

The System Aniline-Acetone-Water
The Affinity Constant of Aniline in
Acetone-Water Mixtures.

by

Edith Margaret Brown B.Sc.

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To Dr. A. N. Campbell who suggested the problem dealt with herein, and who directed and very kindly assisted in this work, the thanks and appreciation of the writer are offered.

(1) Introduction.

The true values of the affinity constants of organic bases are still a matter of considerable doubt. J. N. Pring, (1) after an extensive study of the determination of the affinity constants of bases, states

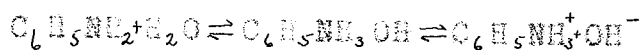
"The data at present available on the affinity constants of bases are derived from measurements made by a number of workers employing different methods such as conductivity, avidity or the competition of two bases for a limited quantity of acid, catalysis, the change in solubility produced on the addition of an acid, and the amount of hydrolysis of salts of the bases with a strong acid as measured by the concentration of free bases acquired in a layer of benzene. On comparing the different results many discrepancies are observed. The methods are all more or less indirect and it is not clear that the different properties such as solubility or catalytic relations are not affected by the operation of other factors which are not understood and are not allowed for. In cases where a series of bases has been investigated by the same method, the results may at most be expected to have a comparative value among themselves which will not strictly apply when the measurements are compared with another series determined by other methods. Though basicity can be regarded as the indirect manifestation of some definite electrical feature of the molecule it does not appear certain that an absolute standard can be determined. The hydroxyl ion concentration which normally defines the basicity cannot be measured in exactly the same medium in the different cases. The presence

of undissociated bases, for instance, affects the dielectric properties of the solvent, the degree of hydration of the ions as probably such factors as association which, apart from the operation of mass action, determine the apparent concentration of hydroxyl ions and modify in a marked manner the so-called dissociation 'constant'."

Fring attempted direct measurements with the hydrogen electrode and the quinhydrone electrode but found that direct methods failed owing to two main difficulties. Of these, he says

"In practice, two difficulties arise in determining low values of hydrogen ion concentration in a solution which is not buffered (i.e. the hydrogen ion concentration of which is not stabilized.). The first is the difficulty of avoiding contamination by the containing vessel and the second is the high resistance of the solution which makes a sharp balance on the potentiometer impossible."

A second objection to the existing values arises in the fact that the measurements are made not of the true basicity constant but of the apparent basicity constant thereby assuming that the whole of the base exists in solution in the hydroxylated form. Thus aniline is assumed to exist entirely in aqueous ^{solution} as $C_6H_5NH_2OH$. In reality, however, two equilibria are involved in an aqueous solution of aniline.



It was thought that these objections might be overcome, the first by using highly purified materials in silica apparatus and by lowering the resistance by bringing the

standard electrode very close to the indicator electrode, and the second by determining the apparent basicity constant in increasing concentration of aniline and extrapolating backward to obtain the true basicity constant, i.e. the apparent basicity constant at an infinite dilution where the ratio of total aniline to the true base would approach unity. Also it was thought that by using other electrodes than the hydrogen and quinhydrone, such as the manganese hydroxide and glass electrodes, more satisfactory results might be obtained.

Therefore in this work attempts were made at direct determination of the affinity constant of aniline in acetone-water mixtures using indicators and electrometric measurements with the hydrogen, manganese hydroxide, and glass electrodes.

Before measurements of hydrogen ion concentration can have any significance it is necessary to know the relative proportions of aniline, acetone and water present in all possible solutions at the temperature of the experiment, viz. 30 C. Therefore a complete study of the system aniline-acetone-water was undertaken.

(2) A Phase Rule Study of the System Aniline-acetone-Water.

(a) Theoretical Considerations.

When two liquids are brought together, they may mix in all proportions and form one homogeneous liquid phase; or only partial miscibility may occur and two phases be formed consisting of two mutually saturated solutions. In the latter case the concentration of the components and also the vapour pressure of the system have, at a given temperature, perfectly definite values.

In the case of three liquid components, a similar behavior may be found, although complete miscibility of three components with the formation of only one liquid phase is of much rarer occurrence than in case of two components. When only partial miscibility occurs, various cases are met with according as the three components form one, two or three pairs of partially miscible liquids. Further, when two of the components are only partially miscible, the addition of the third may cause either an increase or a diminution in the mutual solubility. An increase in the mutual solubility is generally found when the third component dissolves readily in each of the two; but when the third component dissolves only sparingly in the other two, its addition diminishes the mutual solubility of the latter.

In the system aniline-acetone-water there is only one pair of partially miscible liquids, viz. aniline and water, and acetone is very readily soluble in both aniline and water. Therefore this case only will be considered.

The system A. B. C., where A. and B. are the partially

miscible pair, is represented on an equilateral triangle (Fig. a) according to the method of Roozebaum (2).

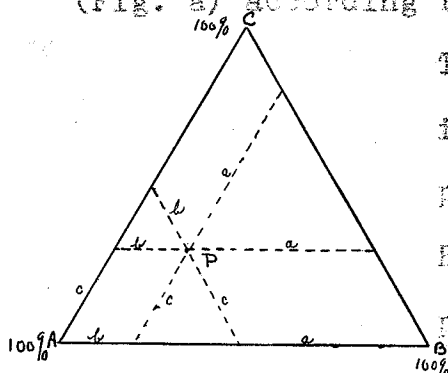


Fig. a.

The composition of a ternary mixture is obtained by determining the distance parallel to the sides of the triangle. Each side is divided into one hundred parts and by plotting the percentage composition of two components the third

is automatically obtained.

If A. is shaken with a larger quantity of B. than it can dissolve, two layers will be formed consisting one of a saturated solution of A. in B. and the other of a saturated solution of A. in B.

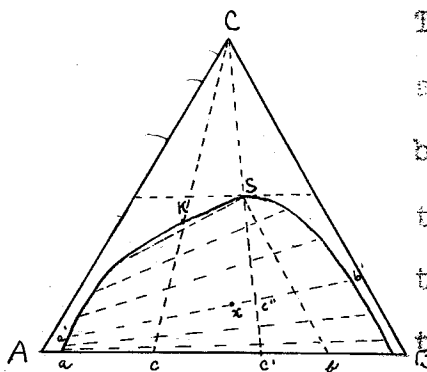


Fig. b.

The composition of these two solutions at a temperature of $y^{\circ}C$. will be represented by the points s and b in Fig. b. If C. is then added it distributes itself between the two liquid layers and two conjugate ternary solutions, consisting of A., B. and C. are thereby produced which are in

equilibrium with one another, and the composition of which will be represented by two points within the triangle. In this way a series of pairs of ternary solutions will be obtained by the addition of C. to the mixture of A. and B. By this addition, since C. is readily soluble in A. and B. not only do the two liquid phases become increasingly rich in C. but the mutual solubility of A. and B. increases. By the

continued addition of C., the composition of the successive conjugate solutions in equilibrium with one another becomes more nearly the same, and a point K. is at length reached at which the compositions of the two solutions become identical. This will therefore be a critical point. Increased addition of C. beyond this point will lead to a single homogeneous solution.

The points on the branch aK. represent compositions of solutions relatively rich in A., those on the curve bK. the compositions of solutions relatively rich in B., and the points on these two branches representing conjugate solutions are joined together by "tie lines". Thus the points a',b' represent conjugate solutions, and the line a'b' is a tie line.

Since C., when added to a heterogeneous mixture of A. and B. does not enter in equal amounts into the two layers, but in amounts depending on its coefficient of distribution between A. and B., the tie lines will not be parallel to A. B. but will be inclined at an angle. Also since the distribution constant will not remain constant because, apart from other reasons, the mutual solubility of A. and B. is altered by the addition of C., the angle will change with increasing amounts of C. Finally the tie lines shrink to a point when the conjugate solutions become identical. For the reason that the tie lines are not, in general, parallel to the side of the triangle, the critical point at which the tie line vanishes will not be at the summit of the curve but somewhere below this as represented by the point K.

The curve aKb forms then the boundary between the

heterogeneous and homogeneous systems. A mixture of A., B. and C. represented by any point outside the curve aKb will form only one homogeneous phase; while any mixture represented by a point within the curve, will separate into two layers having the composition represented by the ends of the tie line passing through that point. Thus, a mixture of the total composition x, will separate into two layers having the composition a and b respectively.

Since, according to the phase rule of Gibbs $F = C - P + 2$ where F is the degree of freedom, C the number of components and P the number of phases present, three components existing in three phases (two liquid and one vapour phase) constitute a bivariant system, the final result, i.e. the composition of the two layers and the total vapour pressure, will not depend merely on temperature as in the case of a two component system, but also on the composition with which we start. At constant temperature, however, all mixtures, the compositions of which are represented by points on one and the same tie line, will separate into the same two liquid phases, although the relative amounts of the phases will vary. If we omit the vapour phases the condition of the system will depend on the pressure as well as on the temperature and the composition of the initial mixture. By keeping the pressure constant, e.g. at atmospheric pressure (by working with open vessels), the system again becomes bivariant. We see, therefore, that the position of the curve aKb will vary with the temperature, and only with the temperature, if we assume either constancy of

pressure or the presence of a vapour phase. Since at the critical point, the condition is imposed that the two liquid phases become identical in composition, one degree of freedom is lost, and therefore only one degree of freedom remains. The critical point, therefore depends on temperature and only on temperature, always on the assumption, of course, that the pressure is constant or that a vapour phase is present. Fig. b, therefore represents an isothermal at $y^{\circ}\text{C}$.

The composition of the different ternary solutions obtained by the addition of C. to a heterogeneous mixture of A. and B. will depend on the composition of the initial mixture of A. and B. as well as the amount of C. added. If we start with a mixture of A. and B. corresponding to the point c' and add increasing amounts of C., the total compositions of the different ternary systems, which will be obtained, must lie on the line Cc' since the relative amounts of A. and B. cannot undergo alteration. These will break into conjugate solutions represented by the ends of the tie lines through these points. Finally at the point S. a homogeneous solution will be obtained. This point is not the critical point where the composition of the two solutions are identical but merely a point at which the amount of one liquid layer has been reduced to nought and only one solution remains. In order that addition of C. shall lead to the critical mixture, it is necessary to start with a binary mixture in the proportion given by the point c. Therefore it is evident that the amount of C. required to produce a homogeneous solution, will

depend on the relative amounts of A. and B. in the initial mixture, and can be ascertained by joining the corner C. with the point in the line A. B. representing the total composition of the initial binary system and determining the concentration of C. where this line cuts the curve akb .

As the temperature changes the boundary curve of the heterogeneous system will also alter. In order to represent this alteration, we make use of the right prism, in which the temperature is measured upward.

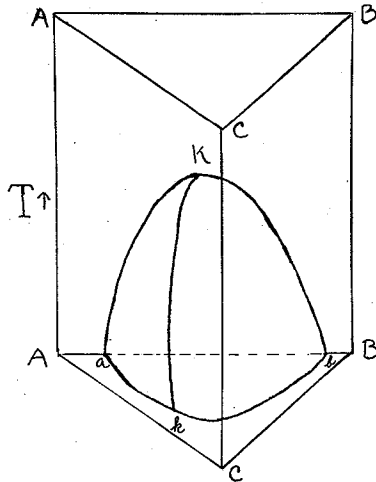


Fig. c.

The boundary curve becomes in this way a boundary surface as shown in Fig. c. The curve akb is the ternary isothermal and the curve aKb shows the change in the binary system A. B. with temperature with a critical point at K. The curve Kk is a critical curve joining together the critical points of the different isothermals. In such a case as is shown in Fig. c. there is no

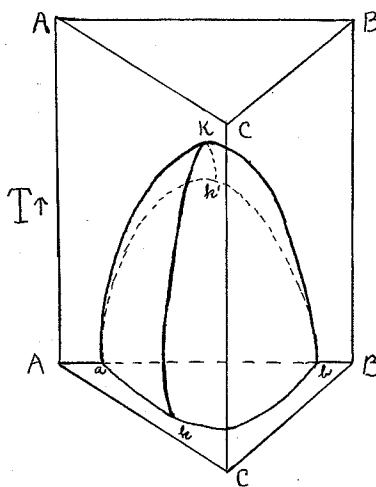


Fig. d.

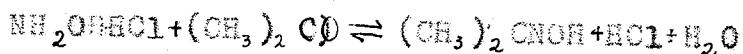
critical temperature for the ternary system. In Fig. d however, a real ternary critical point is found. In this figure akb is an isothermal, $ak'b$ is the curve for the binary system and K. is the ternary critical point. All points outside the helmet-shaped boundary surface represent homogeneous solutions while all points within represent ternary heterogeneous mixtures.

(b) Experimental.

The system aniline-acetone-water was studied in order to ascertain the relative proportions of aniline, acetone and water in all possible solutions at the temperature at which the hydrogen ion concentration were determined, viz. 30° C. Therefore the isothermal at this temperature was first determined.

The three liquids in appropriate proportions were stirred together in a flask in a thermostat bath at 30° C. for twenty-four hours. The aniline present was always more than sufficient to saturate the aqueous layer. After a concentration of about 10% acetone in the total mixture the density of the aniline layer became so reduced by absorption of acetone that the aniline and aqueous layers changed places.

The aniline in both layers was determined by direct titration with $\frac{N}{7}$ HCl using Congo red paper as indicator. The acetone was determined in both layers by a modification of the method of Marasco (3). This method makes use of the reaction of acetone with hydroxylamine hydrochloride.



This reaction however does not proceed to completion but reaches an equilibrium and the constant, actual, apparent amount of acetone must be determined by titrating with weighed quantities of acetone.

The sample is added to an excess of neutral hydroxylamine solution containing methyl orange and the HCl released titrated with $\frac{N}{10}$ NaOH using methyl orange as indicator.

In this experiment however, aniline was present and reacted with the HCl released. Therefore the residual aniline was determined by titration with $\frac{N}{10}$ HCl using Congo red paper as indicator as before. The difference between them, the amount of HCl required for the first titration and that required for the second, gives the amount of HCl released. If excess HCl was released this was determined by titration with $\frac{N}{10}$ NaOH using methyl orange as indicator. The amount of HCl released is then equal to that required by the first titration for aniline added to the amount neutralized by the NaOH used.

The constant was determined for the ratio actual: apparent acetone present using both acetone solutions alone and acetone solutions, acetone solutions containing varying amounts of aniline. It was found that the aniline did not affect the equilibrium in any way. The constant was found to be 1.025 as compared to 1.055 as obtained by Marasco.

The results are contained in Table 1. and are represented graphically in Fig. 1. The points from the binary system curve were obtained from the binary system as given in Seidell (4).

Table 1.

<u>Saturated Aqueous Layer.</u>			<u>Saturated Aniline Layer.</u>		
<u>Aniline.</u>	<u>Acetone.</u>	<u>Water.</u>	<u>Aniline.</u>	<u>Acetone.</u>	<u>Water.</u>
3.35	0	96.65	95.25	0	4.75
3.81	.422	95.767	91.5	3.68	4.82
3.964	.906	95.13	90.04	4.509	5.451
4.15	2.64	93.21	83.19	9.735	7.075
3.85	7.08	98.07	72.66	5.5	11.85
4.105	9.57	86.325	65.5	25.15	9.35
4.27	12.78	82.95	59.39	30.03	10.58
6.1	21.03	72.87	48.32	37.48	14.2
8.78	25.11	66.11	40.13	39.45	20.42
12.95	31.56	55.42	28.83	40.5	30.67
→ 21.1	36.6	42.3	21.1	36.6	42.3

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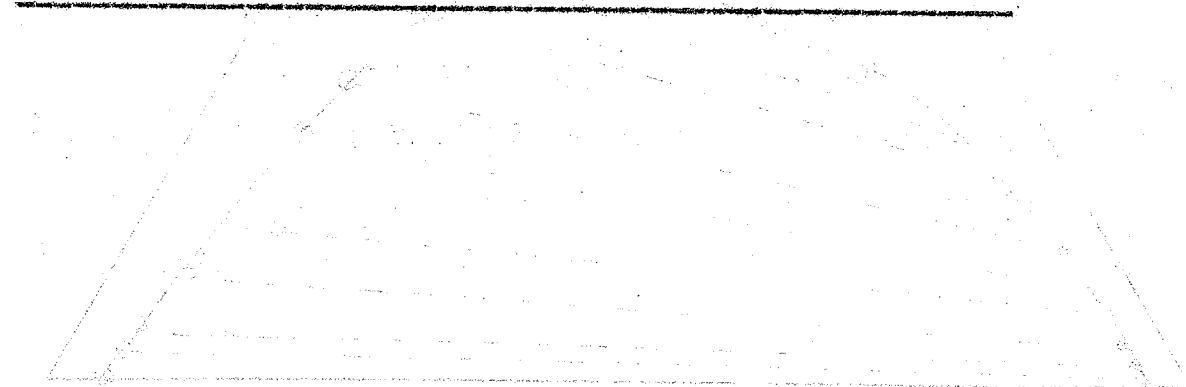


Fig 1

a - Aniline layer
 b - Acetone layer
 c - Critical point

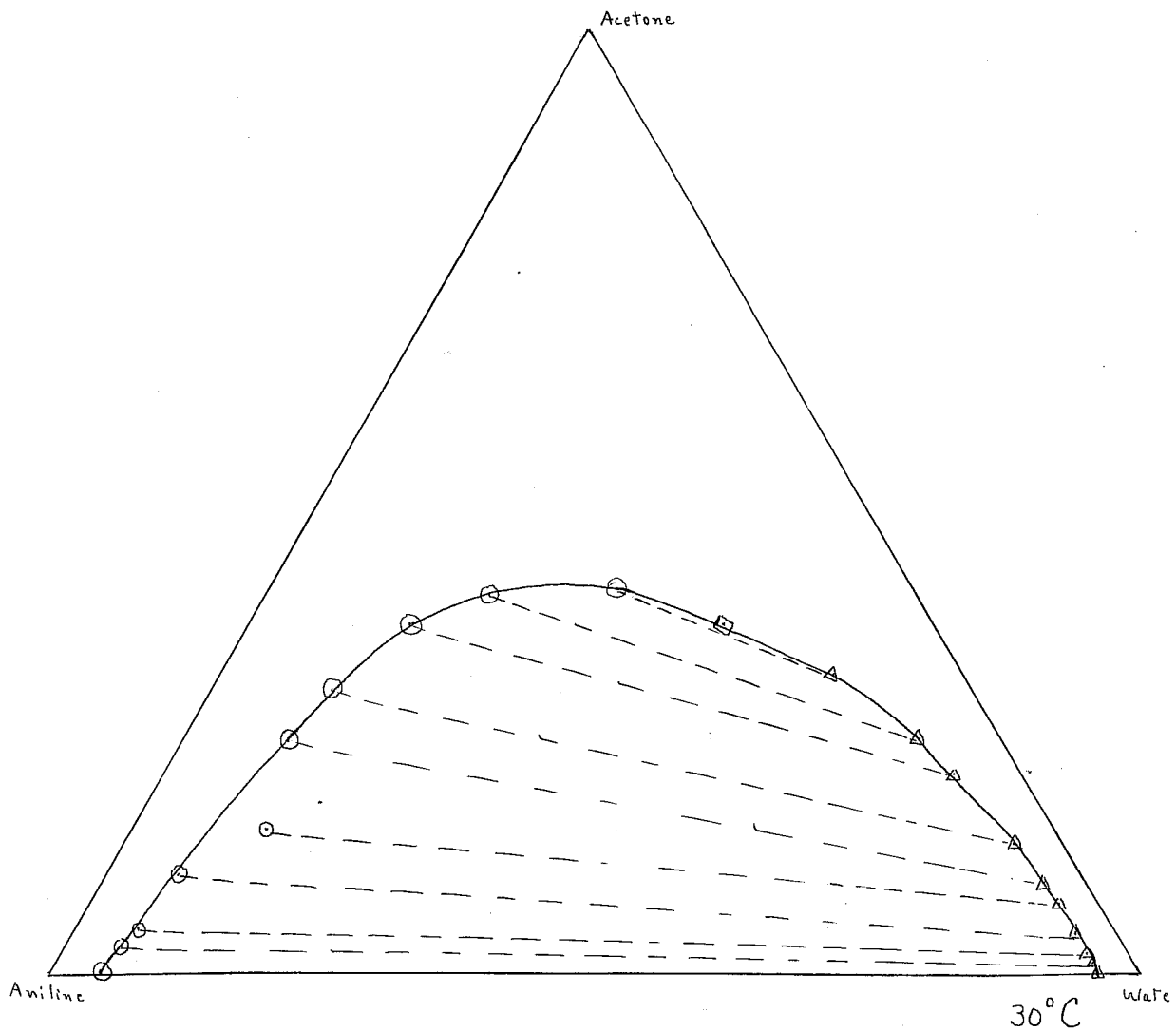


Fig. 1.

- o = Aniline Layer.
- Δ = Aqueous Layer.
- = Critical point.

The solid diagram was then considered. The binary system aniline-water was obtained from Seidell (4).

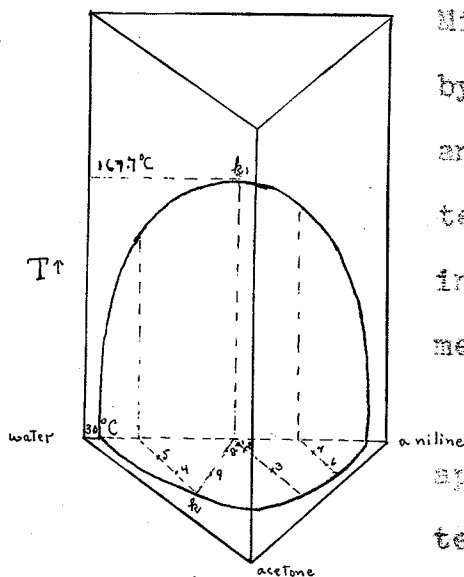


Fig. 2.

Mixtures of total composition as indicated by the numbers 1-9 on Fig. 2 were made up and sealed into hard glass critical temperature tubes. These were then heated in a glycerine bath and the behavior of the meniscus between the two layers noted.

As the tube was heated there was no apparent change in the solution until the temperature approached the temperature for homogeneity. When this temperature region was reached, the solution around the meniscus became decidedly agitated. Heating was continued slowly until finally at a definite temperature the meniscus ceased to be a barrier between the two parts of the solution and the upper solution poured into the lower one. The bath was kept at this temperature and in a very short time the two layers had formed one completely homogeneous solution.

From this data the three dimensional diagram showing the change in the boundary curve of the heterogeneous system with temperature was constructed.

The results are given in Table 2, and are represented graphically in Fig. 3. and Fig. 4. Fig. 3. shows the result of projecting the solid model on the base, i.e. on the 30° isotherm; while Fig. 4. shows the complete solid model.

Table 2.

	<u>Aniline %</u>	<u>Acetone%</u>	<u>Water %</u>	<u>Temperature for Homogeneity</u>
1.	48.6	1.4	50.	166.5 C.
2.	48.6	5.	46.4	156.
3.	48.6	31.68	19.72	104.5
4.	21.	31.68	47.32	86.
5.	21.	15.84	63.16	122.
6.	71.54	15.84	12.62	92.
7.	71.54	7.92	20.54	136.
8.	45.	5.	50.	159.
9.	30.	25.	45.	101.

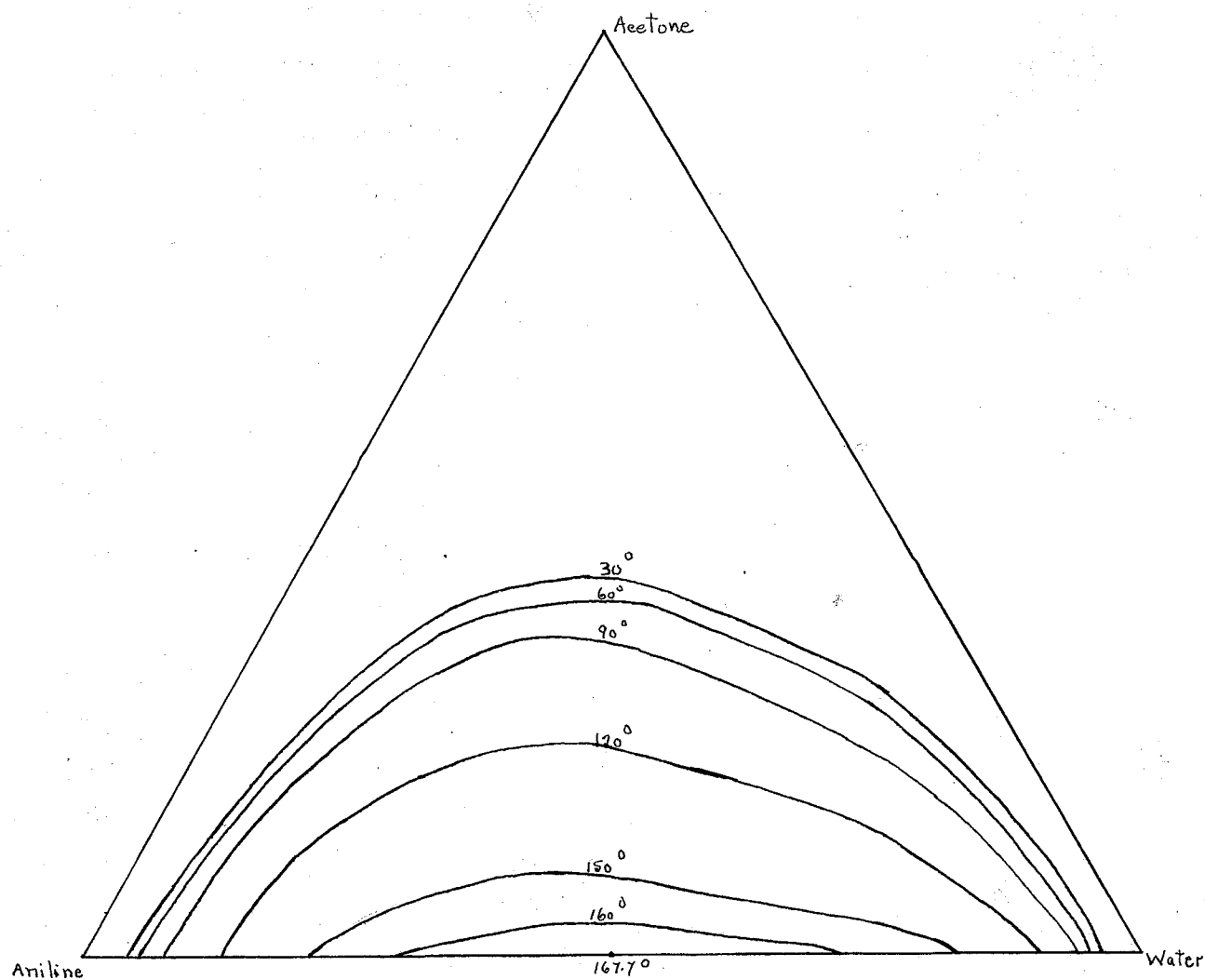


Fig. 3.

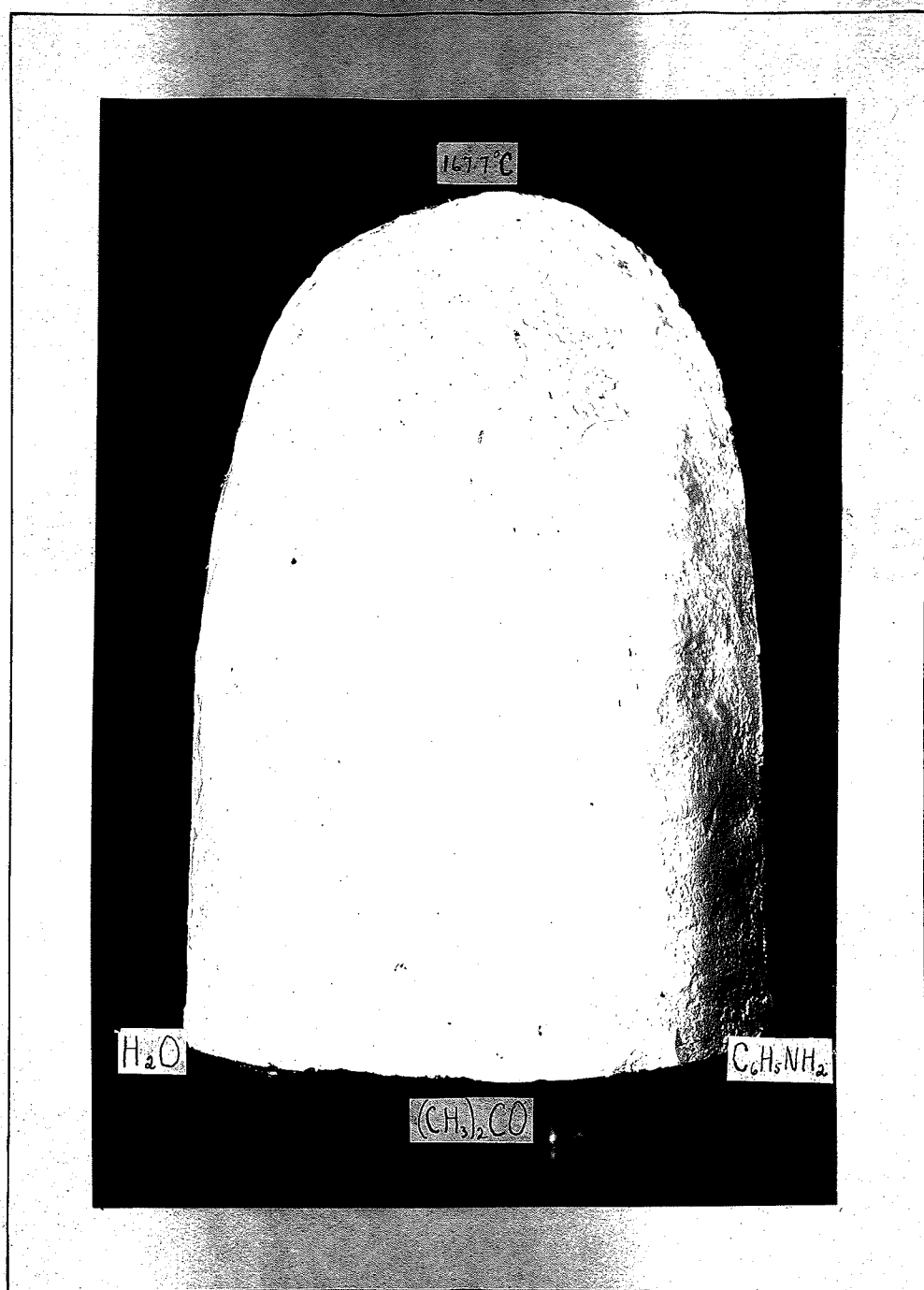


Fig. 4.

(c) Summary.

The curve for the 30 isotherm represents a system with one pair of partially miscible liquids, viz. aniline and water, whose mutual solubility increases with successive addition of a third liquid, acetone, which is readily soluble in each of the other two. The acetone divides itself unequally between the two layers, more entering the layer rich in aniline than the layer rich in water. Therefore the critical point, that is the point at which the composition of the two layers becomes identical is on the side of the maximum of the curve which represents mixtures richer in water than in aniline. This is point K. on Fig. 1. whose composition is 21.1% aniline, 36.6% acetone and 40.3% water.

The solid diagram is one which is similar to Fig. c, which shows no critical ternary, the highest temperature at which aniline, acetone and water can exist together being lower than the critical binary for aniline and water.

(3) Determination of Affinity Constant of Aniline.

(a) General Theoretical Considerations.

The dissociation of a base is represented by the reversible reaction



where B. represents any monovalent metallic radicle.

In equation (1) the rate at which the concentration (BOH) is being diminished by ionization may depend on several physical conditions. To know these is unnecessary for the purpose at hand if we may assume that their effect on the individual molecules of BOH is constant on the statistical average. Then, obviously the rate at which reaction (1) proceeds from left to right will depend upon the concentration of BOH and some constant factor which will be called k.

$$\text{Velocity left to right} = k, (\text{BOH}) \quad (2)$$

The velocity of the reverse reaction wherein the ions recombine to form BOH might be supposed to be dependent only upon the rate at which the ions in their thermal agitation collide. It is difficult to say what degree of approach and what other conditions are necessary before combination is accomplished. It is safer then to assume only that some degree of meeting is necessary, that some average state is to be considered virtual combination and that the physical factors bringing about this state are, on the statistical average, constant. Here again then we ascribe the velocity of reaction first to a factor dependant only upon the numbers of ions concerned and second another factor embracing all known and

unknown influences, exclusive of concentration. Since the number of collisions is proportional to the concentration of both ions present.

$$\text{Velocity right to left} = k_2(B^+)(OH^-) \quad (3)$$

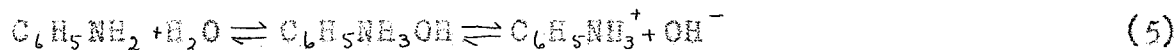
At equilibrium the velocity of reaction in one direction equals the velocity of reaction in the reverse direction.

Then by equating (2) = (3) we get,

$$\frac{(B^+)(OH^-)}{(BOH)} = \frac{k_1}{k_2} = K_b \quad (4)$$

For the ratio of the two constants there is substituted in (4) another constant, K_b , known as the equilibrium constant of the reaction or in this special case as the affinity constant of the base.

In the case of organic bases such as aniline, there are two equilibria to be considered.



The reaction constant of the first is given by

$$K_1 = \frac{(C_6H_5NH_3OH)}{(C_6H_5NH_2)(H_2O)} \quad (6)$$

The reaction constant of the second is given by

$$K_b = \frac{(C_6H_5NH_3^+)(OH^-)}{(C_6H_5NH_3OH)} \quad (7)$$

As in the case of ammonia, there is no information with amines generally of the ratio of the anhydrous compound merely held in solution to the amount of the hydrated but undissociated compound. It denotes the facility with which nitrogen passes from the trivalent to the pentavalent form and is sometimes called the aminolytic constant.

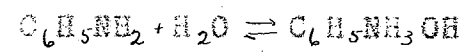
The second ratio is the true basicity constant in analogy

with metallic bases. The basicity as measured is expressed by the equation

$$k_b = \frac{(C_6H_5NH_3^+)(OH^-)}{(C_6H_5NH_2) + (C_6H_5NH_3OH)} \tag{8}$$

That is, the assumption is made that the whole of the base is hydroxylated and we arrive at an apparent rather than the true basicity constant.

From the reaction

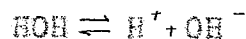


by treatment by the mass action law we arrive at the equation

$$\frac{(C_6H_5NH_3OH)}{(C_6H_5NH_2)} = \frac{(H_2O)}{KV} \tag{9}$$

It therefore appears that to increase the proportion of true base it is necessary either to increase the mass of water keeping the volume of the system constant, or decrease the volume of the system, keeping the mass of water constant. Neither of these procedures is experimentally possible with a purely aqueous solvent, but it is readily possible to adopt the converse procedure, viz. to keep the volume of system constant and decrease the mass of water by dilution with an inert solvent. Such an inert solvent is acetone. As acetone is added to the system the properties of true base should decline and the affinity constant calculated in the ordinary way deviate more and more from the true value. In this way it may be possible to obtain some idea of the true value of the affinity constant by extrapolation backward to zero concentration of aniline although such a procedure involves serious chances of error.

A very important relationship between acids and bases in aqueous solution is brought about by the conduct of water. It dissociates into the hydrogen ion characteristic of acids, and the hydroxyl ion characteristic of bases. The equilibrium of the reversible reaction



is represented by

$$\frac{(\text{H}^+)(\text{OH}^-)}{(\text{HOH})} = k \quad (10)$$

Because the concentration of the undissociated water is so large in relation to the dissociation product, (HOH) will not be changed appreciably by the slight dissociation.

(HOH) may therefore be considered a constant and combined with k .

Equation (10) then becomes

$$(\text{H}^+)(\text{OH}^-) = k_w \quad (11)$$

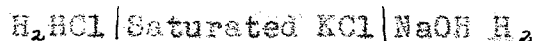
It follows from this equation that, no matter how concentrated the hydroxyl ions may be, there must remain sufficient hydrogen ions to satisfy the above relationship. This permits us to speak of the hydrogen ion concentration of alkaline solutions and to construct a scale of acidity--alkalinity in which we do not discriminate between hydrogen and hydroxyl ion concentrations.

Also from this relationship by determining the hydrogen ion concentration of any solution the hydroxyl ion concentration of that solution can be calculated provided K_w is known.

K_w however is not an absolute constant. It varies with

temperature and also with the ionizing medium. The value of K_w at different temperatures has been determined by many investigators and by many different methods. These are given in Clark (5) and their average value for 30°C used in the present problem.

Pring (1) has made measurements of K_w and also of k_w , $k_w = \frac{(\text{OH}^-)(\text{H}^+)}{(\text{HOH})}$ in acetone-water mixtures. His determination was made by determining the E. M. F. of the cell



the solvent being the same throughout the gas chain. The degree of dissociation of the HCl and NaOH at the concentration employed was determined by conductivity measurements. The E. M. F. of the combination

$$\pi = \frac{RT}{F} \log \frac{c_1}{c_2}$$

where c_1 is the (H) of the HCl and c_2 that of the NaOH. c_1 is known and c_2 is measured. The (OH^-) in the alkali is also known from its conductivity and thus the ionic product $(\text{H}^+)(\text{OH}^-) = K_w$ was determined. The values of K_w for various acetone-water mixtures was obtained from a smooth curve drawn through the point of K_w at zero concentration of acetone at 30°, parallel to the curve drawn through the values obtained by Pring (1) at 20°C. If the pH value of the aqueous layer is determined, and knowing the total composition of the original mixture, the composition of the aqueous layer is readily obtained from the solubility diagram, Fig. 1. The apparent basicity constant, k_b , is obtained from the following calculation:

$$pH = -\log (H^+) \quad (1)$$

$$K_w = (H^+) (OH^-) \quad (2)$$

$$\text{Then total } (OH^-) = \frac{K_w}{(H^+)} \quad (3)$$

Since all the (H^+) present must have arisen through dissociation of water and in the dissociation of water equal numbers of hydrogen and hydroxyl ions are formed, then

$$(OH^-) \text{ due to water} = (H^+) \quad (4)$$

$$\text{Then } (OH^-) \text{ due to the base alone} = \text{total } (OH^-) - (H^+) \quad (5)$$

and since aniline dissociates into equal numbers of OH^- and $C_6H_5NH_3^+$ ions then

$$\text{Total } (OH^-) - (H^+) = (C_6H_5NH_3^+)$$

From these equations k can be determined

$$k_b = \frac{(C_6H_5NH_3^+) (OH^-)}{(C_6H_5NH_2)_{\text{total}}} \\ = \frac{(\text{total } (OH^-) - (H^+)) (\text{total } (OH^-))}{(C_6H_5NH_2)}$$

(b) Determination of Hydrogen Ion Concentration by the Indicator Methods.

(1) Theoretical Considerations.

The chemical indicator may be defined as a substance which when added in small amounts shows the appearance or disappearance of a chemical individual (ion or molecule) by a conspicuous change in colour. In hydrogen ion considerations these substances which show the presence of hydrion or hydroxylion are used as indicators, i.e. indicators which "change colour" when the pH of their solutions change.

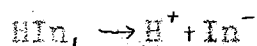
Each indicator exhibits colour change within a characteristic zone of pH. Beyond one indefinite edge of such a zone one characteristic colour appears. Beyond the other indefinite edge the other characteristic colour appears. Within the zone the colour may be treated as if it were a mixture of the characteristic colours. Because the edges of the pH zone are indefinite, the colour or colour mixture in the centre of the pH zone constitutes a useful point of reference. This is called the 50 per cent transformation point and the value of pH at this point is known as the indicator's pK value.

The "acid colour" of the indicator appears when the pH of the solution is about 2 units lower than the pK value and the "alkaline colour" appears when the pH of the solution is about 2 units greater than the pK value of the indicator. These terms refer to the "acid form" and "alkaline form" of the indicator and do not infer acid or alkaline condition of the solution.

According to Ostwald (6) a neutralization indicator is a

slightly dissociated organic acid or base which possesses a different colour from that of the salt into which it is converted by addition of acid or alkali. This theory has been shown to be inadequate and recent investigation has shown that a neutralization indicator always consists of two tautomeric forms (i.e. isomers which tend to go over into each other until equilibrium is reached.) possessing different colours, one of which greatly predominates when the indicator exists in the undissociated state and the other when it exists as the highly dissociated salt.

The end point of a titration, in the presence of an indicator acid, is reached when a portion of the non-dissociating tautomer (HIn) changes into the dissociating tautomer (In⁻) which immediately dissociates into its ions:



This point is not perfectly definite, since a certain quantity of base is required to convert the non-dissociating into the dissociating tautomer. The end point of a titration may be defined, however, as being reached when one-half of the non-dissociating tautomer is transformed into the indicator ion, i.e. when

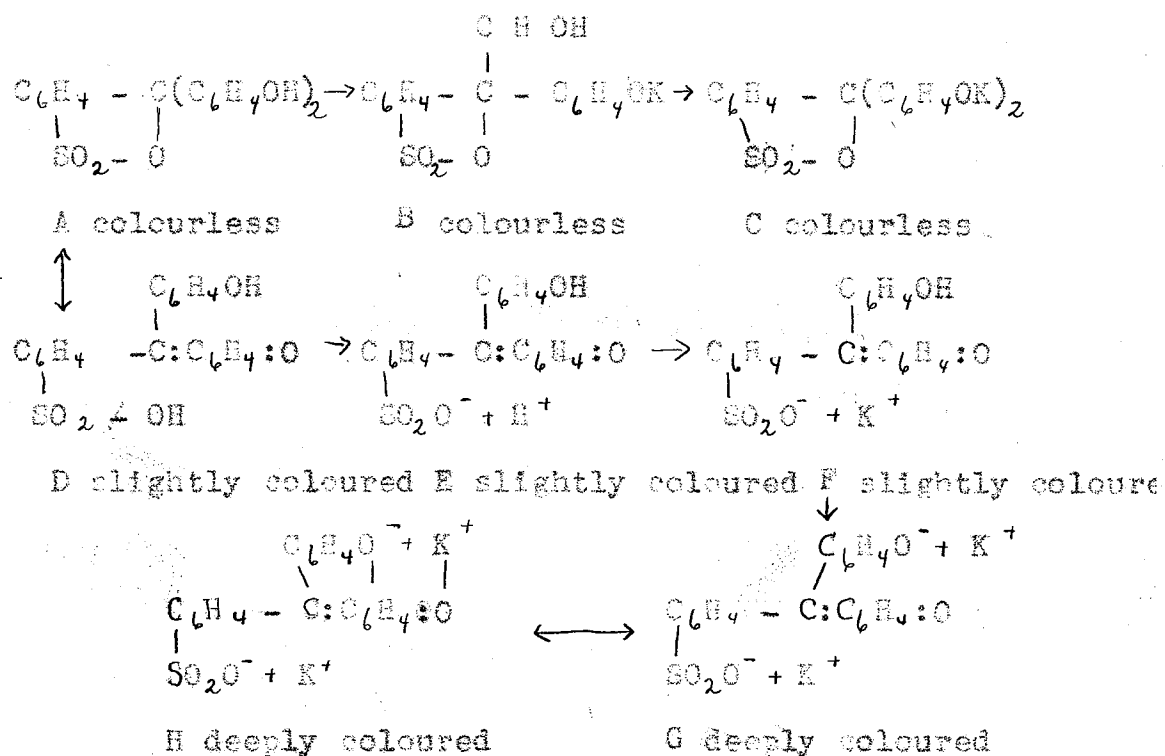
$$(\text{In}^-) = (\text{HIn})$$

This is known as the half-transformation point and the value of the pH of the solution at this point is known as the pK value of the indicator.

In ordinary titration conditions are so chosen that when the "end point" is reached, the pH value of the solution

plunges through the entire range of the indicator's colour transformation. However intermediate colours are important in pH determinations. These can be maintained by buffer solutions which maintain constant values of pH. By means of these reference standards may be prepared. The buffer solution controls only the ratio between the concentration of "acid" and "alkaline" colour-forms of the indicator. Therefore the preparation of a standard colour tube to be judged by eye includes the use of a definite concentration of indicator substance and observation through a definite depth of solution.

The indicator used in these experiments was phenol red (pH 6.8-8.2) or phenol sulphthalein which is typical of all sulphthalein. The various tautomers of this were determined by Lubs and Acres and are given by the following scheme:



The colourless lactoid A. by reason of the strong tendency of the sulphonic group to ionize goes over into the quinoid structure illustrated in the second line which are slightly coloured yellow. It is the transformation of F. to G. and H., the ionization of the phenolic group forming a quinone-phenolate structure which correlates with the intense red colour of phenol red.

Experimental.

In order to save time, pH value determinations by this method were carried out along with the solubility experiments. Contamination of the solution was avoided as far as possible. Accordingly the water was redistilled three times, (a) from alkaline permanganate, (b) from baryta, out of contact with air, (c) through a block tin condenser into a silica receiver with a tin-foil coated stopper. The aniline used was B. D. H. highest purity aniline redistilled (boiling point 182.5-183°C.) in a dull red light and preserved in dark, paper coated bottles. The acetone used was ordinary pure. The three liquids in appropriate proportions were stirred together in a transcendent silica flask (further shielded from light by a bottomless tin can) in a thermostat at 30° for several hours. The aniline present was always more than sufficient to saturate the aqueous layer. The pH value of the aqueous layer was then determined.

A 10 c.c. sample of the aqueous layer was removed and added to 0.5 c.c. of 0.02 per cent solution of phenol red and the resulting colour compared as closely as possible with

standard tubes in the range of 6.8 to 8.2.

From these pH determinations the affinity constant calculated as described. These are given in Table 3.

Table 3.

Concentrated Acetone %	Concentrated Aniline M.	K _b
0	.02	1.016 × 10 ⁻¹¹
0	.04	6.496 × 10 ⁻¹²
0	.08	4.56 × 10 ⁻¹²
0	.1775	3.34 × 10 ⁻¹²
0	.355	2.13 × 10 ⁻¹²
.422	.405	1.467 × 10 ⁻¹²
.906	.42	1.25 × 10 ⁻¹²
2.64	.44	6.560 × 10 ⁻¹³
7.00	.44	5.344 × 10 ⁻¹³
9.57	.455	3.209 × 10 ⁻¹⁴
12.5	.49	1.736 × 10 ⁻¹⁴
12.18	.447	1.42 × 10 ⁻¹⁴
21.03	.63	2.247 × 10 ⁻¹⁵
Extrapolating to 0 conc. of aniline		K _b = 2 × 10 ⁻¹⁰

(c) Electrical Methods.

(1) Theoretical Considerations.

If a metal be placed in a solution of its salt, there will be a difference of electrical potential between metal and solution which will vary in an orderly manner with the concentration of the metal ions. To account for this difference of potential, Nernst assumes that a metal possesses a characteristic solution tension, comparable with the solution pressure of a crystal of sugar--but with the important qualification that it is the metal ions which pass into solution. If a metal is dipped into pure water, the metal tends to go into solution. The metal ions passing into solution carry their positive charges and leave the metal negative. Thus there is established a so-called double layer of electrical charges at the interface between metal and solution. This potential difference opposes further solution and equilibrium is established when the electrostatic control equals the solution pressure.

If there are already ions of metal present in solution, the relative electrostatic field in the solution has already been partially established, fewer ions will escape from the metal and the metal is more positive.

Not only metals but various gases are found to act in the same way under certain conditions. Hydrogen is one of these and acts as a metal electrode when adsorbed in a finely divided platinum, palladium or iridium film. Platinum black deposited on platinum and laden with hydrogen forms a hydrogen electrode. This can be brought into equilibrium with hydrogen ions just as any metal is brought into equilibrium in a solution of its ions.

Considering the energy relations and assuming that we are dealing with an "ideal solution" by which we mean a solution in which the pressure-volume relations of the ions conform to the laws of a "perfect gas", the difference of potential, E , is found to be expressed by the equation

$$E = \frac{RT}{nF} \ln \frac{p}{P}$$

where R is the gas constant, T the absolute temperature, n the valence, F the faraday, p the osmotic pressure of the ions and P the electrolytic solution pressure of the electrode.

Since the solution pressure of a gas is proportional to the pressure of the gas, if we have two hydrogen electrodes under the same gas pressure dipping into two solutions of hydrogen ion concentration c_1 and c_2 and osmotic pressure p_1 and p_2

$$\begin{aligned} E &= E_1 + E_2 = \frac{RT}{nF} \ln \frac{p_1}{P} - \frac{RT}{nF} \ln \frac{p_2}{P} \\ &= \frac{RT}{nF} \ln \frac{p_1}{p_2} \end{aligned}$$

Since the ratio of the pressures may be considered equal to the ratio of the ion concentration,

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2}$$

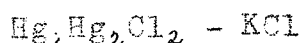
Therefore by measuring the potential difference we have a measure^{of} the ionic concentrations. The junction potential between the two solutions is practically eliminated by using a saturated KCl bridge.

In recent work the term "activity" is substituted for concentration. It is really a corrected concentration γc where γ is the activity coefficient, a correction made necessary

by the fact that no solution is "ideal" just as no gas is a "perfect gas". This coefficient however is difficult to determine except in very dilute solutions and in practical work, the potential is still considered to be a measure of concentration.

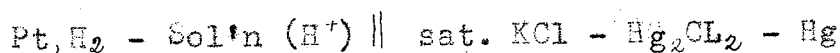
The potential difference between a hydrogen electrode under one atmosphere pressure of hydrogen and a hypothetical solution normal with respect to hydrogen activity is the standard arbitrarily fixed for the difference in potential. This is given the value $E=0$ and the potential difference between any electrode and a solution is referred to it.

However, the hypothetical solution is very difficult to prepare and so standards which are themselves referred to the normal hydrogen electrode are used in general practice. The most commonly used is the calomel electrode, which consists of mercury in contact with mercurous ions and potassium chloride,



Since the mercurous ion concentration depends on the chloride ion concentration, the concentration of KCl determines the potential difference. The calomel electrodes ordinarily used are those containing $\frac{N}{10}$, N or saturated KCl. These exhibit respectively a potential difference, referred to the normal hydrogen electrode of 0.366, 0.281 and 0.246 volts.

In the cell



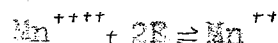
$$E = \frac{RT}{nF} \ln \frac{1}{(\text{H}^+)} + 0.246$$

$$= 0.246 + 0.059 \text{ pH}$$

A saturated KCl bridge practically eliminates the difference of potential formed at the junction of the two electrodes.

Therefore the total E. M. F. is due entirely to E_1 and E_2 ,

the electrode potentials. The manganese hydroxide electrode depends for its difference of potential against a solution, on the reaction



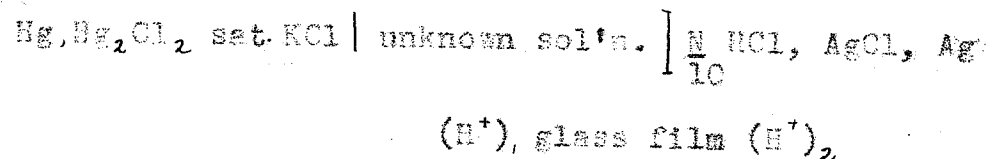
$$E = E_0 - \frac{RT}{nF} \ln \frac{\text{Mn}^{++}}{\text{Mn}^{+++}}$$

but since both hydroxides are only very sparingly soluble and the solid hydroxide is always present $K_1(\text{H}^+)^2$ and $K_2(\text{H}^+)^4$ may be substituted in the equation and

$$E = E_0 + \frac{RT}{F} \ln (\text{H}^+)$$

Therefore the difference in potential is a measure of the hydrogen ion concentration. The electrode must be standardized in buffer solutions of known pH to determine the value of E_0 .

The glass electrode consists of a very thin film of glass separating the unknown solution from a standard solution of HCl into which is dipped a silver--silver chloride electrode. The cell is expressed by



The only unknown difference of potential is produced at the glass film. This film is considered analogous to any barrier which is only permeable to one kind of ion. Haber and Elemen-ziewicz (5) consider the glass as a phase containing water and hydrions and hydroxyl ions at a constant concentration.

The potential difference is expressed by

$$E = \frac{RT}{nF} \ln \frac{(\text{H}^+)}{(\text{H}^+)_2}$$

where the concentration $(M^+)_2$ is known

$$E = \frac{RT}{nF} \ln (H^+), \text{ unknown}$$

and the total difference in potential

$$E = E_1 + E_2 + \frac{RT}{nF} \ln (H^+)$$

A glass electrode must be standardized in buffer solutions before using since the theoretical result is not actually attained and the variation differs with the different kinds of glass used.

(2) Experimental.

Several precautions were taken in order to determine the pH value of the solutions as accurately as possible and to eliminate the difficulties as described by Pring (1).

- (1) The water used was distilled three times.
 - (a) from alkaline permanganate.
 - (b) from baryta.
 - (c) through a block tin condenser into a silica flask out of contact with air.

(2) The aniline was redistilled in a dull red light.

(3) The vessel used was made of silica.

(4) Both chemical and electrolytic hydrogen were used.

It was purified by passing through KOH solution, Hg_2Cl_2 solution, red hot copper turnings, AgNO_3 solution and H_2O .

(5) The calomel electrode was prepared from redistilled mercury, purified calomel, re-crystallized KCl saturated in water redistilled three times.

(6) The hydrogen electrode used was carefully cleaned and the platinum black deposited as described in Clark (5).

(7) The manganese hydroxide electrode was carefully cleaned and prepared as described in Clark (5).

(8) The vessel and calomel electrode were kept at constant temperature $--30^\circ\text{C}$.

(9) The electrical apparatus stood in glass to stop vibration.

(10) The reference electrode was kept close to the indicator electrode to reduce the resistance offered by the solution.

The electrical set-up used was the potentiometer-galvanometer hook up, described in Clark using a Weston cell as the standard cell.

The results obtained were decidedly not satisfactory. The potential difference between the hydrogen electrode and the solution could not be determined at all. The electrode appeared to be poisoned immediately in aniline solutions. There did not appear to be any lack of conductivity but rather poisoning due probably to the adsorption of aniline by the platinum black.

Similarly with the manganese hydroxide electrode poisoning prevented the establishment of equilibrium, and no constant potential difference could be attained. Again poisoning was probably due to adsorption of the aniline by the electrode film.

The glass electrode was prepared by the method of MacInnes and Dole (7). The conductivity is so low across the glass film that the galvanometer is not sufficiently sensitive to record the current. Unfortunately there was no quadrant electrometer available and so results could not be obtained. But it is still thought that the glass electrode would give satisfactory results since there is very little possibility of poisoning and this seems to be the main factor in the failure to get results using the other electrodes.

(d) Summary.

It was attempted to determine the true affinity constant of aniline in unbuffered solutions by measuring the apparent

affinity constant aniline at various concentrations and extrapolating back to zero concentration of aniline at which the apparent affinity constant approaches the value of the true affinity constant very closely. Colorimetric and electrometric methods were tried.

Results were obtained from the colorimetric method giving a value of 2×10^{-10} for the true affinity constant of aniline. This is comparable with 2.13×10^{-10} obtained by Fenwick and Gilman (8) who extrapolated the value of hydrolysis constant for various concentrations of aniline hydrochloride and determined the affinity constant of aniline from these.

Results were not obtained by the electrometric method, but it is thought that by using the glass electrode with sufficiently sensitive apparatus, satisfactory results would be obtained.

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(4) Bibliography.

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