidation of ferrous oxide to ferric oxide, knowing that the heats of formation of the two oxides are 64.3 and 198.5 Cal. respectively.
8. Find the e. m. f. of the reaction whereby $FeSO_4$ is oxidised in an acidic solution by $K_2Cr_2O_7$ at 25°, M solutions being used.
9. Compare the solubilities of FeS in pure water and in 0.01 M Na_2S, the *SP* of FeS being $1.0 \cdot 10^{-19}$.
10. For how many hours is it necessary to conduct the electrolysis of a $FeSO_4$ solution to deposit 279.2 g of pure iron on the cathode at a current intensity of 2 A?

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 82; test tubes and rack; porcelain mortar; test tube holder; three wide-mouth bottles with rubber stoppers and gas-delivery tubes; glass hook; two 100 ml and two 50 ml beakers; 50 ml measuring

cylinder; 15 min sand glass; iron objects for oxidising; three 25 × 80 mm boiler plates; iron nails; piano wire; litmus paper; squared paper; filter paper; iron filings; powdered sulphur; recrystallised ferrous ammonium sulphate; thiourea; meta-nitroaniline; alcohol; ether; fuming HNO_3; concentrated H_2SO_4; 2N and 5% HCl; 2N NaOH; 20% and 2 N H_2SO_4; 2N $(NH_4)_2S$; saturated solution of H_2SO_3; 0.05 N $KMnO_4$; 0.5 N KSCN; N K_3 [Fe $(CN)_6$]; N K_4 [Fe $(CN)_6$]; N $FeCl_3$; 0.5 N $CuSO_4$; solution containing 600 g of NaOH and 60 g of $NaNO_2$ in 1 litre; sandpaper.

1. Attitude of Iron to Acids. Test the action of dilute HCl on iron. Test the action of concentrated H_2SO_4 on iron in the cold and upon heating (careful!). Does a reaction take place in each case? Write the equations of the reactions that have taken place.

What type of H_2SO_4 can be transported in iron tanks? Why is this so?

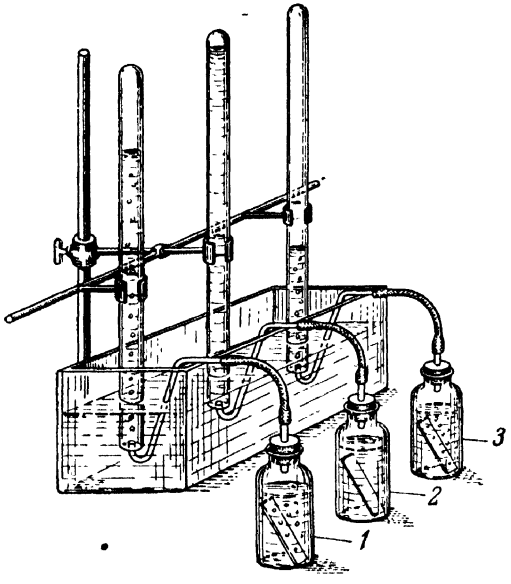


Fig. 82. Set-up for studying speed at which iron dissolves

2. Speed at Which Iron Dissolves in Acid. Immerse three 100 ml eudiometers, fastened in the clamps of a ringstand, in a trough with water (Fig. 82).

Degrease three smooth iron boiler plates (25 × × 80 mm), with small holes at their upper ends, by immersing them on a glass hook first in alcohol and then in ether (close the jars with alcohol and ether immediately). As soon as the ether has evaporated, the plates are placed on a sheet of clean filter paper (the degreased plates can be held only by their edges).

Pour 100 ml of 20% H_2SO_4 into each of three jars (with diameters of 40 mm and heights of 100 mm to the tapering necks). Add 0.001 mol of thiourea $CS(NH_2)_2$ to the second jar, and 0.001 mol of meta-nitroaniline $C_6H_4NO_2NH_2$, to the third. When these substances have dissolved, quickly immerse the plates in the solutions, close the jars with their stoppers, and place the ends of the tubes under the eudiometers. Every 20 minutes now record the volume of water displaced in each eudiometer (conduct other experiments in the meantime!). Conduct the experiment for 120 min. Record the results in the form of a table:

No. of jar	Solution	Volume of H_2 evolved during time (min)					
		20	40	60	80	100	120
1	20% H_2SO_4, pure						
2	20% H_2SO_4 + 0.001 M $CS(NH_2)_2$						
3	20% H_2SO_4 + 0.001 M $C_6H_4NO_2NH_2$						

Plot the experimental results in the form of curves, the ordinate giving the volume of hydrogen evolved, the abscissa, the duration of the experiment in min.

Is the rate of corrosion the same in all three experiments? What role did the thiourea and the meta-nitroaniline play in the process? By what factor was the rate of corrosion retarded or increased?

3. **Passivating and Oxidising Iron.** (a) Immerse a clean iron nail for 3 seconds in a solution of blue vitriol in a test tube and then examine the surface of the nail. What change has it undergone? Write the equation of the reaction that has taken place. Pour some fuming HNO_3 in a small beaker carefully in a ventilated hood; immerse an identical nail in it for 1-2 min. Withdraw the nail carefully, without shaking it, rinse it in a beaker with water, and immerse it in a solution of blue vitriol. Is copper deposited on it?

(b) Clean some iron object with sandpaper, attach a thin wire to it, and wash it first in 5% HCl and then in water. Heat to boiling point 100 ml of a solution containing 600 g of NaOH and 60 g of $NaNO_2$ in 1 litre of water and immerse the iron object in the beaker in which the solution is heated. After intervals of time (3, 5, 10, and 15 min) withdraw the object from the liquid and observe changes in the colour of its surface. What is formed on the metal's surface?

4. **Hydrolysis of Ferrous Salts.** Dissolve 0.5 g of recrystallised ferrous ammonium sulphate in 10-15 ml of boiled distilled water. Test the solution with litmus paper. Write the equation of the hydrolysis reaction that has taken place. Divide the solution into four equal parts for experiments 5, 6, and 7, pouring each part into a test tube.

5. **Preparation of Ferrous Hydroxide.** Prepare ferrous hydroxide by treating the solution of ferrous ammonium sulphate with alkali. Note the change in colour upon exposure to air. Write the equations of the reactions that have taken place.

6. **Reductant Properties of Fe^{2+}.** To the solution of ferrous ammonium sulphate add an equal volume of H_2SO_4 solution and then add

a solution of $KMnO_4$ by drops, noting the disappearance of its colour. Write the equation of the reaction that has taken place.

7. Detection of $Fe^{...}$ Ion. Add a few drops of a solution of red prussiate of potash to the solution of ferrous ammonium sulphate in a test tube and observe the formation of Turnbull's blue. Write the equation of the reaction that has taken place. Now add a few drops of KSCN or NH_4SCN to a solution of ferrous ammonium sulphate in another test tube. Does a crimson colour appear?

8. Hydrolysis of Ferric Chloride. Heat 20 ml of water to boiling point and add 1 ml of $FeCl_3$ solution to the boiling water by drops. Compare the colour of the $FeCl_3$ solution in the bottle with that in the boiling solution and explain the difference. Divide the solution in the beaker into three portions. To the portion in the first test tube add HCl solution; cool the portion in the second test tube, and compare the colours of the solutions in all three test tubes. Explain the differences observed.

9. Detection of Trivalent Iron. Test a ferric chloride solution in separate tes tubes with NaOH, KSCN, yellow prussiate of potash, and $(NH_4)_2S$. Observe the changes that take place and express them in terms of equations.

10. Reduction of $Fe^{...}$. To a ferric chloride solution add a double volume of H_2SO_3 solution; boil the solution. Then divide it into two parts and conduct tests for $Fe^{..}$ and $Fe^{...}$. Write the equation of the reduction reaction that has taken place.

Exercise 41

COBALT, NICKEL, AND THEIR ANALOGUES

SUBJECTS FOR STUDY

The cobalt, rhodium, and iridium series of elements; the structure of their atoms and the positive valence of their ions; the position of cobalt, rhodium, and iridium in the electromotive series; the attitude of cobalt to various oxidising agents; the oxides and hydroxides of cobalt; the simple and complex salts of cobalt.

The nickel, palladium, and platinum series of elements; the structure of their atoms and the positive valence of their ions; properties distinguishing metallic nickel from palladium and platinum; the attitude of nickel to various oxidising agents; the oxides and hydroxides of nickel; the simple and complex salts of nickel.

The atoms of cobalt, rhodium, and iridium have the following electron distribution in their two outer electron shells: Co)8+7)2; Rh)8 + 8)1, and Ir)8 + 7)2. They form positive ions of different charges, of which the most stable are Co^{+2}, Co^{+3}, Rh^{+3}, Ir^{+3}, and Ir^{+4}.

In the electromotive series cobalt is situated above the hydrogen couple; it is therefore oxidised by dilute acids (HCl and H_2SO_4),

with the evolution of hydrogen and the formation of Co^{+2} salts. Rhodium and iridium, on the other hand, undergo practically no oxidation when treated even by strong acids that are oxidising agents.

Cobalt forms the grey-green cobaltous oxide CoO and the black-brown cobaltic oxide Co_2O_3. The corresponding hydroxides $Co(OH)_2$ and $Co(OH)_3$ are insoluble in water and basic in character. The treatment of $Co(OH)_2$ with acids produces cobaltous salts. Cobaltic hydroxide $Co(OH)_3$ does not form salts because, as a strong oxidant, it undergoes reduction to cobaltous salts when dissolving:

$$6HCl^{-1} + 2Co(OH)_3^{+3} \xrightarrow{6e^-} Cl_2 + 2Co^{+2}Cl_2 + 6H_2O$$

The soluble salts of cobalt include $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$.

Salts containing the $[Co(H_2O)_6]^{+2}$ ion are pink; the anhydrous salts are blue. In its complex salts cobalt has the coordination number 4 or (more often) 6. Two illustrations of complex salts will be given here:

(1) ammonium cobaltothiocyanate $(NH_4)_2[Co(SCN)_4]$, a substance that has a blue colour in concentrated solutions and may be prepared thus:

$$CoCl_2 + 2NH_4SCN = Co(SCN)_2 + 2NH_4Cl$$
$$Co(SCN)_2 + 2NH_4SCN = (NH_4)_2[Co(SCN)_4]$$

(2) insoluble potassium cobaltinitrite $K_3[Co(NO_2)_6]$, which is yellow and is prepared in several stages

$$CoCl_2 + \left\{\begin{matrix}2KNO_2 \\ \\ \end{matrix}\right. \rightleftarrows Co(NO_2)_2 + 2KCl \qquad (1)$$
$$2KNO_2 + 2CH_3COOH = 2HNO_2 + 2CH_3COOK \qquad (2)$$

$$Co^{+2}(NO_2)_2 + HNO_2 + \left\{\begin{matrix}HNO_2 \\ \\ \end{matrix}\right. = Co^{+3}(NO_2)_3 + N^{+2}O + H_2O \xrightarrow{1e^-} \qquad (3)$$
$$Co(NO_2)_3 + 3KNO_2 = K_3[Co(NO_2)_6] \qquad (4)$$

The elements nickel, palladium, and platinum are a series of analogues, owing to the fact that their atoms have the same number of electrons in the two outer electron shells: Ni)8 + 8)2; Pd)8 + 10)0, and Pt)8 + 9)1. Typical metals chemically, all three elements form positive ions, of which the most characteristic are Ni^{+2}, Ni^{+3}, Pd^{+2}, Pd^{+4}, Pt^{+2}, and Pt^{+4}. Nickel is a more active metal than either palladium or platinum and is readily oxidised by dilute acids, forming nickelous salts that are various shades of green in colour *.

* Palladium ix oxidised by dilute HNO_3 upon heating and is transferred into the solution in the form of palladium nitrate.

All the metals of this series absorb more or less considerable quantities of gaseous hydrogen (this is especially true of palladium) and are therefore used as catalysts in hydrogenation processes.

Nickel monoxide is green, while the sesquioxide Ni_2O_3 is black. The hydroxides $Ni(OH)_2$ and $Ni(OH)_3$ are basic in character, but when $Ni(OH)_3$ dissolves in acids, salts of bivalent nickel are formed, owing to the reduction of Ni^{+3} to Ni^{+2}.

The salts used mos frequently in the laboratory are the soluble salts $NiSO_4 \cdot 7H_2O$, $NiCl_2 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$.

In complex compounds Ni^{+2} has the coordination number 4 or 6.

With dimethylglyoxime in an ammoniacal or acetic-acid solution, nickel salts form the pinkish red precipitate of nickel dimethylglyoxime.

The reaction* follows the equation:

$$2\begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=NOH \end{matrix} + NiCl_2 + 2NH_3 =$$

$$= 2NH_4Cl + \begin{matrix} & & OH & OH & \\ & & | & | & \\ CH_3-C= & N & & N & =C-CH_3 \\ | & & \diagdown & \diagup & | \\ & & Ni & & \\ | & & \diagup & \diagdown & | \\ CH_3-C= & NO & & NO & =C-CH_3 \end{matrix}$$

The palladium and platinum compounds used are palladium chloride $PdCl_2$, potassium chloroplatinite $K_2[PtCl_4]$, platinic chloride $PtCl_4$, chloroplatinic acid $H_2[PtCl_6]$ and its salts $Me_2[PtCl_6]$, called chloroplatinates.

As ions of noble metals, the ions of palladium and platinum exhibit strong oxidant properties. For example, Pd^{+2} oxidises CO in the cold to CO_2 (a sensitive test for CO). Excess reductant precipitates platinum from $PtCl_4$ solutions. The ions of noble metals display a very marked tendency to form complexes. Among the many complex compounds of platinum, one that is used in the laboratory is chloroplatinic acid, which serves as a reagent for detecting the potassium ion. The reaction product, potassium chloroplatinate, is a substance of low solubility that crystallises in the form of microscopic yellow octahedra. The reaction is employed in microcrystalloscopy, i. e., the identification of substances according to the shape of their crystals under the microscope.

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* The reaction, proposed by L. Chugayev, is one of the best qualitative reactions for detecting nickel.

QUESTIONS

1. Write the equations for the reactions whereby cobalt is dissolved in concentrated HNO_3 and platinum in *aqua regia.*
2. Draw a diagram of an alkaline storage battery. What are the chemical processes that take place when it is charged and when it is discharged?
3. How can $Co(OH)_3$ and $Ni(OH)_3$ be prepared in the laboratory?
4. Which of the isotopes of cobalt is used as a radioactive preparation? Indicate the areas in which it is used. What type of radioactive transformation characterises it? Give the equation for its radioactive transformation.
5. The compound $[Pt(NH_3)_2]Cl_2$ has two isomeric forms: a *cis*-isomer and a *trans*-isomer. How can the isomerism of this compound be explained in terms of coordination formulae?
6. What is the effect of excess NH_4OH on a $NiCl_2$ solution?

Problems

1. The precipitation of potassium from 0.15 g of KCl containing impurities required 0.41 g of chloroplatinic acid. Determine the degree of the salt's purity.
2. The heating of metallic palladium in a chlorine atmosphere at 500° produces $PdCl_2$. What is the volume of chlorine, reduced to N. T. P., that is needed to oxidise 10 g of palladium?
3. Nickelous hydride has the formula NiH_2. What is the volume of hydrogen in ml (at N. T. P.) that can be absorbed by 1 g of nickel?
4. The thermal decomposition of ammonium chloroplatinate follows the equation:

$$3\,(NH_4)_2PtCl_6 = 3Pt + 16HCl + 2NH_4Cl + 2N_2$$

Calculate the amount of it needed to obtain 0.5 kg of platinum.
5. What is the volume of 10% ammonia solution needed to convert 5 g of $NiSO_4 \cdot 7H_2O$ to an ammonia complex compound.
6. Forty millilitres of HCl (relative density 1.19) were used to dissolve a $Co(OH)_3$ precipitate. What was the amount of $Co(OH)_3$ treated?
7. How much metallic nickel of 98.6% purity was dissolved in nitric acid (relative density 1.2) if the amount of acid used up was 120 ml?
8. Twenty millilitres of illuminating gas were passed through a solution of $PdCl_2$, precipitating 0.0076 g of metallic palladium. Determine the percentage content of CO (by volume) in the gas.
9. What is the volume of *aqua regia* needed to dissolve 10 g of metallic platinum, which is converted to H_2PtCl_6?
10. A layer of nickel 0.0034 mm thick is deposited on a 120 × 150 cm sheet of copper. How long was electrolysis conducted if the current intensity was 0.5 A? The density of nickel is 8.9 g/cu cm.

LABORATORY WORK

Apparatus and materials: the apparatus shown in Fig. 69; *camera lucida*; test tubes and rack; crucible tongs; cover of porcelain crucible; object-glass; microscope; cover-glass; thermometer to 150°; cobalt shavings; nickel shavings; crystalline nickelous chloride; cobaltous nitrate; nickelous nitrate; cobaltous chloride; mixture of

ethyl ether and amyl alcohol; ethyl alcohol; concentrated and 2 N HCl; 1 : 1 HNO_3; 10% and 25% ammonia solutions; saturated solution of NH_4Cl in 25% ammonia solution; 2 N CH_3COOH; 30% and 2 N NaOH; N KNO_2; bleaching powder solution; saturated solution of NH_4SCN; 0.5 N solution of nickel sulphate; saturated solution of cobaltous chloride; 5% KCl; N $(NH_4)_2S$; N Na_2CO_3; N NaH_2PO_4; 5% solution of chloroplatinic acid; solution of 75 g of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in 1 litre of water; 3% H_2O_2; 1% solution of dimethylglyoxime in a 10 : 90 mixture of alcohol and water; polishing materials: felt, chamois leather, and polish.

1. Treatment of Nickel and Cobalt with Acids. Put small shavings of these metals into two test tubes and add 3-4 ml of a solution of HCl to each of them. How intensive are the reactions? Write their equations. Pour off the acid, wash the shavings in water thoroughly, and add 4 ml of HNO_3 solution to each test tube. What happens? Write the equations of the reactions that have taken place.

2. Formation of Nickel and Cobalt Oxides. Place one crystal each of cobaltous and nickelous nitrate on the cover of a porcelain crucible and heat it over the flame of a burner. How do the colours of the salts change? Write the equations of the reactions that have taken place. By means of what reactions can cobaltous oxide and nickel monoxide be prepared?

3. Preparation of Cobalt and Nickel Hydroxides. (a) By means of exchange reactions prepare precipitates of $Co(OH)_2$ and $Ni(OH)_2$ and note their colours. Observe that when the cobaltous salt is treated with an alkali, the blue precipitate of a basic salt is formed at first. Write the equations of the reactions that have taken place.

(b) Add some concentrated NaOH to part of the $Co(OH)_2$ precipitate and shake the contents of the test tube. The precipitate is partly dissolved, owing to the formation of sodium cobaltiate $Na_2[Co(OH)_4]$. Write the equation of the reaction. What are the properties of cobaltous hydroxide?

(c) Add some H_2O_2 solution to parts of the $Co(OH)_2$ and $Ni(OH)_2$ precipitates. Do the colours of the precipitates change? Write the equation of the reaction that has taken place. Which of the hydroxides is not oxidised by hydrogen peroxide?

(d) Add lime chloride solution to the nickelous hydroxide precipitate and heat the test tube. How does the colour of the precipitate change? Write the equation of the reaction that has taken place.

(e) (Conduct this experiment in a ventilated hood!) Pour off the solution from the black precipitate of nickelic hydroxide, add 2 ml of concentrated HCl to the precipitate, and heat the test tube. What happens to the precipitate? What chemical property do cobaltic and nickelic compounds exhibit? What is the practical use of this property of nickel sesquioxide?

4. Insoluble Salts of Cobalt and Nickel. Study the action of ammonium sulphide, sodium carbonate, and sodium hydrogen phosphate on soluble salts of cobalt and nickel. Note the colours of the compounds formed and write the equations of the reactions that have taken place.

5. Preparation of Cobaltothiocyanate Complex. Mix equal volumes of concentrated solutions of cobaltous chloride and NH_4SCN; note the colour of the resulting solution. Write the equation of the reaction that has taken place. Now add water to the solution by drops until the blue colour changes to pink. Why does dilution with water affect the colour? Add 2 ml of a mixture of ether and amyl alcohol to the aqueous solution and shake the test tube vigorously. What colour does the ether-alcohol layer acquire? Explain this.

6. Preparation of Potassium Cobaltinitrite. In accordance with the description of this reaction given in the introductory part of this Exercise, prepare the yellow precipitate of $K_3[Co(NO_2)_6]$. Take 2 ml each of cobaltous chloride and acetic-acid solutions and 5 ml of potassium nitrite solution.

7. Detection of Nickel Ion by Chugayev Reaction. Pour 50 ml of water and 5-6 drops of a nickel salt solution into a beaker. Add 5-6 drops of ammonia solution and then add by drops (with vigorous stirring) a solution of dimethylglyoxime in water and alcohol. What is formed?

Write the equation of the reaction that has taken place. Explain why the ammonia has to be added.

8. Preparation and Isolation of Nickel Ammine. Dissolve about 0.5 g of $NiCl_2 \cdot 6H_2O$ in 2 ml of water and add 25% ammonia solution by drops until the precipitate formed dissolves again. Add an equal volume of concentrated ammonia solution saturated with ammonium chloride. A light violet precipitate of hexamminenickel chloride is formed. Write the equations of the reactions that have taken place.

9. Nickel Plating. Use the same apparatus as that used for copper plating in Exercise 21. A copper plate serves as the cathode; a nickel plate, as the anode. The electrodes should be 12-15 cm apart; the voltage applied to the electrodes, 3.5 V; the current density, 0.3 A/ sq dm. The electrolyte should be a solution of 75 g of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in 1 litre of water. The solution should be at room temperature.

Assemble the entire installation and pour enough electrolytic solution into the electrolysis bath to submerge half the electrodes. Switch on the current and by means of the rheostat adjust the voltage to the required figure. Thirty minutes later remove the cathode from the bath, rinse it in a stream of water, and remove the water from its surface by means of filter paper. Polish the dry plate on a felt polishing wheel, using polishes, until it shines.

10. Microcrystalloscopic Test for Potassium Ion. Place a drop each of KCl and chloroplatinic acid solutions on an object-glass a small distance apart and then connect them. After 2-3 minutes cover the drops with a cover-glass and examine the crystals formed under a microscope. Attach a *camera lucida* to the microscope and draw some of the most regular crystals in your notebook.

Exercise 42

SYNTHESIS OF INORGANIC SUBSTANCES

The purpose of the present exercise is to carry out the synthesis of an inorganic compound, employing the techniques studied in previous exercises.

Each student should receive from the instructor of the group an individual assignment and study a description of the methods of synthesising the compound he has been assigned.

I. Choice of Method. The considerations that should dictate the choice of the method of synthesis are: the availability of the necessary reagents, the simplicity of the apparatus required, and the yield of the product.

II. Calculation of the Amounts of Initial Reagents. This calculation should be based on the required amount of the product and the amounts of the initial substances according to the equation of the reaction used for the synthesis.

III. Apparatus for Synthesis. If the synthesis does not require complicated apparatus, draw up a list of what is needed beyond the student's individual apparatus. If the synthesis has to be conducted in special apparatus, draw a diagram of what is required, indicating the purpose of each part.

On completing the synthesis, calculate the yield in per cent and submit the synthesised compound to the instructor, together with a written report.

The following is an example of a synthesis.

The Preparation of Lead Dioxide (12 g).

I. Choice of Method. We shall assume that the method of synthesis chosen is the following.

To a solution of 100 g of analytically pure $Pb(CH_3COO)_2 \cdot 3H_2O$ add a strong solution of 30 g of analytically pure Na_2CO_3; pass an intense stream of chlorine into the solution until the mass acquires a dark brown colour. The chlorine delivery tube should almost touch the bottom of the vessel. When the reaction ends, heat the flask for $1^1/_2$ hours on a water bath and then empty the flask into a beaker. After the precipitate has settled, decant and heat the precipitate with 24-25% HNO_3 to remove the $PbCO_3$ admixture. Finally, wash the precipitate several times by decantation, filter it on a suction filter, and wash it with water to remove Cl' (a sample of the wash water acidified with HNO_3 should not become turbid upon the addition of $AgNO_3$). Yield: 90-95%.

II. Calculation of the Amounts of Reagents. To prepare 12 g of lead dioxide (the required amount) it should be borne in mind that the yield in this method is 90%; accordingly, all the calculations should be for $\frac{12 \cdot 100}{90} = 13.3$ g of the dioxide.

Calculation of the Amount of Lead Acetate $Pb(CH_3COO)_2 \cdot 3H_2O$. A gram-molecule of lead acetate (379.3 g) and a gram-molecule of

lead dioxide (239.2 g) each contain one gram-atom of lead. Calculate the amount of lead acetate that should yield 13.3 g of lead dioxide:

$$\begin{matrix} 379.3 - 239.2 \\ x - 13.3 \end{matrix} \qquad x = \frac{379.3 \cdot 13.3}{239.2} = 21.1 \text{ g}$$

The concentration of the lead acetate is not given in the description of the method. Since lead acetate has a high solubility (100 g of water at 15° dissolves 45.6 g of the salt), it is advisable to prepare, say, an approximately 10% solution, i. e., to dissolve the calculated amount of the salt in 180 g of water.

Calculation of the Amount of Sodium Carbonate Na_2CO_3. The description calls for using 30 g of Na_2CO_3 for 100 g of lead acetate; accordingly, the amount of Na_2CO_3 needed for 21.1 g of acetate will be:

$$\begin{matrix} 100 - 30 \\ 21.1 - x \end{matrix} \qquad x = \frac{21.1 \cdot 30}{100} = 6.33 \text{ g}$$

The description refers to a "strong solution" of Na_2CO_3. Since the term "strong" does not indicate the exact concentration, the description implies that it is necessary to prepare a solution close to a saturated one. From the solubility table of soda it is evident that its solubility at 15° is 14.1%. In 100 g of such a solution there will be 100 — 14.1 = 85.9 g of water. The amount of water needed to dissolve 6.33 g of Na_2CO_3 will be:

$$\frac{6.33 \cdot 85.9}{14.1} = 38.7 \text{ g}$$

This means that 6.33 g of Na_2CO_3 can be dissolved in about 40 g of water.

Calculation of the Amount of Chlorine. From the equation of the reaction

$$Pb(CH_3COO)_2 + Cl_2 + 2Na_2CO_3 = PbO_2 + 2NaCl + 2CH_3COONa + 2CO_2$$

it follows that 70.9 g of chlorine is needed to prepare 239.2 g of PbO_2; accordingly, the amount of chlorine needed to prepare 13.3 g will be:

$$x = \frac{13.3 \cdot 70.9}{239.2} = 3.94 \approx 4 \text{ g}$$

Let us assume that the chlorine is to be prepared by oxidising MnO_2 by concentrated HCl upon heating. Assuming that about 50% of the required amount of chlorine will be lost in passing it into the solution, the total necessary amount of chlorine may be considered equal to 4 + 2 = 6 g.

From the equation of the reaction let us calculate the amounts of MnO_2 and concentrated 37.23% HCl (relative density 1.19) that

will be needed to prepare 6 g of chlorine:

$$\underset{86.9}{MnO_2} + \underset{4\cdot 36.46}{4HCl} = \underset{70.9}{Cl_2} + MnCl_2 + 2H_2O$$

MnO_2 $\quad 86.9 - 70.9$
$\qquad\quad x - 6$
$\qquad x = \frac{86.9\cdot 6}{70.9} \approx 7.4$ g

HCl $\quad 4\cdot 36.46 - 70.9$
$\qquad\quad y - 6$
$\qquad y = \frac{4\cdot 36.46\cdot 6}{70.9} = 12.4$ g

Since the initial acid contains only 37.23% HCl, the required amount of such acid will be:

$100 - 37.23$
$z - 12.4$
$\qquad z = \frac{100\cdot 12\,4}{37.23} = 33.5$ g

Bearing in mind that the relative density of the acid is 1.19, the volume required is $\frac{33.5}{1.19} = 28$ ml. Hence, to prepare 6 g of chlorine we require 7.4 g of MnO_2 and 28 ml of 37.23% HCl.

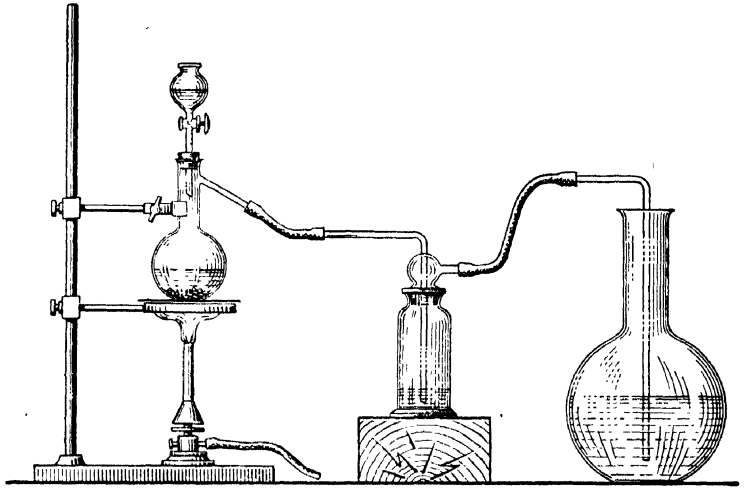

Fig. 83. Apparatus for preparing PbO_2

III. Apparatus. With an eye to the description of the method and the calculated amounts of the reagents, the apparatus that should be prepared is as follows: a 400-500 ml flask, a 50-75 ml flask with a side arm, a 50 ml dropping funnel, and a wash bottle for washing the chlorine (removing HCl admixtures). The apparatus should be assembled according to Fig. 83. Conduct the synthesis in a ventilated hood. The isolation of the PbO_2 at subsequent stages will require

an 0.5 litre beaker, a suction filter with a small porcelain funnel, and filter paper.

If the product weighs, say, 11.6 g, the yield of PbO_2 will be 96.7%.

Described below are methods for preparing various inorganic substances belonging to the classes of simple substances, oxides, hydroxides, acids, acid chlorides, salts (normal, acid, basic, and double), and complex compounds.

1. Metallic silver
(from laboratory waste)

Metallic silver Ag is a white lustrous metal; density 10.49 g/cu cm; m. p. 960.5°. The best solvent for silver is HNO_3. Silver does not dissolve in dilute HCl or H_2SO_4.

Laboratory waste contains both soluble ($AgNO_3$, Ag_2SO_4) and insoluble (AgCl, AgBr, AgI) silver compounds. By the combined action of HCl and Cl_2 all these compounds are converted to chlorides:

$$Ag_2SO_4 + 2HCl = 2AgCl + H_2SO_4$$
$$2AgBr + Cl_2 = 2AgCl + Br_2$$

Silver is obtained from the AgCl by reactions of reduction, e. g.:

$$2H + 2AgCl = 2Ag + 2HCl$$

Procedure. Laboratory waste (solution with precipitate) is evaporated in a porcelain casserole. Concentrated HCl is then poured over the dry residue, a few grams of $KClO_3$ are added, and the contents of the casserole are boiled until all the chlorine has been removed (test). An equal volume of water is then added, the precipitate filtered off and washed with hot water. If necessary, the precipitate is dried. All the work should be done in a ventilated hood.

(a) Reduction by Dry Method. Mix 6 parts by weight of AgCl, 3 parts by weight of soda ash, and 1 part by weight of KNO_3 (the latter helps to fuse and oxidise the admixtures of other metals). Transfer the mixture in small portions to a hot grog crucible. The following reaction takes place:

$$4AgCl + 2Na_2CO_3 + 4Ag + 4NaCl + 2CO_2 + O_2$$

When the entire mixture has been transferred to the crucible, heat it with a blowpipe until all the silver has been fused. Then pour the contents of the crucible carefully into a vessel with water. Boil the lumps of metallic silver for a lengthy time with dilute H_2SO_4, wash them with water, and dry them.

(b) Reduction by Wet Method. Stir equal amounts by weight of AgCl and a 40% formalin solution in a beaker with a mechanical stirrer. Add 30% KOH in small portions whose sum total equals the

weight of the first two substances. Filter off the black precipitate formed and wash it with H_2SO_4 and water until it exhibits a neutral reaction. Dry the precipitate.

2. Crystalline iodine
(from laboratory waste)

Crystalline iodine I_2 has a density of 4.942 g/cu cm; the crystals are violet-grey with a metallic lustre; m. p. 113.5°. Iodine vapour is violet. Iodine dissolves in a KI solution and in organic solvents.

Laboratory waste contains both free iodine I_2 and bound iodine in the form of the I' ion. The latter is oxidised in an acidic solution by $K_2Cr_2O_7$.

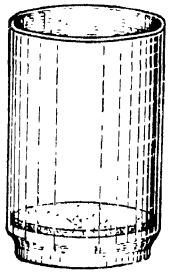

Fig. 84. Filter crucible (Gooch crucible)

Procedure. Add 1-1.5 ml of concentrated H_2SO_4 and 10-40 ml of a solution of $K_2Cr_2O_7$ saturated at 20° (Table II, p. 329) for every 1 litre of the solution containing iodine waste. Five-six hours later the liquid should be siphoned off from the precipitate; the remaining iodine should be filtered off in a filter crucible (Fig. 84), washed 3-4 times with water, and dried in a desiccator over H_2SO_4. The dry iodine should be ground in a mortar with a few crystals of KI and sublimed (see experiment 11, Exercise 36). The iodine crystals formed on the walls of the flask are periodically detached into a weighing bottle by means of a glass spatula.

3. Aluminium oxide aluminate

Aluminium oxide aluminate $(Al_2O_3)_x \cdot NaAlO_2$ has a high adsorption capacity. The heavy white lumps are used as an adsorbent in chromatography.

Aluminium oxide aluminate is prepared from metallic aluminium:

$$2Al + 6HOH + 2NaOH = 2NaAlO_2 + 4H_2O + 3H_2$$

$$2NaAlO_2 + 2CO_2 + 4H_2O = 2NaHCO_3 + 2Al(OH)_3$$

$$xAl(OH)_3 + NaAlO_2 = [Al(OH)_3]_x \cdot NaAlO_2$$

$$2[Al(OH)_3]_x \cdot NaAlO_2 = 3xH_2O + (Al_2O_3)_x \cdot NaAlO_2$$

Procedure. Pour 250 ml of 30% NaOH into a 3 litre battery glass and cool the glass in a vessel with ice. Introduce 25 g of aluminium shavings into the cooled solution in small portions. When all the aluminium has dissolved (if necessary, filter the solution), dilute the solution with water so that it should have a 2% concentration in terms of Al_2O_3. Then pass CO_2 (first washed with water) from the Kipp gas

generator or tank into the solution through a glass bubbler, a spiral-shaped tube with a large number of orifices on its upper side (Fig. 85).

Continue passing the CO_2 into the solution until all the $Al(OH)_3$ has been precipitated. The solution with the precipitate should then be diluted with an equal volume of water. Next filter off 20-30 ml of the solution and pass CO_2 into it again; the absence of slime in the solution indicates that precipitation is finished. Now filter off the precipitate on a suction filter and wash it with hot water on the filter until the addition of a drop of phenolphthalein solution to the filtrate no longer gives it even a pale pink colour. After the precipitate has been washed, dry it in a drying cabinet at 100-130°. Grind the dry residue in a mortar and calcine it in a muffle furnace at 800° for 1 hour. Weigh the product.

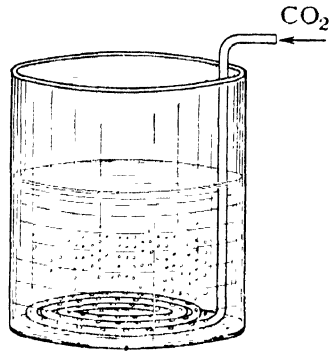

Fig. 85. Spiral-shaped tube in operation

4. Strontium hydroxide

Strontium hydroxide $Sr(OH)_2 \cdot 8H_2O$ has a density of 1.4 g/cu cm. When heated above 100°, the transparent colourless crystals (rhombic system) give up their water of crystallisation. The hydroxide combines avidly with CO_2.

The hydroxide is prepared by an exchange reaction between strontium nitrate and pure NaOH:

$$Sr(NO_3)_2 + 2NaOH + 8H_2O = Sr(OH)_2 \cdot 8H_2O + 2NaNO_3$$

Calculate the amounts of the initial substances needed to prepare 50 g of strontium hydroxide. The amount of NaOH taken should be 20% in excess of the theoretically calculated amount.

Procedure. Dissolve the weighed amount of $Sr(NO_3)_2$, preparing a solution saturated at 20° (the solubility at that temperature reaches 41.5%). The required amount of solid NaOH is rinsed in a beaker with 20 ml of alcohol (to dissolve the surface layer, which contains carbonate); the alcoholic solution is quickly poured off into a jar. Dissolve the remaining NaOH in a triple amount of water and add this solution, while stirring, to the strontium nitrate solution.

The crystals formed should be quickly filtered on a suction filter and washed with a small amount of boiled water (free of CO_2). Dissolve the washed precipitate, preparing a solution saturated at 100°; the solubility of $Sr(OH)_2 \cdot 8H_2O$ at 100° is 47.71%. Allow it to cool

slowly. Filter off the large crystals and dry them between sheets of filter paper. Transfer the crystals to a weighed jar with a ground-in lid and weigh them. Yield: 60-70%.

5. Phosphorous acid

Phosphorous acid H_3PO_3 has a density of 1.15 g/cu cm. The colourless crystals (m. p. 74.4°) deliquesce upon exposure to air. The acid is a strong reducing agent and is kept in airtight bottles.

The acid can be prepared from oxalic acid and phosphorus trichloride:

$$H_2C_2O_4 \cdot 2H_2O + PCl_3 = H_3PO_3 + 3HCl + CO_2 + CO$$

Calculate the amounts of the initial substances needed to prepare 30 g of phosphorous acid. The amount of oxalic acid taken should be triple the theoretical amount.

Procedure. Grind the oxalic acid to a powder, transfer it to a round-bottom flask (200 ml) fitted with a condenser (Fig. 76 on p. 273), add the phosphorus trichloride, and heat the mixture over a small flame until it stops foaming and becomes transparent and mobile.

Pour the heated liquid into a weighed jar with a ground-in lid and cool it. The liquid crystallises. Weigh the jar. Yield based on phosphorus trichloride consumed is 90%.

6. Antimonous iodide

Antimonous iodide SbI_3 melts at 166°. The ruby-coloured crystals dissolve in acetone, benzene, carbon disulphide, and alcohol. The compound undergoes hydrolysis upon exposure to air and is therefore kept in airtight jars.

Antimonous iodide is prepared from antimony and iodine:

$$2Sb + 3I_2 = 2SbI_3$$

Calculate the amounts of the initial substances needed to prepare 20 g of SbI_3.

Procedure. Conduct the synthesis in the apparatus shown in Fig. 76, substituting a sand bath with a thermometer for the wire gauze with an asbestos centre. Pour 20 ml of benzene into a 350-400 ml flask and add the weighed amount of powdered antimony. Close the flask and heat it until the benzene boils violently (b. p. 80°), with the antimony in a suspended state. Through the upper end of the condenser add finely ground iodine in small portions. The total amount of iodine taken should be 10% in excess of the theoretical. The first few portions of iodine quickly lose colour, but subsequent portions do so slowly. Boil for about 30 minutes after all the iodine has been added. Beautiful ruby-coloured plates are precipitated when the solution cools. Filter off the crystals on a suction filter, wash them three times

with 10 ml amounts of carbon tetrachloride, and transfer them to a sheet of filter paper. After drying the crystals for 10 minutes, weigh them, and put them in a jar with a ground-in lid. Yield: 80%.

7. Barium thiocyanate

Barium thiocyanate $Ba(SCN)_2$ dissolves in water, alcohol, acetone, etc. The white needle-like crystals upon heating are dehydrated.

The reaction of $Ba(SCN)_2$ preparation can be expressed by the following equation:

$$Ba(OH)_2 \cdot 8H_2O + 2NH_4SCN = Ba(SCN)_2 \cdot 3H_2O + 2NH_3 + 7H_2O.$$

Calculate the amounts of the initial substances needed to prepare 15 g of barium thiocyanate.

Procedure. Grind the weighed amounts of barium hydroxide and ammonium thiocyanate separately into powders and transfer them to a 100 ml round-bottom flask. Shake the flask vigorously (in a ventilated hood!) until the contents become liquid. Put a drop of the liquid on a phenolphthalein paper and, if it does not become red, add some barium hydroxide. Boil the liquid over a small flame until all the ammonia is eliminated (test!). When the ammonia has been eliminated, filter the solution through a glass filter.

To remove the excess $Ba^{\cdot\cdot}$ ions add 3 M H_2SO_4 to the filtrate until litmus paper shows it to be faintly alkaline. Then pass CO_2 through the solution for 15 minutes. Heat the solution to boiling point next, add 0.1 g of activated charcoal, and, 5 min later, filter it.

Evaporate the filtrate until the temperature reaches 125°; then cool it first to room temperature and, finally, with ice. Filter off the $Ba(SCN)_2 \cdot 3H_2O$ crystals, dry them in air, and weigh them. The yield should reach 75%.

8. Ammonium metavanadate

Ammonium metavanadate NH_4VO_3 is a white or faintly yellow crystalline substance. Heating decomposes the salt to ammonia, water, vanadic anhydride V_2O_5.

The compound is prepared in two stages:

$$V_2O_5 + Na_2CO_3 = 2NaVO_3 + CO_2$$
$$2NaVO_3 + 2NH_4Cl = 2NH_4VO_3 + 2NaCl$$

Calculate the amounts of soda and ammonium chloride needed to react with 10 g of vanadic anhydride.

Procedure. Dissolve the calculated amount of anhydrous soda in 50 ml of water in a 200 ml beaker, heating the water to boiling point and stirring the solution constantly. While continuing the stirring,

add 10 g of vanadic anhydride to the solution in several portions before the evolution of the CO_2 bubbles ends. If the solution turns blue (due to the presence of $VO^{\cdot\cdot}$), a saturated solution of $KMnO_4$ should be added by drops until the blue colour vanishes (an excess of $KMnO_4$ is harmful!).

Filter the liquid through a dense filter (if the filtrate is turbid, run it through the same filter again). Wash the precipitate on the filter with small portions of water until the test for pentavalent vanadium is negative (experiment 11, Exercise 30). Heat the filtrate with the wash water to 60° and add 50 ml of NH_4Cl solution to it. Crystals of ammonium metavanadate are precipitated after a few hours. Filter the crystals off on a suction filter, wash them with water to remove Cl', and dry them in air. Weigh the crystals. Yield: about 80%.

9. Sodium pyrophosphate (disubstituted)

Sodium pyrophosphate (disubstituted) $Na_2H_2P_2O_7$ dissolves slowly in water. The white crystals have the shape of rhombic pyramids. At temperatures not lower than 30° the salt crystallises from solutions in the anhydrous form; below 30° it crystallises in the form of the hexahydrate.

The salt is prepared in two stages:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

$$Na_4P_2O_7 + 2CH_3COOH = Na_2H_2P_2O_7 + 2CH_3COONa$$

Calculate the amounts of all the substances needed to prepare 10 g of the anhydrous salt.

Procedure. Place the calculated amount of di-sodium phosphate in a crucible and calcine it for 5 hours in a muffle furnace at 500°.

Dissolve the product, preparing 100 g of a solution saturated at 40° (the solubility of $Na_4P_2O_7$ at 40° is 11.9%). Add 75 ml of glacial acetic acid and heat to 40°, stirring the solution with a mechanical stirrer. Two and a half hours should pass from the moment when the acetic acid is added to the completion of crystallisation. Thirty minutes after the precipitation of the first crystals lower the temperature of the solution, but not below 30°.

Quickly filter off the crystals on a suction filter, wash them twice with 5 ml portions of ice-cold water, and dry them at 100°. Cool and weigh the salt. Yield: about 45%.

10. Bismuth subnitrate

Bismuth subnitrate $Bi_2O_2OHNO_3$ is a basic nitrate of bismuth, a fine white crystalline powder, which is insoluble in water. The composition of the salt may vary, depending upon the procedure by which it is prepared.

Bismuth subnitrate is prepared by hydrolysis:

$$2Bi(NO_3)_3 + 3HOH = Bi_2O_2OHNO_3 + 5HNO_3$$

Procedure. Grind 2.5 parts by weight of bismuth nitrate and 10 parts by weight of water in a quartz or agate mortar. Pour the resulting suspension into 50 parts by weight of boiling water and boil for 10-15 min. Then allow the precipitate to settle and decant the liquid. Filter off the precipitate, wash it with water, dry it at 30°, and weigh it. The yield should correspond to the theoretical.

11. Potassium chlorochromate

Potassium chlorochromate $KCrO_3Cl$ dissolves in dilute hydrochloric acid, glacial acetic acid, and water (1 : 50). The large crystals have the shape of prisms or tablets and are red. Heating to 100° decomposes the salt, with the evolution of chlorine.

The salt is prepared by a reaction between $K_2Cr_2O_7$ and HCl:

$$K_2Cr_2O_7 + 2HCl = H_2O + 2KCrO_3Cl$$

Calculate the amounts of $K_2Cr_2O_7$ and 25% HCl needed to prepare 25 g of potassium chlorochromate.

Procedure. Pour a double amount of 25% HCl into a flask, heat it on a water bath, and add the powdered $K_2Cr_2O_7$. Continue heating until all the crystals have dissolved. Filter the solution if necessary and then leave it for 2-3 days.

Brownish red crystals in the form of needles and prisms will be precipitated from the solution. Decant the mother liquor as fully as possible and transfer the crystals to a porous clay plate. Recrystallise the crystals from glacial acetic acid, dry them, and weigh them. Yield: 70%.

12. Ammonium cupric chloride

Ammonium cupric chloride $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ dissolves readily in water. The crystals are light blue.

The preparation of the double salt is based on the reaction between concentrated solutions of cupric chloride and ammonium chloride:

$$CuCl_2 \cdot 2H_2O + 2NH_4Cl = CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$$

Calculate the amounts of the initial substances needed to prepare 25 g of the double salt. From the solubility values (Table II, p. 329) of cupric chloride and ammonium chloride derive the quantity of water needed to prepare solutions saturated at 50°.

Procedure. Pour a solution of NH_4Cl saturated at 50° into a saturated solution of cupric chloride, while stirring. Evaporate the solution on a water bath until a crystalline film appears; then cool the

solution. Filter off the crystals and dry them on filter paper at room temperature. Yield: about 70%.

13. Hexamminenickel bromide

Hexamminenickel bromide $[Ni(NH_3)_6]Br_2$ dissolves in hot water and in a concentrated ammonia solution. The crystals are of cubic structure and range in colour from purple to violet-grey. The compound is kept in jars with ground-in lids.

Preparation is in several stages:

$$4NiSO_4 \cdot 7H_2O + 8NaOH = [Ni(OH)_2]_4 \cdot H_2O + 4Na_2SO_4 + 27H_2O$$
$$[Ni(OH)_2]_4 \cdot H_2O + 8HBr = 4NiBr_2 + 9H_2O$$
$$4NiBr_2 + 24NH_3 = 4[Ni(NH_3)_6]Br_2$$

Calculate the amounts of 30% NaOH, 40% HBr (relative density 1.38), and 25% ammonia solution needed to convert 11 g of $NiSO_4 \cdot 7H_2O$ to the complex compound.

Procedure. Dissolve 11 g of $NiSO_4 \cdot 7H_2O$ in 100 ml of water and conduct precipitation with a KOH solution, while heating and stirring. Filter off the precipitate and wash it with warm water until all the $SO_4^{\cdot\cdot}$ ions are removed. Dissolve the precipitate in warm hydrobromic acid, separate the unreacted residue by filtration, add 20-30 drops of HBr solution, and dilute with water to a total volume of 30 ml. Pour six times the theoretical amount of 25% ammonia solution into a beaker, heat it to 60°, and pass an intense stream of ammonia through a bubbler. To this solution add a solution of $NiBr_2$ by drops for 20 min. Then put the beaker in ice. When the solution cools, crystals of the complex compound will begin to appear. Filter the crystals off, wash them five times with a 25% ammonia solution (taking 10 ml portions), and dry them on filter paper. Yield: 90%.

14. Ferrocyanic acid

Ferrocyanic acid $H_4[Fe(CN)_6]$ is soluble in water and in alcohol, but is insoluble in ether. The white crystalline powder becomes light blue upon exposure to air. Heating above 100° decomposes the acid.

The acid is prepared by an exchange reaction:

$$K_4[Fe(CN)_6] + 4HCl = H_4[Fe(CN)_6] + 4KCl$$

Procedure. Add triple the theoretical amount of HCl (relative density 1.19) to 200 g of a 10% solution of yellow prussiate of potash (calculating in terms of the anhydrous salt). If a crystalline precipitate of KCl forms, dissolve it by adding a small amount of water. Add 25 ml of ethyl ether to the cold solution and leave the vessel closed for several hours. The white lustrous tablets that crystallise from the solution are a compound of $H_4[Fe(CN)_6]$ with ether. To

separate the compound from the KCl, dissolve the precipitate in 25 ml of alcohol, filter the solution, and precipitate the substance with an equal volume of ether. Filter off the crystals on a suction filter, wash them with ether several times, and transfer them to a dry round-bottom flask. When all the air has been displaced from the flask by a stream of dry hydrogen (test!), heat the flask for one hour on a water bath at 80-90°, without discontinuing the passage of hydrogen through the flask (careful!). Weigh the product and place it in an airtight jar. Yield: about 45%.

15. Potassium cobaltioxalate

Potassium cobaltioxalate $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ decomposes upon heating and upon exposure to light. The needle-like crystals are emerald green. The compound should be stored in jars of yellow glass with ground-in lids.

The process of preparation involves several stages:

$$2H_2C_2O_4\cdot 2H_2O + 2CoCO_3 = 2CoC_2O_4 + 2CO_2 + 6H_2O$$

$$2CoC_2O_4 + 4K_2C_2O_4\cdot H_2O + PbO_2 + 4CH_3COOH =$$
$$= 2K_3[Co(C_2O_4)_3] + 2CH_3COOK + Pb(CH_3COO)_2 + 6H_2O$$

Calculate the amounts of oxalic acid, potassium oxalate, lead dioxide, and glacial acetic acid needed to convert 11.9 g of cobaltous carbonate to the complex compound.

Procedure. Pour 250 ml of water into a 500 ml beaker and heat it to boiling point. Dissolve the oxalic acid and the potassium oxalate in the hot water; then add the cobaltous carbonate in small portions with mechanical stirring until the evolution of CO_2 ceases. Cool the solution to 40° and add first the lead dioxide and then the glacial acetic acid by drops, while stirring vigorously. An hour later the red colour of the solution should change to dark green.

Filter off the excess lead dioxide and add 250 ml of alcohol to the filtrate to precipitate the complex compound. Filter off the green crystals formed on a suction filter, press them between filter paper until they are dry, and weigh them. Yield: about 70%.

16. Potassium cobaltothiocyanate

Potassium cobaltothiocyanate $K_2[Co(SCN)_4]$ is soluble in amyl alcohol. The large needle-like crystals are dark blue. When the compound is dissolved in water, the complex ion breaks down. The hydrated Co ion imparts a rose-red colour to the solution.

This complex compound is prepared by virtue of the reaction:

$$Co(NO_3)_2\cdot 6H_2O + 4KSCN = K_2[Co(SCN)_4] + 2KNO_3 + 6H_2O$$

Conduct the calculations for 8 g of $Co(NO_3)_2\cdot 6H_2O$.

Procedure. Dissolve the calculated amounts of $Co(NO_3)_2 \cdot 6H_2O$ and KSCN in the smallest possible amounts of water (at 20° the solubilities of these compounds are 100 and 217.5 respectively). Mix the solutions and leave the vessel in a cold place for several hours. Filter off the KNO_3 crystals and wash them with 20 ml of amyl alcohol. Transfer the filtrate with the amyl alcohol to a separating funnel and shake it for some time. Then allow the amyl alcohol to settle at the bottom and drain it off. Add 10 ml portions of amyl alcohol to the remaining aqueous solution twice to extract the rest of the complex compound.

Evaporate the alcoholic solutions (in a ventilated hood) to one-tenth their volume and, after cooling, add 30 ml of ligroin. Filter off the dark blue crystals formed, using a suction filter, wash them with ligroin, and dry them in a desiccator over H_2SO_4. Yield: 55-60%.

17. Ammonium chloroplumbate

Ammonium chloroplumbate $(NH_4)_2[PbCl_6]$ is a heavy yellow crystalline powder. It undergoes hydrolysis readily, forming dark brown lead dioxide.

The formation of the complex salt proceeds in two stages:

$$PbCl_2 + Cl_2 + 2HCl = H_2[PbCl_6]$$
$$H_2[PbCl_6] + 2NH_4Cl = (NH_4)_2[PbCl_6] + 2HCl$$

Procedure. Dissolve 10 g of lead chloride ground to a very fine powder in 200 g of HCl (relative density 1.19). Pass gaseous chlorine (hood!) through the solution at 10-15°, shaking the contents of the flask from time to time. After a few hours a dark yellow liquid forms in the flask. If necessary, filter it through a glass filter, cool it with ice, and add a solution of 4 g of NH_4Cl in 40 ml of water cooled to 0°. A few hours later filter off the yellow precipitate, wash it with alcohol, and dry it. Yield: 80%.

ANSWERS TO PROBLEMS

Exercise 2

1. The first and the third. **2.** The law of multiple proportions. **3.** 12.7 g. **4.** 0.2 g. 5.15.3 g of sulphur. **6.** 3 M. **7.** 0.357 and 4.343 kg. **8.** 406.1 kg. **9.** 27.5%. **10.** 6. 68%.

Exercise 3

1. 30.06. **2.** 17. **3.** 32. **4.** 28.96. **5.** 17.6. **6.** 48.8 and 1.68. **7.** 74 and 2.64. **8.** 37.9 litres. **9.** 0.43 g. **10.** 7.26 kg.

Exercise 5

1. 12. **2.** 35.5. **3.** 65.3 **4.** 50.99. **5.** $C_4H_{10}O$. **6.** $C_2H_4Cl_2$. **7.** CH_2Cl_2. **8.** 93.9% of P; 6.1% of H; 33; 2.28; 2.95. **9.** 8.5%. **10.** 470.3. g and 169.2 litres.

Exercise 6

1. 32.6; 65.2. **2.** 100.2. **3.** 23.1. **4.** 107.9. **5.** 32.7. **6.** 31.5. **7.** 50. **8.** 13.7. **9.** 63.6. **10.** 184.

Exercise 7

1. 98.8%. **2.** 99.4%. **3.** 96%. **4.** 99.1%. **5.** 4%. **6.** 99.2%. **7.** 86%. **8.** 2%. **9.** 84.3%. **10.** 0.14% of Ca; 0.13 of Mg. 0.11% of Al.

Exercise 8

(All quantities in Cal.)

1. 88.9. **2.** 70.9. **3.** 23. **4.** 123.93. **5.** 289.28. **6.** 24. 1. **7.** 198.5. **8.** 11.87. **9.** 53.9. **10.** 373.27.

Exercise 9

1. $[Cl_2] = 0.9$ M. **2.** $[CO] = 0.25$ M; $[H_2O] = 2.25$ M; $[CO_2] = [H_2] = 0.75$ M. **3.** 0.34 M. **4.** 1.22. **5.** 0.69 M. **6.** $K = 0.072$. **7.** $K = 0.75$. **8.** $[H_2] = 0.0017$ M. **9.** 1.76. **10.** 16 and 1.024.

Exercise 10

1. 45.6% and 6.3 M. **2.** 9.9 kg; 72.6 kg; $T = 0.132$. **3.** $T = 0.098$; 9.29%. **4.** 11.5% and 1.94 N. **5.** 10.35%; $T = 0.112$; 0,676 N; 0.338 M. **6.** 422 ml and 578 ml. **7.** 7.12. M. **8.** 52.9% and 11.1 M. **9.** 20%. **10.** $T = 0.296$ and 3.5 N.

Exercise 11

1. 1,271 g and 1,964 g. **2.** 88 and 46.8%. **3.** 0.82 M and 1.64 N. **4.** 250 g and 131.7 g. **5.** 18.3; 15.5%; 1.23 M; 2.46 N. **6.** 1,553 g and 775 g. **7.** 20.8 and 17.2%. **8.** 9. 23. kg and 88.1%. **9.** 11 and $T = 0.107$. **10.** 252.5 g and 247.5 g.

Exercise 12

1. 20.19 kg. 2. 2.0 g. 3. 937.2 litres. 4. 9.38 g 5. CO — 18.2 litres, 2.2%; CO_2 — 822.2 litres, 97.8%. 6. 287.5 g; 700 g; 400 g. 7. 1.43 kg and 0.07 kg. 8. 41.1%; 24.6%; 34.3%. 9. 9.53 litres and 0.28 litre. 10. 2.43 litres.

Exercise 13

1. 180. 2. 0.49°. 3. 128 4. 1.58 atm. 5. 180. 6. 17.15 mm. 7. $C_{14}H_{10}$. 8. 1.65°. 9. 17.1 g. 10. 8 atoms.

Exercise 14

1. 0.3%. 2. $[H^+] = 6.1 \cdot 10^{-3}$; 12. 2%. 3. 0.9 .4. 2; 5.07. 5.4; 4.52. 6. 4.72; 0,003%. 7. 5.86 atm. 8. 120.1. 9. —0.8°. 10. 100.15°.

Exercise 15

1. 0.069 g. 2. $3.27 \cdot 10^{-11}$. 3.68 times. 4. $1.70 \cdot 10^{-10}$. 5. 0.0389 g. 6. Yes. 7. No. 8. 744.6 ml. 9. Yes. 10. No.

Exercise 17

1. 3,517 bombs; 95,238 cu m. 2. 448.8 kg; 620.2 kg. 3. 497.55 litres; 23.6 g. 4. 14.3 litres. 5. 7.3 g. 6. 109.7 kg; 15 bombs. 7. 11.2% of O_3; 88.8% of O_2. 8. 14.1 atm. 9. 12.6 g. 10. 2.6 litres.

Exercise 18

1. HO; H_2O_2. 2. 18.63. 3. 3.95 litres. 4. 5.13%. 5. 100.7°. 6. 10.49 atm. 7. 2.72; 0.95%. 8. 85 ml; 665 ml; $[H^+] = 4{,}9 \cdot 10^{-7}$; 6.31. 9. 56.6 g; 3.16 g. 10. 149 g; 19.8 litres.

Exercise 19

1. E. m. f. = 2.62 V. 2. 482.3 coulombs. 3. 5.79 A. 4. 35.3%. 5. In the first reaction the e. m. f. is positive, while in the second it is negative. 6. 51.8 g. 7. 3.19 V. 8. 2.08 g; 1.39 g. 9. 1.85 A; 1.94 litres. 10. 1 g.

Exercise 20

1. Compounds of this composition are possible. 2. K. 3. 21.4; 6.94%. 4. 85.54. 5. T = 0.0852; 1.52 N. 6. 197.2 litres; 692.3 litres. 7. 11.5%. 8. 100.54°. 9. 49.8 atm. 10. 0.86 g of Na; 0.3 g of O.

Exercise 21

1. 65.3; 2.77%. 2. 74 g. 3. 253.8 litres. 4. $[Ag(NH_3)_2]$ Cl. 5. 0.66 kg KCN; 28.4 litres of O_2; 45.6 g H_2O. 6. 7.8%; 0.62 M. 7. 34.5 Cal. 8. 1,419 coulombs; 4.24 g. 9. e. m. f. = 3.09 V. 10. $1.29 \cdot 10^{-9}$.

Exercise 22

1. 197.2. 2. $[Co(NH_3)_4Cl_2]Cl$. 3. 16.2 g. 4. 28.3 g; 16.5 g. 5. 46.3 litres; 33.7 litres. 6. 0.11 M. 7. 100.15°. 8. 16.2 atm. 9. 107 sec. 10. 1.8 g.

Exercise 23

1. 1.872 g. 2. 9.13 litres. 3. 0.56 kg. 4. 1.9. mg-equiv./litres. 5. 1.2 mg-equiv./litres. 6. 296 kg. 7. 21.72. Cal. 8. 107.8 Cal. 9. 82.2 faradays. 10. E. m. f. = 1.94 V.

Exercise 24

1. They are. 2. 188; 6.3%. 3. One atom. 4. One atom. 5. 69 cu m. 6. T = 0.3235; 1.55 M; 3.1 N. 7. 129.4. litres: 870.6. litres. 8. 1.13 kg; 3.23 kg. 9. $4.3 \cdot 10^{-13}$ g. 10. 100 jars.

Exercise 25

1. 4.3%. 2. 298.9 g. 3. T = 0.008; 0.08 N. 4. 48.5 ml. 5. 143 Cal. 6. $[H^+] = 7.55 \cdot 10^{-7}$; pH = 6.12; $\alpha\% = 0.076$. 7. 1.49 hr. 8. 3.3 A. 9. 1.90 V. 10. 16.8 g; 30 g.

Exercise 26

1. 34.72. 2. CO; 0.96. 3. 50 ml of methane. 4. 28.06. 5. 3.8 tons Na_2SO_4; 66 tons C; 2.7 tons $CaCO_3$. 6. T = 0,0523; 4.5%; 0.49 M; 0.98 N. 7. The Ishim River, 10.42 mg-equiv./litres. 8. 8,832 Cal; 92.6%. 9. 348.74 Cal. 10. pH = 4.73; $\alpha = 1.87\%$.

Exercise 27

1. 59.3. 2. 235.1 litres. 3. 36 litres. 4. 207.25. 5. 15.9%; 1.9 N. 6. 105.3 ml. 7. 0.146 M; 0.292 N. 8. 65% Zr; 26% Fe; 7.7% Al. 9. 110 Cal. 10. 3.57 g.

Exercise 29

1. 765.7 cu m. 2. 30 litres. 3. T = 0.018; 1.06 M. 4. 18%. 5. 113.7 ml. 6. 101.08°. 7. $[N_2] = 0.021$. 8. 385.9 Cal. 9. 280.2 Cal. 10. $[Ca(NH_3)_8]Cl_2$.

Exercise 30

1. By volume: 66.6% NO, 33.4% NO_2; by weight: 56.6% NO, 43.4% NO_2. 2. 46; 1.59. 3. 15.4 g; 59.5 g. 4. 892.8. litres. 5. 488.9 g; 117.3 litres. 6. 10.2 g. 7. 3.45 kg; 1.93 kg. 8. 34.8%; 1.994 g. 9. —0.55°. 10. 40 g; 18.1 g.

Exercise 31

1. 7.8 g. 2. 33.1 litres. 3. 12.14%; 1.53 M. 4. 33.1 kg. 5. 1,193 g. 6. 0.78%. 7. 746.0 mm. 8. $\alpha = 0.076\%$. 9. E. m. f. = 0.63 V; 12,394 coulombs 10. 9.5 g.

Exercise 32

1. 37%; 63%. 2. 81.1; 2.38 times. 3. 34.1; 1.18. 4. 384.1. kg; 638 cu m. 5. 0.0064 g. 6. 709.4 g. 7. Eight. 8. 4.875 Cal. 9. 4.52; 0.3%. 10. $4.7 \cdot 10^{-5}$.

Exercise 33

1. 61.3% SO_2; 38.7% O_2. 2. 2.38 g. 3. 5.17. litres. 4. 0.04 N. 5. 0.08% 6. 2 g. 7. 5.41 kg. 8. 4.6%. 9. It can be because the e. m. f. equals 1.16 V. 10. $8.2 \cdot 10^{-5}$.

Exercise 34

1. 6.9%. **2.** 3 litres. **3.** 1,810 litres. **4.** 871.7 g. **5.** 89.6% Cl_2; 10.4% N_2. **6.** 0.7 kg. **1,** 266 ml; 949 ml; 605 ml. **7.** 12.7 M. **8.** 0.24 mg-equiv. **9.** $7.66 \cdot 10^{-3}$ g. **10.** 9.7 g

Exercise 35

1. 173.7; 5.5%. **2.** 183.9. **3.** 98.3%. **4.** 142.3 g; 86.2 ml. **5.** 88.9%. **6.** 205 ml. **7.** 4.95 kg. **8.** 203.5 Cal. **9.** 0.11 g. **10.** E. m. f. = 0.94 V.

Exercise 36

1. 35.49. **2.** 54.2%; 45.8%. **3.** 9.5 cu m. **4.** 5.07 cu m. **5.** 4.7 ml. **6.** 29.7 g. **7.** I_2. **8.** 0.0017 M. **9.** 10.6 Cal. **10.** 0.75 g NaOH; 209 ml Cl_2.

Exercise 37

1. 45.8% H_2; 54.2% Cl_2. **2.** 89.6%. **3.** 100 ml. **4.** 120 ml. **5.** 14.9%; 4.4 M. **6.** 4,970 g; 1,715 g loss. **7.** 0.06 N. **8.** 0.0137. **9.** 1,686 times. **10.** 5.600 ml; 17.7 g.

Exercise 39

1. 39%; 61%. **2.** 53.4. **3.** Oxygen; 20.6 litres; 29.4 g. **4.** 340 g. **5.** 55 kg MnO_2; 63.9 kg KNO_3; 70.9 kg KOH; 7.1 cu m. Cl_2. **6.** 35.5 g; 11.7 litres. **7.** 2.25 g; 100 ml. **8.** 189 ml; 1,811 ml. **9.** 755 g. **10.** 0.93 g.

Exercise 40

1. 54.4. **2.** 756 g; 1,286 g. **3.** 92.4 ml. **4.** 29.5 g. **5.** 85.5%. **6.** 0.1165 N. **7.** 69.9 Cal. **8.** 0.59 V. **9.** $3.2 \cdot 10^7$. **10.** 134 hrs.

Exercise 41

1. 99.3%. **2.** 2.1 litres. **3.** 381.6 ml. **4.** 1,138 g. **5.** 23.7 ml. **6.** 17.8 g. **7.** 16.5 g. **8.** 8%. **9.** 33.6 ml. **10.** 4.15 days.

APPENDICES

Table I

Relative Densities and Concentrations of Some Salt Solutions

γ_4^{20}	%	γ_4^{20}	%	γ_4^{20}	%	γ_4^{20}	%	γ_4^{20}	%
NaCl				KCl		K_2SO_4		$MgSO_4$	
1.005	1	1.101	14	1.011	2	1.006	1	1.018	2
1.013	2	1.109	15	1.024	4	1.015	2	1.039	4
1.020	3	1.116	16	1.037	6	1.023	3	1.060	6
1.027	4	1.124	17	1.050	8	1.031	4	1.082	8
1.034	5	1.132	18	1.063	10	1.039	5	1.104	10
1.041	6	1.140	19	1.077	12	1.048	6	1.126	12
1.049	7	1.148	20	1.090	14	1.053	7	1.148	14
1.056	8	1.156	21	1.104	16	2.065	8	1.172	16
1.063	9	1.164	22	1.118	18	1.073	9	1.196	18
1.071	10	1.172	23	1.133	20	1.082	9,92*	1.220	20
1.078	11	1.180	24	1.147	22			1.245	22
1.086	12	1.189	25	1.162	24			1.270	24
1.093	13	1.197	26						

* Saturated solution.

Table II

Solubilities of Some Salts (in %)
(in terms of the anhydrous salt)

Salt	Temperature in °C										
	0	10	20	30	40	50	60	70	80	90	100
$NaNO_3$.	42.2	44.6	46.8	49.0	51.2	53.3	55.5	57.6	59.7	61.7	63.5
Na_2CO_3 .	6.6	11.2	17.8	29.0	33.2	32.2	31.7	31.4	—	—	—
KCl . .	22.2	23.8	25.5	27.2	28.7	30.1	31.3	32.6	33.8	34.9	36.0
KNO_3 .	11.6	17.7	24.1	31.5	39.1	46.2	52.5	58.0	62.8	67.1	71.1
K_2SO_4 .	6.87	8.47	10.03	11.49	13.1	14.2	15.4	16.6	17.6	18.6	19.4
$K_2Cr_2O_7$	4.43	7.5	11.1	15.4	20.6	25.9	31.2	36.2	41.1	45.2	50.5
NH_4Cl .	23.0	25.0	27.1	29.3	31.4	33.5	35.6	37.6	39.6	41.6	43.6
$CaSO_4$.	0.176	0.193	0.202*	0.209	0.211	0.208	0.200	—	—	—	0.155
$BaCl_2$.	—	25.0	26.4	27.7	29.0	30.0	31.6	33.0	34.3	35.7	37.0
$Ba(NO_3)_2$	4.8	6.5	8.1	10.4	12.4	14.6	15.9	—	21.3	—	25.5
$CuCl_2$ . .	—	—	42.1	43.6	44.7	45.7	46.7	48.0	49.0	50.8	52.4
$CuSO_4$	12.9	16.2**	—	20.0	22.8	25.1	28.1	31.4	34.9	38.5	42.4
$FeSO_4$.	15.5	17.0	21.0	24.8	28.6	32.7	35.5	35.9	30.3	—	—
$Pb(NO_3)_2$	26.7	30.8	34.3	37.8	41.0	44.0	46.8	49.4	51.8	—	56.0
$Al_2(SO_4)_3$	23.8	25.1	26.6	28.8	31.4	34.3	37.1	—	42.2	—	47.1

* At 18°.
** At 15°.

Table III

Relative Densities of Sulphuric Acid Solutions

γ_4^{15}	% H_2SO_4	γ_4^{15}	% H_2SO_4	γ_4^{15}	% H_2SO_4
1.000	0.09	1.300	39.19	1.590	67.83
1.010	1.57	1.310	40.35	1.600	68.70
1.020	3.06	1.320	41.50	1.610	69.56
1.030	4.49	1.330	42.66	1.620	70.42
1.040	5.96	1.340	43.74	1.630	71.27
1.050	7.37	1.350	44.82	1.640	72.12
1.060	8.77	1.360	45.88	1.650	72.96
1.070	10.19	1.370	46.94	1.660	73.81
1.080	11.60	1.380	48.00	1.670	74.66
1.090	12.99	1.390	49.06	1.680	75.50
1.100	14.35	1.400	50.11	1.690	76.38
1.110	15.71	1.410	51.15	1.700	77.17
1.120	17.01	1.420	52.15	1.710	78.04
1.130	18.31	1.430	53.11	1.720	78.92
1.140	19.61	1.440	54.07	1.730	79.80
1.150	20.91	1.450	55.03	1.740	80.68
1.160	22.19	1.460	55.97	1.750	81.56
1.170	23.47	1.470	56.90	1.760	82.44
1.180	24.76	1.480	57.83	1.770	83.51
1.190	26.04	1.490	58.74	1.780	84.50
1.200	27.32	1.500	59.70	1.790	85.70
1.210	28.58	1.510	60.65	1.800	86.92
1.220	29.84	1.520	61.59	1.810	88.30
1.230	31.11	1.530	62.53	1.820	90.05
1.240	32.28	1.540	63.43	1.830	92.10
1.250	33.43	1.550	64.26	1.840	95.60
1.260	34.57	1.560	65.20	1.8415	97.35
1.270	35.71	1.570	66.09	1.840	98.72
1.280	36.87	1.580	66.95	1.839	99.12

Table IV

Relative Densities of Nitric Acid Solutions

γ_4^{15}	% HNO_3	γ_4^{15}	% HNO_3	γ_4^{15}	% HNO_3
1.000	0.10	1.170	27.88	1.340	54.07
1.010	1.90	1.180	29.38	1.350	55.79
1.020	3.70	1.190	30.88	1.360	57.57
1.030	5.50	1.200	32.36	1.370	59.39

Table IV (continued)

γ_4^{15}	% HNO_3	γ_4^{15}	% HNO_3	γ_4^{15}	% HNO_3
1.040	7.26	1.210	33.82	1.380	61.27
1.050	8.99	1.220	35.28	1.390	63.23
1.060	10.68	1.230	36.78	1.400	65.30
1.070	12.33	1.240	38.29	1.410	67.50
1.080	13.95	1.250	39.82	1.420	69.80
1.090	15.53	1.260	41.36	1.430	72.17
1.100	17.11	1.270	42.87	1.440	74.68
1.110	18.67	1.280	44.41	1.450	77.28
1.120	20.23	1.290	45.95	1.460	79.98
1.130	21.77	1.300	47.49	1.470	82.90
1.140	23.31	1.310	49.07	1.480	86.05
1.150	24.84	1.320	50.71	1.490	89.60
1.160	26.36	1.330	52.37	1.500	94.09

Table V

Relative Densities of Hydrochloric Acid Solutions

γ_4^{15}	% HCl	γ_4^{15}	% HCl	γ_4^{15}	% HCl
1.000	0.16	1.070	14.17	1.140	27.66
1.005	1.15	1.075	15.16	1.145	28.61
1.010	2.14	1.080	16.15	1.150	29.57
1.015	3.12	1.085	17.13	1.155	30.55
1.020	4.13	1.090	18.11	1.160	31.52
1.025	5.15	1.095	19.06	1.165	32.49
1.030	6.15	1.100	20.01	1.170	33.46
1.035	7.15	1.105	20.97	1.175	34.42
1.040	8.16	1.110	21.92	1.180	35.39
1.045	9.16	1.115	22.86	1.185	36.31
1.050	10.17	1.120	23.82	1.190	37.23
1.055	11.18	1.125	24.78	1.195	38.16
1.060	12.19	1.130	25.75	1.200	39.11
1.065	13.19	1.135	26.70		

Table VI

Relative Densities of Ammonia Solutions

γ_{15}^{15}	% NH_3	γ_{15}^{15}	% NH_3	γ_{15}^{15}	% NH_3
1.000	0.00	0.960	9.91	0.920	21.75
0.990	2.31	0.950	12.74	0.910	24.99
0.980	4.80	0.940	15.63	0.900	28.33
0.970	7.31	0.930	18.64	0.890	31.75

Table VII

Relative Densities of KOH and NaOH Solutions at 15°

°Baumé	Rel. den.	% KOH	% NaOH	°Baumé	Rel. den.	% KOH	% NaOH
1	1.007	0.9	0.59	26	1.220	24.2	19.65
2	1.014	1.7	1.20	28	1.241	26.1	21.55
4	1.029	3.5	2.50	30	1.263	28.0	23.50
6	1.045	5.6	3.79	32	1.285	29.8	25.50
8	1.060	7.4	5.20	34	1.308	31.8	27.65
10	1.075	9.2	6.58	36	1.332	33.7	30.00
12	1.091	10.9	8.07	38	1.357	35.9	32.50
14	1.108	12.9	9.50	40	1.383	37.8	35.00
16	1.125	14.8	11.06	42	1.410	39.9	37.65
18	1.142	16.5	12.69	44	1.438	42.1	40.47
20	1.162	18.6	14.35	46	1.468	44.6	43.58
22	1.180	20.5	16.00	48	1.498	47.1	46.73
24	1.200	22.4	17.81	50	1.530	49.4	50.10

Table VIII

Relative Densities and Degrees Baumé at 17.5°
(for liquids heavier than water)

Rel. den.	°Baumé	Rel. den.	°Baumé	Rel. den.	°Baumé
1.000	0.0	1.300	33.3	1.600	54.1
1.050	6.7	1.350	37.4	1.650	56.9
1.100	13.0	1.400	41.2	1.700	59.5
1.150	18.8	1.450	44.8	1.750	61.8
1.200	24.0	1.500	48.1	1.800	64.2
1.250	28.8	1.550	51.2	1.850	66.3

Table IX

Relative Densities and Degrees Baumé at 17.5°
(for liquids lighter than water)

°Baumé	Rel. den.	°Baumé	Rel. den.	°Baumé	Rel. den
10	1.000	40	0.824	70	0.700
15	0.966	45	0.800	75	0.683
20	0.933	50	0.778	80	0.667
25	0.903	55	0.756	85	0.651
30	0.875	60	0.737	90	0.636
35	0.848	65	0.718	95	0.622
				100	0.609

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TO THE READER

Peace Publishers would be glad to have your opinion regarding this book, its translation, design and printing, and to receive any suggestions from you.

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Names of Some Acid Radicals (Anions)
Arranged in alphabetic order of elements)

Element	Anion formula	Anion name
Al	AlO_2'	Meta-aluminate
	AlO_3'''	Ortho-aluminate
As	AsO_3'''	Arsenite
	AsO_4'''	Arsenate
B	BO_2'	Meta-borate
	BO_3'''	Ortho-borate
	B_4O_7''	Tetra-borate
Br	Br'	Bromide
	BrO_3'	Bromate
C	CH_3COO'	Acetate
	CO_3''	Carbonate
	HCO_3'	Bicarbonate
	C_2O_4''	Oxalate
	SCN'	Thiocyanate
	CN'	Cyanide
Cl	Cl'	Chloride
	ClO'	Hypochlorite
	ClO_3'	Chlorate
	ClO_4'	Perchlorate
Cr	CrO_2'	Meta-chromite
	CrO_3'''	Ortho-chromite
	CrO_4''	Chromate
	Cr_2O_7''	Dichromate
F	F'	Fluoride
Fe	$[Fe(CN)_6]'''$	Ferricyanide
	$[Fe(CN)_6]''''$	Ferrocyanide
I	I'	Iodide
	IO_3'	Iodate
	MoO_4''	Molybdate
Mo	MnO_3''	Manganite
Mn	MnO_4''	Manganate
	MnO_4'	Permanganate
N	NO_2'	Nitrite
	NO_3'	Nitrate
P	PO_4'''	Phosphate
	HPO_4''	Hydrogen phosphate
	H_2PO_4'	Dihydric phosphate
Pb	PbO_2''	Plumbite
Pt	$[PtCl_6]''$	Chloroplatinate
Re	ReO_4'	Perrhenate
S	S''	Sulphide
	HS'	Hydrogen sulphide
	SO_3''	Sulphite
	HSO_3'	Hydrosulphite
	SO_4''	Sulphate
	HSO_4'	Hydrogen sulphate
	S_2O_8''	Persulphate
	S_2O_3''	Thiosulphate
Sb	SbO_4'''	Antimonate
Se	Se''	Selenide
	SeO_3''	Selenite
	SeO_4''	Selenate
Si	SiO_3''	Meta-silicate
	SiO_4''''	Ortho-silicate
Sn	SnO_2''	Stannite
	SnO_3''	Stannate
Te	TeO_4''	Tellurate
V	VO_3'	Meta-vanadate
W	WO_4''	Tungstate
Zn	ZnO_2''	Zincate