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A Chemistry Laboratory Manual for First-Year University

N.J. DALY

D.L. SCOTT

B.K. SELINGER

Department of Chemistry
School of General Studies
Australian National University

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TABLE OF RELATIVE ATOMIC WEIGHTS (1961)

Based on the Atomic Mass of $^{12}\text{C} = 12$

The values for atomic weights given in the table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and, further, to natural mixtures that do not include isotopes of radiogenic origin.

ALPHABETICAL ORDER

Name	Symbol	Atomic number	Atomic weight	Name	Symbol	Atomic Number	Atomic weight
Actinium	Ac	89		Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95		Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85		Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97		Nobelium	No	102	
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994 ^a
Boron	B	5	10.811 ^a	Palladium	Pd	46	106.4
Bromine	Br	35	79.909 ^b	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	
Californium	Cf	98		Polonium	Po	84	
Carbon	C	6	12.01115 ^a	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132.905	Promethium	Pm	61	
Chlorine	Cl	17	35.453 ^b	Protactinium	Pa	91	
Chromium	Cr	24	51.996 ^b	Radium	Ra	88	
Cobalt	Co	27	58.9332	Radon	Rn	86	
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96		Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99		Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100		Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086 ^a
Francium	Fr	87		Silver	Ag	47	107.870 ^b
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064 ^a
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797 ^a	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847 ^b	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lead	Pb	82	207.19	Vanadium	V	23	50.942
Lithium	Li	3	6.939	Xenon	Xe	54	131.30
Lutetium	Lu	71	174.97	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.312	Yttrium	Y	39	88.905
Manganese	Mn	25	54.9380	Zinc	Zn	30	65.37
Mendelevium	Md	101		Zirconium	Zr	40	91.22

^a Atomic weights so designated are known to be variable because of natural variations in isotopic composition. The observed ranges are:

Hydrogen	+ 0.00001	Oxygen	+ 0.0001
Boron	+ 0.003	Silicon	+ 0.001
Carbon	+ 0.00005	Sulphur	+ 0.003

^b Atomic weights so designated are believed to have the following experimental uncertainties:

Chlorine	+ 0.001	Bromine	+ 0.002
Chromium	+ 0.001	Silver	+ 0.003
Iron	+ 0.003		

STANDARD ELECTRODE (REDUCTION) POTENTIALS

Half-reaction	log K	E° volt	Half-reaction	log K	E° volt
$Li^+ + e \rightleftharpoons Li$	-51.5	-3.05	$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$	5.8	0.17
$K^+ + e \rightleftharpoons K$	-49.5	-2.93	$AgCl + e \rightleftharpoons Ag + Cl^-$	3.8	0.22
$Rb^+ + e \rightleftharpoons Rb$	-49.5	-2.92	$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	9.1	0.27
$Cs^+ + e \rightleftharpoons Cs$	-49.4	-2.92	$Cu^{2+} + 2e \rightleftharpoons Cu$	11.4	0.34
$Ba^{2+} + 2e \rightleftharpoons Ba$	-98.5	-2.91	$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$	6.1	0.36
$Sr^{2+} + 2e \rightleftharpoons Sr$	-97.6	-2.89	$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$	27.2	0.40
$Ca^{2+} + 2e \rightleftharpoons Ca$	-97.0	-2.87	$Cu^+ + e \rightleftharpoons Cu$	8.8	0.52
$Na^+ + e \rightleftharpoons Na$	-45.9	-2.71	$I_3^- + 2e \rightleftharpoons 3I^-$	18.1	0.54
$Mg^{2+} + 2e \rightleftharpoons Mg$	-80.2	-2.37	$Cu^{2+} + Cl^- + e \rightleftharpoons CuCl$	9.1	0.54
$Al^{3+} + 3e \rightleftharpoons Al$	-84.3	-1.66	$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons HAsO_2 + 2H_2O$	18.9	0.56
$Mn^{2+} + 2e \rightleftharpoons Mn$	-40.0	-1.18	$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	9.7	0.58
$Zn(NH_3)_4^{2+} + 2e \rightleftharpoons Zn + 4NH_3$	-34.8	-1.03	$I_{2(aq)} + 2e \rightleftharpoons 2I^-$	20.1	0.62
$Zn^{2+} + 2e \rightleftharpoons Zn$	-25.8	-0.76	$Cu^{2+} + Br^- + e \rightleftharpoons CuBr$	10.8	0.64
$Cr^{3+} + 3e \rightleftharpoons Cr$	-37.7	-0.74	$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	23.1	0.68
$Ni(NH_3)_6^{2+} + 2e \rightleftharpoons Ni + 6NH_3$	-17.3	-0.51	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	13.0	0.77
$2CO_2 + 2H^+ + 2e \rightleftharpoons (COOH)_2$	-16.5	-0.49	$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	26.8	0.79
$Fe^{2+} + 2e \rightleftharpoons Fe$	-15.9	-0.47	$Ag^+ + e \rightleftharpoons Ag$	13.5	0.80
$Ag(CN)_2^- + e \rightleftharpoons Ag + 2CN^-$	-7.7	-0.45	$Cu^{2+} + I^- + e \rightleftharpoons CuI$	14.5	0.86
$Co(NH_3)_6^{2+} + 2e \rightleftharpoons Co + 6NH_3$	-14.5	-0.43	$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	30.7	0.91
$Cd^{2+} + 2e \rightleftharpoons Cd$	-13.6	-0.40	$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	48.5	0.96
$PbSO_4 + 2e \rightleftharpoons Pb + SO_4^{2-}$	-12.0	-0.36	$Br_{2(aq)} + 2e \rightleftharpoons 2Br^-$	36.8	1.09
$Co^{2+} + 2e \rightleftharpoons Co$	-9.4	-0.28	$Pt^{2+} + 2e \rightleftharpoons Pt$	40.0	1.2
$Ni^{2+} + 2e \rightleftharpoons Ni$	-9.1	-0.27	$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	83.2	1.23
$Sn^{2+} + 2e \rightleftharpoons Sn$	-4.6	-0.14	$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	41.6	1.23
$Pb^{2+} + 2e \rightleftharpoons Pb$	-4.2	-0.13	$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	135	1.33
$Fe^{3+} + 3e \rightleftharpoons Fe$	-2.0	-0.04	$Cl_{2(aq)} + 2e \rightleftharpoons 2Cl^-$	47.2	1.40
$2H^+ + 2e \rightleftharpoons H_2$	0.0	0.00	$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O$	49.4	1.46
$Co(NH_3)_6^{3+} + e \rightleftharpoons Co(NH_3)_6^{2+}$	1.8	0.1	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	127.4	1.51
$S + 2H^+ + 2e \rightleftharpoons H_2S$	4.8	0.14	$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	85.8	1.70
$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	5.1	0.15	$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	59.8	1.77
$Cu^{2+} + e \rightleftharpoons Cu^+$	2.7	0.16	$F_{2(g)} + 2e \rightleftharpoons 2F^-$	96.8	2.87

PREFACE

This manual was produced primarily for use in first-year practical classes in chemistry at the Australian National University. However, the looseleaf construction permits its extension to the requirements of other universities by substitution of appropriate material and it is hoped that eventually there will be available a large pool of exercises from which suitable courses may be selected.

Like all texts the manual owes much to those who have gone before and we acknowledge with thanks the multitude of teachers whose ideas have been incorporated.

Most exercises include some questions which extend the coverage of the fields under examination and provide the bases for many tutorial discussions. Demonstrators at this University are provided with a companion manual containing explanatory notes, marking schedules, and answers to questions.

Canberra
January 1967

N.J.D.
D.L.S.
B.K.S.

PROPERTIES OF GASES

An equation of state is a statement such as $V = f(T, P, n)$, indicating in this case that the volume of a system is some function of the temperature, the pressure, and the number of moles present in the system. For an ideal gas the familiar equation is $V = nRT/P$, where

n is the number of moles of gas present,

R is the gas constant having the value $0.082 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$,

T is the temperature in degrees absolute ($^{\circ}\text{K} = ^{\circ}\text{C} + 273.16^{\circ}$),

V is the volume of the gas expressed in litres.

This equation combines three well-known empirical partial equations of state:

Boyle's Law: If T is constant V is inversely proportional to P ;

Charles's Law: If P is constant V is directly proportional to T ;

Amonton's Law: If V is constant P is directly proportional to T .

The equation of state shows that equal volumes of all ideal gases under the same conditions of temperature and pressure contain the same number of moles. Where w is the weight of the gas sample and M is the weight of one mole, the number of moles of the gas is

$$n = w/M$$

Therefore the molecular weight of a gas can be obtained by comparing, at any convenient definite temperature and pressure, the weight of a known volume of the gas with the weight of an equal volume of a standard gas whose molecular weight is known.

A second method for determination of molecular weights depends on the fact that the temperature of a gas is an expression of the mean kinetic energy of the molecules; for two gases at the same temperature

$$\frac{1}{2} m_1 \bar{u}_1^2 = \frac{1}{2} m_2 \bar{u}_2^2$$

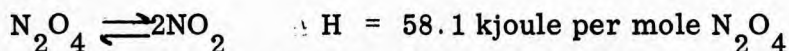
The rate of effusion through a small orifice is proportional to the mean speeds and, in comparing gases

$$\text{rate}_1/\text{rate}_2 = \bar{u}_1/\bar{u}_2 = \sqrt{m_2/m_1} = \sqrt{M_2/M_1}$$

2.2

which is the expression of Graham's Law. The molecular weight can thus be determined by comparing the rate of effusion of a gas with the rate for a standard gas.

At room temperatures, nitrogen dioxide is a mixture of two species in equilibrium



Thus the effective molecular weight of the mixture is intermediate between the values for N_2O_4 (92) and NO_2 (46). If α is the degree of dissociation, then the effective molecular weight is given by the weighted mean

$$\frac{92(1-\alpha) + 46(2\alpha)}{(1 + \alpha)}$$

The equilibrium constants in terms of concentrations (K_c) and partial pressures (K_p) can be expressed as

$$K_c = \frac{(2\alpha)^2}{(1-\alpha)V} \quad K_p = \frac{(2\alpha)^2 P}{(1-\alpha)^2}$$

Where V is the molar volume at the existing conditions and P is the total pressure. It is essential that you understand these equations and are able to derive them.

When a liquid evaporates in a confined space at a constant temperature, an equilibrium between the liquid and the vapour states is soon attained; the vapour pressure assumes a fixed value for a definite temperature. The kinetic energies of molecules in a liquid follow a Boltzmann distribution, and therefore the rate of escape from the liquid surface will be proportional to the number of molecules whose energies exceed some critical value related to the intermolecular attractive forces. This may be expressed by

$$\text{rate of escape} = k_1 \exp(-E/kT)$$

where k_1 is a constant

E is the critical energy which a molecule must exceed to escape

k is the Boltzmann constant

T is the absolute temperature

On the other hand, the rate of condensation of vapour molecules is proportional to their concentrations and thus to their vapour pressures, so that for equilibrium between vapour and liquid

$$k_2 p = k_1 \exp(-E/kT) \quad \text{or}$$

$$\log p = a/T + b$$

where p is the equilibrium vapour pressure, and k_2 , a , and b are constants, a and b may be evaluated by constructing a plot of $\log p$ versus $1/T$. The value of a is related to the heat of vaporisation, (H_{vap}) by

$$a = -(H_{\text{vap}}/2.303R)$$

NOTE: The syringes used in these exercises are fragile and must be handled with care. Hold both the barrel and the plunger firmly during handling to prevent them sliding apart. Before use make sure that they are clean and, where required, are well lubricated with silicone oil so that the plunger moves freely. The natural desire to indulge in horse-play must be restrained. When the syringe is to be weighed, carefully wipe the outside with tissue to remove weighable amounts of moisture and oil deposited from the hands.

PROCEDURE

(a) Determination of molecular weight. Obtain a 50 ml syringe and ensure that it is clean, and that the plunger moves easily in the barrel. Wipe the outside of the syringe with tissue, open the syringe to the 50 ml mark, place it carefully on the balance pan and weigh.

Fit a fine needle to the syringe and, while your partner records the time, carefully insert the needle into the rubber tip of the vacuum hose attached to the water pump. The water pumps should be run full on to minimise fluctuations in pressure. Record the time for the plunger to travel from the 50 ml mark to zero. Again fill the syringe with 50 ml of air and repeat the procedure.

Repeat the entire procedure in duplicate with each of the gases butane, freon, and nitrogen dioxide; obtain the gas samples as shown to you by your demonstrator.

Record the temperature and the barometric pressure.

Use the value of 29 for the mean molecular weight of air and calculate the molecular weights of the other gases from your weight data. Calculate the molecular weights from the effusion results using butane (molecular weight 58) as the standard gas.

From your best data, calculate the degree of dissociation α , and the equilibrium constants K_c and K_p for the nitrogen dioxide system.

(b) Boyle's Law. Place 50 ml of any of the gases but nitrogen dioxide

in a syringe. Seal the tip of the syringe with a polythene cap. Hold the syringe firmly in one hand with the plunger resting on the platform of a 0-22 lb postal balance. Obtain a series of force-volume readings by pressing the plunger against the platform of the balance. Calculate the area of cross-section of the barrel of the syringe and convert the force readings to pressure in kg cm^{-2} ; plot these pressures against the reciprocal of the corresponding volumes ($V^{-1} \text{ ml}^{-1}$).

Remove the polythene cap from the syringe, expel all but about 5 ml of the gas, replace the cap and attach the plunger to the spring extension balance. Obtain a series of measurements for pressures less than one atmosphere. Do not extend the plunger beyond the 40 ml mark. Plot pressure against $1/V$ as above.

If time permits repeat this latter procedure using nitrogen dioxide. Note carefully what happens when the plunger is moved suddenly from the 5 ml mark to the 20 ml mark and held there for about half a minute.

(c) Charles's Law. Place one of the special 273 ml flasks fitted with a rubber stopper which is pierced by a 21 gauge needle in an ice bath. When the flask has reached 0° , fit a syringe to the needle so that the reading is zero at this temperature. Transfer the apparatus to a bath at about 40° and allow the gas to equilibrate at this temperature; from time to time gently press the plunger and allow it to spring back until the volume becomes constant. Record the volume and the temperature.

Repeat the procedure at several temperatures below 40° (about 5° intervals). At the end of the exercise check the volume of the flask by filling it with water and then transferring the water to a measuring cylinder.

Plot V_t/V_0 versus T where V_t and V_0 are the total volumes at T° and 0° respectively; calculate the temperature coefficient of expansion of the gas (deg^{-1}). Estimate the absolute zero of temperature by extrapolation.

(d) Vapour pressure. Admit about 10 ml of air to a syringe and seal the tip with a flexible cap. Make sure that the cap fits tightly and that the plunger moves freely in the barrel of the syringe. Record the volume of air in the syringe and also the barometric pressure. Inject 0.5 ml of methylene chloride from a small syringe through the flexible cap. Shake the syringe gently and after a few minutes record the equilibrium volume.

Place the syringe in an ice-water bath and record the volume when it becomes constant; record the volume at several temperatures up to 35° .

Plot the logarithm of the vapour pressure (calculated as shown on the result sheet) against the reciprocal of the absolute temperature and estimate the boiling point and the latent heat of vaporisation of methylene chloride.

NEAR-INFRARED COLORIMETRY

Molecules absorb energy in various regions of the electromagnetic spectrum. Electronic rearrangements need energies which are associated with light in the visible and ultraviolet regions. Vibration of molecular bonds for which a dipole moment change occurs will absorb energy in the infrared at frequencies which correspond to the vibration frequencies or multiples (overtones) thereof. Changes in the rotational energy of dipolar molecules require far less energy and absorptions occur in the far-infrared and microwave range.

The simple colorimeter with which you are provided has a photo-transistor as a sensing device. The output of this transistor is proportional to the amount of radiation falling on it. Near-infrared light in the range 5000 to 20,000 Å (or 20,000 to 5000 cm^{-1}) produces electrons and associated positive 'holes' in the transistor, and under the influence of an applied potential these migrate to the electrodes, thus generating the photocurrent. This current is amplified by two germanium transistors and is measured on a 0 to 1 milliamp meter. The source of the infrared radiation is a tungsten filament bulb with a filter to remove the visible light. The test solutions are placed in the light path in 1 cm glass cells; it should be noted that glass cells could not be used to make measurements in the far-infrared region since glass absorbs these longer wavelength radiations.

The fundamental frequencies of the various molecular vibrations lie too far into the infrared to be observable with this instrument, but the absorption of the overtone frequencies for some liquids are within its limited range.

Copper solutions are characteristically blue and therefore must absorb red light. The maximum absorption in fact occurs at 8000 Å. This absorption produces a mild electronic rearrangement of the electrons in the hydrated copper ions, $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. When the water ligands are replaced by a more strongly-bound ligand such as ammonia, the absorption shifts towards the visible; thus more infrared light is transmitted to the

detector. On the other hand, when the copper is surrounded by ligands such as chloride ions which are less strongly bound than water, the absorption shifts to lower energy and thus further into the infrared. Thus shifts in the absorption peak for coordinated copper to higher (visible) and lower (infrared) energies are indicated by this instrument as increases and decreases respectively in the transmittance reading.

The basic relationship of colorimetry is the Beer-Lambert Law which states, for absorption of monochromatic light,

$$\log (I_0/I_d) = kcd$$

where I_0 is the intensity of the light beam incident on the sample;

I_d is the intensity of the light beam after it has travelled a distance d through a solution of concentration c ;

k is the constant of proportionality.

In other words, the absorption is proportional to the number of molecules in the light path. When c is expressed as a molar concentration, and d is in cm, the constant k is known as the molar extinction coefficient for the particular absorbing species, at the particular wavelength in use.

PROCEDURE

(a) Standardisation of the instrument. Switch on the nine volt power supply and allow the instrument to stabilise. Adjust the ZERO knob until the reading is steady on 0%. Place an empty cell in the cell-holder as close to the shutter as possible; open the shutter, press the READ button, and adjust the 100% knob until a full scale deflection is obtained on the meter; release this button as soon as possible since heat transmitted from the infrared source causes the zero to drift. Finally check the zero with the shutter closed, resetting if necessary.

(b) The infrared absorption of some liquids. Check the zero position. Fill the cell with carbon tetrachloride (CAUTION. The vapours are toxic) and place it in the holder; press the READ button and record the percentage transmittance of the liquid. In the same manner obtain the percentage transmittance of each of the liquids provided. Include bromine, which is supplied in a special cell, among the liquids. At the conclusion of these readings check the value obtained for carbon tetrachloride.

NOTE: Before each reading check and adjust the zero position (shutter closed). When changing liquid samples rinse the cell thoroughly with acetone and allow it to dry. Wipe the outside of the cells with soft

tissue. Do not place your fingers on the optical faces or drop the cells.

(c) Determination of copper. Fill the cell with distilled water and adjust the ZERO and 100% levels. Dilute the stock solution of copper sulphate to make up a series of about fifteen solutions with concentrations in the range 0.2 to 0.01 M. This may be done by measuring the number of drops needed from your dropper to fill the cell, and to then mix drops of water and copper sulphate in the required ratios. Measure the percentage transmittance for each solution (check the zero in between solutions). Plot $\log(\text{reading}/100)$ versus concentration and draw the line of best fit through the points.

Weigh out accurately about 1 g of the copper alloy and dissolve it in the minimum amount of 6 M sulphuric acid. Make the solution up to 250 ml in a volumetric flask. Measure the percentage transmittance of the solution and use the calibration curve to determine the concentration of the copper in the solution; calculate the percentage copper in the alloy.

(d) Effect of ligands on copper absorption. Use the calibration curve constructed in part (c) to select a concentration of copper which gives about 20% transmittance. Fill the cell to the three-quarters level with copper solution having this concentration, and measure the percentage transmittance; add a sufficient number of drops of concentrated ammonia (15 M) to convert the hydrated copper ions to copper tetrammine ions, and again measure the percentage transmittance. Determine from your curve whether the dilution caused by the addition of ammonia could account for the observed change in absorption.

Select a copper solution to give a transmittance of about 80%. Repeat the above procedure with concentrated hydrochloric acid in place of ammonia. Use just sufficient concentrated hydrochloric acid to form the yellow complex ion CuCl_4^{2-} .

$$2 \text{ in } 10 = \frac{1}{10}$$

$$\begin{array}{r} 1.0000 \\ 18.692 \\ \hline .1308 \end{array}$$

$$\begin{array}{r} .7924 \\ .2076 \end{array}$$

315

.6435
.6232

7634

.6628

.6021

Name Date Mark

NEAR-INFRARED COLORIMETRY(b) Infrared absorption of some compounds

Sample	Reading	Comment
carbon tetrachloride	...102...	
acetone	...84...	
ethanol	...67.5...	
aniline	...83.5...	
water	...48...	
bromine	...105 f...	
carbon tetrachloride	...101...	

(c) Determination of copper

Solution Number	Copper Concentration, M	Reading %	Log (Reading/100)
1	...200...	13.6	
✓ 2 5/30	...033...	74	
✓ 3 10/30	...067...	58	
✓ 4 18/30	...120...	32	
✓ 5 16/20	...16 x .6667...	34	
✓ 6 15/30	...1...	42	
✓ 7 14/30	...14 x .6667...	44	
✓ 8 12/30	...080...	46	
✓ 9 20/30	...133...	26	

DROPS

52

3 in 20

5 .033

8

10 .067

12 .080

13

14

15 .1

16

17

18 .120

20 .133

25 .167

~~for 500 - 900~~ $\frac{9}{15} \times \frac{2}{5}$ $\frac{2}{5} \times \frac{2}{5}$
 $\frac{5}{12} \times \frac{1}{5}$
 $\frac{1}{12}$ $\frac{1}{5}$ $\frac{8}{15} \times \frac{2}{5}$ $\frac{1.6}{15} - \frac{.16}{1.5}$ $\frac{2}{15} \times \frac{2}{5}$
 $= \frac{1.4}{15}$ $.16 \times .6667$

3.6

Solution Number	Copper Concentration, M	Reading %	Log (Reading/100)
✓ 10 8/30	.08 x .6667	62	
✓ 11 25/30	.1667	18	
✓ 12 17/30		33	
✓ 13 13/30		40	
14			
15			

Weight of watchglass + alloy g
 Weight of watchglass g
 Weight of alloy g
 Meter reading 3.7 %
 Concentration of copper M
 Percentage of copper in alloy

Calculations:

$$\frac{4}{15} \times .2 = \frac{.8}{15} \quad \frac{5}{6} \times .2 = \frac{1}{6}$$

Name

(d) Effect of ligand on copper absorption

22/30

Transmission for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ solution 12 %Transmission for $\text{Cu}(\text{NH}_3)_4^{2+}$ solution 4 %Comments:Transmission for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ solution 75 %Transmission for CuCl_4^{2-} solution 40 %Comments:

QUESTIONS

1. Why does bromine show no absorption in the infrared?

What might you expect if some iodine were dissolved in the bromine?

Would you expect any absorption for hydrogen or hydrogen chloride?

3.8

2. The infrared spectra of celestial bodies can provide much useful information about the nature of the surface composition. However, it is virtually impossible to carry out such studies from the surface of the earth. Why?

DETERMINATION OF WATER OF CRYSTALLISATION

This exercise is a very simple application of gravimetric analysis, which, as its name implies, involves the process of weighing in order to obtain information on the composition of a system. If a pure compound of known composition can be isolated from a known weight of mixture, the proportion of one or more constituents can be calculated from the weight of the separated sample. This method of analysis is capable of a very high degree of accuracy, but it may involve considerable skill on the part of the operator and may be, in comparison with modern instrumental techniques, excessively time-consuming. However, the simple stoichiometric basis of gravimetric analysis is fundamental and there still remain some analyses which are best carried out this way. For these reasons, and to teach you careful handling and weighing techniques, some standard gravimetric determinations are included in the course.

Two of the most common separation techniques are thermal decomposition and precipitation; the present exercise utilises the first, which relies on the fact that many substances when heated to a particular temperature undergo partial decomposition to yield products of definite composition. Perhaps the simplest of these decomposition reactions is the loss of water by a hydrated salt and this exercise is the first stage in a complete analysis of reputedly-pure $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Later, both barium and chlorine will be determined by precipitation and the chlorine will also be estimated volumetrically.

As there will be several long periods of waiting during this exercise, you are also asked to investigate qualitatively the effects of heat on several other compounds.

PROCEDURE

(a) Water of crystallisation. Place a clean crucible with its lid in the oven rack, and, after displacing the lid slightly to facilitate drying, leave for about 1 hour. Using your tongs transfer the crucible to a

11.2

desiccator; allow to cool for about 20 minutes and weigh quickly. Return it to the oven for a further 15 minutes; allow to cool and weigh as before. If the two weights so obtained differ by more than about 0.2 mg consult your demonstrator.

Place 0.4 to 0.5 g of barium chloride dihydrate in the crucible and weigh accurately. Replace the crucible in the oven rack and leave for at least 1 hour. Cool, weigh, and repeat the cycle as before. Calculate the percentage of water in the sample. If you are proceeding to the determination of barium you should retain the dried salt.

(b) Effects of heat on some compounds. While you are waiting during the drying periods, heat a small quantity of each of the compounds as directed on the result sheet. Record full observations and equations.

Name Date Mark

DETERMINATION OF WATER OF CRYSTALLISATION(a) Water of crystallisation

Weight of crucible g

Weight of crucible + $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ gWeight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ gWeight of crucible + BaCl_2 gWeight of BaCl_2 g

Weight of water driven off g

Percentage of water in hydrate

Theoretical percentage

Calculations:

11.4

(b) Effects of heat on some compounds

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Heat strongly in a crucible. Allow to cool. Add a little water and a drop of phenolphthalein.

NH_4Cl . Heat gently in a casserole.

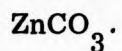
HgI_2 . Heat gently in a casserole. Allow to cool.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Heat rather strongly in a casserole. Allow to cool and add a drop of water.

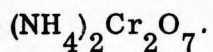
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Heat strongly in a crucible. Allow to cool and add a drop of hydrochloric acid.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Heat gently and then strongly in a crucible. Test the vapour evolved with blue litmus paper.

Name



Heat strongly in a crucible. Allow to cool.



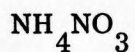
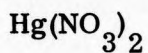
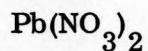
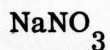
Heat gently in a casserole.

QUESTIONS

1. Do you think that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ would be a suitable salt for this determination?

2. How is water of crystallisation held in the crystal lattice?

3. Write equations to illustrate the thermal decomposition of

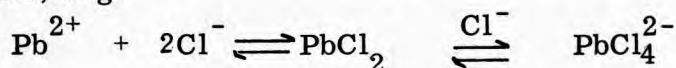


DETERMINATION OF BARIUM

This determination employs the second of the gravimetric separation techniques, namely that of precipitation. For an exposition of the many fundamental principles and problems involved in precipitation processes the student should consult a standard analytical text. The main points are summarised as follows:

(1) Precipitates made up of large particles are usually more easily filtered and handled. The production of large particles is favoured by maintaining a low degree of supersaturation of the solution with respect to the precipitate; the precipitant should therefore be dilute and should be added slowly and with stirring to a hot solution. Digestion of the precipitate in contact with the solution tends to increase the particle size since the smaller particles redissolve as the larger particles grow; in special cases, however, this process may cause contamination of the solid.

(2) A large excess of the precipitating reagent is generally undesirable since, as well as tending to precipitate electrolytes with higher solubilities, the precipitate itself may partially redissolve in the form of complex ions, e.g.



(3) The precipitate should be thoroughly washed. In some cases the use of pure water for washing is to be avoided as the solid may be peptised - i.e. the solid may become dispersed as a colloid and pass through the filter. To avoid peptisation silver chloride is washed with dilute nitric acid. In other cases the washing solutions may contain an ion common to the precipitate to reduce loss by solution, or may be acidic to reduce losses due to hydrolysis.

(4) Substances which interfere with the normal precipitation must be removed before the precipitation process. Additionally there may be impurities which could be coprecipitated with the desired compound - i.e. they are incorporated into the precipitate by mechanical trapping, by

substitution in the lattice, or by adsorption on the surface. Coprecipitation must be controlled by suitable choice of experimental conditions, by digestion, or by redissolving the solid in a suitable solvent and precipitating again. This last procedure cannot be employed for barium sulphate, for which there is no suitable solvent, but an example of its use is the precipitation of iron as the hydrated oxide. Barium sulphate exhibits a remarkable ability to coprecipitate many other ions, e.g. chloride, nitrate, sodium, potassium, calcium, aluminium, ferric. The solution is therefore kept very dilute and the precipitate is digested.

(5) Once the precipitate has been formed it must be collected in a form suitable for weighing; this is usually achieved by filtering the suspension. At times it is necessary to ignite the precipitate in order to obtain the desired product; in such cases the precipitate is collected on a low ash filter paper which is subsequently burned off. At other times the precipitate needs only to be dried, and is then readily collected in a sintered glass crucible which can be placed in a drying oven. Barium sulphate is not readily removed from sintered glass crucibles and in this exercise the barium sulphate will be collected on a low ash filter paper. Barium may also be precipitated as the chromate, which can be collected in the sintered glass crucible; the chromate is readily soluble in dilute hydrochloric acid and can easily be removed from the crucible.

PROCEDURE

(a) Determination of barium as barium sulphate. Suspend a clean porcelain crucible and its lid in a ceramic triangle and heat strongly for fifteen minutes. During this waiting period proceed with the precipitation. After the fifteen minutes have elapsed, remove the burner and allow the crucible to cool for three minutes; transfer the crucible to the desiccator in which it is allowed to reach ambient temperature. Weigh the crucible (together with the lid) after a further twenty minutes have elapsed. Ideally the heating, cooling, and weighing cycle should be repeated until the weight is constant to within 0.2 mg.

Weigh out accurately about 0.4 to 0.5 g of barium chloride dihydrate and transfer the sample quantitatively to a 600 ml beaker; use your wash-bottle to rinse the weighing bottle and allow the washings to fall into the beaker. Add deionised water to the beaker until the total volume of the solution is about 300 ml. Heat the solution to incipient boiling. Calculate the quantity of the 2 M sulphuric acid necessary just to precipitate

the barium; dilute twice this amount of the acid to about 50 ml and add it to the barium solution.

Keep the solution near boiling for about ten minutes and stir occasionally. Under these conditions the barium chloride particles grow and the proportion of coprecipitated impurities is minimised. Refer to the data below and select a suitable grade of filter paper.

Characteristics of Whatman Filter Papers

<u>No.</u>	<u>General</u>	<u>Retention</u>	<u>Speed</u>	<u>Use</u>
1	qualitative grade	medium	medium	general purpose
2	ash 0.06%	high	slow	fine precipitates
5		good	slow	hardened, Buchner
40	double acid-washed	medium	medium	general purpose
41	with HF and HC	poor	rapid	$\text{Al}(\text{OH})_3$ etc.
42	ash 0.01%	high	slow	Buchner, fine BaSO_4

540, 541, and 542 correspond to the preceding series but are hardened, have very high wet strength, are resistant to acids and alkalis, and will not pulp readily in water; they are ideal for Buchner use and precipitates are readily scraped off them.

Filter the hot solution, taking care to decant most of the clear supernatant liquid through the filter before transferring any of the solid. Test the filtrate with sulphuric acid to ensure that the precipitation is complete. Rinse the beaker with hot water and transfer the washings to the filter paper; repeat the rinsings until all the particles have been transferred to the filter and the washings are free from acid.

Fold the paper carefully around the precipitate and place it in the weighed crucible. Heat the crucible gently to drive off moisture and to smoke off the filter paper; if the paper catches fire place the lid squarely on the crucible and remove the burner for a few moments. After the paper has stopped smoking heat the crucible strongly, rotating it periodically so that no tar is deposited on the sides. Hold the crucible at red heat for ten minutes then allow it to cool as described above; weigh the

crucible and the barium sulphate. Repeat the process of heating, cooling, and reweighing until the successive weighings agree to within 0.02 mg. Calculate the percentage of barium in the sample.

(b) Determination of barium as barium chromate. Dry a sintered glass crucible to constant weight in an oven at 120° following a procedure similar to that described in part (a).

Accurately weigh about 0.4 to 0.5 g of barium chloride dihydrate and quantitatively transfer the sample to a 250 ml beaker; rinse the weighing bottle with deionised water placing the washings in the beaker. Make the volume of the solution up to about 100 ml with deionised water. Add 10 ml of 1 M acetic acid and 5 g of solid ammonium chloride.

Heat the mixture to boiling and stir so that the solid is dissolved; stir the solution continuously and slowly add 10 ml of 10% potassium chromate solution. After the addition is complete boil the solution gently for several minutes, and allow it to stand for some time, preferably overnight.

Filter the mixture through a sintered glass crucible; rinse the beaker with cold water and pour the rinsings through the crucible. Test the filtrate to make sure that precipitation is complete. Dry the crucible and the chromate to constant weight at 120° . Calculate the percentage of barium in the original sample.

Mechanically remove as much of the precipitate as is possible, and dissolve the remainder in dilute hydrochloric acid. Rinse the crucible thoroughly with water.

Name Date Mark

DETERMINATION OF BARIUMWeight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (BaCl_2) gWeight of crucible + BaSO_4 (BaCrO_4) g

Weight of crucible g

Weight of BaSO_4 (BaCrO_4) g

Percentage of Ba in sample

Weighing details and calculations:**QUESTIONS**

1. Indicate, with reasons, what effect you would expect the following variations in experimental procedure to have on the result of this determination :

As sulphate: (a) The filter paper was not completely burned off before the crucible was strongly heated.

12.6

(b) Sodium sulphate was used as a precipitant.

(c) The precipitate was washed with dilute sulphuric acid.

(d) A concentrated solution of the precipitant had been added quickly.

As chromate: The precipitate was washed with dilute sulphuric acid.

2. Assuming that your sample contained 2×10^{-3} moles of barium, that it was dissolved in 300 ml of water and that exactly twice the required amount of sulphuric acid was added, would there have been any calcium sulphate precipitated if very hard tap water, containing 100 ppm of calcium, had been used for making up the solution (K_{so} for $\text{CaSO}_4 = 2.5 \times 10^{-4}$)? Would this have affected the chromate determination?

Calculations:

Name

3. In a variation of this procedure the sulphate ions are generated in the solution by the slow hydrolysis of sulphamic acid ($\text{NH}_2\text{SO}_3\text{H}$). What is the advantage of this?

4. Why were acetic acid and ammonium chloride added before the barium chromate was precipitated?

If ammonium chromate had been used as precipitant instead of the potassium salt what change could have been made in the procedure?

5. The solubility of barium sulphate in dilute hydrochloric acid solution varies as follows (Kolthoff and Vogelenzang, Zeit. anal. Chem., 58, 49, 1919):

Concentration of acid (M)	0.0	0.1	0.5	1.0
Solubility (mg litre ⁻¹)	2.6	11	31	54

Calculate the solubility product of BaSO_4

Given that K_2 for sulphuric acid ($\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$) is 10^{-2} mole litre⁻¹, determine whether the solubility of BaSO_4 in acid solution is attributable simply to the formation of the bisulphate.

The data for the solubility of BaSO_4 in acid solution vary widely from source to source. How do you account for this?

12.8

Calculations:

DETERMINATION OF CHLORIDE

The quantitative precipitation of silver chloride for the determination of either silver or chloride involves a number of experimental problems. The precipitate tends to be colloidal and thus difficult to filter. The addition of dilute nitric acid to the solution renders the silver chloride less soluble and thus assists in the coagulation process; also nitric acid prevents the precipitation of other salts such as the phosphate and carbonate. The use of a slight excess of precipitant also reduces the solubility of the chloride, but a large excess is to be avoided as the precipitate adsorbs common ions from the solution and will form a soluble complex if the concentration of silver or chloride ions becomes sufficiently high.

Further, silver chloride is photochemically sensitive, being decomposed by light to metallic silver and chlorine. It quickly turns purplish in colour on exposure to sunlight and therefore all operations should be carried out in subdued light.

The precipitate is washed with dilute nitric acid to reduce losses by dissolution and to prevent peptisation.

PROCEDURE

Dry a sintered glass crucible to constant weight in an oven at 120° .

Weigh out accurately sufficient barium chloride dihydrate to contain about 0.1 g of chlorine. Dissolve the sample in about 150 ml of deionised water in a beaker and add 5 ml of 2 M nitric acid. Estimate approximately how much 0.1 M silver nitrate will be required to precipitate the chloride and then add this volume slowly and with constant stirring. Check for completeness of precipitation by adding a few drops more of precipitant; repeat this process until there is a slight excess of silver ions present.

Heat the suspension and maintain near boiling for several minutes until the precipitate is coagulated and the supernatant liquid is clear. Again check that precipitation is complete. Allow the suspension to settle in a dark place for at least one hour.

13.2

Decant as much as possible of the supernatant liquid through the filter crucible. Wash the precipitate several times by adding 0.02 M nitric acid to the beaker and decanting. Transfer the precipitate to the filter as a suspension in dilute nitric acid and rinse out the beaker with the acid, making sure that there are no solid particles clinging to the wall. The residue in the filter must now be washed with 1 ml quantities of dilute nitric acid until any silver ions which may have been absorbed on the precipitate have been removed. This removal is complete when the filtrate collected from the last washing gives no precipitate when treated with dilute hydrochloric acid solution.

Dry to constant weight at 120°.

Clean the crucible mechanically and by backwashing.

The crucible should then be washed with ammonia solution, followed if necessary by hydrochloric acid.

Name Date Mark

DETERMINATION OF CHLORIDEWeight of watchglass + $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ g

Weight of watchglass g

Weight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ g

Approximate weight of chlorine g

Approximate volume of 0.1 M AgNO_3 required mlWeight of crucible
+ precipitate g

Weight of crucible g

Weight of precipitate g

Percentage of chloride in sample

Calculations:

13.4

Complete analysis of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

	Theoretical	Found
Barium	 %	 %
Chloride		
Water		

QUESTIONS

1. Indicate, with reasons, what effect you would expect the following variations in experimental procedure to have on the result of this determination:

- (a) Pure water was used for washing the precipitate
- (b) A large excess of precipitant was added
- (c) The experiment was carried out in bright sunlight
- (d) The solution was not acidified before precipitation

2. Would it have been reasonable to use either hydrochloric or sulphuric acid for acidifying the solution?

3. If this method were to be used for the determination of silver, what would be the effect on the result of adding a large excess of chloride ion during the precipitation?

Name

4. A standard method for determining chloride and bromide in a mixture is to precipitate both with silver nitrate, weigh the product, convert the bromide to chloride by heating in a stream of chlorine and weigh again. In one determination, the weights obtained were 1.810 and 1.676 g; calculate the weights of AgCl and AgBr in the original precipitate.

AgCl g AgBr g

Calculations:

5. Despite the fact that AgCl is about six hundred times more soluble than AgBr , the precipitate resulting from the addition of 0.1 mole of silver nitrate to a solution containing 0.1 mole each of chloride and bromide ions is not pure AgBr , but contains a few percent of AgCl . Discuss.

ACIDIMETRY

Volumetric analysis involves the determination by titration of the volume of a solution of unknown strength that is required to react completely with an aliquot of a standard solution of known concentration. In some cases, the unknown or the standard may be solids. The standard solution, if one is used, is normally placed in the burette, but this is by no means always the case.

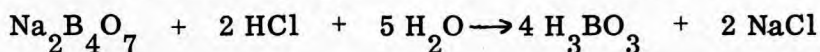
There are a number of types of titrations - iodimetry, acidimetry-alkalimetry, redox, precipitation, complexometric - the names being self-explanatory. When the desired reaction has proceeded to completion, the equivalence-point is said to have been reached. The true equivalence-point may, in fact, not be recognised in a titration, but rather an end-point is determined. The method for recognising the end-point is usually chosen so that the difference between this and the equivalence-point is negligible for the purpose.

The most common means of detecting the end-point of an acid-base titration is by the use of an indicator, which changes from one distinct colour to another over a given pH range, adopting intermediate colours within that range. When it is desired to define a particular pH more closely, a mixed indicator may be used; e.g., a mixture of neutral red and methylene blue changes colour very sharply near pH 7 and is thus useful for titrating weak acids against weak bases. Alternatively, a mixture of an indicator with an indifferent dye, called a screened indicator, may be used; e.g., methyl orange and xylene cyanol changes from green to grey to magenta sharply at pH 3.8. Some common indicators are:

methyl orange	red	3.1 - 4.4	yellow
bromocresol green	yellow	3.8 - 5.4	blue
methyl red	red	4.2 - 5.4	yellow
bromothymol blue	yellow	6.0 - 7.6	blue
phenolphthalein	colourless	8.3 - 10.0	red
thymolphthalein	colourless	9.3 - 10.5	blue

Other means for recognising the end-point include following the electrical conductance of the solution and measuring the emf of a suitable electrode pair.

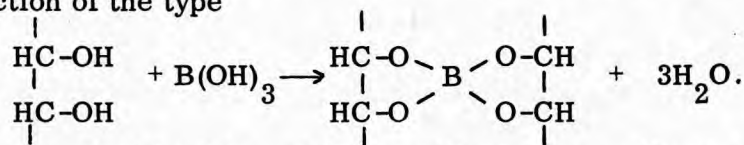
In the first part of this exercise you will standardise some approximately 0.1 M hydrochloric acid against solid samples of borax (disodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) according to the equation



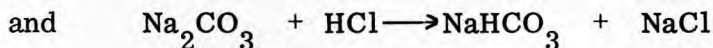
The advantages of borax over sodium carbonate are:

- (i) it has a high molecular weight
- (ii) it is easily and economically purified by recrystallisation from water, thus eliminating the need for heating to constant weight. Since the decahydrate changes to the pentahydrate at 61° , the recrystallisation must take place below this temperature.
- (iii) it is practically non-hygroscopic.

Boric acid is a weak acid, but in the presence of organic compounds with adjacent hydroxy-groups it behaves as a strong acid and can be titrated using phenolphthalein. This interesting property is apparently due to an interaction of the type



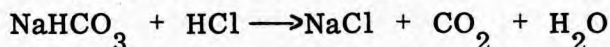
Having standardised the acid, you will use it to estimate the proportion of sodium carbonate in a solution of sodium hydroxide by carrying out two titrations with different indicators. Free carbon dioxide in the solution renders it sufficiently acid to decolourise phenolphthalein so that, if we titrate first using this indicator, the titre, T_1 , will correspond to the reactions



If the dissociation constants of carbonic acid are K_1 and K_2 , the pH at this stage is given approximately by $\frac{1}{2}(\text{p}K_1 + \text{p}K_2) = 8.3$. Since the phenolphthalein indicator does not give a particularly sharp end-point, it is preferable to use a mixture of 6 parts of thymol blue and 1 part of cresol red, which is blue at pH 8.4, violet at 8.3 and rose at 8.2. As the pH range of thymol blue is 8.0-9.6 in its second range, this mixture

is a mixed indicator.

If the titration is repeated with a fresh sample, using an indicator with a range below the pH of a saturated solution of carbon dioxide, the sodium hydrogen carbonate will be titrated as well



and the titre, T_2 , will correspond to the total concentration of base.

Methyl orange could be used, but a sharper end-point is obtained with the screened indicator, methyl orange - indigo carmine, which changes from yellowish-green to grey at pH 3.8 and then to violet (magenta) at pH 4.0.

PROCEDURE

(a) Standardisation of hydrochloric acid. Weigh out accurately two 0.4-0.5 g samples of borax, transfer them to separate titration flasks with about 20 ml of water and add a few drops of a suitable indicator. Answer Question 3 at this stage to assist you in the choice of indicator.

Titrate each sample with the stock acid. It is suggested that you keep the first solution when it has reached what you consider to be the end-point and titrate the second to the same colour. Calculate the concentration of the acid.

(b) Titration of carbonate-hydroxide mixture. Obtain from your demonstrator a mixture of sodium carbonate and hydroxide solutions. Make this up to 250 ml in a standard flask and titrate 25 ml aliquots with the standardised acid, using the mixed thymol blue indicator, until satisfactory agreement (better than 0.1 ml) is obtained between titres.

Repeat the titrations using the methyl orange screened indicator.

Calculate the weights of sodium hydrogen carbonate and sodium hydroxide in the original sample.

(c) Titration of boric-hydrochloric acid mixture. Determine the concentration of some 0.1 M sodium hydroxide by titrating it against the hydrochloric acid standardised above.

Obtain from your demonstrator a mixture of boric and hydrochloric acids. Make this up to 250 ml in a standard flask and titrate 25 ml aliquots with sodium hydroxide, using methyl orange indicator.

Repeat the titrations, using phenolphthalein and adding, before titration, 10 ml of 10% mannitol solution to each 25 ml aliquot.

Calculate the weights of hydrogen chloride and boric acid in the original sample.

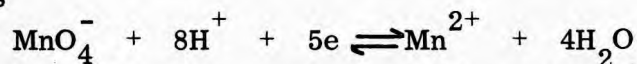
(d) Determination of ammonia in an ammonium salt. Take two conical flasks to your demonstrator and obtain duplicate aliquots of solution of ammonium chloride. Add to each 50 ml of the standardised sodium hydroxide from a burette. Place a small funnel in the neck of each flask and boil gently until a piece of filter paper moistened with mercurous nitrate no longer turns black when placed in the vapour above the boiling liquid. Cool the solutions and titrate the unconsumed sodium hydroxide with standard hydrochloric acid, using methyl red or methyl orange as indicator. Calculate the weight of ammonium chloride in your sample.

PERMANGANATE TITRATIONS

Potassium permanganate is a powerful oxidising agent and is extremely valuable for volumetric work. It is, however, difficult to obtain pure, and in solution is readily decomposed by light, heat, and traces of organic material (e.g., filter paper, rubber); additionally, the solutions tend to deposit manganese dioxide which catalyses further decomposition. For these reasons potassium permanganate is not used as a primary standard. Nonetheless, provided that your apparatus is clean, an initial standardisation of the solution provided will be valid for the duration of this assignment.

A useful discussion of the stabilities of certain volumetric solutions is given by B. W. Durham, J. Chem. Educ., **28**, 387, 1951, and also in many texts.

In acid solutions the partial ionic equation for the reaction of permanganate ions is



The electrode potential of the $\text{MnO}_4^-/\text{Mn}^{2+}$ couple is given by

$$E = E^0 - \frac{RT}{nF} \frac{(\text{Mn}^{2+})}{(\text{MnO}_4^-)(\text{H}^+)^8} \quad E^0 = 1.52 \text{ volt}$$

By manipulating the pH of the solution it is possible to vary E and thereby to oxidise selectively several components of a mixture.

PROCEDURE

(a) Standardisation of permanganate solution. Use your 500 ml volumetric flask to collect 300 ml of approximately 0.02 M permanganate solution from the store. Note that this volume is more than adequate for your requirements and you may have trouble obtaining more; it would be necessary to standardise any further permanganate solution you might collect.

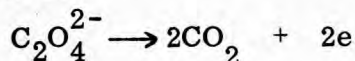
Calculate the quantity of sodium oxalate required to make 250 ml of

0.05 M solution. Accurately weigh this quantity from a bottle of dry salt, dissolve it in warm deionised water, and make up to 250 ml in a standard flask.

NOTE: Oxalates are very poisonous, and attack glass slowly.

Pipette 25 ml of the oxalate solution into a conical flask and acidify with 25 ml of 1 M sulphuric acid. Warm the mixture to 60° and titrate slowly with the permanganate solution until the warm solution retains a slight pink colouration after standing for 30 seconds.

All titrations should be carried out in duplicate. The partial ionic equation for oxalate ions is



Calculate the molarity of the permanganate solution.

(b) Determination of oxalate in the trioxalatoferrate complex.

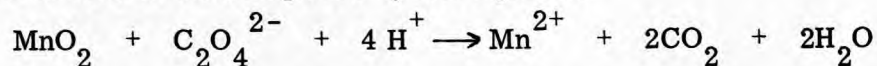
Accurately weigh about 0.2 g of the potassium trioxalatoferrate complex prepared previously. Boil this sample with 50 ml of 1 M sulphuric acid in a conical beaker. Allow the mixture to cool to about 60° and titrate with the permanganate solution as before. Repeat the determination.

Calculate the percentage by weight of oxalate in the sample and compare with the theoretical value.

(c) Determination of iron. Use the approximate value supplied for the percentage of iron in the ferrous salt to calculate the amount of salt required to give a titre of about 40 ml with the permanganate solution. Accurately weigh out this quantity, dissolve in 100 ml of water, add 10 ml of 3 M sulphuric acid and titrate with the permanganate solution. Carry out a duplicate determination.

Calculate the percentage of iron in the sample.

(d) Determination of manganese. In this analysis, an amount of oxalate in excess of that required by the equation



is added to a sample of manganese dioxide and the excess is determined by titration with permanganate solution.

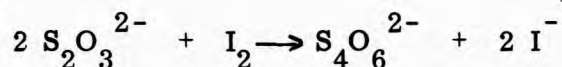
Accurately weigh out about 0.5 g of the impure manganese dioxide sample and transfer to a 400 ml beaker; add 0.1 g more than the amount

of sodium oxalate that would be required if the sample were pure. Add 25 ml of water and 50 ml of 3 M sulphuric acid. Cover the beaker with a watchglass and warm gently until the evolution of carbon dioxide ceases and the residue is free from black particles. Dilute the solution to about 250 ml, warm to 60° , and titrate with the permanganate solution.

Calculate the percentage of manganese dioxide in the sample. This back-titration technique can also be used for cations such as calcium that form insoluble oxalates.

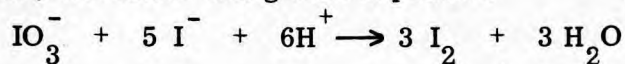
IODIMETRIC TITRATIONS

Iodine is so widely used in volumetric analysis that a special term, iodimetry, is often applied to these determinations. Free iodine is reduced quantitatively by sodium thiosulphate which is oxidised to the tetrathionate



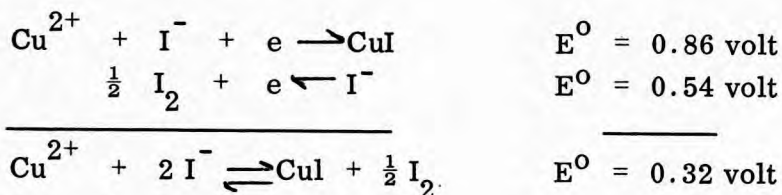
The end-point for the disappearance of free iodine is detected by using starch indicator, which forms a blue addition complex with iodine. Since the release of iodine from the complex may be slow, most of the iodine is titrated and the solution diluted before the indicator is added. The indicator should be freshly prepared and cannot be used in alcoholic or strongly acid solutions.

The best way of standardising the thiosulphate solution is against the iodine liberated from potassium iodide by oxidation with potassium iodate or bromate, the latter being less expensive



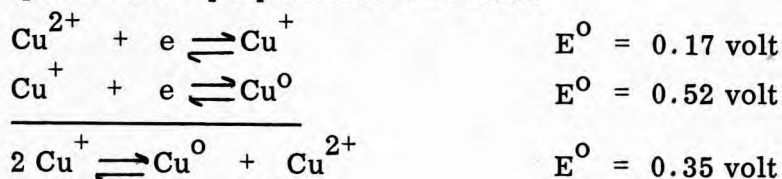
Alternatively, but less desirably, permanganate or dichromate can be used. Direct standardisation against iodine solutions is complicated by the low solubility of iodine in water and by the volatility of iodine. These difficulties are overcome by dissolving iodine in potassium iodide solution, in which it is very soluble and less volatile because of the formation of the triiodide ion, I_3^- .

Of the many determinations in which iodine is involved one of the most interesting is that of copper. When solutions of copper and iodide ions are mixed, part of the iodide is oxidised to iodine, while the copper is reduced to the cuprous state



The liberated iodine is then titrated.

The cuprous ion disproportionates in water



This value of 0.35 volt is a function of the logarithm of the equilibrium constant and corresponds to

$$K = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2} = 10^6$$

Cuprous ions can exist in contact with water only when they are effectively isolated by precipitation or complex formation.

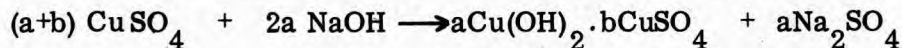
For accurate results the pH of the copper solution should be adjusted to about 4 and this is done by means of a buffer - in this case, sodium acetate-acetic acid. If the pH is too high the reaction does not proceed quantitatively to the right; if it is too low, the iodide ions are liable to be re-oxidised by the air, a reaction which is catalysed by copper ions.

Cuprous iodide is white but the precipitate at the end of the titration will be faintly buff-coloured owing to the triiodide ions adsorbed on the surface. Besides introducing an error of up to about 0.3%, this adsorption also renders the end-point somewhat difficult to detect. This may be overcome by adding, just before the titration is complete, about 1 g of potassium thiocyanate. The cuprous thiocyanate is less soluble than the iodide and hence sharpens the end-point. In addition the thiocyanate ions will tend to displace the adsorbed triiodide ions. In fact, the less-expensive thiocyanate can be used to replace the iodide, provided a trace of iodide is still present



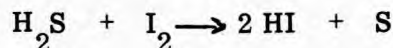
A further reaction of interest occurs when dilute sodium hydroxide is added to excess copper sulphate; the pale blue gelatinous precipitate

that separates is not a simple hydroxide, but a basic sulphate



The values of a and b can be determined by adding a known amount of sodium hydroxide to an excess of copper sulphate solution, filtering off the precipitate and titrating the residual copper. In practice, it is better to make several determinations using varying amounts of sodium hydroxide, when a and b are estimated graphically.

The iodimetric determination of sulphides utilises the reversible reaction



The simple, direct procedure provides satisfactory results, provided the concentration of hydrogen sulphide is not greater than 0.01 M. At this concentration, loss of the gas is avoided, side reactions are eliminated, and the precipitated sulphur does not carry down significant amounts of iodine.

NOTE: Iodine is an expensive substance. Therefore, all solutions containing iodine in any form should be returned to the Iodine Residues Bottle.

PROCEDURE

(a) Preparation and standardisation of 0.1 M thiosulphate solution.

Weigh out accurately about 6.2 g of the sodium thiosulphate pentahydrate prepared previously. Dissolve the sample in water and make up to 250 ml in a standard flask. Place 25 ml of the standard 0.05 M iodine solution provided in a titration flask and add thiosulphate solution from a burette until the colour due to the iodine has changed to light yellow. Dilute this solution to about 200 ml with deionised water, add 2 ml of starch solution, and titrate carefully until the blue colour disappears. Allow the solution to stand for a few minutes to make sure the titration is complete. Carry out a duplication determination. Calculate the concentration of the thiosulphate solution and the 'purity' of your preparation, basing your calculations on $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

(b) The reaction between copper sulphate and sodium hydroxide.

Place 25 ml of the copper solution provided in a titration flask and add dilute sodium carbonate until a faint permanent precipitate appears. Redissolve this by adding dilute acetic acid dropwise and then add 30 ml

of 10% potassium iodide solution. Titrate with the iodine solution using the starch indicators as described in (a). Carry out a duplicate determination. Calculate the concentration of the copper solution.

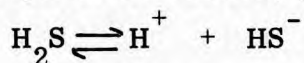
Add to 25 ml of copper solution the volume (up to 25 ml) of 0.1 sodium hydroxide assigned by your demonstrator. Filter off the precipitate and wash through with a little water. Titrate the copper in the filtrate and the washings. Combine your results with those of the rest of the group. Plot the volumes of copper solution used to form the precipitate against the volumes of sodium hydroxide added. Select any suitable point on the line of best fit and determine a and b.

(c) The solubility of hydrogen sulphide. Put about 200 ml of water in your 500 ml standard flask and then run in from the dispenser 50 ml of water saturated with hydrogen sulphide; make up to 500 ml. Pipette two 25 ml samples of this solution into titration flasks containing 25 ml of 0.05 M iodine solution which has been acidified with 5 ml of 2 M sulphuric acid. Back-titrate the residual iodine in the usual way. Calculate the solubility of hydrogen sulphide

(i) in mole litre⁻¹ and

(ii) in ml of gas per ml of water at laboratory conditions.

Calculate also the pH of the solution, given that, for the equilibrium



$$K_1 = 1.1 \times 10^{-7} \text{ mole litre}^{-1}$$

Name

(c) Solubility of hydrogen sulphide

Titres ml

Volume of residual 0.05 M iodine ml

Amount of iodine consumed mole

Concentration of hydrogen sulphide M

Solubility of hydrogen sulphide ml ml⁻¹

pH

Calculations :**QUESTIONS**

1. Indicate, with reasons, what effect you would expect the following variations in experimental procedure to have on the results of the copper determinations

(a) The standard iodine solution was exposed to the atmosphere for some time

23.8

(b) the pH was too high

(c) The pH was too low

(d) The starch indicator is added at the beginning of the titration

2. Given the reduction potential



would you expect potassium chloride to react with copper ions in the same way as the iodide?

3. Comment on the figure you obtained for the purity of your sodium thiosulphate preparation.

4. A well-known analytical text (Kolthoff and Sandell) says, of the iodimetric determination of copper : 'A reasonable excess of iodide is always added to insure the complete reduction of copper.' Do you consider this to be a reasonable statement?

5. The interference of ferric iron with this determination of copper is reduced by the addition of ammonium hydrogen fluoride. Write equations to illustrate the interference of the iron and the action of the

Name

fluoride. Note also that the fluoride acts as a buffer.

6. Although the reversible oxidation of hydrogen sulphide by iodine produces hydriodic acid, the titration is carried out in weakly acid solution to prevent the production of sulphate by a side-reaction. Write a partial ionic equation to illustrate this.

7. Devise and perform a simple test for the presence of iodine in the 'iodised' table salt provided.

PREPARATION OF TIN (IV) IODIDE

The bond between a pair of atoms acquires increasing covalent character and becomes more localised as the electronegativity difference between the two atoms decreases. Such increasing covalent character in the bond leads to a crystal lattice which is composed of discrete molecules between which the forces of interaction are relatively weak.

In contrast to the behaviour of ionic lattices, the dissolution of such molecular lattices in water may result in the decomposition of the compound. For this reason the preparation of tin (IV) iodide is carried out in the absence of water, which is removed by reaction with acetic anhydride to give acetic acid; acetic acid is used as the medium for the reaction.

PROCEDURE

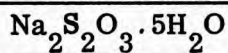
Reflux 3 g of stannous chloride dihydrate with 25 ml of a 1 : 1 mixture of glacial acetic acid and acetic anhydride for fifteen minutes in a 50 ml round-bottom flask fitted with a condenser. Allow the mixture to cool.

Remove the condenser and add 3.3 g of iodine in portions, shaking the mixture well between additions. Replace the condenser and boil the solution for a few minutes. If the solution is not completely clear at this stage, pour a few crystals of iodine down the condenser. On cooling, deep orange crystals should form. Filter off the product and dry the crystals between filter papers. Preserve the sample in the usual manner.

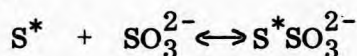
INORGANIC PREPARATIONS

While it is probably true that pure synthetic inorganic chemistry, i.e., the making of a compound for its own sake, is much more popular than it deserves to be, nevertheless every experimental chemist needs raw material and the search for and the application of new synthetic methods is an important field.

Each preparation should be preserved in a suitable vessel labelled with the names of the substance and the preparer, the yield and date and, if known, the approximate purity. If the preparation involved several steps, the approximate yield at each stage should be recorded for later reference.

PREPARATION OF SODIUM THIOSULPHATE PENTAHYDRATE

In the same way as sulphites may be oxidised to sulphates by atmospheric oxygen, so they may also be oxidised by sulphur to yield thiosulphates in which one of the sulphate oxygen atoms is replaced by sulphur. The two sulphur atoms in the thiosulphate molecule are not equivalent; this can be shown by preparing the thiosulphate with sulphur that has been labelled with the radioisotope ^{35}S . When such labelled thiosulphate is decomposed with acid all the radioactivity is retained by the liberated sulphur, indicating that there has been no exchange between the sulphur atoms in the thiosulphate molecule.



The only difficulty that is likely to be encountered in the preparation arises from the high solubility of sodium thiosulphate. At 20° , 100 g of water will readily dissolve about 150 g of the salt; hot solutions readily become highly supersaturated on cooling and the salt may not crystallise. During the preparation do not add excess water to the system and, if

crystals have not formed by the next session, add a tiny seed crystal to the solution. If crystallisation does not then begin immediately it will be necessary to boil off some of the water carefully and then perhaps to re-seed.

PROCEDURE

Place 15 g of anhydrous sodium sulphite, 5 g of finely powdered sulphur and 40 ml of water in a conical flask. Place a small filter funnel in the neck of the flask to reduce loss of water by evaporation; boil the mixture gently for about two hours. From time to time replace the water that has boiled off, but do not add excess. Filter the hot solution to remove unreacted sulphur. Allow the filtrate to crystallise in a small beaker. If crystallisation does not occur, proceed with the seeding operations described above.

Dry the crystals between filter papers and allow them to stand in the air until thoroughly dry. Do not heat the product in an attempt to accelerate the drying as sodium thiosulphate melts incongruently at 49° . Weigh the crystals and store for later use.

Name Date Mark

PREPARATION OF SODIUM THIOSULPHATE PENTAHYDRATE

Theoretical yield g

Actual yield g

Percentage yield

Weighing details and calculations:**QUESTIONS**

1. Write equations to show how the following reagents might be used to differentiate between thiosulphates, sulphites, and sulphates:

(a) Dilute acid

(b) Lead acetate solution

(c) Iodine solution

31.4

2. What do you think is the best assignment for the oxidation numbers of the two sulphur atoms in thiosulphate?

3. Suggest a molecule in which you would expect two or more atoms or ions to be equivalent and hence to exchange with one another.

VOLUMETRIC GLASSWARE

You should remember that the success of many exercises will depend on the precision of your measuring equipment and that this in turn will depend on the care that you take of it and the skill with which you use it. This exercise is designed to introduce you to the function, use, and care of your glassware.

(a) Volumetric glassware

Cleaning: When water is poured from a clean glass vessel there should remain on the inner surface an unbroken film of water. A few minutes spent, as opportunity offers early in the year, in cleaning your glassware will save you much time and trouble later. Usually a thorough washing with detergent and warm water, followed by rinsing, will be adequate. If you are unable to clean some apparatus satisfactorily, consult your demonstrator, who may suggest some more vigorous method.

Volumetric Flasks: These are calibrated to contain a fixed volume of liquid at a specified temperature and are used for the preparation of standard solutions. They are not reagent bottles for the storage of solutions. B-grade 250 ml flasks have a tolerance of ± 0.2 ml.

Transfer Pipettes: These are calibrated to deliver a fixed volume of liquid under specific conditions. If the solution to be measured out is corrosive or toxic, do not suck it into the pipette by mouth. The level of liquid in the pipette is controlled by a finger, not the thumb. The pipette should be vertical when adjusting the meniscus to the calibration mark. When the pipette is discharging the solution, the tip should be in contact with the walls of the receiving vessel and should be kept there for about 15 seconds after the flow has apparently stopped. Some liquid should remain in the tip even after delivery is complete; the pipette is calibrated to allow for this. Never blow through a pipette. It is easy to chip the tip of a pipette, thereby rendering it useless for any accurate work. Check yours at frequent intervals. The specifications of a B-grade 25 ml pipette are an outflow time of 20-50 seconds, a drainage time of 15 seconds and a tolerance of ± 0.05 ml.

Graduated Pipettes: These are a hybrid between a transfer pipette and a burette. They are used for measuring out variable volumes slightly more accurately than by measuring cylinder.

Burettes: Before using a burette, check that it is clean, that there is no grease in the vicinity of the tap or in the tip and that the tap is well-lubricated and moving freely. Greasing a tap well is quite a skilled task and you would be well advised to seek your demonstrator's assistance. In use, the burette should be clamped vertically. Before taking the reading, allow at least 10 seconds after delivery has ceased for drainage to be complete. You should fix on a method for reading the meniscus and adhere to it. The tolerance of a B-grade 50 ml burette is ± 0.1 ml.

Measuring Cylinders: These are useful only for the approximate measurement of liquids.

Beakers and Flasks: These are used as containers for carrying out reactions. They usually have a capacity about 10% greater than that engraved on the side.

(b) Calibration of a pipette. This exercise is designed to introduce you to your balance and to the handling of a pipette. You are asked to determine the weights of three samples of water delivered from your 25 ml pipette and to apply some corrections to compensate for the fact that experimental conditions are not standard.

Weigh a clean, dry 100 ml beaker covered with a small watchglass; you should handle the beaker with cloth or tissue to prevent transfer of moisture from your fingers to the glass. Add 25 ml of deionised water from the pipette and weigh again. Add two further 25 ml samples, weighing after each addition. Calculate the mean weight of water delivered by the pipette and the variation about the mean.

Because, according to Archimedes' Principle, the apparent weight of an object immersed in a fluid is less than the true weight by the weight of the amount of fluid displaced, it is necessary to apply a correction for buoyancy when the density of the object is significantly different from that of the weights used (here 8.4 g cm^{-3}). This correction can be readily calculated, but you may read it from the nomogram supplied in the laboratory.

In order to convert the corrected weight of water to a volume it is necessary to know the density of the water at the temperature of the laboratory. Obtain this value from the table in the Appendix.

For the most precise work there are other corrections that should be applied. Notice, for example, that if the pipette is used at a temperature other than that for which it was calibrated, allowance should be made for the thermal expansion of the glass. The cubical expansion of pyrex glass is approximately 10^{-5} deg^{-1} , which, for a 25 ml pipette at 30° (ten degrees above the standardisation temperature), produces an increase in volume of $25 \times 10 \times 10^{-5} = 0.0025 \text{ ml}$; this is clearly negligible for normal use.

Name Date Mark

VOLUMETRIC GLASSWARE

Experimental conditions °C mm Hg

Weight of beaker

(1) (2) (3) (4) g

+ water (2, 3, 4) (1) (2) (3) g

Weight of water g

Mean weight of water g

Variation about mean ml

Buoyancy correction factor + %

Corrected mean weight of water g

Density of water at laboratory temperature g ml⁻¹

Corrected mean volume of water ml

QUESTIONS

1. Which holds more, when filled to the graduation mark: a 25 ml pipette or a 25 ml volumetric flask?

2. What is the meaning of the inscription 250 ml/C20°C/B (or its equivalent) on your volumetric flask?

3. Under what circumstances is a pipette, operated in the ordinary way, NOT to be used for measuring out liquids?

4. List at least four variables that affect the volume of liquid delivered by a pipette and indicate, with reasons, what you would expect to be the effect on the delivered volume of increasing each one of these variable quantities.

5. The following titres were obtained with a B-grade burette when weighed portions of potassium hydrogen phthalate were titrated with 0.101 M NaOH using phenolphthalein indicator:

Sample weight	Titre
0.408 g	19.8 ml
0.594	28.7

Are these results within the limits of experimental accuracy?
Discuss.

6. The corrected weight of water in a volumetric flask filled to the mark at 15° was 998.87 g. A solution of 16.988 g of silver nitrate was made up to the mark in this flask at 25° . Calculate, with appropriate precision, the concentration in mole litre⁻¹ of this solution. (Coefficient of cubical expansion of glass = $2.5 \times 10^{-5} \text{ deg}^{-1}$, density of water at 15° = 0.99913 g ml⁻¹, AgNO₃ : 169.88).

Name

7. At what temperature would a Fahrenheit and a Celsius thermometer have the same reading?

8. The temperatures of two beakers of liquid are such that the Fahrenheit temperature of one is -3 times the Fahrenheit temperature of the other. Further, the same relationship obtains between the Celsius temperatures. What are the temperatures of the liquid?

PRECIPITATION TITRATIONS

Precipitation reactions may be used in volumetric analysis if the ions to be determined can be precipitated as insoluble compounds by the addition of known amounts of suitable reagents. For example, in the titration of chloride (or other halides with the exception of fluorides) with silver nitrate, one finds the exact amount of a silver nitrate solution of known concentration which is just sufficient to precipitate completely the chloride as silver chloride. At the equivalence-point, the amount of silver solution added from the burette (precipitant) is exactly equivalent to the amount of chloride in the sample.

Indicators in precipitation titrations function by producing a suitably coloured precipitate or colour in solution as soon as an excess of precipitant has been added. The point at which the colour can first be observed is termed the end-point. If the indicator has been properly chosen and the titration performed carefully, the end-point should be very close to the equivalence-point.

(a) Mohr's method. In the determination of chlorides and bromides by titration with silver nitrate, a solution of potassium chromate can be used to detect the end-point. Silver halides are much less soluble than silver chromate, and, as long as there is an appreciable concentration of halide ions in the solution, no silver chromate is precipitated on addition of silver nitrate. When all the halide has been precipitated, the first excess of silver nitrate precipitates the brown silver chromate, indicating the end-point of the titration.

The relationship between equivalence-point and end-point can be derived by considering the solubility products of silver chloride and silver chromate.

The equivalence-point: At this point the amount of silver added is equivalent to the chloride; the concentrations of silver ions and chloride ions in equilibrium with solid silver chloride are equal.

$$K_{so}(\text{AgCl}) = 1.7 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

$$[\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ mole litre}^{-1}$$

The end-point: At this point silver chromate just begins to precipitate. A typical indicator concentration is reached by adding 1 ml of 0.2 M potassium chromate to the titration mixture. If we choose the reasonable figure of 50 ml as the final volume of the titration mixture, the concentration of chromate ions is:

$$[\text{CrO}_4^{2-}] = \frac{1 \times 0.2}{50} = 0.004 \text{ mole litre}^{-1};$$

the concentration of silver ions can now be calculated.

$$K_{so}(\text{Ag}_2\text{CrO}_4) = 1.1 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$[\text{Ag}^+]^2 = 1.1 \times 10^{-12} / 4 \times 10^{-3} = 2.8 \times 10^{-10}$$

$$[\text{Ag}^+] = 1.7 \times 10^{-5} \text{ mole litre}^{-1}$$

Therefore the end-point lies very slightly beyond the equivalence-point; the difference, expressed in millilitres of precipitant, is termed the theoretical indicator error. In the above example, the difference between the silver concentrations at the equivalence-point and the end-point is $(1.7 \times 10^{-5} - 1.3 \times 10^{-5})$ which is $4 \times 10^{-6} \text{ mole litre}^{-1}$. This amounts to $2 \times 10^{-7} \text{ mole}$ in the actual volume (50 ml). If the precipitant is a 0.1 M solution of silver ions, the volume required to increase the concentration of silver ions from the equivalence-point to the end-point is $(\frac{2 \times 10^{-7}}{0.1} \times 1000)$ or 0.002 ml. The theoretical indicator error is thus insignificant. In practice the indicator error is greater than the theoretical value since a finite amount of silver chromate must be present before the colour change can be observed.

The Mohr titration can be carried out only in neutral solutions (see Question 4).

(b) Adsorption indicators. Precipitates have a tendency to adsorb their own ions. When halide solutions are titrated with silver nitrate the excess of silver ions, which is present in the solution beyond the equivalence-point, is adsorbed on the surface of the silver halide precipitate (primary adsorption); there is thus a positively charged layer on the surface of the precipitate, and this can adsorb ions with a negative charge

(secondary adsorption). Anions of some organic acids such as fluorescein and eosin, are adsorbed much more strongly than nitrate ions, and silver halides precipitated in the presence of these acids give brightly coloured 'adsorption complexes' at the end-point. The colour change at the end-point occurs on the surface of the silver halide precipitate.

Silver halides with a layer of indicator adsorbed on the surface are especially sensitive towards decomposition by light. Titrations using adsorption indicators must be carried out with a minimum exposure to sunlight or fluorescent light.

PROCEDURE

(a) Determination of chloride using Mohr's method. Accurately weigh about 3 to 3.5 g of the barium chloride used in the earlier assignments. Dissolve the sample in water and make the solution up to 250 ml in a standard flask taking care to mix thoroughly. Pipette 25 ml of the solution into a conical flask and add between 5 and 10 ml of 0.5 M sodium sulphate. Shake the flask and allow it to stand for a few minutes; use a graduated pipette to add 1 ml of 0.2 M potassium chromate. Titrate the mixture with the standard silver nitrate solution until the reddish colour, formed by the addition of each drop of the precipitant, begins to disappear more slowly. This indicates that most of the chloride has been precipitated and the titration should now be continued dropwise. The first permanent brown tinge represents the end-point. Repeat the determination until concordant results (differing by no more than 0.1 ml) are obtained. Use the mean of these to calculate the percentage of chlorine in the sample.

Combine these results with the percentages of barium and water obtained in previous assignments and calculate the empirical formula of the barium sample (i.e. the proportions $\text{H}_2\text{O} : \text{Cl} : \text{Ba}$).

(b) Determination of chloride using an adsorption indicator. Pipette 25 ml of the barium solution prepared above into a conical flask; add about 25 ml of water and 10 drops of fluorescein. Titrate this solution with the silver nitrate while agitating the flask continuously. As the end-point is approached the silver chloride begins to coagulate, and the local development of a pink colour as silver nitrate is added becomes more pronounced. At the end-point the precipitate suddenly assumes a pink or red colour. Repeat the determination until titration figures agreeing within 0.1 ml are obtained.

Calculate the percentage of chlorine in the sample.

Name Date Mark

PROPERTIES OF CRYSTALS

(a) Crystal habit

1. Examine under the microscope and sketch the following crystals: (i) sodium chloride grown from aqueous solution (ii) potassium chloride grown from aqueous solution (iii) silver chloride grown from an ammoniacal solution (iv) sodium chloride grown from 2 M urea solution in water.

2. All these crystals belong to the cubic system and have the same packing of cations and anions. Discuss the relationships and explain the differences between their habits.

(b) Polymorphism

1. Recall earlier exercises on the precipitation of mercuric iodide and the effect of heat on this substance.

2. (i) Ammonium chloride changes from one cubic form to another at 183° ; one form has the face-centred cubic (sodium chloride) structure, while the other is body-centred cubic (caesium chloride structure). Which form would you expect to be stable above the transition temperature?

(ii) Place the sealed tube containing ammonium chloride and 1, 2, 4 trichlorobenzene in a paraffin bath at about 170° and maintain at this temperature for about 30 minutes. Raise the temperature to 190° and maintain. Record your observations. Assuming that the tube did not explode, what would you expect to observe on raising the temperature still further?

(iii) A dilatometer containing 10 g of ammonium chloride and 100 ml of paraffin oil is placed in a bath at 150° and the volume is recorded after equilibrium is attained. The increases in the equilibrium volume are then recorded at 170° (1.55 ml), 190° (4.43 ml), and 210° (5.98 ml). Calculate:

(a) the coefficient of expansion of paraffin in deg^{-1} , assuming that it is constant over the range, and

(b) the density of the high-temperature form of the chloride, given that the density at room temperature is 1.47 g ml^{-1} .

Name

3. Ammonium nitrate can exist in at least six polymorphic forms. Can you explain why this is so?

(c) Allotropy

1. (i) Place about 3 g (1 level teaspoon) of sulphur and 10 ml of xylene (or toluene) in a large test tube. Heat CAREFULLY over a bunsen until the sulphur has completely dissolved and the solution is boiling gently. Suspend the tube in a beaker of boiling water and allow the sulphur to crystallise. After some time allow the bath to cool slowly so that crystallisation continues. Pour off the xylene into a beaker and transfer some of the crystals to a watchglass. Examine them under a microscope, sketch and explain your observations. Return all sulphur and xylene to the appropriate Residues Bottles.

(ii) Would you expect the rhombic or the monoclinic sulphur to be more soluble in carbon disulphide?

(iii) Rhombic and monoclinic sulphur are packing allotropes; i.e., the forms differ only in the way in which the S_8 rings are packed. Can you suggest how and why the two structures differ?

2. The red and yellow forms of phosphorus are bonding allotropes. Ex-

plain, in terms of the difference in bonding, the much greater volatility and chemical reactivity of the yellow form.

3. White tin changes to another allotrope, grey tin, below 13° , but the rate of transformation is normally very slow and it is thus difficult to determine the transition temperature. However, if electrodes of white and grey tin are placed in a solution of stannous chloride at any temperature other than 13° , a potential difference exists between them and the transition temperature can readily be determined as the temperature at which the potential difference becomes zero or at which the polarity of the cell is reversed. What is happening at the grey tin electrode at say 25° ? Would you expect this electrode to be negative or positive with respect to the white tin at this temperature?

(d) Defect structures

1. Recall the effect of heat on zinc oxide. Explain what is happening.

2. (i) Subject the sodium chloride crystals sealed into an evacuated tube to the high-frequency discharge from the Tesla coil. Observe and explain the colour change that occurs.

(ii) The alkali metal halides are known to take up small amounts of alkali metal or halogen when heated in the appropriate vapour. Suggest how these excess atoms might be accommodated in the lattice.

Name

3. Using the cell provided, measure the resistance at room temperature of a disc of silver mercuri-iodide, which undergoes a crystallographic transition at 51° . Place the cell in an oven at about 40° and record the resistance after about 40 minutes. Repeat at about 60° and 80° . Note any colour change and show that the transition is accompanied by a large increase in the conductivity of the substance.

Temperature, $^{\circ}\text{C}$	Resistance, ohm
.....	
.....	
.....	
.....	

4. It is well known that zinc sulphide fluoresces in UV light. However, when it is freshly prepared, it has no fluorescence. When heated above 500° , some sulphur sites become vacant and some zinc atoms occupy interstitial positions, and the solid fluoresces blue. If the substance is heated above 1100° with a trace of copper (about 1 copper atom to 10^4 zinc atoms), the fluorescence becomes yellow-green and the substance also exhibits phosphorescence. Observe the behaviour under UV light of the samples provided.

(e) Isomorphism

1. Discuss the following observations:

(i) Potassium chloride and potassium bromide form a complete range of solid solutions; potassium chloride and sodium chloride form solid solutions over limited composition ranges only, and potassium chloride and lithium chloride show no miscibility in the solid. All these compounds have the sodium chloride structure.

(ii) Sodium chloride and calcium fluoride belong to the same crystal class but are not isomorphous.

(iii) Silver bromide has the sodium chloride structure, while silver iodide has the zincblende arrangement (at room temperature).

(iv) Silver bromide can dissolve up to 70% of silver iodide but it shows little solubility itself in silver iodide.

(v) Sodium chloride, ammonium iodide, and potassium cyanide are isomorphous.

2. When one considers an isomorphous pair such as sodium nitrate and calcium carbonate it is clearly unnecessary that isomorphous salts be chemically similar. However, mixed crystals of these two salts cannot be prepared. Explain.

3. What can you suggest concerning the nature of the mixed precipitate of copper hydroxide and sulphate prepared in the exercise on iodimetric titrations ?

4. Examine the crystals provided which show oriented over-growths of potassium alum on chrome alum.

Name

5. Under what circumstances does the addition of A to B increase the melting point of B? Is it necessary that A and B be isomorphous?

(f) Clathrate compounds

Place about 5 ml of the aqueous solution of hydroquinone in a test tube and immerse the tube in an ice-bath. Pass hydrogen sulphide slowly through the solution until a precipitate forms. Show that this is not a normal covalent compound by centrifuging off some of the precipitate, dissolving it in water and adding a drop of lead nitrate solution. Suggest how the formation of a clathrate can be used to purify a chemical compound.

(g) Packing of spheres

1. Using spheres of the same size, prepare models to illustrate face-centred cubic and hexagonal close packing and body-centred cubic packing.
2. Using suitably-sized spheres, prepare models of the sodium chloride and caesium chloride structures and relate these to the appropriate models in 1.

(h) Relationships between properties and crystal structure

1. Record for each of the substances below the type of crystal lattice (ionic, molecular, etc.) and on the basis of this, predict the melting point, hardness, solubility in water and carbon tetrachloride, and electrical conductivity. Explain any apparent anomalies.

(i) Silica

(ii) Iodine

(iii) Potassium bromide

(iv) Naphthalene

(v) Lead

(vi) Calcium carbonate

(vii) Silicon carbide

2. Compare the resistances at room temperature of nichrome, germanium and carbon.

(i) Effect of rate of crystallisation on particle size

(i) Mix 10 ml of solution A (containing 175 g of di-ammonium hydrogen phosphate per litre) with 10 ml of solution B (containing 175 g of tartaric acid per litre). Add 15 ml of solution C (containing 575 g of magnesium chloride per litre) and mix thoroughly. Now add sufficient 3 M ammonia to dissolve the precipitate, and then 2 ml excess. Divide the mixture into two parts. Allow one to stand, and shake the other vigorously for 30 seconds and allow to stand. Compare the particle sizes under the microscope.

(ii) What are the compositions of the two precipitates that form?

(iii) What is the function of the tartaric acid?

FACTORS INFLUENCING CHEMICAL REACTION RATES AND EQUILIBRIA

Some of the many factors that may affect the rate of a chemical reaction and the final position of an equilibrium are

1. Extent of contact between reactants. Homogeneous reactions will proceed faster than equivalent reactions in which there is more than one phase present. A heterogeneous reaction may be accelerated by increasing the area of the interface between the phases by stirring two liquids vigorously, by finely grinding a solid reagent, by bubbling a gas, and so on. Notice the curious facts that the vapour pressure of small drops of liquid is greater than that of the liquid in bulk and that a solid is more soluble when finely powdered, indicating that physical as well as chemical equilibria may depend on the state of subdivision.

2. Concentration. The overall dependence of the rate of a reaction on the concentration of the reactants may be complex because the reaction may proceed in several steps. However, it is clear that an increase in the concentration of the reactant molecules should accelerate the rate by increasing the frequency of collisions between the molecules.

3. Temperature. The rate of reaction increases with temperature according to the relation

$$\text{rate of reaction} \propto 1/\text{time of reaction} \propto \exp(-E/RT)$$

where E is called the activation energy. From this we obtain

$$\log(1/t) = K/T$$

where $K = -E/2.303R$

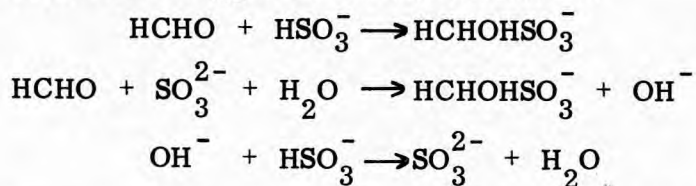
4. Radiation. The energy barrier opposing a particular reaction may be overcome by irradiating the system. This results in the production of high-energy species such as excited molecules, free atoms and radicals, and ions. Irradiation may initiate a chemical reaction or provide an alternative mechanism for one that proceeds slowly under normal thermal activation.

5. Catalysis. By providing an active surface for the reaction or by

entering into an intermediate compound, catalysts may accelerate a reaction enormously, but they do not alter the position of the final equilibrium.

Many reactions begin with an induction period, during which there is no apparent change. This may be due to the fact that the reaction proceeds in several steps, one of which is relatively slow or, alternatively, the reaction may be auto-catalytic, so that one of the products catalyses the forward reaction. The first type is exemplified in this exercise, while a well-known example of the second is the titration of hydrogen peroxide with permanganate, which proceeds very slowly until sufficient manganous ions are present to catalyse the reaction. There are many interesting examples of these 'clock reactions' and the one you will be observing here - the addition of the hydrogen sulphite ion to aldehydes - is an important characterising reaction in organic chemistry. You will be discussing this later in the year.

The mechanism suggested for this addition is



The last reaction is virtually instantaneous but the first two are much slower. As soon as the hydrogen sulphite ions are consumed, the pH of the solution rises owing to the free hydroxyl ions present and this is indicated by the change of the phenolphthalein indicator to the red form. By keeping the concentration of formaldehyde much higher than those of the other reactants, the interpretation is much simplified. If the ratio of the concentrations is kept constant, simply by diluting the mixture with varying amounts of water, then the reaction rate is a linear function of the dilution (consult R.L. Barrett, J. Chem. Educ., 32, 78, 1955).

In the following exercise, you should record all observations and interpret them as fully as you can. Provide equations where applicable.

PROCEDURE

(a) Effect of particle size and concentration. Compare the rates of evolution of hydrogen in the following systems:

1. Place small amounts of granulated zinc and zinc dust in separate test tubes. Cover the samples with 1 M sulphuric acid.

2. Place a small piece of granulated zinc in a third tube and cover with 3 M sulphuric acid.

3. Add one drop of 0.5 M copper sulphate to the tube containing granulated zinc in (1) above.

(b) The action of light. Add 1 ml of 5% bromine solution in carbon tetrachloride to 10 ml of petroleum ether (60 - 80° BP range). Divide into two parts. Keep one portion dark by placing it in your locker and place the other in direct daylight on the windowsill. Compare the colours of the samples from time to time.

(c) Effect of temperature. Place 10 ml of the permanganate solution (containing 1 g of potassium permanganate per litre of 2.5 M sulphuric acid) in a large test tube. Drop in a nail and warm the solution, by placing the tube in a beaker of warm water until the colour disappears. Rinse the nail. This pre-treatment is necessary to prepare the surface of the nail by removing any impurities likely to interfere with the desired reaction.

Prepare a beaker of water at about 30° and maintain the temperature as closely as possible. Place a large test tube, containing 10 ml of the permanganate solution and a second thermometer, in the beaker. When the solution has attained the bath temperature, drop in the nail and record the time, t sec, required for decolorisation. Record also the average temperature for the solution for the period of the reaction.

Wash the nail and repeat the experiment at about 50°, 70°, and 90°. Plot a graph of $\log (1/t)$ against the reciprocal of the absolute temperature.

(d) A clock reaction. Place 10 ml of 0.3 M formaldehyde solution in a 250 ml flask and add 0.5 ml of phenolphthalein solution and 40 ml of water. Pipette 10 ml of sulphite solution (0.2 M in sodium hydrogen sulphite and 0.05 M in sodium sulphite) into a large test tube. Add the sulphite solution rapidly to the formaldehyde, swirling vigorously to ensure thorough mixing. Record the time in seconds for the colour to appear.

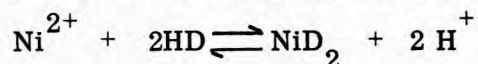
Repeat this with three more 10 ml samples of formaldehyde, but adding different amounts of water so that the reaction time varies over a suitable range. Plot a graph of time against volume of water added. Comment on your results.

If time permits, repeat one of the mixtures but warm the solutions to about 10° above the ambient temperature by placing them in a water

bath before mixing. Compare the reaction times.

(e) Chemical equilibria

1. Add 3 ml of 1% dimethyl glyoxime solution to 20 ml of 0.05 M nickel nitrate solution; shake the mixture, allow it to stand, and filter. Place 2 ml aliquots of the filtrate into six test tubes and add (i) a few drops of 2 M ammonia solution (ii) solid calcium carbonate (iii) a few drops of 3 M sodium acetate solution (iv) a few drops of dimethyl glyoxime solution (v) a few crystals of nickel nitrate and (vi), after suspending a little of the original precipitate in the solution, 2 M sulphuric acid drop-wise. Explain your observations by considering dimethyl glyoxime as a weak acid, HD, which gives a slightly-soluble nickel complex, NiD_2



2. Mix 1 ml of 0.1 M ferric chloride solution with 1 ml of 0.1 M ammonium thiocyanate. Dilute to 20 ml and divide the solution into seven parts. Retain one for comparison and treat the others as follows (i) add some more ferric solution (ii) add some more thiocyanate solution (iii) add some sodium fluoride solution (iv) warm and allow to cool (v) cool in ice and allow to return to room temperature and (vi) add some solid ammonium chloride. Comment on your observations.

(f) The ethyl acetate equilibrium. Place exactly 5 ml of 3 M hydrochloric acid in your 10 ml measuring cylinder. This acid acts as a catalyst for the reaction and its concentration remains unchanged. Now add as accurately as possible one of the following mixtures, as assigned by your demonstrator:

Mixture Number	Volume, ml, of			
	Water	Acetic Acid	Ester	Ethanol
i	5	0	0	0
ii	0	0	5	0
iii	1	0	4	0
iv	3	0	2	0
v	0	0	4	1
vi	0	1	4	0
vii	0	1	0	4

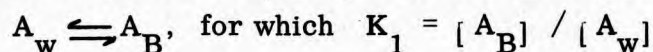
DISTRIBUTION EQUILIBRIA

For the ideal distribution of a solute, A, between two immiscible solvents, P and Q, the Nernst distribution law holds, i.e.,

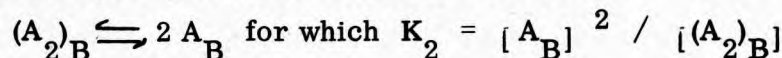
$$K = \frac{[A]_P}{[A]_Q} = \text{distribution or partition coefficient.}$$

This equation applies for dilute solutions where the solute is in the same molecular state in both solvents, but it must be modified to allow for any association or dissociation of the solute molecules. Thus distribution investigations may provide useful information concerning the molecular complexity of a substance in solution.

For the system formed when acetic acid is distributed between water and benzene we have both the simple distribution equilibrium



and the association equilibrium of the acid in benzene



From these equations it can be readily shown that the ratio of the total concentrations of acetic acid in benzene (C_B) and in water (C_w) is given by

$$\frac{C_B}{C_w} = K_1 + \frac{2K_1^2}{K_2} C_w$$

Thus the observed partition ratio should increase linearly with total concentration in the aqueous layer. A plot of C_B/C_w against C_w should have a slope of $\frac{2K_1^2}{K_2}$ and an intercept of K .

Similarly, the effective concentration of free solute molecules will be reduced by reaction of the solute, either with the solvent, as in hydrolysis, or with a second solute, as in the formation of a complex. For

example, it is possible to determine by distribution the concentration of free ammonia molecules in an aqueous solution of the copper tetrammine complex. The solution of the complex is shaken with chloroform and the ammonia extracted into the organic phase is titrated. If the distribution coefficient for ammonia between chloroform and water is known and if it is assumed that the distribution and complex formation equilibria are independent of one another, then the proportion of the total ammonia coordinated to the copper is readily calculable.

NOTE: It is essential for this work, particularly when the solute has very different solubilities in the two solvents, that equilibrium be attained and that the two phases be completely separated before analysis. The separating funnel should be shaken vigorously for at least two minutes, with frequent relief of pressure by inverting and opening the tap, and then set aside to allow separation to occur. Discard all fractions that are likely to be mixtures of the two phases and rinse out all measuring and titration vessels after each step. Return all waste organic solvents to the Residues Bottle.

PROCEDURE

(a) The association of acetic acid in benzene. Prepare about 30 ml of approximately 0.5 M acetic acid by diluting the stock acid in a measuring cylinder. Add about 30 ml of benzene and transfer the mixture to a separating funnel. **CAUTION:** Benzene is very poisonous and can be assimilated into the body by ingestion, inhalation, and absorption through the skin; do not pipette benzene or spill it on your hands.

Shake the mixture thoroughly as directed in the introduction and allow the layers to separate. Run off most of the aqueous layer into a beaker. Then run the intermediate fraction, which is likely to be a mixture, into a second beaker and, finally, run exactly 20 ml of the benzene layer into a clean measuring cylinder.

Pipette 1 ml of the aqueous layer into a titration flask containing about 20 ml of water, add a few drops of phenolphthalein and titrate with 0.02 M sodium hydroxide to obtain the titre T_W .

Transfer the 20 ml benzene sample to a titration flask. Rinse the cylinder several times with water and add these washings to the flask. Titrate as before and record the titre T_B .

Return all mixtures containing any benzene to the funnel. Allow to settle and discard as much as possible of the aqueous layer. Add about

50 ml of distilled water, shake and again discard the water layer. Now add about 30 ml of acetic acid of suitable concentration and repeat the entire procedure.

Carry out at least five determinations using acetic acid concentrations in the range 0.1 - 1 M. Plot C_B/C_W against C_W and estimate the values of the two equilibrium constants from the graph.

(b) Formula and stability of the cuprammonium ion. Place 50 ml each of 1.2 M ammonia solution and chloroform in the separating funnel and equilibrate the mixture as described in the introduction. If necessary, swirl the contents of the funnel gently during the settling period to assist in separation of the layers.

Draw off 10 ml of the aqueous layer with a pipette and run into about 100 ml of water in a titration flask. Titrate with 0.5 M hydrochloric acid, using methyl orange, to obtain the titre T_1 .

Place a 100 ml measuring cylinder containing about 80 ml of water under the funnel and run in exactly 20 ml of the organic phase. Transfer to a titration flask, rinsing out the cylinder several times with water. Titrate as before, but using 0.05 M hydrochloric acid, to obtain the titre T_2 . At the conclusion of the titration, decant off and discard as much as possible of the aqueous layer in the flask. Return the remainder to the measuring cylinder. Add water until the volume of the aqueous layer in the cylinder is 10 ml. Now return the contents of the cylinder to the separating funnel. Shake and repeat the entire procedure. Repeat the process several times. Return the chloroform to the Residues Bottle. Calculate the distribution coefficient for ammonia between water and chloroform.

Place 5 ml of 0.5 M copper sulphate solution, 45 ml of 1.2 M ammonia and 50 ml of chloroform in the separating funnel. Equilibrate and allow to settle. Discharge from the funnel into a measuring cylinder containing about 50 ml of water as much as possible of the chloroform layer. Do not allow any drops of the aqueous layer to pass through the tap. Titrate with 0.05 M acid as before and record T_3 .

The chloroform may be used for further distributions as before. For successive partitions, use 5 ml of copper solution and varying volumes (35, 25, 20 ml) of ammonia solution, making the volume of the aqueous layer up to 50 ml each time with water.

Return the chloroform to the Residues Bottle. Calculate the formula of the complex and its stability constant.

THE SODIUM SULPHATE - WATER SYSTEM

This system contains several interesting examples of the phase relationships observed in two-component systems at physical equilibrium. These relationships are subject to the Phase Rule, $P + F = C + 2$, which describes the interdependence of the number of phases, P (solid, liquid, vapour), the number of degrees of freedom, F (temperature, pressure, concentration) and the number of components, C (sodium sulphate, water); notice that the hydrates of sodium sulphate are not regarded as separate components in the sense of the Phase Rule because their compositions can be expressed in terms of the basic constituents of the system.

Systems such as the present one are often studied in open vessels at atmospheric pressure. Thus one degree of freedom is taken up and we may apply the Phase Rule for condensed systems, $P + F = C + 1$; i.e., the vapour phase is ignored in determining the values of the parameters P , F , and C .

Because there exists a metastable heptahydrate of sodium sulphate as well as the stable decahydrate, the temperature-composition diagram for this system (Question 1) is in effect a composite of two diagrams. You will find it helpful to answer Question 1 before starting the exercise.

The incongruent melting point, or transition point, of sodium decahydrate, which lies at 32.383° under one atmosphere is sharply defined and readily reproducible and therefore is used as a fixed point for the calibration of thermometers. If the exercise were carried out in a closed vessel under the vapour pressure of the system, this quadruple point - four phases in equilibrium - would be found to occur at 32.4° and 30.8 mm.

PROCEDURE

(a) Examination of thermometer. Obtain a 50° thermometer and examine the inscriptions on it. Place it in a mixture of ice and water and record the ice point indicated by the thermometer.

(b) The transition $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Take about 5 g of the

decahydrate in a test tube containing a 50° thermometer. Place the tube in a beaker of hot water until the temperature reaches about 40° . Stir well but carefully with the thermometer. Stand the tube in an empty flask and allow the temperature to fall below 31° . Seed the solution with a small crystal of decahydrate, stir, and record the maximum temperature attained during crystallisation. WARNING: if at any stage during this exercise the thermometer becomes firmly embedded in a mass of crystals, do not attempt to withdraw it; warm the tube until the mass liquefies.

(c) The transition $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Reheat the tube in hot water and allow the solution to cool to room temperature. Place the tube in a bath at 15° and when the temperature falls below 17° stir carefully. Record the maximum temperature attained during crystallisation. If metastable equilibrium is achieved the temperature should remain constant at 24.2° . Otherwise it will rise immediately to 32.4° and the decahydrate will crystallise. The addition of a seed of the decahydrate will cause the heptahydrate to transform very rapidly to the stable phase.

Now add 1 ml of water to the crystals in the tube, warm, and then cool to about 17° as before. Add 10 ml of cooled alcohol to the solution. The heptahydrate should precipitate. Pour off the supernatant liquid and warm the tube slowly. Observe the temperature arrest at 24.2° .

(d) Lowering of the transition temperature. Weigh out about 5 g of decahydrate and place it in a clean test tube. Add 0.5 g of dextrose. Heat to 40° , stir well and allow to cool to about 28° . Seed, stir, and record the maximum temperature attained during crystallisation.

Weigh out a second 5 g sample of decahydrate and repeat the procedure but adding 0.5 g of sodium chloride in place of the dextrose.

(e) The eutectic $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Ice}$. Weigh out about 10 g of ice. Place in a large test tube and add about 1.1 g of decahydrate. Stir well and record the minimum temperature attained.

Name Date Mark

THE SODIUM SULPHATE - WATER SYSTEMRecorded temperatures

- | | |
|--|----------|
| (a) Ice point | °C |
| (b) Transition temperature of decahydrate | |
| (c) Transition temperature of heptahydrate | |
| (d) Transition temperature with added dextrose | |
| Transition temperature with added salt | |
| (e) Eutectic temperature | |

Weighing details:**QUESTIONS**

1. Temperature - Composition Diagram:

(i) Identify the points M, E, E', Q, Q', C, X, and Y. Considering the system as composed of condensed phases only, at atmospheric pressure, list the phases present at each point and the number of degrees of freedom, e.g., Q : Triple (transition) point; decahydrate, anhydrous, solution; $F = 0$,

M

E

E'

Q'

C

X

Y

(ii) Consider carefully the application of the Phase Rule to the mixture represented by K.

2. Under normal conditions the decahydrate effloresces when open to the atmosphere. Explain.

The dissociation pressure of the decahydrate at 25° is 19.0 mm. Calculate the minimum relative humidity of the atmosphere necessary to prevent efflorescence.

3. Discuss the reasons why your thermometer may not have read 32.4° at the decahydrate transition point.

Name

4. Arrange in order of increasing magnitude the vapour pressures at 25° of the decahydrate, the heptahydrate, and a saturated solution of sodium sulphate.

5. Why did the addition of dextrose lower the decahydrate transition temperature?

Why was the lowering greater when sodium chloride was added?

What would be the nature of the solid that separates from these systems below the eutectic E?

6. What would have been observed on cooling if some decahydrate had been warmed to 40° and sufficient water added to dissolve all the anhydrous salt?

7. Explain how a eutectic mixture of ice and sodium chloride (-22.4° at 23% of salt) can be used to maintain a constant temperature.

What happens to the volume of the solution in equilibrium with the eutectic if the water vapour above the solution is pumped off?

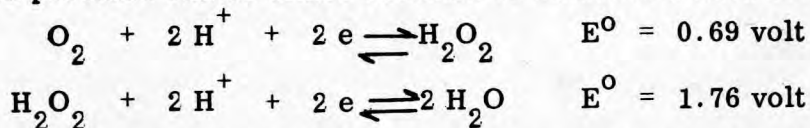
RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE

The decomposition of hydrogen peroxide is a first-order process, i.e., the concentration c will change according to the differential equation $-dc/dt = kc$, where k is the rate constant with units of reciprocal time. Integration of this equation yields $\ln(c_0/c_t) = kt$, where c_0 is the initial concentration and c_t is the concentration at time t . Thus a plot of $\log(c_0/c_t)$ against t should be a straight line, with slope $= k/2.303$.

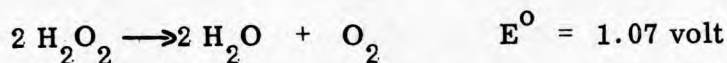
One way of checking a set of kinetic data to see whether they relate to a first-order process, without going to the trouble of plotting them out, is to calculate the fractional change in concentration, c_1/c_2 , for several equal time intervals, $t_2 - t_1$. It is clear from the equation that these should be equal. One such time interval commonly used is the half-time, i.e., the time required for the concentration to be reduced to a half of its initial value. Here $c_1/c_2 = 2$, so that $kt = 2.303 \log 2 = 0.693$. The half-life is often used to characterise radioactive species, which decay according to the first-order law.

The rate of decomposition of hydrogen peroxide is normally small, but it is increased in the presence of heterogeneous catalysts such as finely-divided platinum and manganese dioxide. Decomposition can also be accelerated by homogeneous catalysts such as enzymes (blood catalase and amylase) and certain ions (ferric, manganous, and bromide).

Hydrogen peroxide can be either oxidised or reduced in acid solution

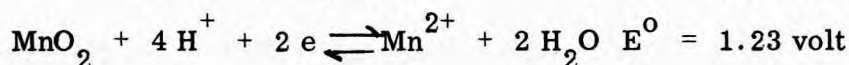


and should therefore be unstable to disproportionation in the same way as Cu(I)

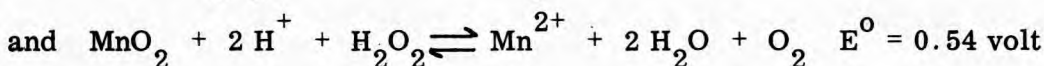
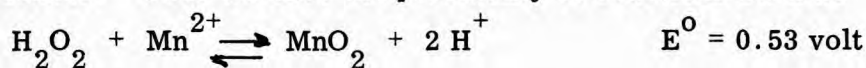


However, there exists a considerable energy barrier to this reaction and hydrogen peroxide is relatively stable. Homogeneous catalysts

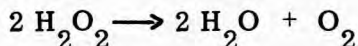
obviate the need for crossing this barrier by providing an alternative mechanism for decomposition and function because the reduction potentials of the appropriate couples



lie intermediate between the potentials for the oxidation and reduction of hydrogen peroxide. Thus we have the possibility of reactions such as



with the net reaction



The decomposition can be retarded - negative catalysis - by the addition of dilute mineral acids, ether, and glycerol. These inhibitors act by 'poisoning' the surfaces of dust particles, which act as catalytic centres, and commercial peroxide usually contains one of these retardants.

In this experiment, ferric ions at a concentration of 20 mmol litre⁻¹ are used as the catalyst. The addition of copper ions, themselves having negligible catalytic activity, at a concentration of only 1 mmol litre⁻¹, produces a marked increase in the reaction rate. The copper ions are said to promote the ferric-ion catalyst.

PROCEDURE

Dilute 25 ml of 'ten-volume peroxide' solution to 200 ml in an Erlenmeyer flask. Place the flask in a large dish of water, the temperature of which should be maintained as close as possible to some agreed value, say 20 or 25°. When the solution has attained the temperature of the bath, add 10 ml of the ferric catalyst solution, and immediately withdraw two 10 ml samples for titration. Begin timing the reaction from just before the withdrawal of the second sample.

Transfer these samples to titration flasks containing 10 ml of 2N

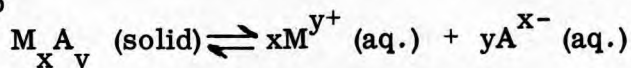
sulphuric which, besides providing an acid medium for the titration, should also effectively quench the decomposition reaction. Titrate as quickly as possible with 0.02 M permanganate to obtain T_0 , the titre at zero time.

After about ten minutes, withdraw another 10 ml sample, record the time and titrate as before. Continue titrating 10 ml samples at intervals of about ten minutes for the remainder of the session, noting the time in each case. You should try to follow the reaction for at least one hour.

Plot $\log (T_0/T_t)$ against the elapsed time and estimate the value of k from the slope.

THE SOLUBILITY PRODUCT OF SILVER ACETATE

In a saturated solution of a sparingly soluble salt the following equilibrium is set up

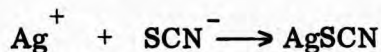


The solubility product, K_{so} , is given by

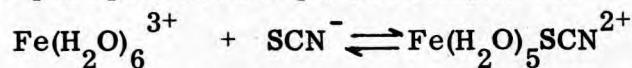
$$K_{so} = [M^{y+}]^x [A^{x-}]^y$$

where K_{so} is constant for a definite temperature. Consideration of the equilibrium shows that any increase in the concentration of either of the ions by the addition of an electrolyte containing a common ion causes a decrease in the solubility of the salt $M_x A_y$; conversely a decrease in the concentration of either of the ions brought about by some means causes an increase in the solubility of the salt $M_x A_y$.

Silver acetate is a convenient salt for the purposes of this exercise; the solubility is such that the concentrations of ions in equilibrium with the solid are sufficient to enable the solubility product to be determined by titrimetric analysis of the silver ions present. In the Volhard method, silver thiocyanate is precipitated from saturated solution of silver acetate by titrating with a solution of thiocyanate ions; a ferric salt (e.g., ferric alum) is used as the indicator. Up to the equivalence-point the reaction is:



After the equivalence-point has been reached there is no appreciable concentration of silver in the solution; further addition of the precipitant increases the thiocyanate concentration. The ferric indicator reacts with the excess precipitant forming a red complex ion



The first appearance of a red colour in the solution corresponds to the end-point. The titration should be carried out in acid solution to prevent the formation of insoluble ferric compounds.

PROCEDURE

Add 0.5 g of silver acetate to each of three conical flasks; number the flasks 1, 2 and 3 respectively. Use a burette to add:

40 ml of deionised water to flask 1

40 ml of 0.05 M sodium acetate solution to flask 2

40 ml of 0.05 M silver nitrate solution to flask 3

Shake the flasks vigorously several times during the next two hours, then leave to stand in a dark place till the next laboratory session.

Record the temperatures of the solutions and filter about 25 ml of each of these solutions into dry flasks. Analyse each of the solutions in turn as follows: pipette 10 ml of the filtered solution into 15 ml of deionised water and add 5 ml of 2 M nitric acid; add 1 ml of the ferric indicator solution and titrate the solution with 0.05 M potassium thiocyanate solution till the first appearance of a red colour. Carry out a duplicate titration in each case. Record the results for each solution in the report sheet.

From your experimental data, calculate the solubility product of silver acetate and its solubility in mole litre⁻¹ in each of the solutions.

Name Date Mark

THE SOLUBILITY PRODUCT OF SILVER ACETATE

Temperature of saturated solutions	 °C		
	Flask 1	Flask 2	Flask 3
Thiocyanate titres, ml			
			
Concentration of silver in solution, mole litre ⁻¹			
			
Concentration of acetate in solution, mole litre ⁻¹			
			
Solubility product of silver acetate, mole ² litre ⁻²			
			
Solubility of silver acetate in solution, mole litre ⁻¹			
			

QUESTIONS

1. The solubility product of silver oxide, which is precipitated when hydroxide ions are added to silver solutions, is of the order of 2×10^{-8} . Do you think it would have been wiser to have used ammonium acetate instead of the sodium salt as a source of acetate ions?

2. What are the units for solubility product?

3. The solubility product of silver acetate can be determined by analysis of the saturated solution as described. The solubility product for lead chloride is quoted as 2×10^{-5} at 25° ; do you think that the solubility product of lead chloride could be obtained with reasonable accuracy by analysis of the saturated solution?

4. What would have been the effect on your experimental solubility product if you had acidified 25 ml of the saturated silver acetate solution with one drop of concentrated nitric acid:

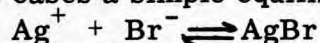
(a) before filtration

(b) after filtration

and then removed a 10 ml aliquot for analysis?

SOLUBILITY PRODUCTS AND IONIC EQUILIBRIA

(a) Precipitation and solubility effects. Although the solubility product expression describes the behaviour of sparingly soluble salts accurately in dilute solutions there are occasions when the experimental solubility is much greater than the value calculated from the solubility product. In these cases a simple equilibrium such as

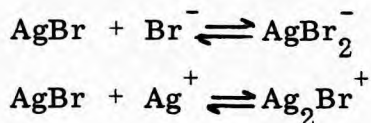


is not adequate to explain the process of solution. The increased solubility is generally explicable in terms of complex formation or the formation of colloidal suspensions.

Consider firstly the solubility of silver bromide in the region where there are roughly equimolar amounts of silver and bromide ions; this is the normal solubility region and the solubility observed is that which can be calculated from the solubility product. The process is completely described by the equilibrium written above. Outside this region, when either silver or bromide ions are present in a moderate excess, the solubility product is exceeded, but the silver bromide forms extremely small particles, which adsorb free ions onto their surface. These colloidal particles are all either negatively charged or positively charged depending upon which ions were in excess; these charges stabilise the suspension and no precipitate is observed. The apparent solubility of the salt is increased.

Addition of either silver or bromide ions beyond this second region also involve the addition of an ion of charge opposite to the charge on the colloid. At suitable concentrations these oppositely charged ions can neutralise the charges on the colloids with resultant destabilisation and concomitant precipitation of the silver bromide.

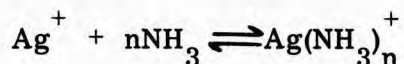
At concentrations of either silver or bromide ions which are higher than in any of these regions, the salt may again appear completely soluble. In such cases this increased solubility may be explained by the formation of complex ions, e.g.,



The object of this section of the assignment is to examine qualitatively these different solubility regions. The student should consult E. Matijevic *et al.*, *J. Chem. Educ.*, **38**, 397, 1961, and R. Ramette, *J. Chem. Educ.*, **37**, 348, 1961, for more complete discussions.

(b) The sensitivity of analytical reactions. Common analytical tests such as the precipitation of silver and the formation of the blue copper ammine complex have a lower limit to their sensitivity. A negative test may indicate that the reactants were not present in quantities sufficient to produce a detectable change. The sensitivity of such tests is related to the solubility product or some equivalent equilibrium constant pertaining to the observable phenomenon. This exercise compares the sensitivity of two tests for copper.

(c) The formula of the silver ammine complex ion. Treatment of a solution of silver ions with an excess of ammonia establishes the equilibrium



for which the equilibrium constant K is

$$K = \frac{[\text{Ag}(\text{NH}_3)_n^+]}{[\text{Ag}^+][\text{NH}_3]^n} \quad (1)$$

Addition of potassium bromide to this equilibrium mixture until silver bromide just begins to precipitate brings into operation the further equilibrium



This equilibrium is described by the solubility product

$$K_{\text{so}} = [\text{Ag}^+][\text{Br}^-] \quad (2)$$

Equations (1) and (2) are simultaneous and substitution of the expression for $[\text{Ag}^+]$ from (2) enables K to be written

$$K = \frac{[\text{Ag}(\text{NH}_3)_n^+][\text{Br}^-]}{K_{\text{so}}[\text{NH}_3]^n} \quad (3)$$

Rearranging this equation and taking logarithms gives the form

$$\log [\text{Br}^-] = \log \frac{K K_{\text{so}}}{[\text{Ag}(\text{NH}_3)_n]^+} + n \log [\text{NH}_3] \quad (4)$$

Since K is large, almost all the silver in solution will be present as the diammine. Further, if the total concentration of ammonia is made sufficiently high, the proportion present in the complex may be neglected. If the concentration of silver be kept constant over a series of mixtures, then under the conditions above, equation (4) reduces to

$$\log v_2 = n \log v_1 + \text{constant}.$$

Here, v_1 is the volume of ammonia solution added to a particular mixture and v_2 is the volume of bromide solution necessary to bring about incipient precipitation of silver bromide; clearly, v_1 and v_2 are proportional to the respective concentrations. Thus, a plot of $\log v_2$ against $\log v_1$ should be a straight line, with slope n .

PROCEDURE

(a) Precipitation and solubility effects. Clean seven 6 x $\frac{1}{2}$ inch test tubes and number them 1 - 7. Place in them 5 ml of silver nitrate solution at the concentrations listed in the result sheet. Now add 5 ml of potassium bromide solution as directed, taking care to mix rapidly as you add it. Allow the solutions to stand for about ten minutes and record your observations.

Filter about 5 ml of each of the solutions showing any turbidity into clean test tubes. Record the turbidity of the filtrate.

To all solutions now add three drops of 2 M magnesium sulphate and record your observations.

(b) The sensitivity of analytical reactions. Dilute 10 ml of the stock 1000 gamma ml^{-1} copper solution (1 gamma = 10^{-6}g) to 100 ml in a graduated cylinder; set aside 20 ml of this 100 gamma ml^{-1} solution. Dilute 10 ml of the remainder to 100 ml and again set aside 20 ml; repeat the dilution procedure until you have 20 ml of solution for each of the concentrations 1000, 100, 10, and 1 gamma ml^{-1} of copper.

Add 1 ml of 2 M ammonia solution to 10 ml of each of these copper solutions and to 10 ml of deionised water. Determine the minimum concentration of copper detectable by viewing the samples against a white background. If time permits, you might attempt to fix the limit more closely by preparing solutions with concentrations intermediate between the limits already found.

Repeat the procedure using 0.1 ml of 0.1 M potassium ferrocyanide as the test reagent in place of ammonia.

(c) Formula of the silver ammine complex ion. Dilute 40 ml of the stock 0.05 M silver nitrate solution to 200 ml with deionised water; this does not need to be done with great accuracy. Prepare two burettes for dispensing 2 M ammonia and 0.02 M potassium bromide respectively.

Burette 25 ml of the 0.01 M silver solution into a conical flask and add a measured volume, v_1 , of about 40 ml of the ammonia solution. View the solution against a dark background and titrate with the bromide solution until the first permanent turbidity appears. Record the volume, v_2 , of bromide solution added and the total volume, V , of the mixture.

Repeat the procedure using the same quantity of silver solution but using each of the volumes 30, 20, 17, 12.5, and 10 ml of ammonia solution. In each case, just before the end-point is reached, add sufficient deionised water to bring the total volume of the solution to V ml.

Plot $\log v_2$ against $\log v_1$ and evaluate n for the complex from the gradient of the line of best fit.

POTENTIOMETRIC TITRATIONS

The Nernst equation

$$E = E^{\circ} - \frac{RT}{nF} \log \frac{[\text{reduced form}]}{[\text{oxidised form}]}$$

shows that the potential of an electrode or half-cell varies as the relative concentrations of the oxidised and reduced forms in the solution vary (see Exercise 73). If such an electrode is coupled with a reference electrode whose potential remains constant throughout, then the titration of one of the species in the half-cell will cause the emf of the couple to vary with the extent of the titration. Measurement of this change in emf leads to a convenient and accurate method for determining the end-points of titrations.

A glass and a calomel electrode form the couple commonly used in acid-base titrations. The glass electrode is essentially a glass tube terminating in a thin-walled bulb and containing a silver-silver chloride electrode in dilute hydrochloric acid. The potential difference between the test solution and the glass electrode is a linear function of the pH of the solution.

$$E = \text{constant} - \frac{RT}{nF} \text{ pH}$$

No standard electrode potential can be cited for the glass electrode as it varies with the construction. The potential of the glass-calomel pair must therefore be standardised by means of a buffer of known pH. The variation in potential during the course of titration is measured against the reference calomel electrode which consists of a tube containing a paste of mercury and mercuric chloride (calomel) in a potassium chloride solution; electrical contact with the titration solution is made through a fine fibre or a sintered glass disc.

The electrical resistance across the bulk of the glass electrode is high (c. 10^8 ohms) and the emf of the couple is amplified before being measured. The pH meter amplifies this signal which is read on a scale

directly calibrated in pH units.

As an acid-base titration approaches the end-point the concentration of hydrogen or hydroxyl ions becomes very small, and continued small additions of titrant cause increasingly large changes in the pH of the solution. Consequently the pH rises most steeply at the end-point, and a plot of pH versus ml of titrant added enables the end-point to be determined.

In redox systems many electrodes consist of an inert metallic conductor such as platinum in contact with the oxidised and reduced forms of a material. Thus a platinum electrode in a solution of either a reduced or oxidised form of a material will form a half-cell as soon as the first drop of titrant is added. The glass electrode is suitable as a reference electrode in redox titrations. pH meters generally have a scale marked in millivolts and are used to follow the change in potential of the couple as the titration proceeds.

In Section (b) of this exercise you will be titrating a sample of ferrous ions with a standard dichromate solution using the platinum-glass electrode system. Up to the end-point the meter measures the emf of the (Pt), $\text{Fe}^{2+}/\text{Fe}^{3+}$ - glass electrode system; beyond the end-point all the ferrous ions are consumed, and chromic ions have been produced in their place; the meter then measures the emf of the (Pt), $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ - glass electrode system. The end-point is characterised by a jump in potential corresponding to this change from one system to the other. Plotting emf against ml of titrant added enables the end-point to be found.

PROCEDURE

(a) Acid-base titration curves. In this section you will be preparing titration curves for the systems strong acid-strong base, strong acid-weak base, weak acid-strong base, and weak acid-weak base, by plotting the pH measured after successive additions of titrant versus the volume of titrant added. At the same time record the colour changes in an indicator suited to each particular system.

The strong acid and base may be taken as completely dissociated into ions, but the dissociation constants of the weak acid and base are to be calculated from the experimental observations. This may be done in two ways

- (i) Record the pH of the 0.1 M solution of each and combine these with the concentrations at the equivalence-points determined by titration; and
- (ii) Use the relationship $\text{pH} = \text{pK}$ when half the equivalent amount of

titrant has been added to read off pK from the graph of pH versus ml of titrant.

For each titration, choose a suitable indicator from those provided. The end-point for titrations such as these carried out without using a pH meter is a matter of subjective observation and may differ slightly from the equivalence-point; in general, both of these may be appreciably different from the neutral-point.

The instruments will have been standardised against a buffer solution before the session commences and should hold this standardisation throughout the session. There should therefore be no need to adjust any control, except to switch from CHECK to pH when the meter is being used. The electrode assembly is FRAGILE and must be treated with utmost care. When a series of measurements is complete, return the meter to the CHECK position, lift the electrodes from the solution and rinse them thoroughly with a jet of water from a washbottle; it is not necessary for the present purpose to dry the electrodes. Store the electrodes in deionised water or buffer when not in use; they must not be allowed to dry out.

In the following titrations assume that the original concentration of all the reagents is 0.5 M and, using the determined values for the dissociation constants of the weak acid and base, calculate from the theoretical relations the pH of each titration mixture initially, at the equivalence-point, and after 5 ml of excess titrant has been added.

(i) Strong acid-strong base. Place 20 ml of 0.5 M hydrochloric acid in a 250 ml beaker and add 80 ml of water, followed by a few drops of a suitable indicator. Lower the electrodes into the solution and record the pH. Add 2 ml of 0.5 M sodium hydroxide from a burette, stir well with a glass rod (KEEP CLEAR OF ELECTRODES) and again read the pH. The successive volumes of titrant added need not be equal, but may be varied in accordance with the rate of change of pH. Where the pH is changing rapidly, the increments of titrant should be small, although, in this particular titration the break in the curve is so sharp that you will probably overshoot it. Carry the titration at least 5 ml past the end-point.

Record all results in the tabulations provided, noting as you proceed any significant changes in the indicator colour.

(ii) Weak acid-strong base. Repeat the procedure using 0.5 M acetic acid instead of hydrochloric acid.

(iii) Strong acid-weak base. Pipette 20 ml of the ammonia solution

into a 250 ml beaker and dilute with 80 ml of water. Add a few drops of a suitable indicator and titrate with the 0.5 M hydrochloric acid as before.

(iv) Weak acid-weak base. Repeat the procedure in (iii) but titrate the ammonia with the 0.5 M acetic acid solution instead of the hydrochloric acid.

(b) Redox titration. Place 20 ml of 0.1 M solution of ferrous sulphate in a 250 ml beaker and add 80 ml of water and 5 ml of 2 M sulphuric acid. Replace the calomel electrode with the platinum electrode provided. Switch the instrument to CHECK and lower the electrode system carefully into the ferrous solution. Ask your demonstrator to adjust the instrument to a suitable reading on the millivolt scale. Switch the instrument to the 0-14 pH setting and titrate the ferrous solution with the 0.02 M dichromate solution, adding 2 ml quantities of the titrant and then recording the millivolt reading after stirring the mixture. The successive volumes of titrant added need not be equal, but should be varied to suit the rate of change of meter reading (see Section a (i)). Record your results and plot meter reading v the volume of titrant added. Determine the end-point for the titration. Carry out a duplicate titration and note the reproducibility of the method.

[illegible]

Name

Calculation of concentrations and dissociation constants

Concentration of HCl (provided)	 M
Equivalence-point for NaOH <u>v</u> HCl	ml
Concentration of NaOH	 M
Equivalence-point for CH ₃ COOH <u>v</u> NaOH	ml
Concentration of CH ₃ COOH	 M
Equivalence-point for NH ₃ <u>v</u> HCl	ml
Concentration of NH ₃	 M
Equivalence-point for NH ₃ <u>v</u> CH ₃ COOH	ml
Concentration of NH ₃	 M
pH of diluted (0.1 M approx.) CH ₃ COOH	
pK _a by method (i) above	
pK _a by method (ii) above	
pH of diluted (0.1 M approx.) NH ₃	
pK _b by method (i) above	
pK _b by method (ii) above	

Calculation of titration curvesSystem HCl/NaOH

- (i) Initial pH
- (ii) pH at equivalence-point
- (iii) pH after 25 ml of NaOH added

System CH₃COOH/NaOH

- (i) Initial pH

63.8

(ii) pH at equivalence-point

(iii) pH after 25 ml of NaOH added

System NH_3/HCl

(i) Initial pH

(ii) pH at equivalence-point

(iii) pH after 25 ml of HCl added

System $\text{NH}_3/\text{CH}_3\text{COOH}$

(i) Initial pH

(ii) pH at equivalence-point

(iii) pH after 25 ml of CH_3COOH added

(b) Redox titration

[illegible]

Name

Volume $K_2Cr_2O_7$ added, ml	Meter reading, millivolt	Volume $K_2Cr_2O_7$ added, ml	Meter reading, millivolt
.....			
.....			
.....			
.....			
.....			
.....			
.....			
.....			

Concentration of dichromate solution M

Titresml

Accepted titreml

Concentration of ferrous solution M

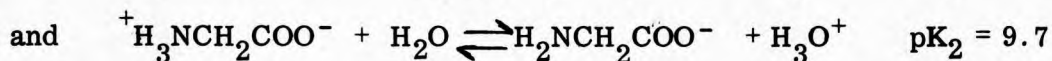
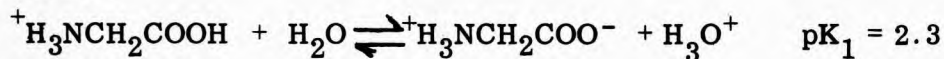
QUESTIONS

1. (i) What percentage error would have resulted in the standardisation of acetic acid against sodium hydroxide if the neutral-point had been taken as the end-point, instead of the equivalence-point?

(ii) What would have been the determined concentration of acetic acid if the methyl red end-point had been taken?

2. The dissociation constants for the tribasic acid, orthophosphoric acid, are $K_1 = 7 \times 10^{-3}$, $K_2 = 6 \times 10^{-8}$ and $K_3 = 4 \times 10^{-13}$. What indicators would you select for titration with strong base to the first and second equivalence-points?

3. The acid dissociation of the amino acid glycine may formally be represented as



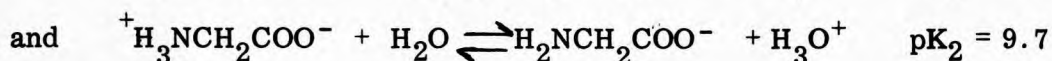
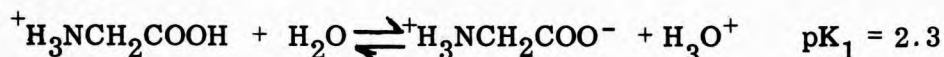
Calculate the pH of the isoelectric point, at which the concentrations of the positive and negative ions are equal (and small) and the substance exists mainly in its zwitterion form, $^+\text{H}_3\text{NCH}_2\text{COO}^-$.

4. Explain the indicator action of phenolphthalein in terms of its molecular structure. If the phenolphthalein is added to sodium hydroxide of sufficient concentration, say 2 M, it immediately turns pink, but the colour slowly fades on standing. Explain.

(ii) What would have been the determined concentration of acetic acid if the methyl red end-point had been taken?

2. The dissociation constants for the tribasic acid, orthophosphoric acid, are $K_1 = 7 \times 10^{-3}$, $K_2 = 6 \times 10^{-8}$ and $K_3 = 4 \times 10^{-13}$. What indicators would you select for titration with strong base to the first and second equivalence-points?

3. The acid dissociation of the amino acid glycine may formally be represented as



Calculate the pH of the isoelectric point, at which the concentrations of the positive and negative ions are equal (and small) and the substance exists mainly in its zwitterion form, $^+\text{H}_3\text{NCH}_2\text{COO}^-$.

4. Explain the indicator action of phenolphthalein in terms of its molecular structure. If the phenolphthalein is added to sodium hydroxide of sufficient concentration, say 2 M, it immediately turns pink, but the colour slowly fades on standing. Explain.

Name

5. An unknown student takes an unknown weight of an unknown weak acid, dissolves it in an unknown amount of water and titrates it with a strong base of unknown concentration. After 10.00 ml of base has been added, the pH concentration of hydrogen ion in the solution is 1.0×10^{-5} M. He continues the titration and estimates from the titration curve that 22.22 ml of base are required to reach the first equivalence-point. Calculate the first dissociation constant of the acid.

6. Why is it unnecessary to standardise the millivolt reading before carrying out the ferrous-dichromate titration?

If the readings obtained during this titration were in fact the actual potentials of the electrode system, show how you could obtain the standard electrode potential for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system from your titration curve and a known value for the potential of the glass electrode.

7. In some redox titrations the glass electrode would not be suitable as a reference. Why?

Why can it be used in this particular case?

ACID-BASE BUFFER SOLUTIONS

As described by Le Chatelier's Principle all systems in equilibrium are in general terms buffered in that a given addition of one of the components of the equilibrium produces a rather smaller change in the concentration of that component. In practice, however, the term buffer solution is applied specifically to solutions that resist marked changes in hydrogen ion concentration despite the addition of strong acid or base. In this restricted sense a solution containing an acid and its conjugate base in concentrations of the same order of magnitude is a buffer solution. The usual equilibrium considerations apply; if, for example, hydrogen ions are added they react with the base to produce the conjugate acid; similarly, added hydroxyl ions react with the acid to produce the conjugate base, and in each case the pH is relatively unaffected.

If the general buffer solution of a weak acid and one of its alkali-metal salts is considered, it can be shown that

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

while for a weak base and one of its salts the relationship is

$$\text{pH} = \text{pK}_w - \text{pK}_b - \log \frac{[\text{salt}]}{[\text{acid}]}$$

where $\text{pK}_w - \text{pK}_b = \text{pK}_a$ for the base.

In these equations both the salt and acid concentrations may be taken as those used in making up the solution; these approximations are valid only in the pH range 4 to 10. Outside this range these concentrations would have to be calculated from the appropriate equilibrium constants.

The buffer capacity of a solution may be regarded as the amount of strong acid or alkali required to change the pH by a given amount. The larger this quantity the better the buffer. The buffer capacity is at a maximum when the concentrations of acid and salt are equal.

In this exercise you will study the behaviour of acid-base buffers with the aid of the colour changes of indicators. Indicators are weak acids or

bases, and within the working range both the acid form, In_a , and the base form, In_b , are present in varying amounts according to the relationship

$$\text{pH} = \text{pK}_{\text{In}} - \log \frac{[\text{In}_a]}{[\text{In}_b]}$$

The working range, i.e., the range over which the indicator appears to change colour, is approximately two pH units, from $\text{pH} = \text{pK}_{\text{In}} + 1$ to $\text{pK}_{\text{In}} - 1$. The value of pK_{In} is determined from the pH of the solution in which the concentrations of In_a and In_b are equal.

Citric acid, $\text{CH}_2\text{COOH} - \text{COH} \cdot \text{COOH} - \text{CH}_2\text{COOH}$ (MW = 210), is a tribasic acid with dissociation constants of $K_1 = 8.4 \times 10^{-4}$, $K_2 = 1.8 \times 10^{-5}$, and $K_3 = 4.0 \times 10^{-6}$. Because these constants are so close together it is possible to prepare a sequence of overlapping buffers involving consecutively the species citric acid (H_3Cit), NaH_2Cit , Na_2HCit and Na_3Cit . This is not possible in the case of phosphoric acid, for which the dissociation constants are widely separated (7×10^{-3} , 6×10^{-8} , and 4×10^{-13}).

PROCEDURE

(a) Determination of the indicator constant. Choose one acid-base indicator from the following

thymol blue	red	1.2 - 2.8 yellow
methyl orange	red	3.1 - 4.4 yellow
bromocresol green	yellow	3.8 - 5.4 blue
methyl red	red	4.2 - 5.4 yellow

and, by mixing appropriate volumes of the sodium citrate solution (containing 21.0 g of citric acid in 1 litre of 0.2 M sodium hydroxide) with either 0.1 M hydrochloric acid or sodium hydroxide according to the table below, prepare a series of buffer solutions, A, B, ... which straddle the working range of the indicator. Add 1 ml of the indicator to each solution.

Citric Acid - Citrate Buffers

Volume 0.1 M HCl	Volume citrate	pH	Volume 0.1 M NaOH	Volume citrate	pH
9.0 ml	1.0 ml	1.17	0.0 ml	10.0 ml	4.96
8.0	2.0	1.42	0.5	9.5	5.02
7.0	3.0	1.93	1.0	9.0	5.11
6.67	3.33	2.27	2.0	8.0	5.31
6.0	4.0	2.97	3.0	7.0	5.57
5.5	4.5	3.36	4.0	6.0	5.98
5.25	4.75	3.53	4.5	5.0	6.34
5.0	5.0	3.69	4.75	5.25	6.69
4.5	5.5	3.95			
4.0	6.0	4.16			
3.0	7.0	4.45			
2.0	8.0	4.65			
1.0	9.0	4.83			
0.5	9.5	4.89			

Also prepare solutions X and Y by adding 0.5 ml of indicator to 10 ml of 0.1 M acid and alkali respectively.

Place tube X in front of Y and observe the resultant colour against a light background; this is the colour shown by the indicator when equal amounts of the acid and base forms are present. Compare this colour with that shown by A, B, ... and choose the best match. Hence determine pK_{In} .

(b) Determination of degree of hydrolysis and dissociation constant.

Prepare a series of citrate buffers in the range 4.96-5.57 and add 0.5 ml of methyl red to each. Add the same amount of indicator to 10 ml of ammonium chloride solution and cork the tube. The ammonium chloride solution contains 5.352 g of salt dissolved in distilled water free from carbon dioxide.

Match the colour of the salt solution with the indicator solutions, interpolating if necessary. Calculate (i) the degree of hydrolysis of the ammonium ion and (ii) K_a and K_b for the acid NH_4^+ and its conjugate base NH_3 .

(c) Construction of a buffer solution. From the concentrations of the

solutions of disodium hydrogen phosphate and sodium dihydrogen phosphate provided, calculate what volumes of these solutions must be mixed to give 20 ml of buffer solution at pH 6.8. The second dissociation constant of phosphoric acid is 6.2×10^{-8} ; $pK_a = 7.21$. Prepare the buffer and add a little bromothymol blue indicator (yellow 6.0 - 7.6 blue). Check the pH of the mixture on the meter. Divide the solution into equal parts and determine its buffering capacity towards acid and base as before.

(d) Determination of buffer capacity. Use two burettes to make up the following five buffer solutions

	A'	B'	C'	D'	E'
0.5M acetic acid, ml	18	15	10	5	2
0.5 M sodium acetate, ml	2	5	10	15	18

In addition take 20 ml of 0.25 M ammonium acetate and call it solution F'. Measure the pH of each of these solutions on the pH meter and use a burette to find

(i) the volume of 0.5 M hydrochloric acid solution necessary to change the pH of 10 ml of each solution by 1 pH unit;

(ii) the volume of 0.5 M sodium hydroxide necessary to change the pH of 10 ml of each solution by 1 pH unit.

Record and comment upon your results.

Name ... JACK !**QUESTIONS**

1. Is a 0.1 M solution of ammonium acetate an efficient buffer?
Would you expect it to have a buffer capacity as great as a mixture of 0.1 M sodium acetate and 0.1 M acetic acid?

2. Given that $pK_{In} = 7.0$ for bromothymol blue, calculate for Part 3 of the exercise

(i) the proportion of the indicator in the acid form at $pH = 6.8$

(ii) the volumes of 0.1 M acid and alkali required to adjust the pH of the buffer to the formal limits of buffer capacity, i.e., $pK_a \pm 1$.
Compare these volumes with those observed.

3. A solution is 0.04 M in H_2CO_3 , for which $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$. Sufficient sodium hydroxide is added stepwise to the solution to raise the pH successively to 5, 7, 9, and 11. Calculate for

64.8

each pH the fraction of total carbonate material present as H_2CO_3 , HCO_3^- and CO_3^{2-} and sketch a plot of each of these fractions against pH.

pH	Fraction as		
	H_2CO_3	HCO_3^-	CO_3^{2-}
5			
7			
9			
11			

4. Can you explain why the successive dissociation constants should be very much closer for citric acid than they are for phosphoric acid?

HEAT OF REACTION

The heat of reaction at constant pressure, ΔH joule mole⁻¹, can be directly determined by measuring the change of temperature of the system when the reaction is carried out under carefully controlled conditions in a calorimeter. Since the various components of the calorimeter will absorb some heat as well as the reaction system, it is necessary to determine the heat capacity of the calorimeter by carrying out in it a process in which a known amount of heat is liberated. This standard amount of heat may be supplied in several ways, but chemically the usual source is the neutralisation reaction, $H^+(aq) + OH^-(aq) \rightarrow H_2O$, for which $\Delta H = -(61160 - 203t)$ joule mole⁻¹, where t is the Celsius temperature.

When sulphuric acid is added to water, heat is produced by the hydration of the ions formed from the acid. A number of distinct hydrates can be recognised. If a calibration curve is prepared for a particular calorimeter by adding fixed amounts of sulphuric acid of different concentrations to a given amount of water, this curve can then be used for the routine determination of the concentration of the acid. This procedure is used industrially for process control, particularly in the case of the oleums. In preparing the curve, it is clearly unnecessary to know the heat capacity of the calorimeter and since the curve that you will prepare will be plotted from the combined results of your group, we must assume that the heat capacities of the various calorimeters are equal.

PROCEDURE

(a) Heat of precipitation of silver chloride. The calorimeter consists of a dewar flask fitted with a stopper, stirrer, and a -5 to 50°C thermometer, graduated in 0.1°. Place 250 ml of standardised 0.2 M hydrochloric acid in the calorimeter and stir gently. Record the temperature at two-minute intervals, until it becomes constant to within 0.05°. Add quickly from a measuring cylinder, 50 ml of 1.1 M sodium hydroxide, which should be as nearly as possible at the same temperature as the acid. Stir and record the temperature every 30 sec. Plot the temperature

against time and determine the temperature rise. Assuming that the solution has a density of 1 g ml^{-1} and a heat capacity of $4.2 \text{ joule gm}^{-1}$, calculate the heat capacity of the calorimeter.

Repeat the above procedure with 250 ml of standardised 0.1 M silver nitrate and 50 ml of 0.6 M sodium chloride. Place the silver chloride suspension in the Silver Residues Bottle and rinse the calorimeter with a little ammonia solution to remove the last traces of silver chloride. (See H.L.Clever, *J. Chem. Educ.*, **38**, 470, 1961).

(b) Heat of dilution of sulphuric acid. Place 100 ml of water in the calorimeter. When the temperature has become steady add the 10 ml of sulphuric acid (between 50 and 97 per cent) assigned to you from a pipette with the tip below the surface of the water.

CAUTION: Do not operate the pipette with your mouth.

Replace the stopper and thermometer in the dewar and record the temperature rise. Calculate the composition by weight of the original sample from the data on the label, given that concentrated sulphuric acid has a density of 1.84 g ml^{-1} and contains 97% by weight of sulphuric acid.

Plot temperature rise against composition from the results of the group.

Obtain a sample of acid of unknown concentration from your demonstrator and determine the temperature rise as before. Read off from the curve the composition of the sample. Transfer the diluted acid to a 500 ml flask and make up to the mark with water; if the temperature of the acid is high, it would be advisable to add some crushed ice before transferring it to the flask. Titrate 25 ml of the acid in the flask with standard 0.5 M sodium hydroxide and compare the molar concentration so obtained with the composition by weight determined by calorimetry; use densities interpolated from the following table:

Density of Sulphuric Acid, 20°C

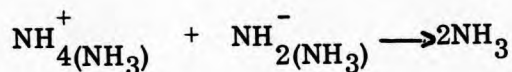
Percentage by weight	Molarity	Density g ml^{-1}	Percentage by weight	Molarity	Density g ml^{-1}
50	7.12	1.395	80	14.10	1.727
55	8.11	1.445	85	15.43	1.779
60	9.17	1.498	90	16.66	1.814
65	10.30	1.553	95	17.78	1.834
70	11.50	1.610	97	18.17	1.836
75	12.77	1.669	100	-	1.831

(See E.Wolthuis *et al.*, *J. Chem. Educ.*, **38**, 472, 1961.)

Name

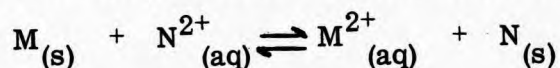
present; 20% oleum contains 20% by weight of SO_3 and 80% of H_2SO_4 . Calculate the weight of pure sulphuric acid obtained by diluting 100 lbs of 65% oleum. 45% oleum (melting point 35°) is not made in large quantities and is usually shipped as a mixture with nitric acid. Explain.

8. The heat of vaporisation of liquid ammonia at its boiling point, -33° , is $1.37 \text{ Kjoule g}^{-1}$. Find the heat of reaction for the neutralisation process



from the fact that the reaction of 0.948 g of ammonium bromide (MW = 98) with an equimolar amount of potassium amide dissolved in liquid ammonia liberates 0.845 g of ammonia gas.

9. The heat of the displacement reaction for two metals, M and N,



can be expressed as the sum of the differences between the ionisation energies, heats of atomisation, and heats of hydration of the gaseous ions of the metals involved. A set of data below gives the energies of the processes in Kjoule mole^{-1} for five metals. For the systems Zn/Cu, Mg/Pb, and Fe/Cu, decide which term makes the most significant contribution to the heat of reaction. From your knowledge of the properties of the metals and their ions, rationalise why this should be so in each case.

81.10

	Mg	Zn	Fe	Pb	Cu
Heat of atomisation	150	130	420	190	340
Ionisation energy	2185	2640	2320	2320	2715
Heat of hydration	1915	2105	2065	1475	2045

