

The same product was obtained when the experiment was repeated with potassium amide instead of potassium metal, the amide being prepared in the apparatus.

*Anal.* Found: Zr, 42.75, 42.60; K, 36.43, 36.50; N, 18.80, 17.70.

When potassium amide was added in an equivalent amount to zirconium bromide, a mixture of zirconium imide and a monopotassium derivative of zirconium imide were formed.

*Anal.* Calcd. for an equimolar mixture of  $Zr(NH)_2$  and  $ZrNHNK$ : Zr, 65.03; K, 13.93; N, 19.96. Found: Zr, 65.52, 65.02; K, 13.15, 13.33; N, 20.39, 20.65.

The first reaction product between potassium and zirconium bromide will be studied further in a solvent in which solvolysis is less than in ammonia.

Thorium bromide underwent no color change on being treated with potassium in liquid ammonia. There was, however, a slow reaction and potassium bromide was formed and hydrogen was evolved. It is possible that on account of the very slight solubility of the thorium salt, saturation of a very small amount of a reduction product by the  $NH_2$  group, or  $NH$  group, would occur without any visible evidence of reduction. Another possibility is an initial formation of potassium amide and a subsequent metathesis with thorium bromide. If ammonolysis of the salt took place, potassium would then react with the ammonium bromide formed. In the course of the reaction between potassium and thorium bromide, which was very slow, there was, of course, a continually increasing reaction between the metal and the solvent to form the amide. Approximately the same molecular proportions of salt and metal were used as in the reaction with zirconium bromide and potassium, but in the majority of cases the composition of the product approached that represented by the formula  $ThNKNH \cdot NH_3$ .

*Anal.* Calcd. for  $ThNHNK \cdot NH_3$ : Th, 73.17; K,

12.32; N, 13.29. Found: Th, 72.73, 73.90; K, 15.35, 15.40; N, 9.25, 10.03.

A larger percentage of potassium could be introduced in the product by continued action, and analyses of samples were obtained which showed that the hydrogen of the second imide group was partially replaced by the metal. With excess potassium amide, however, the reaction was more nearly complete, the analysis of the final product pointing to a replacement of both imide hydrogen atoms by potassium and a molecular compound with the amide.

*Anal.* Calcd. for  $Th(NK)_2 \cdot KNH_2$ : Th, 59.00; K, 29.81; N, 10.67. Found: Th, 59.89, 60.11; K, 27.10, 26.70; N, 9.75, 10.41.

### Summary

Zirconium tetrabromide was found to be soluble in liquid ammonia and was reduced in this solvent by potassium metal to form a black precipitate and red solution. The reduction product reacted further with evolution of hydrogen to form a compound  $Zr(NK)_2 \cdot NH_3$  which was also formed by the reaction of zirconium bromide with potassium amide in excess. In equivalent proportions, however, the imide, together with a monopotassium derivative, was formed.

No reduction of thorium bromide was observed when it was treated with potassium in liquid ammonia. Reaction took place, however, with evolution of hydrogen and a product  $ThNHNK \cdot NH_3$  was isolated.  $Th(NK)_2 \cdot KNH_2$  was formed by reaction between thorium bromide and excess potassium amide.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Solubility of Noble Gases in Aqueous Salt Solutions at 25°

BY GÖSTA ÅKERLÖF

### Introduction

The influence of strong electrolytes on the thermodynamic properties of non-electrolytes in solution has been studied for a large number of different substances, mostly with a rather complicated structure, like ethyl acetate, phenyl thiourea, diacetone alcohol and others. Numerous measurements with simpler substances like hydrogen, oxygen and other gases have, however, also been carried out and the data available give on the whole, as shown in the exhaustive summary of Randall and Failey,<sup>1</sup> about the same picture as that of the behavior of more

(1) Randall and Failey, *Chem. Rev.*, **4**, 271, 285, 291 (1927).

complicated substances. Therefore, at the suggestion of Professor H. S. Harned, it was considered to be worth while to make a study of the solubility changes in solutions of strong electrolytes of the simplest molecules known, those of the noble gases, which are mono-atomic, non-polar and chemically inactive. As will be shown below, also in this case the general results of the measurements carried out do not differ from those obtained with non-electrolytes having a relatively very complicated structure.

### Experimental Method

The principle of the method employed for the solubility measurements is extremely simple and consists in the direct

substitution of a known volume of mercury by exactly the same volume of the solution to be used. Thus, provided no gas absorption took place, the gas pressure in the apparatus would remain constant. However, due to the absorption of gas which begins when the solution is introduced, the pressure does change and the amount of this change was utilized to measure directly the amount of gas dissolved with an ordinary gas buret.

A schematic diagram of the principal parts of the apparatus is shown in Fig. 1. The noble gas enters at N and passes first slowly through the previously evacuated vessel I, filled to about two-thirds with a solution of exactly the same concentration as the one to be used for the solubility measurements. In vessel I the gas takes up water vapor but since the establishment of complete equilibrium is very essential to the accuracy of the method used, the stopcock between vessel I and the rest of the apparatus was kept open until the measurement was started about twenty-four hours later.

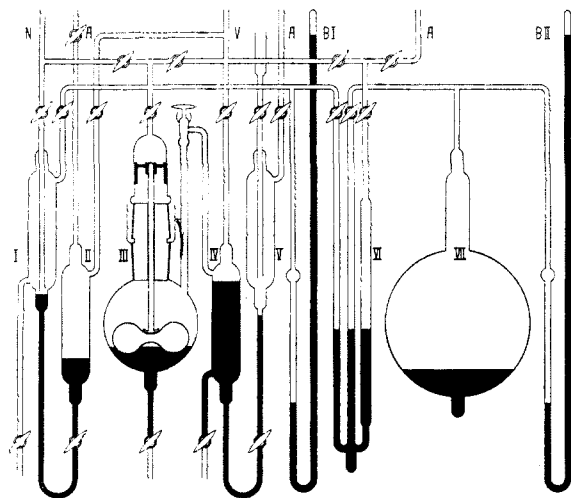


Fig. 1.

From vessel I the noble gas, saturated with water vapor, passes on to the reaction vessel III. The latter with the manometer BI and the connection to the gas buret VI had beforehand been thoroughly evacuated. Vessel III contains about 1600 cc. of mercury and is provided with an efficient stirrer in the form of a glass dumbbell balanced to sinking in pure water with an iron ring as shown in Fig. 1. The iron ring was given an up and down motion by switching off and on by means of a commutator device a 0.5-amp. d. c. current through two large coils around the outside of the large upper outlet tube from the reaction vessel. The vertical shaft for the stirrer was held in a double cone of stainless steel, drilled with a number of holes to provide an easy passage for the gases. In dismantling the apparatus for occasional repairs or cleaning, a glass cone would have been impossible to remove without breakage.

When the gas pressure in the reaction vessel had increased to a value of about 760 mm., the mercury levels in the measuring tubes of the gas buret were adjusted until they had reached a few inches from their lower end. Then the gas inlet to vessel I was closed. To avoid errors and corrections due to changing barometric pressure during

the run of a measurement the gas buret was connected to a large flask VII. The latter was connected with the control manometer BII and weighted down with mercury to prevent strain in the connecting tubes when the apparatus was submerged in water.

The solution to be used for the solubility measurement had previously been heated and then boiled in vacuum for about three-quarters of an hour and it was introduced into the thoroughly evacuated vessel IV simultaneously with the filling of vessel I (interconnections for the filling and washing of the apparatus are not shown in Fig. 1). A hard click was usually heard at the very end of the filling of vessel IV or when the stopcocks in the solution inlet lines for this vessel or vessel I were closed. The concentration of the solution employed was calculated from its density as measured with a Mohr-Westphal balance and using the density tables given in Volume III of "Int. Crit. Tables." Before the solution to be used was introduced into the apparatus its temperature was adjusted to 25°, since it was important that it should give the correct vapor pressure in vessel I. The introduction of the noble gas was delayed until about half an hour after that of the solution.

Before the solution was introduced in the reaction vessel III the stopcock to vessel I was closed and the zero point on the gas buret was determined by reading with a cathetometer the mercury levels at several points and interpolating to zero difference with an accuracy of  $\pm 0.05$  mm. Twenty-four hours were always allowed to elapse before the zero point was determined, but, as found a large number of times, it always seemed to remain unchanged during this period. Then in order to introduce the solution in

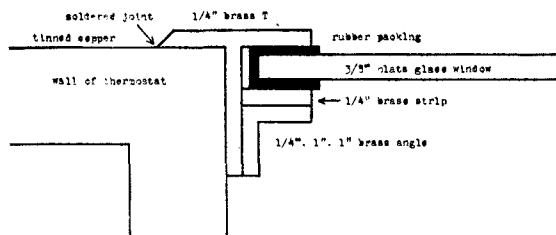


Fig. 3.—Detail of seal for thermostat window.

vessel IV into the reaction vessel, the stopcock for the upper outlet tube for the latter vessel was closed and mercury allowed to flow out through its lower outlet tube into an evacuated flask until this was filled. The inner volume of the flask had been determined accurately to be 1051.2 cc. by weighing it empty and filled with water at 25°. The mercury thus withdrawn from vessel III was immediately introduced into vessel V and allowed to

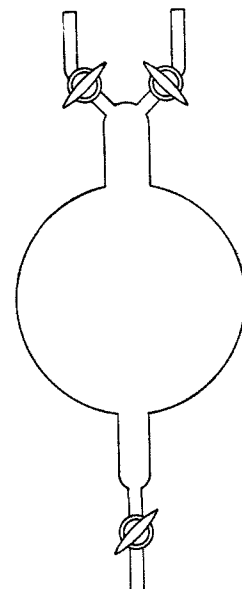


Fig. 2.—Vessel for mercury transfer.

flow into vessel IV, pushing the solution in this vessel into vessel III until a previously observed mark on the outlet from vessel V again had been reached and thus the volume of mercury taken out from vessel III had been replaced by an equal volume of solution.

After the solution had been introduced into the reaction vessel the upper stopcock to the same was opened again and the magnetic stirrer was started. The speed and the force of the stirring could be regulated over a fairly large range but variations did not seem to have any noticeable effect on the amount of gas dissolved. The mercury left in the reaction vessel served as an elastic cushion for the dumbbell, which always was completely submerged in the solution used. The absorption of the gas by the solution in the reaction vessel was followed by raising the mercury levels in the gas buret until further changes could not be observed.

Due to the raising of the mercury levels the zero point previously observed needs a correction since both sides of the gas buret are connected to closed volumes. The correction necessary varied within the reading errors on the cathetometer linearly with the amount of gas absorbed. A very slight correction of the correction might be observed but it is entirely negligible and has been neglected. The calibration of the gas buret was carried out in the usual manner by sealing a stopcock to one end of the measuring tube and for approximately equally spaced intervals weighing the mercury column representing a measured distance.

The apparatus shown in Fig. 1 was supported by a heavy framework of angle brass and submerged in water in a large thermostat one side of which was provided with a large plate glass window through which the entire apparatus could be observed. The temperature of the thermostat was regulated to 25° with a precision of 0.01° but controlled with far greater accuracy by a large grid-like mercury thermoregulator. To facilitate the operation of the apparatus a few of the necessary stopcocks were placed in front of the thermostat and the connecting glass tubes drawn out under the bottom of the tank. Possible temperature variations of the connections outside the tank were estimated to have an entirely negligible influence on the accuracy of the solubility measurements. After a measurement had been finished, about 80% of the gas used could be returned to its reservoir by means of only two operations of a simple gas pump. The solution inside the apparatus could be drained practically quantitatively and used over again. All parts of the apparatus that needed to be washed out for a new measurement could be alternately completely flooded and drained in rapid succession. After the washing had been finished most of the remaining drops of water in the glass tubing were blown out with compressed air and complete drying was accomplished by evacuation. When all visible water drops had disappeared the final stage of the drying was aided by a very efficient diffusion pump and the vacuum attained tested twice with a McLeod gage.

### Experimental Results

The noble gases used for the solubility measurements were helium and argon. The former was 98% and the latter 99% pure. The impurity

present in the greatest amount was nitrogen but since its solubility in aqueous solutions is of the same order of magnitude as that of both helium and argon the correction of the observed solubilities for the noble gases to their pure state is considerably smaller than the average experimental errors and it has therefore been neglected. The rate of the absorption of the noble gases by the solutions employed was found to be very rapid with a half period of only a few minutes. The stirring was, however, kept up for about two hours and then the system was allowed to come to equilibrium during another two-hour period. After this time the final end-point and pressure were observed. All solutions were made up with chemicals of the analyzed variety. Their concentration is in the following expressed in moles per 1000 g. of solvent.

A summary of all the experimental results obtained is given in Table I. In the case of helium the data given represent as a rule the mean of three and in the case of argon of two

TABLE I

THE SOLUBILITY  $\alpha$  OF HELIUM AND ARGON IN VARIOUS SALT SOLUTIONS AT 25°

A. Solubility of Helium				
Electrolyte	$m$	$\alpha$	$\gamma$	(log $\gamma$ )/ $\mu$
	0.00	0.0086	1.00	..
Potassium chloride	4.72	.0048	1.81	0.055
Sodium chloride	5.81	.0043	2.02	.053
Lithium chloride	6.18	.0136	0.640	-.015
Lithium iodide	2.40	.0109	.801	-.038
Sodium nitrate	6.95	.0039	2.23	.050
Perchloric acid	6.89	.0187	0.466	-.048
B. Solubility of Argon				
	0.00	0.0332	1.00	..
Potassium chloride	3.00	.0220	1.51	0.060
	4.55	.0174	1.91	.062
Sodium chloride	3.23	.0216	1.54	.058
	5.98	.0149	2.23	.058
Lithium chloride	3.35	.0248	1.34	.038
	6.78	.0187	1.78	.037
Sodium nitrate	3.51	.0204	1.63	.060
	7.37	.0123	2.59	.056
Perchloric acid	4.05	.0411	0.81	-.023
	9.32	.0521	0.64	-.021
Calcium chloride	2.95	.0216	1.54	.021
	5.37	.0180	1.84	.016
Strontium chloride	2.10	.0203	1.64	.034
	3.56	.0150	2.22	.032
Barium chloride	1.25	.0185	1.79	.068
	1.74	.0141	2.35	.071
Magnesium chloride	3.02	.0248	1.34	.014
	5.02	.0228	1.46	.010
Aluminum chloride	0.98	.0247	1.34	.022
	1.56	.0179	1.86	.020

separate determinations. In calculating the results, all pressure and volume readings have been reduced to 0° and 760 mm. partial pressure using the correction tables given in Landolt-Börnstein. The vapor pressure of the salt solutions employed was estimated from data given in Volume III of "Int. Crit. Tables," and second "Ergänzungsband" of Landolt-Börnstein (aluminum and magnesium chlorides) and some recent investigations of Pearce and co-workers.<sup>2</sup> The solubility values  $\alpha$  in Table I give the volume of gas in liters absorbed under standard conditions of 0° and 760 mm. in an amount of solution containing 1000 g. of solvent. The estimated accuracy of the data is about 2% in the case of helium and 1% in the case of argon. The data in the last column of Table I have been calculated using the empirical equation of Setschenow

$$km = \log (s_0/s) \quad (1)$$

where  $s_0$  is the solubility of the gas in the pure solvent and  $s$  the solubility at the concentration  $m$ .  $k$  is a constant which in the following will be called the salting out constant. The accuracy of equation (1) seems never to have been tested carefully and it is used here because it appears to be able to express in a very simple manner and within the probable experimental errors the results of a considerable number of salting out studies. In this connection it may be pointed out that at very high concentrations the variation of the activity coefficient of a very large number of strong electrolytes as a good approximation may be given by the same equation. As an example the data of Randall and Young<sup>3</sup> for hydrochloric acid at 25° give the following result

HCl $m$	9	10	12	14	16
$\log \gamma$	0.900	1.019	1.236	1.437	1.628
$(\log \gamma)/m$	.100	0.102	0.103	0.103	0.102

It has been shown by the author<sup>4</sup> that at high ionic strengths the following simple relationship

$$\log \gamma_A/\gamma_B = k_1m \quad (2)$$

where A and B are two strong electrolytes of the same valence type, is consistent with the solubility data for numerous aqueous ternary systems. By adding a constant term equation (2) may be applied to two electrolytes of different valence

(2) Pearce and Nelson, *THIS JOURNAL*, **54**, 3544 (1932), lithium, sodium and potassium chloride; Pearce and Nelson, *ibid.*, **55**, 3075 (1933), perchloric acid.

(3) Randall and Young, *ibid.*, **50**, 989 (1928).

(4) Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934); Åkerlöf, *ibid.*, **56**, 1439 (1934).

types. Thus equation (1) should be applicable to very concentrated solutions of all strong electrolytes and the higher the valence type of the electrolyte considered the lower the concentration limit below which this relationship ceases to be at least approximately valid.

The value obtained for the solubility of helium in pure water,  $0.0086 \pm 0.0001$ , represents the mean of five measurements and agrees very well with the value of 0.0087 found by Lannung.<sup>5</sup> In the case of argon, however, the agreement is not so good. Lannung found at 25° the value 0.0314 while the value given in Table I representing the mean of four measurements is  $0.0332 \pm 0.0002$ . On the other hand, this latter value is in far better agreement with the old measurements of Winkler<sup>6</sup> which give a solubility of 0.0326 for argon at 25°. The sensitivity of the method presented in this paper is approximately the same as that of the method employed by Lannung even though, due to practical reasons, it was necessary to use a fairly large gas volume of about 600 cc. The main difference between the two methods seems to be the manner in which the gas and the liquid were brought in contact. In the case of the apparatus used by Lannung the contact surface must have been quite small and accordingly the movement of the surface layer of the liquid might have been rather slow. In our case the contact surface was at least fifty times larger and the surface layer was given a rapid, soft movement by the dumbbell bobbing up and down in the liquid. It has been pointed out by Cady, Elsey and Berger<sup>7</sup> that improper violent stirring gives completely erroneous and far too high solubility values. This possibility is, however, definitely ruled out since it was found that after half an hour of stirring, the end-point did not change visibly although the stirring was continued hour after hour.

### Discussion of the Experimental Results

Modern theories of the effect of strong electrolytes on the thermodynamic properties of non-electrolytes are as yet to be considered as first approximations to be applied only in the case of very dilute solutions. Therefore the present status of the theory will not be discussed in this place but we will instead first compare the results of the measurements carried out with helium

(5) Lannung, *ibid.*, **52**, 68 (1930).

(6) Winkler, *Z. physik. Chem.*, **55**, 344 (1906).

(7) Cady, Elsey and Berger, *THIS JOURNAL*, **44**, 1456 (1922).

TABLE II  
 SALTING OUT CONSTANTS OF VARIOUS NON-ELECTROLYTES

Electrolyte	Non-electrolytes <sup>a</sup>									
	1	2	3	4	5	6	7	8	9	10
HCl	..	0.020	0.022	0.016	0.006	..	..	..	..	..
LiCl	0.037	.066	..	.081	..	..	0.088	0.077	..	0.181
NaCl	.058	.094	.132	.101	..	0.093	.166	.139	0.140	.220
NaBr	..	..	..	.089	..	.077	.119	.109	..	..
NaI	..	..	..	..	..	..	.024	.041	.029	..
NaNO <sub>3</sub>	.058	.080	..	.072	.053 <sup>b</sup>	.050	.074	..	.019	..
Na <sub>2</sub> SO <sub>4</sub>	..	..	..	.110	.109 <sup>b</sup>	.098	..	.159	.133	..
KCl	.061	.078	..	.085	.059	.062	.143	.118	.118	.245
KBr	..	..	..	.063	.045	.049	.105	.090	.055	..
KI	..	..	..	.058	.032	..	.037	.034	.057	..
KNO <sub>3</sub>	..	.061	..	.047	.025	.030	.060	..	.013	..
H <sub>4</sub> NNO <sub>3</sub>	..	..	..	.007	..	..	.027	..	.057	..
BaCl <sub>2</sub>	.070	..	..	.073	.060	.067	.080	..	.074	.069
SrCl <sub>2</sub>	.033	..	..	..	..	..	..	..	..	.064
CaCl <sub>2</sub>	.018	.065	..	.064	..	.058	..	..	..	.062
Ca(NO <sub>3</sub> ) <sub>2</sub>	..	..	..	.041	..	.028	.022	..	..	.062
MgCl <sub>2</sub>	.012	..	..	..	..	.055	..	.060	..	.060
MgSO <sub>4</sub>	..	.057	..	.070	..	.064	.127	.105	.080	..
AlCl <sub>3</sub>	.021	.028	..	..	..	.044	..	.043	.063	..
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	..	..	..	.045	..	.043	..	.076	..	..

<sup>a</sup> 1, Argon; 2, hydrogen; 3, oxygen; 4, nitrous oxide; 5, carbon dioxide; 6, acetylene; 7, ethyl acetate; 8, diacetone alcohol; 9, phenyl thiourea; 10, phenol. <sup>b</sup> Iodine. References: 2, 3, 4, 5, 6 and 9, Randall and Failey, *Chem. Rev.*, **4**, 271 and 285 (1927). 7, Glasstone and Pound, *J. Chem. Soc.*, **127**, 2660 (1925); Glasstone, Dimond and Jones, *ibid.*, **128**, 2935 (1926); 8, Åkerlöf, *THIS JOURNAL*, **51**, 984 (1929); 10, Herz and Hiebenthal, *Z. anorg. allgem. Chem.*, **177**, 363 (1929).

and argon with the results obtained using various other non-electrolytes.

The effects of a given electrolyte on different non-electrolytes may easiest be compared by using the salting out constants calculated according to equation (1). In Table II is given a summary of the values obtained for a number of different non-electrolytes in the presence of various strong electrolytes. The constants given have been computed using the experimental data particularly for more concentrated solutions since in the case of dilute solutions the probable errors of the values obtained in a number of cases might be larger than the constants themselves. All concentrations have been calculated as the ionic strength of the solutions.

A study of the data in Table II shows first of all that the salting out coefficients are all of the same order of magnitude. Second, for a given electrolyte individual variations for different compounds must be present. In some cases the variations appear to be very small, as, for instance, in the case of solutions of barium chloride where the differences may be well within the experimental errors. In other cases up to fourfold variations are observed and they are without much doubt largely caused by differences in

individual behavior. Even the sign of the salting out constant may change and as an example argon is salted out and helium is salted in by lithium chloride. It should also be remembered that the solubility of the compounds the behavior of which has been studied varies within very wide limits. The solubility of helium is a few milligrams per liter of solution while diacetone alcohol and water are completely miscible.

Due to the reasons just given the relative distribution of the salting out curves for different electrolytes varies with the neutral compound present. It is further also evident that the magnitude of the salting out constants cannot be given by some definite simple rule. They do not arrange themselves in the order of the curves for the activity coefficients of the electrolytes used or the magnitude of their mean ionic radii as previously pointed out by Randall and Failey. The closest approach to a definite relationship seems to be given by a distinct tendency to parallelism between salting out constants and the volume changes occurring when strong electrolytes are dissolved in water. As a matter of fact, it has been found that these volume changes, in the case of contraction, may be expressed very accurately by an exponential function identical

in form with equation (1). In case of an expansion taking place at higher concentrations, the entire curve for the volume changes may be given with a surprisingly high degree of accuracy simply by the addition of a positive linear term.

A relationship such as the one suggested would require that all non-electrolytes give salting out curves of the same sequence. As already mentioned this does not seem to be the case. It should be stressed, however, that the probable errors in a substantial portion of the data in Table II are

very large and a really precise study of the whole field is very much needed.

### Summary

The solubility of helium and argon in various salt solutions at 25° has been studied. The salting out constants obtained have been found to have the same order of magnitude as those of any other non-electrolyte studied. A short discussion of the salting out studies that have been presented in the literature shows the need for an investigation of real precision.

NEW HAVEN, CONN.

RECEIVED APRIL 20, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

## The Change in the Surface Tension of a Solution of Methyl Acetate Due to Hydrolysis<sup>1</sup>

BY BENJAMIN H. HANDORF AND E. ROGER WASHBURN

The possibility of measuring the rate of hydrolysis of ester solutions by measuring the changes in surface tension which accompany hydrolysis has been suggested.<sup>2</sup> It was the purpose of this study to carry out such an investigation. The rate of change of the surface tension of a 2 molar solution of methyl acetate was compared with the rate of hydrolysis as measured by titration with standard barium hydroxide.

### Purification of Materials and Preparation of Solutions

Methyl acetate of c. p. grade was further purified by the method used by Young<sup>3</sup> in the preparation of samples for the determination of its physical constants. The intermediate fractions distilling over within less than 0.5° range in temperature were used in making up the solutions. The specific gravity of the methyl acetate used was  $d^{25}_4$  0.9275  $\pm$  0.0003 as compared with the value in the literature,<sup>4</sup>  $d^{25}_4$  0.9273.

Synthetic methyl alcohol of a high degree of purity was fractionally distilled through an efficient fractionating column to remove minute traces of water. The specific gravity of the purified alcohol was  $d^{25}_4$  0.7867  $\pm$  0.0001 as compared with the value in the literature,<sup>4</sup>  $d^{25}_4$  0.7867.

Acetic acid of c. p. grade was purified by repeated fractional crystallization and then by fractional distillation through an efficient fractionating column. The specific gravity of the acid used was  $d^{25}_4$  1.0446  $\pm$  0.0001 as compared with the value in the literature,<sup>4</sup>  $d^{25}_4$  1.0443.

Conductivity water was used for making up the solutions.

Barium hydroxide solutions, standardized by means of benzoic acid and phenolphthalein, were used for titrating the liberated acetic acid.

### Measurement of Surface Tension and Percentage Hydrolysis

The ring method of measuring surface tension was used in this investigation to determine the surface tension of the solutions. One purpose for its choice was for testing its accuracy and applicability as a means of following the changes in the surface tension of hydrolyzing solutions containing ingredients of varying volatility.

In measuring the surface tension the force required to break the ring from the surface was determined by means of a chainomatic balance especially constructed for surface tension measurements. The magnitude of the force was read directly in grams. The ring was constructed of platinum wire, 0.31 mm. in diameter. The circumference of the ring as calculated from its measured diameter, 1.272 cm., was 3.996 cm. The surface tension measurements were made at suitable intervals of time on samples withdrawn from the solutions in a constant temperature bath. A suitable quantity of solution from each sample was titrated with standard barium hydroxide for determining the percentage hydrolysis. During the titrations the solutions being titrated were kept in ice water to retard the hydrolyzing effect of the barium hydroxide on the methyl acetate. Data beyond the equilibrium point between methyl acetate and water and methyl alcohol and acetic acid were obtained by studying the methyl alcohol-acetic acid solutions as the acid and alcohol reacted to form the ester and water.

In making the surface tension measurements the precautions recommended by Harkins<sup>5</sup> were observed with one exception, the instrument was not immersed in a thermostat, and constant temperature was not maintained in the instrument during succeeding measurements. During a

(1) Presented at the Twelfth Midwest Regional Meeting of the American Chemical Society, May 4, 1934, at Kansas City, Missouri.

(2) Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

(3) Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 26.

(5) Harkins, *Science*, **64**, 333 (1926).