A METHOD FOR MEASURING THE ACTIVITY OF SALTS

IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS

By

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I. INTRODUCTION

INTRODUCTION

The chemical potential, or partial molal free energy, of any component in a liquid solution is related to its chemical potential in some reference solution of the components at the same temperature and pressure by the equation

$$u = u^O + RT \ln a \qquad (1)$$

u = chemical potential of component in solution

u^O = chemical potential of component in reference solution

a = activity of component in solution relative to its

activity in the reference solution.

This equation, applied to a solute, may be written in terms of the molal concentration, m, of the solute through the introduction of a parameter known as the activity coefficient, γ, defined as

$$a = \gamma m \qquad (2)$$

The introduction by G. N. Lewis of the activity function and the activity coefficient into the thermodynamic treatment of solutions has resulted in the development of a set of relations which can be applied to non-ideal solutions independently of the factors producing the deviations[1]. As a result of the general usefulness of activities in solution thermodynamics, the evaluation of activity coefficients has constituted a very important area of experimental investigation.

References to methods for determining the activity coefficient of the solute in two-component liquid solutions are readily found in standard reference works on chemical thermodynamics[2]. These methods may be classified dependent upon whether it is a property of the solvent or of the solute that is measured. Since there seems to be no method ideally appli-

cable to all solutions, each method must be considered in relation to its suitability for the system under investigation.

Of the methods depending upon measurement of a property of the solvent, one of the simplest in principle is the measurement of the vapor pressure. If the solute is relatively nonvolatile (as in the case of a salt dissolved in water), the vapor in equilibrium with the solution will be essentially that of the solvent only. The chemical potential of the solvent and its vapor pressure in the solution is then related to its potential in a reference solution by the well-known transformation of equation (1)

$$u_1 = u_1^0 + RT \ln p_1/p_1^0 \qquad (3)$$

$p_1/p_1^0 =$ activity of the solvent.

Knowing values of the ratio p_1/p_1^0 as a function of the solute molality permits the computation of the chemical potential of the solvent as a function of the solute molality. By means of yet another useful equation in thermodynamics, known as the Gibbs-Duhem[3] relation, the chemical potential of the solute is related to the chemical potential of the solvent as follows:

$$n_1 \, du_1 + n_2 \, du_2 = 0 \qquad (4)$$

$n_1 =$ moles of component 1

$n_2 =$ moles of component 2

$u_1 =$ chemical potential of component 1 in the solution

$u_2 =$ chemical potential of component 2 in the solution.

Aside from the experimental and mathematical difficulties in the evaluation and use of the quantities in equations 1 - 4, the problem is straightforward in its solution.

The experimental methods for the measurement of the lowering of the vapor pressure of a solvent may be classified into five groups: direct

static, direct dynamic, transpiration, dew-point, and isopiestic.

In the direct static method[4], a mixture of known composition is placed in an evacuated container and the pressure directly read with a manometer. The accuracy of this method is limited by both the amount of dissolved air and other impurities which may be present, and the difficulty encountered in measuring the pressure exactly.

The direct dynamic method[5] consists of boiling a liquid at a fixed temperature by adjusting the external pressure and condensing the vapor for analysis. Superheating and change in the boiling point during the collection of a sample make temperature measurement difficult. Further difficulty is encountered in quantitatively condensing and analyzing the vapor.

In the transpiration method[6], a measured amount of inert gas is saturated with the vapors of the liquid by passing the gas through a series of saturators and analyzing the vapors to determine their partial pressures. The experimental difficulties involved are: completely saturating the inert gas with the vapors of the liquid being measured, constructing a gas-tight apparatus, and absorbing the vapors for analysis.

The dew-point method[7] is also available for determining vapor pressure and consists of cooling the vapor to a point where it starts to condense. This method is limited to binary solutions of nonvolatile solutes because of the difficulty in finding surfaces which would separately indicate the dew-points of two volatile components as in a mixed solvent.

In the isopiestic method[8], two vessels containing different concentrations of solute in the same solvent are placed in a closed space and, because the vapor pressures of the two solutions are different, solvent will distill from one vessel into the other until the vapor pressures of

the solutions are the same. If the vapor pressure of one solution is known accurately at all compositions, then the vapor pressure of the isopiestic solution can be found. The chief difficulty with this method is the time required to reach equilibrium, but this has been overcome by Robinson and Sinclair[8] by selecting a solution having a known vapor pressure close to the one being examined. This method is capable of high precision.

In the case of a liquid solution of three components consisting of a solvent and two solutes, a knowledge of the chemical potential of the solvent as a function of the composition of the solution is not sufficient to determine the activity of the other components since the extended Gibbs-Duhem equation relating the chemical potentials now has the form

$$n_1 \, du_1 + n_2 \, du_2 + n_3 \, du_3 = 0$$

This equation has three variables of which two are completely independent. Consequently, many of the methods available for measuring the activity of a solute which have been found useful in the case of binary solutions by study of some property of the solvent related to its chemical potential are not applicable to ternary solutions. Indeed the problem is theoretically and experimentally far more difficult, and those methods which have been applied in a few cases are subject to rather severe limitations. Examples of some of these methods which may be used under special conditions are ion-exchange resin equilibria[9], partition of salts between immiscible solvents[10], and electromotive force studies[11].

The extended Gibbs-Duhem equation for a three-component system in principle can be made the basis for the estimation of the activity of a salt in concentrated aqueous solutions of hydrochloric acid by the measurement of the partial pressures of water and hydrogen chloride in equilibrium with the solution. Consider equation (5). By dividing each term by n_1

and setting the ratio of n_2/n_1 equal to a constant, k, one obtains

$$du_1 + kdu_2 + n_3/n_1\, du_3 = 0 \qquad (6)$$

Equation (6) can be written to show the variation of chemical potential with respect to n_3, the number of moles of the nonvolatile component:

$$\left(\frac{\partial u_1}{\partial n_3}\right)dn_3 + k\left(\frac{\partial u_2}{\partial n_3}\right)dn_3 + \frac{n_3}{n_1}\left(\frac{\partial u_3}{\partial n_3}\right)dn_3 = 0 \qquad (7)$$

Substitution into equation (7) of the relations between the chemical potential and the equilibrium partial pressure and activities of the volatile and nonvolatile components, respectively, gives

$$\left(\frac{\partial \ln p_1}{\partial n_3}\right)dn_3 + k\left(\frac{\partial \ln p_2}{\partial n_3}\right)dn_3 + \frac{n_3}{n_1}\left(\frac{\partial \ln a_3}{\partial n_3}\right)dn_3 = 0 \qquad (8)$$

Consider now a function, ϕ, defined by

$$\phi = \ln p_1 p_2^k = \ln p_1 + k \ln p_2 \qquad (9)$$

Differentiation of ϕ with respect to n_3 gives

$$d\phi = \left(\frac{\partial \ln p_1}{\partial n_3}\right)dn_3 + k\left(\frac{\partial \ln p_2}{\partial n_3}\right)dn_3 \qquad (10)$$

It can be seen by comparison of equations (8) and (10) that equation (8) can be rewritten as

$$d\phi = -\frac{n_3}{n_1}\left(\frac{\partial \ln a_3}{\partial n_3}\right)dn_3 \qquad (11)$$

Integration of equation (11) leaves

$$\frac{n_1}{n_3}\int_{\phi'}^{\phi''} d\phi = -\int_{a_3'}^{a_3''} d\ln a_3 \qquad (12)$$

It can be seen from equation (12) that from a knowledge of the equilibrium partial pressure of both water and hydrogen chloride as a function of the concentration of the nonvolatile salt at constant water/acid composition, k, the relative activity of the salt can be calculated.

Aside from the necessity of performing a graphical integration of equation (12) and preliminary treatment of the data to best perform this integration, the main problem involved is the experimental one of obtaining the vapor pressure lowerings of the HCl-H_2O "mixed solvent" by the salt.

Of the several ways of determining vapor pressures, the transpiration or gas-saturation method was considered to be the best adapted to measure the vapor pressure lowerings in a salt-H_2O-HCl system. Based on practical considerations the hydrochloric acid solutions should be sufficiently concentrated to have a measurable vapor pressure of hydrogen chloride and water, and the salt solution must be concentrated enough to cause detectable change in the partial pressures from their values when no salt is present. The method is therefore limited to acid concentrations in excess of seven molal where there is a significant vapor pressure of hydrochloric acid.

If a measured volume of inert gas is saturated with the vapors of a two-component solvent, and the vapors analyzed for the volatile components, the partial pressures can be determined by the following calculations.

By Dalton's law of partial pressures, which holds within experimental limits for pressures of one atmosphere,

$$P = P_1 + P_2 + P_3$$

P = total pressure

P_1, P_2 = partial pressures of the components in the mixed solvent

P_3 = partial pressure of inert gas.

If the vapors behave as ideal gases, then their partial pressures are proportional to their mole fractions

$$P_1 = \frac{n_1}{n_1 + n_2 + n_3} \, P$$

P_1 = the partial pressure of component 1

n_1, n_2, n_3 = moles of gases

P = external pressure

The experimental problems offered by the method are then: (1) to accurately measure the moles of gas saturated, (2) to selectively absorb the vapors of the "mixed" solvent, and (3) to completely saturate the gas.

II. PURPOSE AND SCOPE OF INVESTIGATION

PURPOSE AND SCOPE OF THE INVESTIGATION

Because of the increasing importance of organic solvent extraction processes involving aqueous solutions of inorganic salts, fundamental studies on the nature of such processes are of practical importance. Aqueous hydrochloric acid solutions of many salts have been found to partition the metal salt favorably into the organic phase in cases where no partition occurs in the absence of the acid. It is, therefore, essential to have data on the activity of these salts in hydrochloric acid solutions in gaining a better understanding of this phenomenon.

This investigation was undertaken to provide an apparatus which could be used in obtaining activity data through a measurement of the vapor pressure lowering of hydrochloric acid-water mixtures by salts. The gas saturation apparatus of Pearce and Snow[6] was suitably modified, and preliminary experiments were made employing pure water and aqueous hydrochloric acid solutions.

III. EXPERIMENTAL

EXPERIMENTAL

APPARATUS

The gas-saturation method as applied in this work involved the electrolytic generation of a measured amount of hydrogen and oxygen gas which was passed first through a pre-saturator maintained at a temperature approximately five degrees higher than the final saturation temperature, and finally through eight saturators in a constant-temperature bath maintained at 30°C. The exit vapors were selectively absorbed in a suitable train, and the increase in weight of the absorbers was measured. From the observed increase in weight the number of moles of vapors carried in the exit gas stream and hence the mole fractions were calculated.

Gas Generators: Originally six electrolysis cells, shown in Figure I, were constructed using three-liter, wide-mouth bottles a filled to within one-half inch of the bottom of the rubber stopper with 25% sodium hydroxide solution prepared from C.P. sodium hydroxide. The electrodes b were made from electrolytic nickel sheet, 9 cm. x 6 cm. x 0.1 cm., and were suspended by nickel wire leads which were welded to the nickel sheet. The leads were enclosed in pyrex glass tubes inserted through the stopper. These tubes were fused to the nickel leads at the bottom, and filled with sealing wax at the top. The electrodes inside the bottle were separated by a glass cylinder c extending through the middle two-thirds of the solution to prevent catalytic recombination of the hydrogen and oxygen. The tops of the stoppers were coated with sealing wax and finally painted with Fisher "Sealit" paint.

The first several calibration attempts, using distilled water, gave vapor pressure values for distilled water which were from two to five percent lower than the accepted value. Since the original cells were
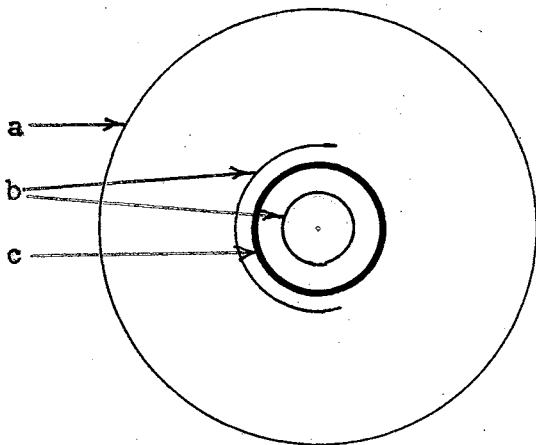
FIGURE I

Original Gas Generators
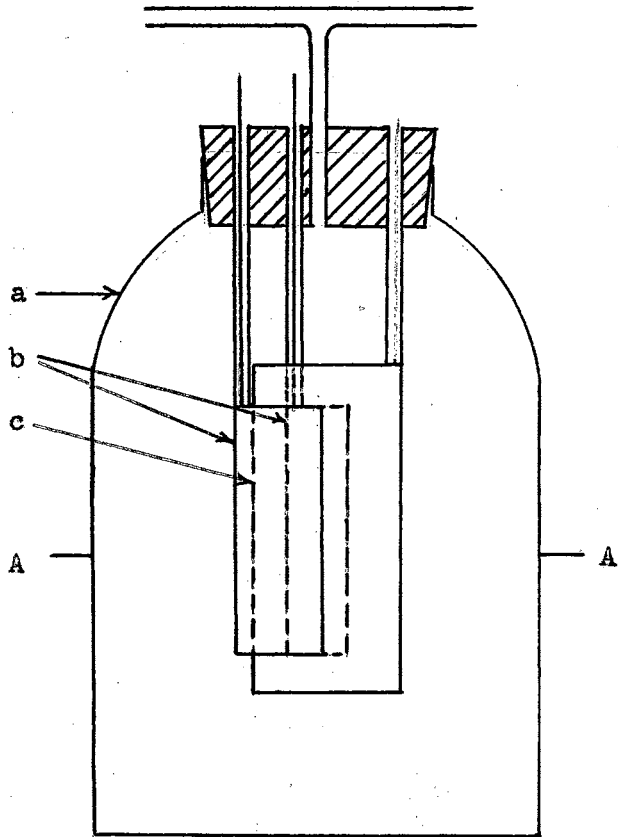
a   3-liter bottle

b   nickel electrodes

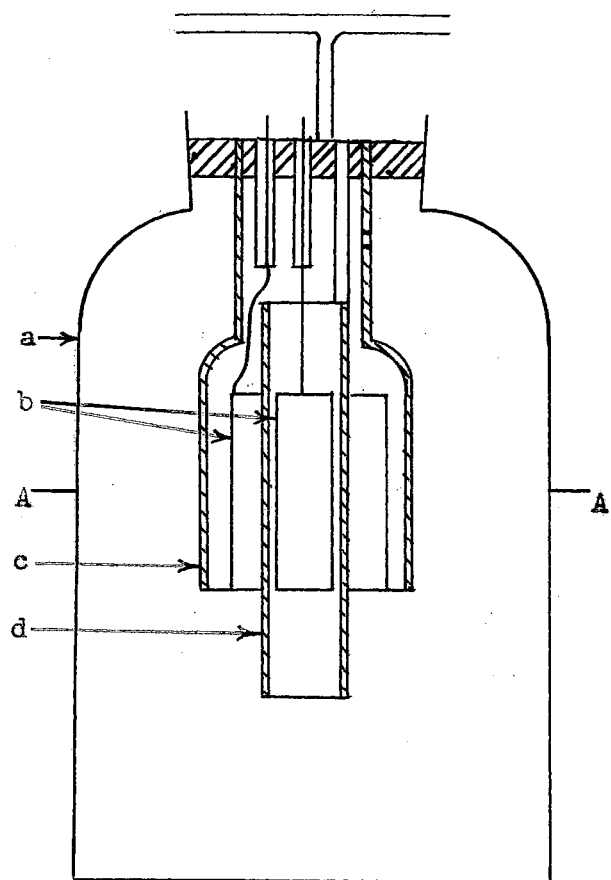c   glass cylinder

Cross section A-A

constructed of amber glass, changes in the appearance of the electrodes passed unnoticed. No mention of difficulty in the use of similar electrodes had been mentioned in the work of Pearce and Snow[6]. Later in carefully checking the apparatus to find the source of the errors a black deposit was observed on the cathode. This deposit was analyzed and found to contain nickel, probably as metallic nickel. Upon further experimentation it was found that a black deposit was formed on the anode at higher current densities. Attempts to remove the trouble by electrodepositing a fresh nickel surface were unsuccessful, and the nickel electrodes were abandoned in favor of platinum gauze electrodes since no electrode reaction except the formation of hydrogen and oxygen could be tolerated.

The final design of the electrolysis cells which proved to be entirely satisfactory is illustrated in Figure II. Six two-liter, wide-mouth bottles a were filled to within two inches of the bottom of the stopper with 20% sulfuric acid. The platinum electrodes b were of the conventional type used in electroanalysis and were suspended by platinum wire leads enclosed in two mm. capillary tubing. The tubing was inserted through the cork stopper and sealed at the bottom with polystyrene since all attempts to fuse the heavy platinum leads into soft glass were unsuccessful. The electrodes were separated by a glass cylinder c extending through the middle two-thirds of the solution to prevent catalytic recombination of the hydrogen and oxygen. The electrodes, exit tube, and glass cylinder were enclosed in a second glass cylinder d fitted with a pyrex wool plug at the upper end. A hole was blown in the side of this cylinder to allow equalization of the pressure in the electrolysis cell. The first experiments using platinum electrodes and H_2SO_4 had shown that the sulfuric acid
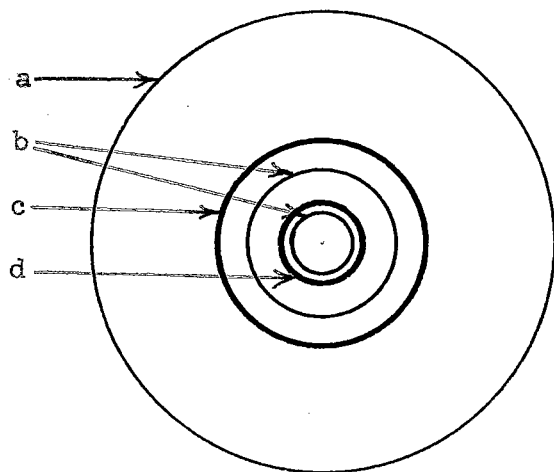
FIGURE II

Final Gas Generators

Cross Section A-A

a 2-liter bottle

b platinum electrodes

c glass cylinder

d glass cylinder

spray on the bottom of the stopper readily diffused through the holes where the electrode tubes were inserted and attacked the sealing material, thus causing the cell eventually to leak. A flat cork stopper was selected of the proper size so that it could be countersunk one-fourth inch into the mouth of the bottle. All glass tubing, except for the exit tube, was then brought out flush with the top of the stopper. The capillary tubes were filled with mercury and a copper wire inserted into the mercury. The recess above the stopper was now filled with a thick coating of "Picein" and heated with an infrared lamp to bake out trapped air. A mercury manometer was attached to the manifold tube of the gas generators. After a pressure had been built up by the generation of gas, the apparatus was left to stand for four hours to check for leaks. No detectable change in pressure was noted.

Saturators: The saturators, shown in Figure III, were of the type used by Pearce and Snow[6]. These were made from 38 mm. x 300 mm. pyrex test tubes a, into one end of which was sealed at a slight inclination a 9 mm. tube b containing a 7 mm. bubbling tube c drawn down to a 2 mm. capillary tip. A hole d was blown in the bottom of the 9 mm. tube, just behind the tip of the capillary, to promote stirring. Each saturator was provided with an 8 mm. tube e to permit filling and cleaning and was made gas-tight by means of a mercury seal f. A lead-weighted inverted cup completed the seal. The overall length of each saturator was 23 cm. and its approximate volume was 250 cc.

The saturator train consisted of a pre-saturator kept in a separate constant-temperature bath and two sets of four saturators. Each set of four saturators were glass sealed together, and the connections between the pre-saturator and the two sets were made with ball-and-socket joints.

FIGURE III

Saturator
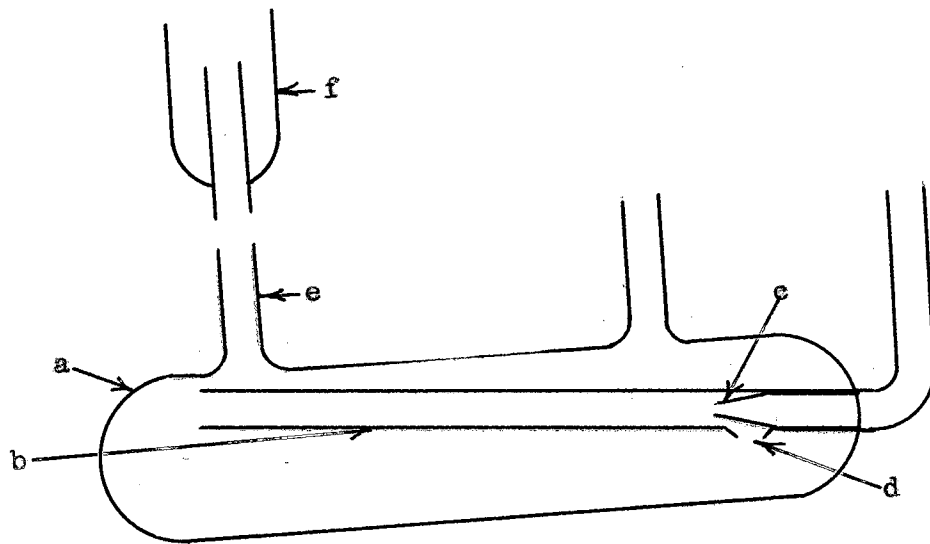
a 38 mm. x 300 mm. pyrex test tube

b 9 mm. pyrex tube

c 7 mm. bubbling tube

d hole to promote stirring

e 8 mm. pyrex tube

f mercury seal

Coulometer: Considerable thought was given to methods for measuring the volume of the inert carrier gas. To obtain the accuracy of 0.1% desired, some method of electrical generation seemed necessary since electrical measurements are capable of high precision. The quantity of gas used in each experiment was measured by measuring the quantity of electricity needed to generate the gas by means of a silver coulometer of the type suggested by Rosa, Vinal and McDaniel[12]. This coulometer has the advantages of being simple to construct and having an accuracy of at least 0.2%.

The silver coulometer used in this work is shown in Figure IV. It consisted essentially of a one-liter beaker a; a silver cylinder b, 10 cm. x 8 cm. x .08 cm.; and a platinum cylinder c, 10 cm. x 5 cm. x 0.004 cm. The platinum cylinder was suspended in a ten percent solution of reagent grade silver nitrate by means of a watch glass d to which a glass rod had been fused at the center. A glass cylinder e was suspended between the two electrodes with its lower end just beneath the surface of the solution to serve as a barrier in preventing any floating silver particles from reaching the platinum electrode. Ordinarily, in exact coulometric work, reagent grade silver nitrate is purified by recrystallizing from a nitric acid solution and fusing the crystals for several minutes at $300^{\circ}C$. Rosa and Vinal[12], however, report an error of only three parts in ten thousand when using reagent grade silver nitrate in their coulometers. The accuracy of 0.1% sought in this investigation, therefore, would allow the use of this simple form of the silver coulometer employing reagent grade silver nitrate.

In the first several trials a simple copper coulometer was used although it was recognized that the desired accuracy could not be obtained

FIGURE IV

Silver Coulometer
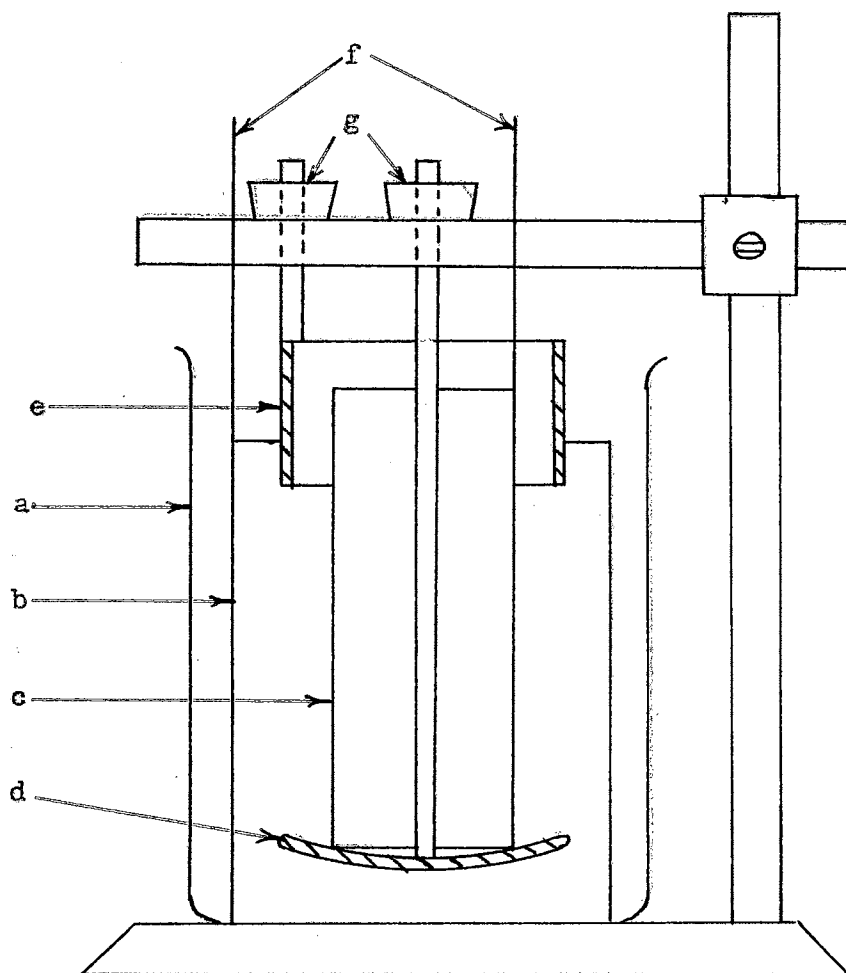
a   1-liter pyrex beaker

b   silver electrode

c   platinum electrode

d   watch glass

e   barrier

f   electrode leads

g   rubber stoppers

from the instrument. When the parts for the silver coulometer became available, the copper coulometer was discarded.

Absorbents: After investigating the possible absorbents which would selectively absorb hydrochloric acid and water vapors, it was decided to use anhydrous magnesium perchlorate and "Ascarite". Anhydrous magnesium perchlorate is reported as being as efficient as phosphorus pentoxide in absorbing water vapor at gas rates of not more than five liters per hour and is a suitable drying agent for hydrochloric acid vapors because of its neutral nature[13]. Several tests were conducted to determine if the magnesium perchlorate could remove the water vapor without affecting the hydrochloric acid vapor. Air was bubbled rapidly through a seven molal solution of hydrochloric acid and then passed first through an absorber containing anhydrous magnesium perchlorate, and finally through an absorber containing both "Ascarite" and anhydrous magnesium perchlorate. The gas from the last absorber was bubbled through a solution of dilute silver nitrate to test for the presence of hydrogen chloride. At the end of eight hours the silver nitrate solution was examined against a dark background, and no silver chloride precipitate was visible. Similarly the magnesium perchlorate was dissolved in distilled water, treated with dilute silver nitrate, and allowed to stand for one hour. No silver chloride precipitate was visible when examined against a dark background.

The absorption tubes as shown in Figure V were made by removing the curved portions of U-shaped 150 mm. glass-stoppered drying tubes, and sealing the two straight portions together. A heating coil of nichrome wire was wrapped around the mercury seal of the last saturator to prevent condensation in the arm of the first absorber.

FIGURE V

Absorber
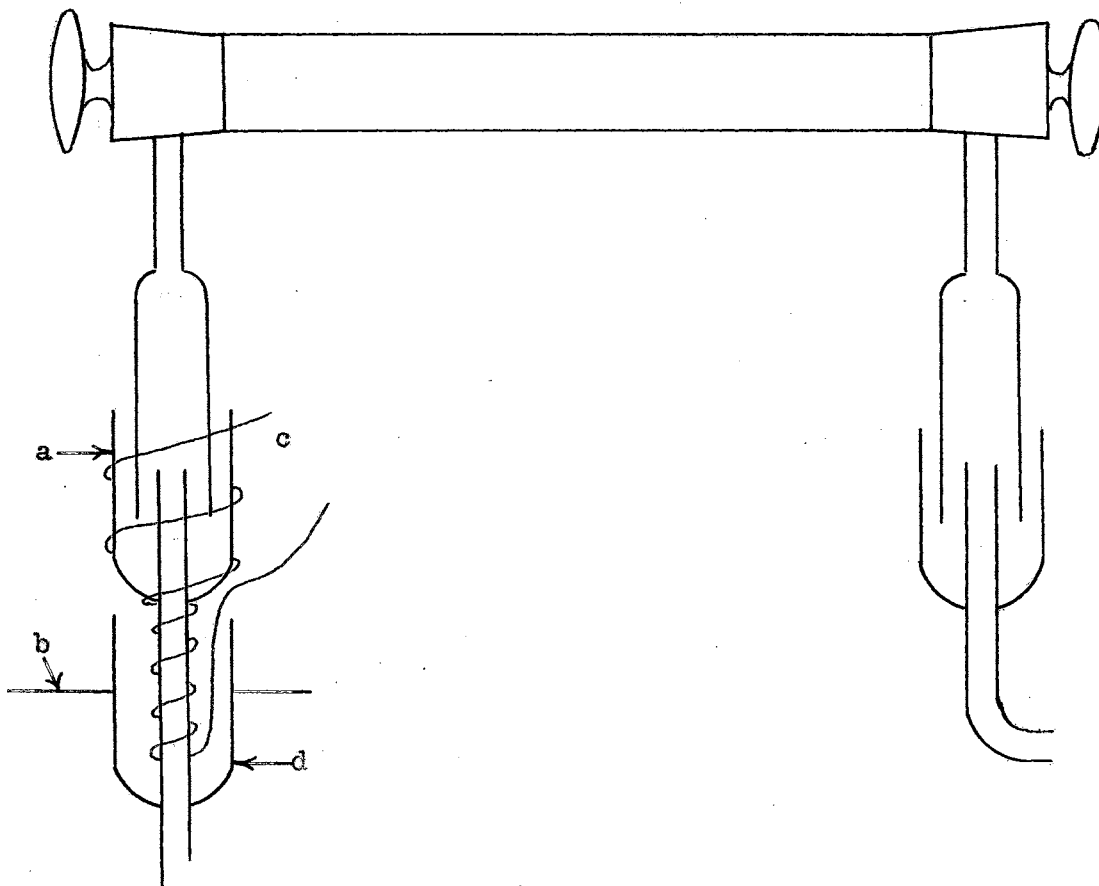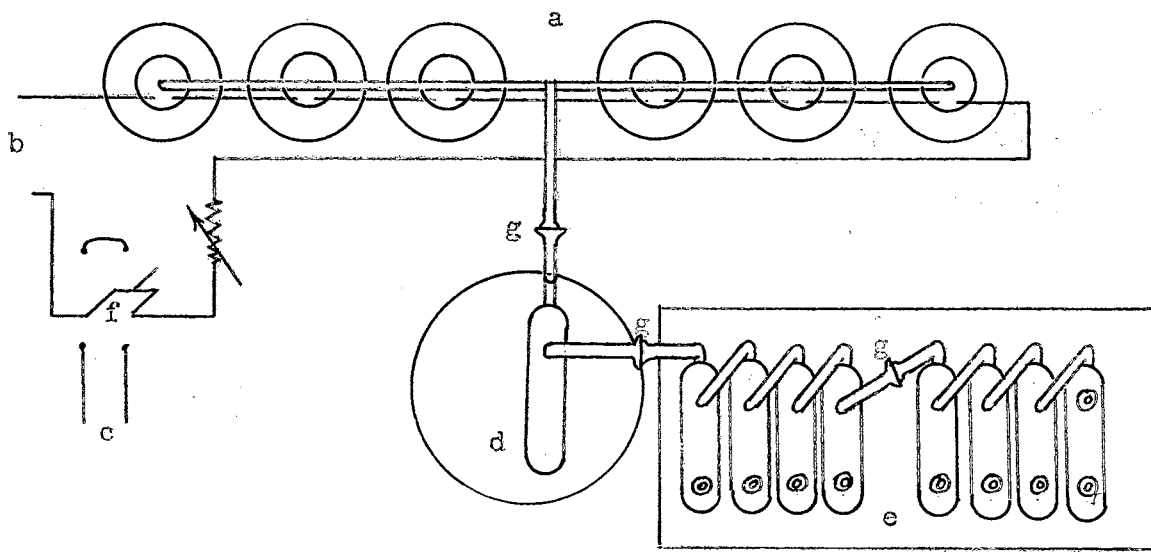

a   mercury seal on last saturator

b   water level

c   heating coil

d   protection tube for heating coil

FIGURE VI

Assembled Apparatus
(Absorption train not shown)

a   electrolysis cells

b   leads to power supply

c   leads to coulometer

d   pre-saturator

e   saturators

f   double-pole, double-throw switch

g   ball-and-socket joint

Top View

Front View
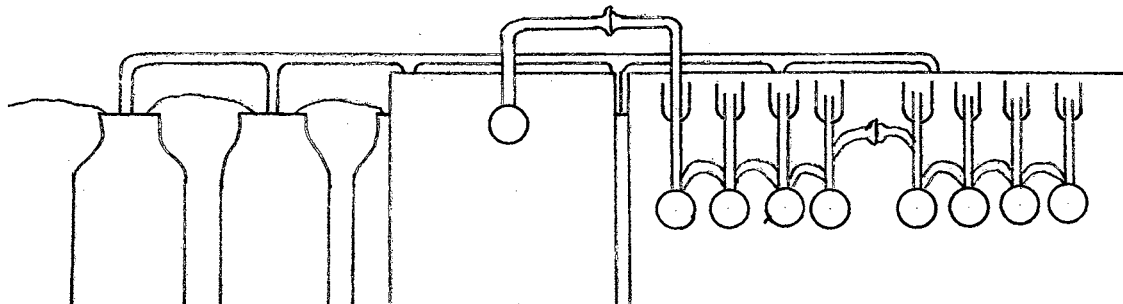
Miscellaneous parts: The temperature of the water bath was controlled by a "Thermocap" capacitor-type electronic relay and set to the desired temperature with a thermometer graduated to 0.05° which was calibrated with Bureau of Standards' thermometer No. 87266. Temperature regulation was $\pm 0.02^{\circ}$C.

The water bath was heated with a 75-watt light bulb connected to the "Thermocap" electronic relay, and cooled by running tap water directly into the bath. Constant water level was maintained with an automatic siphon.

The power supply for the electrolysis cells consisted of four six-volt automobile storage batteries connected in series with a rheostat and milli-ammeter for current regulation.

EXPERIMENTAL PROCEDURE

Gas was first passed through the saturators for a period of one hour to allow the system to come to equilibrium. The circuit was then opened, the coulometer assembled, the absorbers attached, and the calibration started. At the end of the experiment the circuit was opened, the coulometer disassembled, and the absorbers removed. The platinum coulometer electrode was placed in a half-liter beaker and rinsed several times with distilled water until the rinse water gave no test for silver. The rinse water was removed by siphon, leaving only a few ml. of water after each rinse which was examined for particles of silver. The coulometer electrode was finally dried in an oven at 120°C. for two hours. The absorbers were wiped with a chamois skin, placed in the balance case overnight, and weighed in the morning. All weighings were made to an accuracy of 0.2 mg.

The silver deposited on the platinum electrode was replated onto the silver electrode by reversing the polarity of the coulometer and using a small current of approximately 0.3 amperes. After the silver was replated, the silver electrode was heated with an air torch until the silver crystals just began to fuse. This treatment made the silver much more resistant to mechanical disintegration on use.

The barometric pressure readings were made at intervals of one-half hour during the run, averaged, and then corrected to 0°C. and 45° latitude.

Calculations of partial vapor pressures were made in the following manner:

$$P_1 = \frac{n_1}{n_1 + n_2 + n_3} P$$

P_1 = partial vapor pressure of component 1

n_1 = moles of component 1

n_2 = moles of inert gases

n_3 = moles of component 2

P = corrected atmospheric pressure.

One faraday of electricity generated 0.75 mole of gases in each electrolysis cell according to the reaction

$$e^- + H_2O \longrightarrow \tfrac{1}{2}H_2 + \tfrac{1}{4}O_2$$

or a total for six cells of 4.5 moles of gas. Therefore, for every equivalent of silver plated, there were a total of 4.5 moles of gases generated.

TABLE I

Results of Calibration with Copper Coulometer

Calibra-tion Exp.	Current Amps.	Gr. of H_2O	Moles of H_2O	Gr. of Cu	Moles of Inert Gas	Total Moles of Gas	Press. Corr. mm.	Vapor Press. H_2O mm.	Time of Exp. hrs.	Rate of Gas Flow cc/sec.
1	0.98	0.2168	0.0120	2.6392	0.3736	0.3856	738	22.95	2.75	2.64
2	0.90	0.4305	0.0239	3.8993	0.5521	0.5759	734	30.45	4.33	2.40
3	0.78	0.3011	0.0167	2.6466	0.3747	0.3914	734	31.33	3.39	2.15
4	0.95	0.3223	0.0179	3.9320	0.5567	0.5746	740	23.02	3.50	3.07
5	1.05	0.3470	0.0193	4.3530	0.6163	0.6355	734	22.42	3.42	3.56

Notes: (1) Calibration experiments #1, #4, and #5 made at 25°C.

(2) Calibration experiments #2 and #3 made at 30°C.

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TABLE II

Results of Calibration with Silver Coulometer

Calibration Exp.	Current Amps.	Gr. of H_2O	Moles of H_2O	Gr. of Ag	Moles of Inert Gas	Total Moles of Gas	Press. Corr. mm.	Vapor Press. H_2O mm.	Time of Exp. hrs.	Rate of Gas Flow cc/sec.
6	0.47	0.2199	0.0122	6.7369	0.2810	0.2932	737	30.66	3.56	0.49
7	0.59	0.2951	0.0164	12.5206	0.5227	0.5386	737	22.40	4.66	0.69
8	0.39	0.0685	0.0038	4.7269	0.1972	0.2010	740	13.99	3.00	0.41
9	0.53	0.4742	0.0263	14.2774	0.5956	0.6219	735	31.11	6.66	0.56
10	0.37	0.3511	0.0495	10.4757	0.4370	0.4565	734	31.32	7.00	0.39
11	0.24	0.1947	0.0108	6.1670	0.2572	0.2583	737	30.81	5.34	0.30
12	0.25	0.2283	0.0127	7.5644	0.3155	0.3282	740	28.56	7.51	0.31
13	0.31	0.2543	0.0141	7.8985	0.3295	0.3436	737	30.28	6.32	0.32
14	0.30	0.3938	0.0219	11.9511	0.4985	0.5204	739	31.03	9.99	0.32
15	0.36	0.3664	0.0203	9.5122	0.5290	0.5494	738	27.31	6.56	0.42
16	0.25	0.4189	0.0233	10.1245	0.5631	0.5863	734	29.10	10.05	0.34
17	0.23	0.2983	0.0166	10.0209	0.4877	0.5042	736	24.16	10.81	0.33
18	0.24	0.1224	0.0068	3.5966	0.2000	0.2068	736	24.98	3.72	0.31

Notes: (1) All calibration experiments made at 30°C. except #7 which was made at 25°C.

(2) Nickel electrodes replaced after calibration experiment #12.

(3) Electrolysis cells completely redesigned after calibration experiment #18.

	TABLE III	TABLE IV
	Vapor Pressure of H_2O at 30 C.	Partial Pressures of H_2O and HCl at 30°C.
Calibration Exp.	19	20
Current Amps.	0.19	0.19
Gr. of H_2O	0.2951	0.1529
Gr. of HCl	———	0.0140
Moles of H_2O	0.0161	0.0085
Moles of HCl	———	0.0004
Gr. of Ag	8.7195	8.4656
Moles of Inert Gas	0.3637	0.3531
Total Moles of Gas	0.3801	0.3620
Pressure Corrected mm.	738	742
Time of Exp. hrs.	11.39	11.06
Rate of Flow cc/sec	0.20	0.20
Vapor Press. of H_2O mm.	31.78	17.38
Literature value, vapor press. of H_2O at 30°C.	31.82	17.37[*]
Vapor Press. of HCl mm.	———	0.76
Literature value, vapor press. of HCl mm.	———	0.69[**]

[*] Partial pressure of H_2O at 30°C. obtained from data of Akerlof and Teare[14], Robinson and Stokes[15].

[**] Partial pressure of HCl at 30°C. obtained from data of Bates and Kirschmann[16].

IV. DISCUSSION

DISCUSSION

The results of the calibration experiments are given in tables I-IV. It can readily be seen that the first efforts to calibrate the apparatus by employing pure distilled water in the saturators gave results which were consistently low. At first it was believed the error might be due to the use of a copper coulometer the accuracy of which is limited by the reaction

$$Cu^{++} + Cu \longrightarrow 2Cu^{+}$$
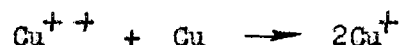
However, the substitution of the silver coulometer failed to improve the accuracy.

Electrochemical changes on the nickel electrodes of the gas generators would account for some of the low results since some electrical energy would be used in bringing the changes about and hence this quantity would not be available for the generation of hydrogen and oxygen. While this doubtless contributed to the error, the amount of this contribution could not be estimated, and the redesign employing platinum electrodes in sulfuric acid eliminated this source of error completely.

Probably the chief source of error in the measurements occurred in the leakage of gas, particularly hydrogen. Confinement of hydrogen under pressure is not easy in as extensive an apparatus as was employed here and over the extended period of time (approximately ten hours) required for each run. After several changes in the design the final apparatus described earlier was found to be satisfactorily gas-tight.

"Ascarite" and anhydrous magnesium perchlorate were found to be very satisfactory in selectively absorbing hydrochloric acid vapors and water vapors. In future work, it would be worthwhile to determine the minimum length of absorbent necessary to quantitatively absorb the vapors and

thus reduce the back pressure of the absorption tubes to a point where it could be neglected.

No difficulty was experienced in handling the silver coulometer if the previously mentioned technique was followed. The acidity of the silver nitrate solution increased slightly with each calibration attempt, indicating the possible need to purify the silver nitrate crystals and use conductivity water in making the coulometer solution.

In table III is presented the comparison between the experimental values of the vapor pressure of water and the literature value. The agreement is quite satisfactory, being a little greater than 0.1%.

In table IV is contained the experimentally measured partial pressures of both water and hydrogen chloride above a 7.284 molal hydrochloric acid solution. The agreement is again quite satisfying. In obtaining the partial pressure of water from the literature, the experimental data of Akerlof and Teare[14] were consulted to obtain the partial molal heat contents needed to convert from $25^{\circ}C$. to $30^{\circ}C$. the water activities calculated from the osmotic coefficient of Robinson and Stokes[15]. The partial pressure of hydrogen chloride was taken from the direct measurements of Bates and Kirschmann[16] who also used the transpiration method in their work. Although the agreement is not as good, the experimental uncertainty in both this work and in theirs is large since the partial pressure of the HCL is quite small. The agreement is, however, within the experimental uncertainty.

Although time did not permit further calibration experiments on solutions of higher HCl molality nor the application of the vapor pressure lowerings of HCl and H_2O by a salt to the measurement of solute activities,

the apparatus seems to be sufficiently reliable to permit such measure-
ments; however, the values (as in the case of activities determined by
vapor pressure lowerings in general) would likely not be highly precise.
Nevertheless, since no other methods are available for obtaining
activities in such solutions, this type of data would be very useful.

V. SUMMARY

SUMMARY

1. A transpiration apparatus was constructed which can be used in obtaining activity data through measurement of the vapor pressure lowering of hydrochloric acid-water mixtures by salts.

2. Anhydrous magnesium perchlorate and "Ascarite" were entirely satisfactory as absorbents.

3. The problem of hydrogen leakage was eliminated by properly redesigning the gas generators.

VI. BIBLIOGRAPHY

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BIOGRAPHY

Russell David Ring, son of Harry Ring and Rose Johnson Ring, was born in Oak Park, Illinois, September 22, 1924. He attended the public schools in Chicago, Illinois, graduating from Carl Schurz High School in June, 1942. After working one year as an apprentice machinist he served two and one-half years in the Army of the United States. Following his discharge in February, 1946, he returned to his previous employment. In July, 1946, he was married to Beverly Ann Johanson and has a son and daughter.

He enrolled in Coe College, Cedar Rapids, Iowa, in September, 1947, and received his Bachelor of Arts degree in July, 1950. He spent one year of graduate study at Oklahoma Agricultural and Mechanical College in Stillwater, Oklahoma, completing the requirements for a Master of Science degree. During this time he was employed as a graduate fellow.

Typed by Beverly A. Ring