



The equilibrium of silver chloride, silver hydroxide, potassium hydroxide, and potassium chloride in aqueous solution at different temperatures and varying concentrations of potassium hydroxide : the calculation of the heat of the reaction

by William Wallace Harrity

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

Montana State University

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Abstract:

1. The reaction  $\text{AgCl} + \text{KOH} = \text{KCl} + \text{AgOH}$  was carried out at  $30^\circ$ ,  $40^\circ$  and  $50^\circ$  using different concentrations of aqueous potassium hydroxide and the equilibrium constants were obtained.

2. It was found that the concentration of potassium hydroxide used had little if any effect on the equilibrium of the reaction.

3. The heat of the reaction at the various temperatures was calculated by use of van't Hoff's reaction isochore equation.

4. The heat of the reaction was found to decrease quite rapidly as the temperature was increased.

5. Comparisons are given with data submitted by Newton,<sup>3</sup> and the heat of the reaction calculated by use of the above mentioned data.

6. Data will have to be secured for the activities of ions in solutions of higher concentration before the true equilibrium constants for these solutions can be determined.

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THE EQUILIBRIUM OF SILVER CHLORIDE,  
SILVER HYDROXIDE, POTASSIUM HYDROXIDE, AND POTASSIUM  
CHLORIDE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES  
AND VARYING CONCENTRATIONS OF POTASSIUM HYDROXIDE.  
THE CALCULATION OF THE HEAT OF THE REACTION.

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THE CALCULATION OF THE HEAT OF THE REACTION.

INTRODUCTION

G. Wetzlar in 1828, and J. Percy<sup>5</sup> in 1880, found that at ordinary temperatures an aqueous solution of sodium or potassium chloride would react with moist silver oxide to give a white precipitate of silver chloride and a solution of the alkali hydroxide. The action, however, was not complete, and if the solution was boiled the reverse action took place producing silver oxide. This was found to be true of all the alkaline earth chlorides.

W. Gregory in 1839, and F. Mohr<sup>6</sup> in 1848, made silver oxide by boiling freshly precipitated silver chloride with a solution of aqueous potassium hydroxide. The silver oxide thus made was washed with water to remove the alkali and dried on filter paper.

In 1902, Noyes and Kohr<sup>4</sup> published a paper on the measurement of the equilibrium between silver oxide, silver chloride, potassium hydroxide, potassium chloride, and water. They found the value of the equilibrium constant at 25° to be 0.00937. Noyes and Kohr's results were not very consistent and in 1928, Newton<sup>3</sup>, working at Purdue University, published a paper on "The Equilibrium of Silver Oxide and Silver Chloride with Aqueous Potassium Chloride and Potassium Hydroxide." The method used by Newton was to place varying proportions of silver oxide and silver chloride in ground-glass-stoppered Pyrex Erlenmeyer flasks, and add the desired quantities of potassium hydrox-

ide, potassium chloride, and water and rotate the samples in a thermostat at  $25^{\circ} \pm 0.02^{\circ}$  for periods of time varying from several hours to three days. The equilibrium was approached from both sides. No consistent differences were observed. Samples of the liquid portions were then filtered from the flasks and titrated with 0.5 N sulphuric acid, using phenolphthalein as an indicator. The solution was then carefully evaporated to small bulk and titrated electrometrically with 0.01 N silver sulfate solution, using a silver-silver chloride electrode and connecting to a saturated potassium sulfate-mercurous sulfate-mercury electrode. The samples of silver oxide were prepared in different ways but the values obtained did not differ significantly from one another. The average value of the equilibrium constant using an approximately 0.1 N solution of potassium hydroxide at  $25^{\circ} \pm 0.02^{\circ}$  was found to be 0.00905.

The results of Newton's experiment give values somewhat below those obtained by Noyes and Kohr, but in all probability they agree within the limits of experimental error. The equilibrium constant for 0.05 N and 0.1 N solutions appears to be the same within experimental error.

The purpose of this paper is: (1) to determine the equilibrium constant for the reaction



in aqueous solution at different temperatures and varying concentrations of potassium hydroxide, and (2) to determine by calculation the heat of the reaction.

PREPARATION OF MATERIALS

The greatest difficulty encountered in preparing materials was in the preparation of carbonate-free potassium hydroxide. The general method used was to electrolyze an aqueous solution of a potassium salt using a mercury cathode and a platinum anode. By this method the potassium amalgam was made. Then by reversing the current the amalgam was broken down and the potassium hydroxide obtained.

An attempt was first made to prepare the potassium hydroxide by electrolyzing a saturated solution of potassium oxalate. The saturated solution of potassium oxalate was placed in an electrolytic cell and mercury placed in the bottom of the cell. A platinum anode was suspended in the solution and another platinum wire sealed in a glass tube was placed in contact with the mercury. Electrolysis at 2.5 to 2.7 amperes and 4.5 to 5 volts was carried on for five hours. The solution was then removed from the top of the mercury and the amalgam was washed with cold distilled water until it gave no trace of oxalate when tested with one drop of a 0.01 N potassium permanganate solution. The washed amalgam was then placed in a desiccator into which carbon dioxide-free air was passed and covered with distilled water. The current was reversed using a platinum wire suspended in the solution as the cathode and another platinum wire connected to the amalgam as an anode. The current used was 0.10 to 0.15 amperes and the voltage was 1.0 to 1.2 volts. When the hydroxide had been formed tests were made for the presence of mercuric, mercurous, carbonate, and oxalate ions. The first three were found to be absent but the oxalate ion was present in sufficient quantity to reduce four to five drops of a 0.01 N potassium permanganate solution. This method had to be discarded as unsatisfactory.

The same general method was then used with a saturated solution of high grade potassium hydroxide. The yield of amalgam in this case was too small to permit its use.

Finally it was found that by using a saturated solution of C. P. potassium chloride a very satisfactory amalgam could be prepared and the potassium hydroxide obtained was free from chloride, carbonate, mercurous and mercuric ions. A saturated solution of C. P. potassium chloride was electrolyzed using a platinum anode and a mercury cathode. The lead wire to the mercury was sealed in a glass tube to prevent contact with the solution. The anode was a flat spiral of platinum which was parallel to the surface of the mercury and submerged in the solution to a depth of 2.5 to 3.0 centimeters. The electrolysis was carried on for 4 to 5 hours at 2 amperes and 4.5 volts. The amalgam was removed from the cell and washed with cold distilled water until it gave no trace of chloride ions on testing it with silver nitrate in a nitric acid solution. When the amalgam was washed with cold distilled water very little decomposition took place, but with warm distilled water considerable hydrogen was evolved. The washed amalgam was then placed in a desiccator into which carbon dioxide-free air was passed and was covered with distilled water. A platinum cathode was suspended in the solution and another platinum wire sealed in a glass tube was connected with the amalgam. During the process of breaking down the amalgam to form the potassium hydroxide the current used was 0.10 to 0.15 amperes and 1.2 to 1.5 volts. The low current was used to prevent as much as possible the formation of mercurous oxide. The potassium hydroxide prepared in this manner was approximately 1.5 N and it was diluted with distilled water to obtain the required solutions. The potassium hydroxide solutions were stored in waxed

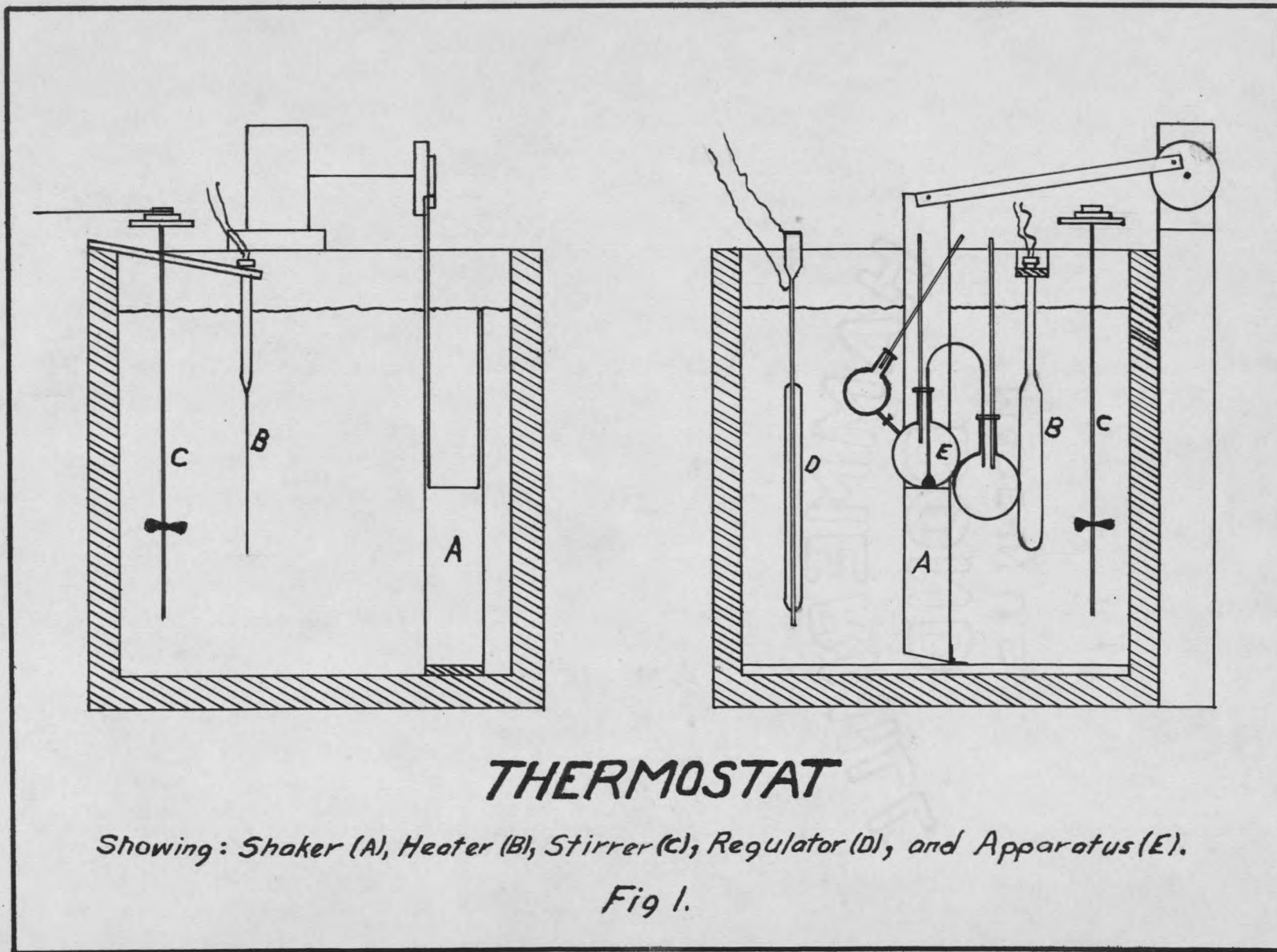
bottles and kept free of carbonate by means of soda lime tubes.

The silver chloride was made by thoroughly mixing an approximately 0.1 N silver nitrate solution with an approximately 6 N hydrochloric acid solution. The precipitated silver chloride was stirred and washed with hot distilled water. The residue was filtered off by means of a filter pump and suction flask. The partially dried silver chloride was then placed in a drying oven held at a temperature of 120° for six hours. The silver chloride thus obtained was finely divided and showed no reduction to free silver. The silver chloride was stored in a dark place until ready for use. In no case was silver chloride used which had stood in the dark room for more than three days.

A thermostat was constructed and insulated by packing excelsior around it. The temperature was controlled by means of a mercury-toluene thermo-regulator and a 500 watt knife heater. A constant stirring kept the temperature the same throughout the apparatus. Figure 1, shows the relative positions of the heater, the thermo-regulator, the shaker, the stirrer, and the reaction apparatus.

To insure thorough mixing the shaker, shown in figure 2, was employed and kept the reacting mixture in constant motion. The shaker was fastened to the bottom of the thermostat by means of a hinge and the bottom of the upright was cut at an angle to allow the backward and forward motion to take place. A strip of wood was connected to the top of the upright and then fastened to a pulley in such a manner that the upright was shaken back and forth as the pulley revolved. The pulley was connected directly to a low speed motor.

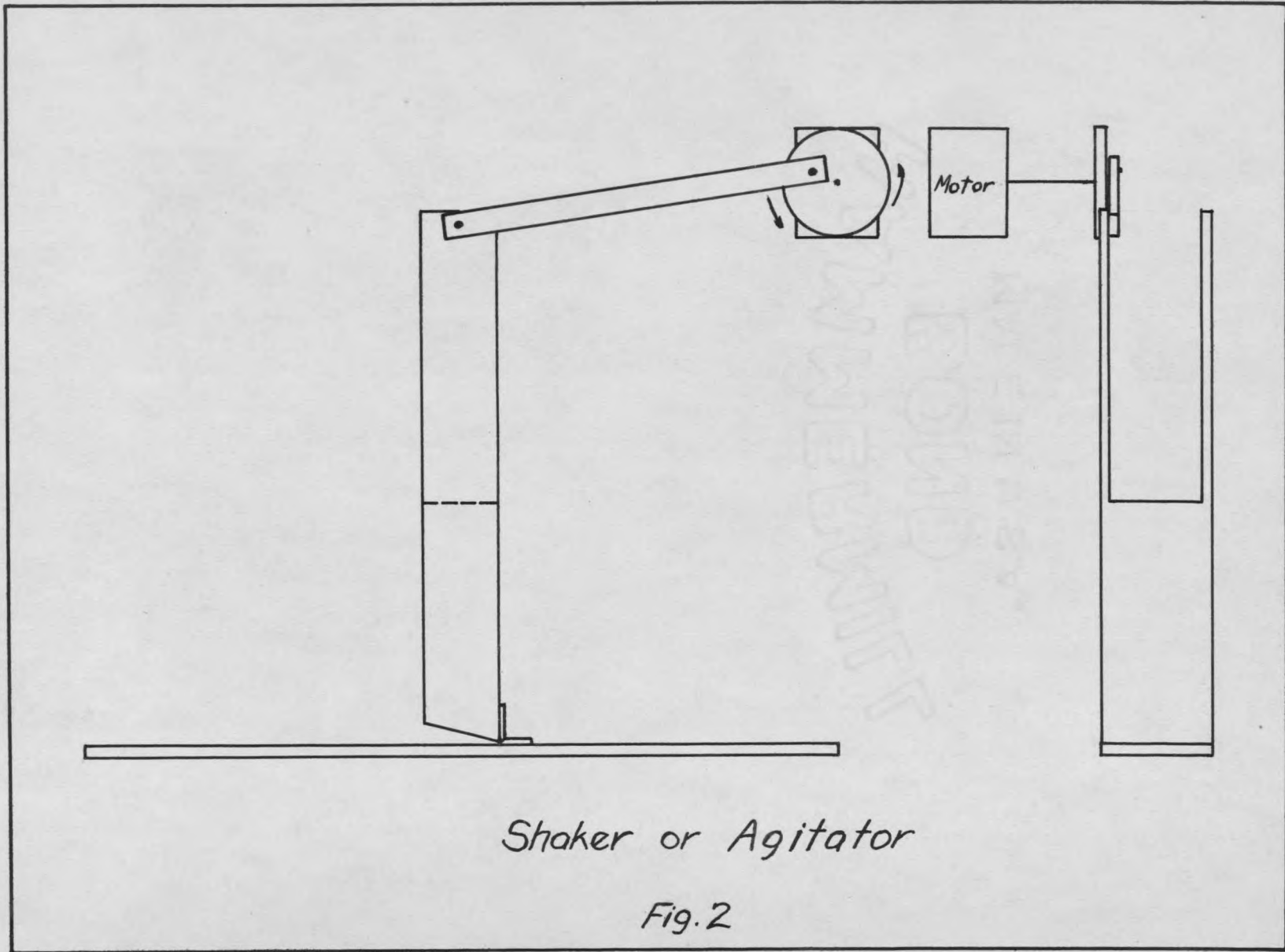


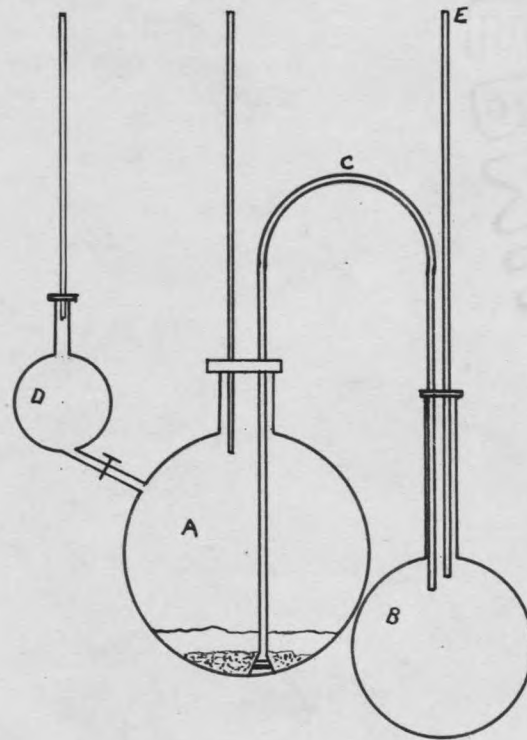


## THERMOSTAT

Showing: Shaker (A), Heater (B), Stirrer (C), Regulator (D), and Apparatus (E).

Fig 1.





*Reaction Apparatus  
Fig. 3.*

The reaction apparatus, figure 3, was designed to facilitate the filtering off of the liquid portions of the reaction mixture without making it necessary to remove the apparatus from the thermostat. The reaction chamber, A, was a 200 cc. round bottom Pyrex flask, the container, D, for the wash water, was a 60 cc. Pyrex florence flask, and the filter flask, B, was a 125 cc. Pyrex round bottom flask. The method of operation will be described under the procedure:

#### PROCEDURE

Twenty-five cubic centimeters of aqueous potassium hydroxide of known concentration were placed in reaction chamber A, figure 3, and an amount of silver chloride which was in excess of the theoretical amount necessary for complete reaction was added. Flask D was filled with distilled water and the whole apparatus was shaken in a thermostat at a constant temperature for a period of time varying from three and one-half to twelve hours. Equilibrium was assumed to have been established when the results of three or more runs, taken over time intervals varying enough to allow for further reaction, showed no variation in the equilibrium constant that could not be accounted for on the basis of experimental error. Obviously, longer time intervals were necessary for the establishment of equilibrium at low temperatures than at high temperatures.

When equilibrium had been reached a filter pump was attached to the tube E, figure 3, and the liquid contents of reaction chamber A were removed to filter flask B by means of tube C which had a Gooch filter plate held in place in the funnel by means of the usual asbestos mat. When all of

the liquid had been removed; the residue was washed with the distilled water from container D. Portions of twenty cubic centimeters each were used for the washing and the mixture was shaken during the washing to insure complete washing. After each washing the liquid in reaction chamber A was removed to filter flask B. The entire apparatus was removed from the thermostat and the liquid portion in the filter flask B was titrated by means of a standardized hydrochloric acid solution which was approximately one-half the normality of the potassium hydroxide used in the reaction. Phenolphthalein was used as an indicator.

As a check on the results, the titrated solution was evaporated on a steam plate and the dry potassium chloride was weighed. The potassium chloride contained a negligible quantity of silver hydroxide and silver chloride. The error introduced is calculated below:

Solubility product<sup>l</sup> of AgOH at 25° is  $1.74 \times 10^{-8}$

Solubility product<sup>l</sup> of AgCl at 25° is  $1.56 \times 10^{-10}$

Mols KOH at equilibrium is .0022

Mols KOH/liter is  $.0022 \times 40 = .088$

$\frac{17.4 \times 10^{-9}}{8.8 \times 10^{-2}} = 1.97 \times 10^{-7}$  mols Ag / liter from AgOH

Mols KCl at equilibrium is .000028

Mols KCl/liter is  $.000028 \times 40 = .00112$

$\frac{15.6 \times 10^{-11}}{1.12 \times 10^{-3}} = 13.9 \times 10^{-8}$  mols Ag / liter from AgCl

$\frac{13.9 \times 10^{-8}}{4 \times 10} = 3.47 \times 10^{-9}$  mols Ag in 25 cc. from AgCl

$\frac{19.7 \times 10^{-8}}{4 \times 10} = 4.925 \times 10^{-9}$  mols Ag in 25 cc. from AgOH

Molecular weight of AgOH is 124.9

$$124.9 \times 4.925 \times 10^{-9} = 4.976 \times 10^{-7} \text{ gms. AgOH}$$

Molecular weight of AgCl is 143.3

$$143.3 \times 3.47 \times 10^{-8} = 6.15 \times 10^{-6} \text{ gms. AgCl}$$

Total weight of AgOH and AgCl is .000006647 gms.

The weighed amount of KCl is 0.2223 gms.

$$\% \text{ error is } .000006647 \text{ divided by } .2223 \times 100 = .00299 \%$$

This shows that the error due to the amount of AgOH and AgCl is less than experimental error and in addition to this if we consider the common ion effect of the silver ion in AgCl the solubility would be even less than that shown above. The error then would be smaller than calculated.

The amount of silver chloride was neglected. The amount of potassium chloride from the titration was calculated and this was subtracted from the weight of the dry potassium chloride obtained. In this manner the amount of potassium chloride from the reaction of silver chloride and potassium hydroxide was found. By dividing the weight of potassium chloride by its atomic weight the mols potassium chloride formed in the reaction were calculated and this value was checked against the total mols of potassium hydroxide used in the reaction (see tables I, II, and III).

This same procedure was used with standardized solutions of potassium hydroxide of various concentrations and at temperatures of 30°, 40° and 50° ± .025°. The temperatures were measured by means of a Beckmann thermometer which was set by means of thermometers guaranteed to meet Bureau of Standards specifications. The data is given on pages 14, 15 and 16.

TABLE I.

Temperature  $30^{\circ} \pm .025^{\circ}$ .

Time of run in hours	Titration cc. .06925 N HCl	Mols KOH at equilibrium	Mols KOH at start. (25cc. sample)	Mols KCl at equilibrium	Wt. of KCl on evaporation in grams	Total mols KCl on evaporation Check column 4	Equilibrium Constant
$3\frac{1}{2}$	32.7	.002264	.002295	.000031	.1792	.002402	.0136*
5	32.75	.002267	.002295	.000028	.1741	.002334	.0123
6	32.75	.002267	.002295	.000028	.1737	.002328	.0123
$5\frac{1}{2}$	32.75	.002267	.002295	.000028	.1742	.002335	.0123

Constant for the 0.0918 N KOH solution ----- .0123

cc. .2655 N

	HCl						
$4\frac{1}{2}$	54.0	.01433	.01452	.00019	1.0997	.01474	.0132
10	54.0	.01433	.01452	.00019	1.1026	.01478	.0132
5	54.02	.01434	.01452	.00018	1.1001	.01464	.0125
4	54.0	.01433	.01452	.00019	1.0855	.01455	.0132
$3\frac{1}{2}$	53.97	.01432	.01452	.00020	1.0973	.01471	.0139

Constant for the 0.5808 N KOH solution ----- .0132

cc. .531 N

	HCl						
$4\frac{1}{2}$	42.45	.02254	.02284	.00030	1.7293	.02318	.0133
5	42.45	.02254	.02284	.00030	1.7269	.02315	.0133
7	42.45	.02254	.02284	.00030	1.7434	.02337	.0133
$3\frac{1}{2}$	42.47	.02255	.02284	.00029	1.7785	.02384	.0128*

Constant for the 0.9137 N KOH solution ----- .0133

\*These values were not used in calculating the mean for the equilibrium constant since in each case the time of the run was shorter and equilibrium may not have been established.

TABLE II.

Temperature  $40^{\circ} \pm .025^{\circ}$ 

Time of Titration run in hours	cc. HCl	Mols KOH at .0629 N equilibrium	Mols KOH at start. (25cc. sample)	Mols KCl at equilibrium	Wt. of KCl on evaporation in grams	Total mols KCl on evaporation Check column 4	Equilibrium constant
6	41.0	.002839	.002907	.000068	.2300	.003083	.0240
7	41.0	.002839	.002907	.000068	.2216	.002971	.0240
6½	41.0	.002839	.002907	.000068	.2243	.003006	.0240
4	40.9	.002837	.002907	.000070	.2234	.002994	.0246*
Constant for the 0.1163 N KOH solution -----							.0240
0.2655 N HCl							
4	53.4	.01417	.01452	.00035	1.0959	.01469	.0247
4½	53.4	.01417	.01452	.00035	1.0900	.01461	.0247
6	53.4	.01417	.01452	.00035	1.0011	.01472	.0247
3½	53.4	.01417	.01452	.00035	1.0951	.01468	.0247
Constant for the 0.5808 N KOH solution -----							.0247
0.531 N HCl							
5	42.0	.02250	.02284	.00054	1.7538	.02351	.0242
4½	42.0	.02250	.02284	.00054	1.7670	.02366	.0242
6	42.0	.02250	.02284	.00054	1.6293	.02318	.0242
7	42.0	.02250	.02284	.00054	1.7397	.02332	.0242
Constant for the 0.9137 N KOH solution -----							.0242

\*This value was not used in calculating the mean for the equilibrium constant since the time of the run was shorter than in the other cases and equilibrium may not have been established.



TABLE III.

Temperature 50° ± .025°

Time of Titration run in hours	cc. .0629 N HCl	Mols KOH at equilibrium	Mols KOH at start. (25cc. sample)	Mols KCl at equilibrium	Wt. of KCl on evaporation in grams	Total mols KCl on évaporation Check column 4	Equilibrium constant
12	31.95	.002213	.002295	.000082	.1732	.02317	.0370
5	31.95	.002213	.002295	.000082	.1723	.02308	.0370
8	31.95	.002213	.002295	.000082	.1729	.02311	.0370
7	31.93	.002212	.002295	.000083	.1737	.02320	.0375*
Constant for the 0.0918 N KOH solution -----							.0370
cc. .2655N HCl							
6	54.2	.01439	.01493	.00054	1.1437	.01533	.0375
9	54.2	.01439	.01493	.00054	1.1332	.01519	.0375
7	54.2	.01439	.01493	.00054	1.1362	.01523	.0375
5	54.15	.01438	.01493	.00055	1.1512	.01542	.0382*
Constant for the 0.5808 N KOH solution -----							.0375
cc. .531 N HCl							
6	45.95	.02440	.02531	.00091	1.9114	.02562	.0373
7	45.95	.02440	.02531	.00091	1.9176	.02570	.0373
8	45.96	.02438	.02531	.00093	1.9197	.02573	.0381
5	45.89	.02439	.02531	.00092	1.9167	.02569	.0377
Constant for the 0.9137 N KOH solution -----							.0376

\*These values were not used in the calculation of the mean for the equilibrium constant since the time of the run was shorter and equilibrium may not have been established.

TABLE IV.

Newton's values at 25° - .02° \*

(For comparison).

Conc. of OH <sup>-</sup> mols/Kg water	Conc. of Cl <sup>-</sup> mols/Kg water	Conc. Ratio Cl <sup>-</sup> / OH <sup>-</sup>
.0939	.000852	.00907
.1011	.000925	.00915
.1098	.000981	.00893
.1072	.000944	.00881
.1038	.000973	.00937
.0997	.000921	.00924
.0978	.000875	.00895
Average for solutions approximately 0.1 N -----		.00905
.0529	.000471	.00889
.0542	.000483	.00891
.0520	.000465	.00894
.0531	.000481	.00906
.0536	.000485	.00905
Average for solutions approximately 0.05 N -----		.00897

\* These values were taken from the Journal of the American Chemical Society 50, 3258 (1928).

The equilibrium constants determined from the data show that the concentration of the potassium hydroxide has little or no effect on the equilibrium. The constants are in close agreement with each other and experimental error may easily take care of the differences found.

Calculation of the equilibrium constant:

The reaction we are considering may be written



The mass-action expression for this reaction is then written

$$\frac{C_{\text{KCl}} \cdot C_{\text{AgOH}}}{C_{\text{KOH}} \cdot C_{\text{AgCl}}} = K$$

The AgCl, AgOH, and Ag<sub>2</sub>O which is undoubtedly present are all in the solid form and are very insoluble as was shown earlier in the discussion. On the basis of this their concentration is practically a constant and can be included as such in the constant K. When the common ion effect is considered the amount of these salts in solution is so small that it is negligible and with stronger concentrations of potassium hydroxide the solubility decreases to a greater extent. Many attempts have been made to determine the solubility of these salts but the values given by various experimenters vary so widely that the agreement is in magnitude only. Errors are so large due to the small amount of these salts that go into solution that the values are almost useless and will remain so until more accurate methods of analysis can be developed. The silver hydroxide and the silver chloride in the above equation will then be considered as constant and the new mass-action equation will be written

$$\frac{C_{\text{KCl}}}{C_{\text{KOH}}} = K'$$

The mols of potassium hydroxide which is added at the start of

the reaction is known and by titration with a standard hydrochloric acid solution at equilibrium the mols of potassium hydroxide at equilibrium may be determined. The difference in these amounts will then be the mols of potassium chloride formed in the reaction. The equilibrium constant is then obtained by dividing the concentration of potassium hydroxide in mols per liter into the concentration of potassium chloride in mols per liter at equilibrium.

A review of the tables will show that the constant obtained for the 0.0918 N KOH solution at  $30^{\circ} \pm .025^{\circ}$  is the only one that varies to any great extent from the values with the other concentrations at the same temperature. The total concentrations of potassium hydroxide and potassium chloride are used in calculating the constants. This involves the assumption that these substances are 100% dissociated in solution, an assumption which certainly can not be justified either from the standpoint of the older electrolytic dissociation theory or from that of the newer interionic attraction theory as applied to strong electrolytes.

While it is realized that the activities or "effective concentrations" of the ions involved in this equilibrium should be used in calculating the values of the equilibrium constants the difficulty attending the evaluation of the individual activities in such a system are great enough to preclude such a calculation at this time.

However, using the hypothesis of the independent activity coefficients of the ions<sup>2</sup>, viz, -- "In dilute solutions the activity coefficient of any ion depends solely upon the total ionic strength of the solution" -- and using the data given in the same reference for hydroxyl and

chloride ions at ionic strength of 0.1 molal solution as being comparable with the 0.0918 N KOH solution used in this work it is found that the activity of the hydroxyl ion is 0.81 and that of the chloride ion is 0.79. This means that only 0.81 of the total hydroxyl ion concentration measured analytically is effective at equilibrium and that only 0.79 of the total chloride ion as measured analytically is effective at equilibrium. In other words only 0.81 of the hydroxyl ions potentially available and 0.79 of the chloride ions potentially available in solution are actually involved in the equilibrium.

This means that in order to arrive at the more exact value of the equilibrium constant where the 0.0918 N KOH solution is involved the equilibrium constant given in the tables should be multiplied by  $0.79/0.81$ . This would give a series of values running about 2.5% lower than those tabulated above.

The hypothesis of the independent activity coefficients of the ions stated above contains the rather vague phrase "dilute solutions". In a case like this some explanation of the phrase seems necessary. Lewis and Randall<sup>2</sup> comment as follows, "When we use the rather vague phrase "dilute solutions" in a case like this we mean that the principle as stated approaches complete validity as the dilution is indefinitely increased. It becomes then a matter of experiment to determine at what concentrations such a principle may be regarded as valid within certain limits of permissible error, say 1%." With such an interpretation it is our belief that the hypothesis is correct over the same range as our previous rule of mixture, namely, up to an ionic strength of a few hundredths to a few tenths, according to the nature of

the ions. The degree of departure in concentrated solutions doubtless depends upon numerous factors, such as the amount of hydration of the ion."

While this rule can be applied in solutions corresponding to the 0.0918 N KOH solution used here it is doubtful if it can be extended to include even approximately 0.5 N KOH solutions although further experimentation in connection with this work may show that the "few tenths" of the above quotation may prove to be as many as five tenths. This is a possibility to which we can do no more than call attention at this point.

Because of the uncertainty involved in attempting to evaluate the activities of the ions in the more concentrated solutions it is felt that it is better to present the actually determined values of total concentration of the ions from which the necessary activity data can be obtained as soon as a suitable and satisfactory treatment of the concentrated solutions of the strong electrolytes are available. It is possible that this data is available<sup>7</sup> for all the concentrations involved but considerable work will have to be done in order to arrive at values which will apply to the exact concentrations and temperatures involved in this study. It is again emphasized that sufficient data are available<sup>2</sup> for the 0.0918 N KOH solution and possibly also for the 0.5808 N and the 0.9137 N KOH solutions and when taken together with the data of this paper, would allow of a calculation of the equilibrium constants in terms of the more significant activity ratios.

#### THE HEAT OF THE REACTION

In the study of the chemical kinetics of a reaction nothing is of more interest or of more importance than the energy changes involved in the

action. The chemical energy involved in a chemical reaction carried out under the conditions of this study (namely, in solution and under conditions where none of the reactants appear as volatile gases, and no light is absorbed or liberated and no electrical energy is absorbed or liberated) is absorbed or evolved almost entirely in the form of heat.

For a long time it was assumed that the heat evolved in a chemical reaction was a direct measurement of the chemical affinity of the various reactants for each other, that is, if a large amount of heat was liberated in a reaction there was a large affinity displayed by the reacting atoms or molecules. On the other hand if small thermal effects accompanied a reaction the atoms or molecules involved were said to have small affinity. While this is known to be true only in a qualitative sense and another physical quantity the change in free energy of a system, is to be taken as the quantitative measure of chemical affinity, the thermal effects accompanying chemical change are still of prime importance. In fact the whole study of chemical thermodynamics and of thermo-chemistry is based upon the heat changes accompanying chemical reaction.

Calculation of the heat of the reaction:

A very important equation is used for calculating heats of reaction from the equilibrium constants measured at two different temperatures and it was derived by van't Hoff. The unintegrated expression has the following form:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant, T the absolute temperature, R the molar gas constant and  $\Delta H$  the heat of the reaction.

This expression can be integrated if  $\Delta H$  is constant to give the following form:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \cdot \frac{T_2 - T_1}{T_2 T_1}$$

where  $K_2$  is the equilibrium constant at temperature  $T_2$  and  $K_1$  is the equilibrium constant at temperature  $T_1$ , and  $R$  and  $\Delta H$  have the same significance as before, and are measured in calories.

By means of this equation it is possible to calculate the heat of the reaction if the equilibrium constants at two different temperatures are known, or if the equilibrium constant at one temperature and the heat of the reaction are known, the equilibrium constant at another temperature may be calculated. In most cases, however,  $\Delta H$  is not constant over a very long temperature range so that one must be careful not to apply the equation over excessively large temperature intervals. The temperature interval usually employed is  $10^\circ \text{C}$ , it having been found that the equation holds fairly well due to the fact that the value of  $\Delta H$  does not change greatly in such an interval. It is emphasized, however, that the equation is strictly applicable only in cases where  $\Delta H$  is a constant, that is, where a plot of the logarithms of the equilibrium constants against the reciprocal of the corresponding absolute temperatures is a straight line. For cases where  $\Delta H$  is not a constant the accuracy of the data calculated from the equation becomes increasingly more accurate as the temperature interval decreases.

When the equilibrium constant data of this paper are substituted into the equation it is found that  $\Delta H$  is far from constant, but it is found to decrease quite rapidly as the temperature rises.



The heat of the reaction was calculated as shown in the sample calculation given below:

Referring to the table on page 25 for the 0.0918 N KOH solution at 30° to 40°  $\pm$  .025° the values may be obtained for  $T_2$ ,  $T_1$ ,  $K_2$  and  $K_1$ . Substituting these values in van't Hoff's equation isochore we have

$$2.303 \log \frac{.0240}{.0123} = \frac{\Delta H}{2} \frac{313 - 303}{313 \times 303}$$

Upon solving the above equation for  $\Delta H$  we have

$$\Delta H = \frac{4.606 (\log .0240 - \log .0123) 303 \times 313}{313 - 303}$$

$$\Delta H = 12,656 \text{ calories per mol.}$$

The following table contains the values of the heat of the reaction at different temperatures as calculated from the data of this paper and from the value of  $K$  obtained by Newton<sup>3</sup> at 25°  $\pm$  .02°.

TABLE V.

Calculated heat of the reaction:

30° to 40°  $\pm$  .025°

KOH Solution	$K_2$	$K_1$	$T_2$	$T_1$	Heat of reaction calories / mol
0.0918 N	.0240	.0123	313	303	12,656
0.5808 N	.0247	.0132	313	303	11,871
0.9137 N	.0242	.0133	313	303	11,351

40° to 50°  $\pm$  .025°

0.0918 N	.0370	.0240	323	313	8,735
0.5808 N	.0375	.0247	323	313	8,441
0.9131 N	.0376	.0242	323	313	8,889

30° to 50° ± .025°

KOH Solution.	K <sub>2</sub>	K <sub>1</sub>	T <sub>2</sub>	T <sub>1</sub>	Heat of reaction calories / mol
0.0918 N	.0370	.0123	323	303	10,756
0.5808 N	.0375	.0132	323	303	10,220
0.9137 N	.0376	.0133	323	303	10,177

Newton's data for 0.1 N and .05 N KOH solutions at 25° ± .02°

Author's data for 0.0918 N and .5808 N KOH solutions at 30° ± .025°

KOH Solution	K <sub>2</sub>	K <sub>1</sub>	T <sub>2</sub>	T <sub>1</sub>	Heat of reaction calories / mol
Approx. 0.1 N	.0123	.00905	303	298	11,035
Newton 0.05 N	----	.00897	---	298	
Author 0.5808 N	.0132	-----	303	---	*13,916

\* In this calculation the constant obtained by Newton for the 0.05 N solution was used as shown above with the constant obtained by the author for the 0.5808 N solution. It appears that this comparison can be made since the concentration of the solution seems to have such a small effect on the equilibrium. The value .00897 was substituted for K<sub>1</sub> and the corresponding absolute temperature T<sub>1</sub> is 298° The value .0132 was substituted for K<sub>2</sub> and its corresponding absolute temperature is 303°. The value obtained for the heat of the reaction seems to agree fairly well with the values obtained at the other temperatures.







