CHAPTER II

A STATEMENT OF THE PROBLEM

The primary objective of this investigation is the determination of the dependence of solvolysis rates of butyl bromide upon the dielectric constant of methanol-water mixtures at 50° Centigrade.

A secondary objective is the utilization of the kinetic data obtained to explore mechanisms of solvolyses in these systems.

CHAPTER III

EXPERIMENTAL

A. Reagents

1. Standards

Distilled water. All water used in preparing the solutions was previously distilled through a Barnstead still.

Hydrochloric acid of the desired normality (approximately 0.5 N) was prepared by diluting 44 ml. of concentrated HCl (Analytical Grade) with water to a volume of one liter. The other three acid solutions were prepared by diluting quantitatively appropriate aliquots. These solutions were standardized with sodium carbonate and found to be 0.5145 N, 0.2561 N, 0.1029 N and 0.0617 N, respectively. They were stored in glass-stoppered bottles or automatic-filling burets.

Karl Fischer reagent (Eimer and Amend Co.,) was prepared by adding chilled solution number 1, (containing sulfur dioxide in pyridine), to solution number 2, (containing iodine in methanol solution), in a screw-capped brown glass bottle. The reagent

was stored in the refrigerator.

Commercial methanol-water standard (Eimer and Amend Co.), 1 ml. equivalent to 1 mg. water, was used to standardize the Fischer reagent each time before it was used.

Potassium acid phthalate crystals, (Bureau of Standards, Analytical Grade), were dried in an oven for four hours at 110° C. and then cooled in a desiccator before using. (The dried salt, 2.0421 g. and 1.0211 g., was used to standardize the approximately 0.25 N and 0.1 N sodium hydroxide solutions, respectively.)

Potassium thiocyanate crystals (Matheson, Coleman and Bell Company, Inc., assay 99.93%) were dried in a desiccator at room temperature and then in an oven at 120-150° C. for two hours, fused for a few minutes at 190-200° C., and cooled in a desiccator before using. The crystals were protected from light and acid fumes. The pure, dry salt, (4.6323 g.), was dissolved in water and diluted to a volume of 500 ml. A second solution was prepared from 5.5027 g. of the pure, dry salt diluted to a final volume of 500 ml. Both of these solutions (0.0952 N and 0.1131 N, respectively), were stored

in glass-stoppered bottles.

Silver nitrate solution (approximately 0.1N) was prepared by dissolving 17.0152 g. (Reagent Grade, Matheson, Coleman and Bell, Inc.,) in water and diluting to a volume of one liter. The solution was stored in a 5 liter screw-capped brown glass bottle. The salt used to prepare this solution was not heated in an oven prior to mixing.

Sodium bromide crystals (C.P. Grade, Eimer and Amend Co., assay 99.7%) were dried in an oven at 120° C. for three hours, and cooled in a desiccator before using. A solution(0.1028 N) was prepared by dissolving 5.3085 g. of the pure, dry salt in water and diluting to 500 ml. The solution was stored in a glass-stoppered bottle.

Sodium carbonate (pulverized crystals of micro-analysis quality, Mallinckrodt Chemical Works) was heated in a porcelain crucible in an electric furnace for one hour at 270-300° C., then placed in a clean, dry, tared weighing bottle and cooled in a desiccator before using (approximately 1 g., 0.31-.36 g., 0.22-.25 g., 0.13-.15 g., were used to standardize the 0.5, 0.25, 0.1 and 0.06 N HCl solutions, respectively).

Sodium chloride (Reagent Grade, ACS, crystals, Matheson, Coleman, and Bell, Co.,assay 99.97%) was heated in an oven at 500-600^{0} C. for three hours and cooled in a desiccator before using. A solution (0.1001 N) was prepared by dissolving 2.9232 g. of the pure, dry salt in water and diluting to a volume of 500 ml. The solution was stored in a glass-stoppered tincture-type bottle.

Carbonate-free sodium hydroxide solution was prepared by filtering through a sintered porcelain crucible a 50% aqueous solution of sodium hydroxide pellets, (Analytical Grade, ACS, Matheson, Coleman and Bell, Inc., minimum assay 97.7%), in carbon dioxide-free water. During the filtering process, the solution was protected from atmospheric carbon dioxide and suction was used. The filtered solution (50 ml.) was transferred to a one liter volumetric flask and diluted to volume with carbon dioxide-free water by siphoning. Mixing was accomplished by inversion. This solution was then siphoned into a clean, dry, paraffin-lined 2 $^{1}/2$ liter bottle which was protected by indicating soda lime (Mallinckrodt Chemical Works, 8-14 mesh, USP XIV) for storage. Base solutions of the desired normality were pre-

pared by siphoning an estimated quantity (100-200 ml.) of this stock base solution into a one liter volumetric flask, diluting to volume with carbon dioxide-free water and mixing by inversion. The resulting solutions were transferred by siphoning from the volumetric to a second stock base bottle, also paraffin-lined, which was connected to an automatic-filling buret. Both the bottle and buret were protected by indicating soda lime tubes. (The buret and its connections were of base-resistant glass.)

2. Indicators

Bromcresol green indicator solution was prepared by grinding 0.1 g. of the dry material (National Aniline Co.) in a mortar with 6.2 ml. 0.2297 N sodium hydroxide solution and diluting the mixture with distilled water to an indicated volume of 250 ml. in a graduated cylinder.

The eosin bluish solution (0.1%) was prepared by dissolving about 0.1 g. of the material (Distillation Products Industries) in 30 ml. of 95 % ethanol and this was followed by dilution with distilled water to an indicated volume of 100 ml. in a graduated cylinder.

Two grams of ferric ammonium sulfate hydrate crystals (Merck and Co.), Reagent Grade, ACS, were dissolved in 25 ml. of distilled water that had been acidified by the addition of 1 ml. concentrated white nitric acid.

Methyl orange indicator solution (0.1%) was prepared by dissolving 0.1 g. of the dry material (Distillation Products Industries) in distilled water and diluting to an indicated volume of 100 ml. in a graduated cylinder.

Phenolphthalein indicator solution (1%) was prepared by dissolving 1 g. of the dry material (Mallinckrodt Chemical Works) in 60 ml. of 95% ethanol and diluting with distilled water to an indicated volume of 100 ml. in a graduated cylinder.

Sodium dichlorofluoresceinate solution (0.1%) was prepared by dissolving 0.1 g. of the dry material (Distillation Products Industries) in distilled water and diluting to an indicated volume of 100 ml. in a graduated cylinder.

TABLE II

INDICATOR SOLUTIONS[b]

Indicator	Solution	pH Range[e] (Virage)	Reference
Acid-Base:			
Bromcresol green	.04% sodium salt in water[a]	3.8--5.4[c] Yellow--Blue	Ref. a, p. 348; c, p. 429.
Methyl orange	0.1% in water[d]	3.1--4.4[c] Red--Yellow-orange	Ref. c, p. 429; d, p. 994.
Phenolphthalein	1% in 70% alcohol	8.0--9.8[c] 8.3--10.0[d] Colorless--Red-violet	Ref. c, p. 429; d, p. 996.

[a]S. B. Arenson and G. Rieveschl, Jr., "Introduction to Quantitative Analysis," Crowell, New York, 1944; [b]C. W. Foulk, H. V. Moyer and W. M. Mac Nevin, "Quantitative Chemical Analysis," McGraw-Hill, New York, 1952, p. 176; [c]I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, 1952; [d]N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Ohio, 1952; [e]at room temperature.

3. Solvents

The solvents used were absolute methanol, distilled water, and methanol-water mixtures in various weight percent compositions (25%, 50%, 60%, 75% and 90% methanol).

Commercial synthetic methanol, (Fisher Scientific Co., acetone-free), assay 99.5% MeOH, was dehydrated by the method of Lund and Bjerrum[29] and purified by fractionation through the Todd column. About 800 ml. methanol was placed in the one liter flask of the Todd apparatus and 5-10 g. clean Grignard magnesium turnings was added. A vigorous reaction followed when the methanol contained only about 1% water by volume. At times the reaction became so vigorous that external cooling of the flask using crushed ice wrapped in a towel was required. When this vigorous initial reaction had subsided and the magnesium had almost completely dissolved, the flask was connected to the Todd apparatus, heated and the contents were refluxed for 24 hours to complete the dehydration. In this stage, a "cake" composed of magnesium hydroxide and magnesium methoxide formed. The dry alcohol was carefully distilled from this residue using the Todd fractionation apparatus under the following conditions.

The column, (10 mm. internal diameter and 90 cm. length, packed with Pyrex glass helices of 4 mm. diameter), was not heated. The stillpot was heated to a temperature of 65° C., the voltage being controlled by a Powerstat. At this temperature the (total) reflux rate was about 33 ml./min., the collection rate of the material (b.p. 64.5° C., 760 mm. Hg) was about 0.5 ml./min. The middle cut of the alcohol distilling at a constant head temperature of 65° C., 767 mm. Hg, was taken. This material analyzed 0.005% water or less with standard Fischer reagent. The water content was checked periodically by the Karl Fischer method[30] and did not increase on storage. The pure dry methanol ($n_D^{27°}$ = 1.3310) was stored in a large brown glass bottle provided with Pyrex glass tubing connections, a stopcock, and was protected from atmospheric moisture with indicating Drierite (W. A. Hammond Drierite Co., 8 mesh) and from carbon dioxide with Ascarite (A. H. Thomas Co.). The stopcock was greased with Apiezon M (Fisher Scientific Co.,) which is thought to be insoluble in methanol. The methanol was transferred by siphoning from the distillate receiver (5 l. brown glass bottle) into a stock bottle (5 l. brown glass). During the

siphoning process, the methanol was protected from atmospheric moisture with Drierite and from the water aspirator by a trap (suction flask, also protected with Drierite). Whenever the methanol was needed, it was obtained by siphoning from this stock bottle and it was protected at all times from moisture during the process.

Preliminary analysis of the distilled water (Barnstead still water) for ammonia (with Nessler's reagent), carbon dioxide (with limewater) and chloride ion (with silver nitrate solution) showed that it was "free" from these impurities. The specific conductivity of the water was 1.2×10^{-6} ohm as measured using a Wheatstone Bridge at room temperature. The pH at 25° C. was 6.92 as measured by a Beckmann pH meter (model G). The water was stored in a 5 gallon glass carboy closed with a rubber stopper wrapped in aluminum foil and sealed with muslin and tape.

Mixed solvents were prepared from the pure components gravimetrically or volumetrically at 25° C. The mixed solvents were stored in clean, dry Pyrex infusion bottles closed with screw caps on muslin. X per cent methanol is the solvent obtained by adding 100 volumes of methanol to Y volumes of water at 25° C.

For example, 75% methanol was prepared by adding 500 ml. pure methanol to 130 ml. water. Table III gives the volumes of the pure components required in preparing the mixed solvents.

TABLE III

MIXED SOLVENTS DATA[e]

X[c]	Y[d]	N_{H_2O}	D_{50}^{o}
0		1.000	69.94[a]
100	0	.000	27.44[b]
10.0	713		65.66[b]
20.0	317		61.06[b]
25.0	238	.842	58.91[b*]
30.6	180		
40.2	118		
50.1	79	.636	47.98[b*]
61.3	50		
70.0	34		38.81[b]
75.3	26	.371	36.84[b*]
79.8	20		
89.7	9		

[a]Calculated from J. Wyman Jr., Phys. Rev., 35, 623 (1930); [b] From G. Akerlof, J.Am. Chem. Soc., 54, 4125 (1932); [b*] calculated from Akerlof s data; [c] Weight per cent methanol in solvent; [d] milliliters of water to be added to 100 milliliters methanol at 23.7° C. to give X % methanol-water; [e] using density of water =.99739 g./cc. and density of methanol = .79223 g./cc. at 23.7° C.

4. Miscellaneous reagents

N-butyl bromide was washed successively with dilute hydrochloric acid, aqueous sodium carbonate solution, and distilled water; dried with anhydrous magnesium sulfate overnight (about 8 hours); filtered through Whatman no. 1 semi-quantitative paper and distilled through the Todd apparatus. The material used was the middle cut distilling at constant head temperature (b. p. 101.5° C., 760 mm. Hg).

Mercury was purified by layering with diluted nitric acid (25 volumes of concentrated white nitric acid diluted with water to make 100 volumes of total mixture) and slowly bubbling air through the mixture by attaching the side outlet of a suction flask to an aspirator. After a few hours, the mercury was decanted, washed with water several times, patted dry with filter paper, and filtered through a pinhole in ordinary semi-quantitative paper. The thermoregulators were filled with this mercury using suction.

3-5 Dinitrobenzoyl chloride and 3-nitrophthalic anhydride (Eastman Organic Chemicals) were used to prepare n-butyl 3-5 dinitrobenzoate[31] and n-butyl 3-nitrophthalate,[32] respectively, without preliminary treatment.

B. Apparatus and calibrations

1. Balance and weights

For all precise weighings, a chainomatic analytical balance (Voland and Sons, Inc.) with a magnetic damping device and Permas (Fisher Scientific Co.) Class S weights were used. The 10 g. weight was compared with a standard 10 g. weight which had been calibrated with certification by the Bureau of Standards.

2. Burets

Burets (and pipets) were calibrated[33,34] by a direct weighing method. Macroburets were calibrated at 10 ml. intervals (i.e., 0-10, 0-20, 0-30, 0-40, 0-50) and microburets, at 1 ml. intervals (i.e., 0-1, 0-2, 0-3, 0-4, 0-5). The deviations of the burets were just within the tolerances of the Bureau of Standards[35] and the calibration curves showed no abrupt changes in direction.

Five ml. microburets were used for titrations involving hydrochloric acid, silver nitrate, and sodium hydroxide whenever these solutions were concerned in the kinetic measurement. Fifty ml. burets were used for all other titrations.

The burets were arranged for automatic

filling and their connections were protected by appropriate adsorbents. The buret and its connections containing the sodium hydroxide solution were of base-resistant glass.

3. Density measurement

The density measurements were made by using a density bulb of conventional design (U-shaped). The temperature of the apparatus and solutions was controlled by immersion in a constant-temperature bath. The observed values were corrected to vacuo.

4. Refractive index measurement

All refractive index measurements were made by using an Abbe Refractometer and by employing the usual procedure(i.e., air as the standard of comparison, sector adjusted to the sodium D line of the spectrum, temperature regulation of the prisms by circulating tap water).

5. Distillation apparatus

A Todd fractionation apparatus (Todd Scientific Co.) was used to distill the dried n-butyl bromide and methanol and to separate the fractions in the reaction product analyses. The column used had an internal diameter of 10 mm., a length of 90 cm., and was packed with Pyrex glass helices of 4mm. diameter.

Indicating Drierite was used to prevent moist air from entering the apparatus, take-off and receiver. When the methanol was distilled, the receiver was protected also by seals of Cenco-Sealstix and by Drierite and Ascarite.

Preliminary distillations of ethyl ether in the extraction procedures was accomplished by a Vigreaux column (1 in. diameter, 26 in. length) with ground glass joints.

An ordinary microdistillation apparatus was used in some separations of reaction products.

6. Thermometers

Each constant-temperature bath was provided with two thermometers. One of these was an immersion thermometer, range -1° to 101° C., graduated to one-tenth degree divisions. The other was a Beckmann differential thermometer. The one-tenth degree thermometers were calibrated by comparison with one certified by the Bureau of Standards. Temperature readings were accurate to about ± 0.05°.

One thermometer used in the determination of melting points was an hexane-filled immersion thermometer (Central Scientific Co.), range -200° to 30° C., graduated to one degree divisions.

The low temperature thermometer and the standard taper thermometer of the Todd apparatus were not calibrated.

7. Precision timer

The reaction was timed in seconds and tenths of seconds by a Time-it (Precision Scientific Co.) precision timer. The timer was calibrated for a period of one week with a timing device, certified by the Bureau of Standards, at a local radio station. The precision timer and certified timer were in excellent agreement over this range of time.

8. Reaction flasks

Aliquots of the reaction mixture were contained in 25 ml. glass-stoppered volumetric flasks for the duration of a "run."

In order to determine whether there was a vapor loss during the course of a "run," appropriate portions of the different reaction mixtures were added at 25° C. to the 25 ml. volumetric flasks. The flasks were stoppered, weighed on the analytical balance, sealed with aluminum foil, and placed in the thermostats for the time of the longest run. At this time, the flasks were removed from the thermostats, dried, cooled, dried in a desiccator and then reweighed on

the same balance. It was observed that a small vapor loss (411 mg.) occurred in flask no. 70, the total weight of which was 35.4942 g., when it contained a 75% methanol-25% water solution. Negligible or no losses occurred from all other flasks in this same period. These tests were performed in duplicate.

9. Constant-temperature baths

Two constant-temperature water baths of conventional design were constructed for this work.

One of the baths consisted of a round Pyrex glass and felt insulated container, 11 $^{1}/_{4}$ in. diameter, 12 in. height. It contained a Beckmann differential thermometer, a calibrated one-tenth degree thermometer, a heating coil (375 watts) composed of a heating element in copper tubing, a cooling coil composed of copper tubing through which water from the tap circulated at its own pressure, a three-armed mercury thermoregulator, a solenoid-type relay, connecting wires, a Fisher Tork Labmotor having a 12 in. length fin-type blade. The motor of the stirrer was cooled by a small external fan (8 in. diameter). The bath was provided with a large round-bottomed 2-hole rubber stoppered flask having two glass tube inserts and supported in an inverted position at a height such

that one tube was flush with the surface of the water in the bath, the other tube slightly above this water level. This device, as long as it contained water, automatically added water to the bath whenever the level decreased due to evaporation. (It was found that a 2l. flask for the round bath, 3 l. for the square bath, held the water level constant over-night--a period of 8 hours.)

The second bath consisted of a square metal container, 15 in. by 15 in., 16 in. deep. This bath contained items similar to those just described, but there were two important distinctions. The square bath had two heaters and an electronic relay (Deltron Inc., model 300A). For this thermostat, a Fisher Jumbo stirrer with a 17 in. length fin-type blade was used. The motor of this stirrer also was cooled by a small external fan (8 in. diameter). One of the heaters was a nickel-plated, Cenco Lagless, immer-sion, knife-type heater (250 watts) which was connec-ted directly to the wall circuit (line voltage 115 v). The second heater (500 watts), of the copper coil type, was plugged into the "closed" side of the relay.

For the round bath, a sample holder made of wood, suspended and secured the 25 ml. volumetric

flasks at the necessary height for complete immersion of their contents and for free circulation of water about each flask. For the square bath, the sample holder was of similar design, although larger and made of stainless steel.

The thermostats maintained the temperature at 50° C. ± .05 for the kinetic runs.

10. Karl Fischer titration apparatus

The water content of pure methanol was determined by using the Karl Fischer reagent. This was delivered from an ordinary, calibrated 50 ml. buret arranged for automatic filling and protected from oxygen (by pyrogallol), moisture (by Drierite), and carbon dioxide (by Ascarite). The titrated solution was stirred by means of a magnetic stirrer (Mag-Mix, Precision Scientific Co., catalog no. 65904).

The commercial methanol-water standard solution was provided with an identical set-up.

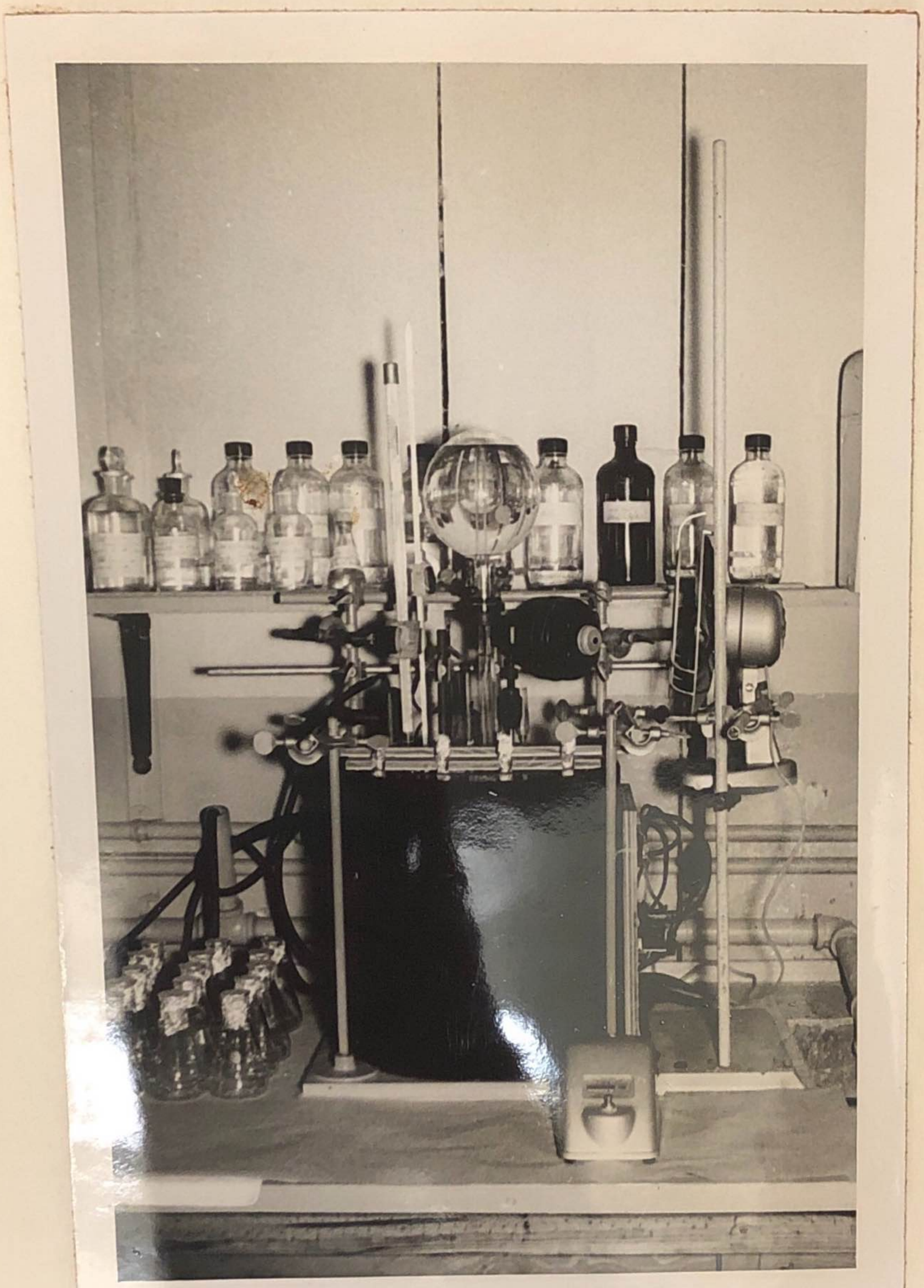

Fig. 3. Thermostat

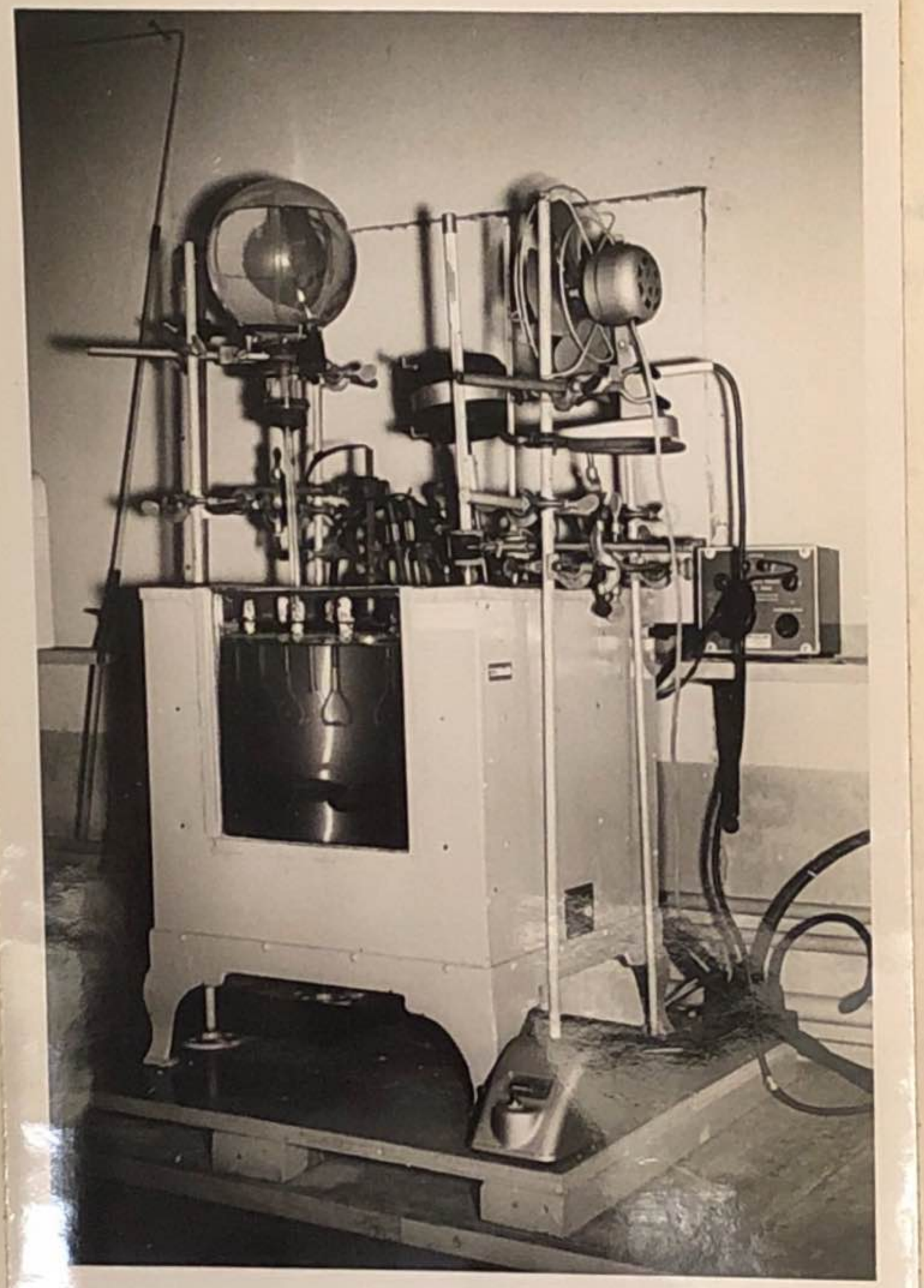

Fig. 4. Thermostat

C. Methods

1. Details of titrations

The analytical methods were those customarily used in precise work. The value given for the normality of a solution is the average value obtained from at least three separate samples determined by the given method. The standards used have been described previously as reagents.

The water content of "absolute" methanol (obtained as described previously by fractionation through the Todd apparatus) was determined by the Karl Fischer method.[30] This method involves the use, ordinarily, of two separate solutions and the completion of two separate titrations. The reagent proper is a methyl alcohol solution of iodine, sulfur dioxide, and pyridine. The standard solution (containing a known weight of water per unit volume) was, in this case, a commercially obtained methanol-water solution (1 ml. $\equiv$ 1 mg. water).

The method involved first, the standardization of the Fischer reagent by determining gravimetrically and volumetrically the water equivalence of the reagent with 10 ml. weighed portions of the standard. Next, 25 ml. weighed portions of methanol of un-

known water content were titrated with the freshly standardized reagent. Since the weight (in mg.) of water equivalent to 1 ml. of the reagent was known from the standardization and the volume (in ml.) of the reagent required for the 25 ml. sample of methanol had been determined in the second step, it was possible to find the apparent water content of the methanol. The apparent water content is the value calculated on a per cent basis from the weight of water (in mg.) found equivalent to the volume of the reagent necessary to titrate it. (The calculation[36] accounts for the reaction of the methanol .)

Although the complete stoichiometry of the reaction(s) involved in this method is not known with certainty, (viz., reaction with pyridine), it is usually stated that water is consumed by the reagent according to the equation

$$H_2O + I_2 + SO_2 + CH_3OH \longrightarrow 2HI + CH_3HSO_4 .$$

The Karl Fischer reagent has an intense brown color that is due to the presence of iodine in an alcoholic pyridine solution. In practice, the iodine color is immediately discharged when the reagent (added from the buret) meets an aqueous environment, (in the present case, methanol containing trace

amounts of water). When all the water in the medium has reacted with the reagent, the next drop of the reagent colors the solution being titrated. (This point, in chemical parlance, is termed the end point.) The end point of the titration is indicated by the appearance of the amber color of free iodine. As the end point is approached, the straw color of the solution changes from canary yellow to chromate yellow; beyond this point, the solution exhibits a red-brown color due to the presence of a large excess of iodine.

Considering the equation given above, it may be noted that an iodine-iodide couple is operative. For this reason, oxygen was excluded from the atmosphere in which the titrations were performed. Small pH changes were prevented by protection from atmospheric carbon dioxide.

The reproducibility and accuracy of the Karl Fischer method for the determination of the water content of "pure" methanol was tested in the following manner. Additional methanol-water standard solutions were prepared gravimetrically at 25° C. from the pure components. In these, the weight of water was varied in multiples of two (from 5 mg. to 80 mg.).

Titration of the resulting solutions with the standard Fischer reagent showed that the amount of water present could be determined accurately. Whenever the Fischer reagent was used in a determination, it was first standardized with 10 ml. portions of the commercial methanol-water standard.

The silver nitrate solution (approximately 0.1N) was titrated with standard KCNS solution in a microburet to a salmon pink end point and employed the otherwise ordinary procedure.[37] The Ag^{+}-CNS^{-} ratio was 1.07. This solution was titrated also with standard sodium chloride by a modified Volhard method,[38] with standard sodium bromide by the Volhard method,[39] and with both of these standards by the Fajan's method.[40] A third titration involving adsorption phenomena was performed using eosin indicator.[41] These methods are described in following remarks.

Titration of bromide and chloride ions by Fajan's method using sodium dichlorofluoresceinate indicator was by the following procedure. To 25 ml. halide solution (approximately .005- .12 N), glacial acetic acid was added dropwise (about 4 drops) until the pH of the solution was approximately 5 as determined by

Hydrion test paper. Four drops of the indicator were added and the sample was titrated with standard silver nitrate solution (0.1N) in a dropwise manner, with constant swirling in diffuse light. Approximately one per cent before the equivalence point, the silver halide sol flocculates. Dropwise titration was continued with vigorous agitation until the white precipitate suddenly exhibited a peach color. The indicator blank cannot be determined directly owing to the great sensitiveness of the precipitate toward light; the correction fortunately is negligibly small with 0.1 N silver ion.

Titration of bromide and chloride ions by a Volhard method was performed using the following procedure. To 25 ml. of the halide solution (approximately .05-0.1 N) were added 8-16 drops concentrated white nitric acid. Standard silver nitrate solution (0.1N, 17-34 ml.) was added from a buret (the silver nitrate was 2-5 ml. in excess); then 1-2 ml. of purified nitrobenzene and 10-20 drops of ferric alum indicator were added. The excess silver ion was titrated in a dropwise manner with standard KCNS solution (.0952N) until the solution suddenly turned reddish-brown.

When bromide ion was titrated in this way, the use of nitrobenzene was unnecessary.

Titration of bromide ion with eosin bluish was performed using the following procedure. To 25 ml. halide solution (approximately .001-.05N), glacial acetic acid was added dropwise (about 4 drops) until the pH of the solution was approximately 5 as determined by Hyrion test paper. Two drops eosin were added and the sample was titrated with standard silver nitrate solution (0.1N) in a dropwise manner, with constant swirling in diffuse light. Approximately one per cent before the equivalence point, the silver halide sol flocculates. Dropwise titration was continued with vigorous swirling until the precipitate suddenly became bluish-gray. The indicator blank is negligibly small using 0.1 N silver ion.

Pure, anhydrous sodium carbonate was used to standardize the HCl solutions. Methyl orange indicator only was used in the titrations[42] of the approximately 0.5 N and 0.25 N acid solutions; methyl orange and bromcresol green were used in the titrations[43] of the approximately 0.1 N and 0.06 N solutions.

The carbonate-free NaOH solutions analyzed

0.2297 N and 0.1151 N, respectively. The solutions were standardized with pure, dry potassium acid phthalate[44] and standard hydrochloric acid solution,[45] using phenolphthalein indicator in both cases.

2. Determination of physical constants

The boiling point, melting point, density and refractive index were determined on either purified samples of materials or freshly distilled samples.

The boiling point was determined by a modification of Elmich's method.[46]

The melting point of derivatives was determined in the usual manner by the capillary method.[47] The melting point of liquids was determined by the cooling curve method using a liquid nitrogen cooling bath (Florida Gas and Chemical Corp., Dania, Fla.) and the low temperature thermometer. The liquid sample was placed in an ordinary 6 in. Pyrex test tube which rested inside an 8 in. Pyrex test tube. The thermometer was placed directly into the sample and immersed to the appropriate height. Two large beakers insulated by Pyrex glass wool were fitted into each other and the liquid nitrogen was sprayed into the smaller beaker (1 l.) from a wide-mouthed insulated one gallon thermos bottle. In practice, the sample was cooled until completely frozen, then the double test tube was removed from the cooling bath and its contents thawed. Temperature readings were

taken on freezing and thawing at thirty second intervals. When the readings became constant for five minutes, the temperature was recorded as the freezing point or the melting point. The average of these values is given as the approximate melting point of the sample.

The density was determined by using an apparatus already described and the following procedure. The clean, dry, air-filled density bulb was weighed on the analytical balance. Freshly boiled, cooled distilled water, which had been placed in a thermostat at the assigned temperature for at least one hour, was drawn into the bulb and this was thermostated for one-half hour at the same temperature. The water-filled bulb was then dried and weighed. The water was removed, the bulb rinsed with ethanol, dried by suction for a few minutes, and thoroughly dried in an oven. After cooling in a desiccator, the bulb was filled with the liquid sample, (previously thermostated for one hour at the assigned temperature), thermostated and weighed as before. The density was computed by using the formula

$$d_4^{t^\circ} = \frac{W'D}{W} - D_a \frac{(W' - W)}{(W)} ,$$

in which d is the density of the sample, W' is its weight in air, D is the density of water, W is the weight of an equal volume of water in air, t is the temperature in $^{\circ}C$, and D_a is the density of air at the temperature and pressure of the weighings.[48]

The refractive index was determined with an Abbe Refractometer and is recorded as n_D^t, where n is the index of refraction referred to air, t is the temperature, and D refers to the wavelength of the light source---in this case, the D line of sodium vapor.

3. Analysis of reaction products

The general procedure for the analysis of the reaction products was the following. Definite weights of butyl bromide and sodium hydroxide in various methanol-water mixtures were allowed to react under kinetic conditions at 30° C. After a suitable time, the reaction was "stopped" by cooling in shaved ice at 0° C. Six 2 ml. aliquots of the reaction product mixture were taken and these were used to determine titrimetrically the concentrations of unreacted halide and hydroxide ions with standard silver nitrate solution (using sodium dichlorofluoresceinate indicator) and standard hydrochloric acid solution (using phenolphthalein indicator), respectively. (The details of these titrimetric methods were given in part 1 of this section[1].)

The remainder of the reaction product mixture was filtered from any solid that was present. Concentrated hydrochloric acid was added drop by drop to this chilled mixture until it was neutral to Hydrion paper. Two drops of the acid were then added in excess. The slightly acidic solution was fractionated through the Todd column without previous drying and the products were collected in flasks of

known weight or the volumes of the fractions were recorded. The ordinary general and specific class tests were applied to the fractions and the refractive indices of the fractions were determined.

Two or more fractions isolated in this procedure were thought to be azeotropes (butyl alcohol-water, methyl butyl ether-methyl alcohol, methyl butyl ether-water mixtures).

Butyl alcohol was separated from the water by salting out with sodium sulfate, then extracting with ethyl ether, drying the mixture with anhydrous potassium carbonate and finally, distilling the ethyl ether from the alcohol product. As the amount of the butyl alcohol was small, it is thought to be the minor product. It was identified by the determination of its boiling point (b.p. 117.5° C., 767 mm. Hg) and refractive index ($n_D^{27^\circ}$ =1.3963) and by the general and specific class tests. A 3-nitrophthalate derivative was prepared[32] which melted at 145° C. (first crystallization) and 144° C. (second crystallization). An authentic sample of the derivative was prepared in the same way from butyl alcohol. Small portions of these samples were combined and the melting point of the mixture was determined (m.p. 144° C.). The

yield of n-butyl 3-nitrophthalate of the alcohol product was 72 mg.

Extractions with solvents for the separation of the methyl butyl ether azeotropes were unsatisfactory. The ether product was isolated by diluting the mixture (azeotrope, b.p. 55-57° C., 767 mm. Hg) with water (about 100-200 ml.), adding water during stages in the distillation and in later stages, of calcium chloride, and distilling the precipitated ether once from fused barium oxide and twice from potassium. The boiling point and index of refraction of the product were determined (b.p. 71° C., 767 mm. Hg; $n_D^{27^\circ}$=1.3772). The product was identified as an ether by the general class tests. The ether was cleaved to confirm the identification by preparation of a derivative. The procedure for this identification was a standard one.[31] The 3-5 dinitrobenzoate derivative of the cleavage product melted at 62.5° C., and an authentic sample of the ether treated in the same way formed a material which melted at 63.0°C. A mixed melting point (m.p. 63.0° C.) confirmed that the product was methyl butyl ether. A higher boiling fraction (b.p. 78° C., 767 mm. Hg) was not identified. The yield of n-butyl 3-5 dinitrobenzoate

of the ether product was 4 mg.

4. Details of Rate Measurement

Freshly prepared solutions of n-butyl bromide (A) in the suitable methanol-water mixture were made by siphoning the solvent mixture into a volumetric flask containing a weighed amount of solute (approximately 28 millimoles), diluting to an indicated volume of 50 ml. at room temperature and mixing by inversion. The solution was placed in a thermostat at 50° C. ±.05° for one hour in order to attain temperature equilibrium. Solutions of sodium hydroxide (B) in the same methanol-water mixture were prepared and thermostated in an identical manner. Reaction mixtures were prepared by mixing the two solutions in a volumetric flask and diluting to an indicated volume of 250 ml. with the same solvent mixture. The latter had been placed in a thermostat at 50° ± .05° for at least one hour prior to mixing.

As quickly as possible, aliquots of the reaction mixture (10 ml. for most runs, 20-25 ml. for run 2) were placed in 25 ml. glass-stoppered volumetric flasks and thermostated at the assigned temperature. At suitable intervals, the flasks were removed from

the thermostat and chilled in crushed ice at 0° C., to "stop" the reaction. The contents of the flask were transferred to 125 ml. Erlenmeyer flasks immersed in ice at 0° C. The reaction flask was washed twice with small portions of cold absolute methanol and the washings were added to the Erlenmeyer flask. The reaction mixture was analyzed for hydroxide ion by titrating with standard acid (HCl) using phenolphthalein indicator. A separate reaction mixture sample was analyzed for bromide ion by titrating with standard halide-free silver nitrate using either eosin or sodium dichlorofluoresceinate indicator. (The details of these titrimetric methods were described previously in part 1 of this section.) The titrations were performed in the cold following the method of Zuter and Cook.[49]

Initial titers of hydroxide and bromide ions were determined as soon as possible after mixing and diluting solutions A and B. The process of diluting and quenching the reaction took about one minute. The concentrations given in the tables as "a" and "b" are the values determined in this way. Control experiments showed that both titrations

were reliable within experimental error.

It has been stated above that the reaction was timed in seconds and tenths of seconds. The $t_{min.}$ values in the tables represent the time of the nearest whole minute. "Zero" time was called the mean time of addition of the two solute mixtures (B to A).

Reactions were followed to about 30-80 % completion, and initial concentrations were checked by "infinity" titers whenever this was feasible. The "infinity" titer was usually determined after a period of about three weeks. The "infinity" titer of bromide ion agreed well with the concentrations determined initially. In some cases, the "infinity" titers of hydroxide ion were unreliable by a few % , probably due to reaction of the glass.

It is possible to titrate a single reaction mixture sample for both hydroxide and bromide ions, precisely, provided the base concentration is low. If this is done, the hydroxide ion is, of course, determined first.

Eosin was the indicator used initially and when the bromide ion concentration was less than 0.01N. Simultaneous determinations were performed using sodium dichlorofluoresceinate; usually, the bromide

ion concentration recorded in the tables is that observed by the latter indicator.

No correction has been made for the error due to solvent expansion.

D. Results

1. Physical constants data is summarized in tables IV and V.

2. Reaction product data is summarized in table VI.

3. Kinetic data is given in tables VII to XII; data for the calculations of the rate constants and the least squares computations, in appendix C. Other kinetic summary data may be found in tables XIII and XIV. Plots of C (OH^-, Br^-, and BuBr, butyl bromide, respectively) versus $t_{min.}$ are shown in figures 5, 6, and 7; log C (OH^- and BuBr, respectively) versus $t_{min.}$, in figures 8 and 9.

Rate constants were calculated [50] from classical first- and second-order kinetic equations (k_1 and k_2, respectively), from slopes of the plots of log C versus t ($\overline{k}_1$), by the least squares computation for the curves of log C versus t (k_s), from another second-order equation (k_2'), and by the arithmetical mean method (k_m).[50c]

The dielectric constant data for the acetone-water, ethanol-water, and methanol-water systems were calculated from Akerlof's[51] equations or were