

used to calculate the polarizations of the substances and the electric moments of their molecules.

The polarizations show that the branched carbon chain of the *tert.*-butyl group has no measurably greater screening effect upon the force field of the dipole than the straight chain of the *n*-butyl group, while the larger triphenylmethyl group has a greater screening effect.

A theory of induced moments has been applied to explain the values here obtained, together with those of other investigators of alkyl halides. The moments of the molecules increase from the normal to the secondary to the tertiary compound because of the increase in the number of carbon atoms subjected to the inductive influence of the principal dipole, while the moment of the iso compound is the same as that of the normal if the branch in the chain is at least two carbons away from the halogen because only these two carbons are measurably affected by the principal dipole.

As previously observed, the moments do not show differences corresponding to the differences in chemical behavior.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

DIFFERENTIAL POTENTIOMETRIC TITRATION.

IV. (a) AN ADAPTATION OF THE METHOD TO THE USE OF HYDROGEN ELECTRODES.

(b) A TEST OF STANDARDS FOR PRECISE ACIDIMETRY

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In the third paper of this series¹ an improved apparatus for differential potentiometric titrations, involving a simple gas lift pump, was described, and data were given showing the usefulness of the method for measurements of high precision. We are, however, in this Laboratory, much interested in solutions of acids. Until recently our measurements on conductances, transference numbers, etc., have been hampered by the lack of precise (0.01% or better) methods for acidimetry. This has been especially true with regard to solutions of weak acids. Our attempts to use the quinhydrone electrode for acidimetry were not successful. This was probably due to the rapid oxidation of this substance as soon as the solutions approach the neutral point. An effort was also made to get the desired accuracy by means of indicators, using color standards, without greater success. Either of these methods might, with further investigation, have been developed to give adequate precision. It was, however,

¹ The papers already published in this series are (a) MacInnes and Jones, *THIS JOURNAL*, **48**, 2831 (1926); (b) MacInnes, *Z. physik. Chem.* (Cohen Festband), 217 (1927); (c) MacInnes and Dole, *THIS JOURNAL*, **51**, 1119 (1929).

decided to adapt the differential potentiometric method to the use of hydrogen electrodes. With such electrodes the results are more nearly unambiguous than when some indicating substance is added, since no allowance need be made for such an addition.

The Apparatus

The apparatus now in use utilizes the gas lift pump described in a previous paper,¹ operated by a stream of hydrogen. It was found in our early tests that for correct re-

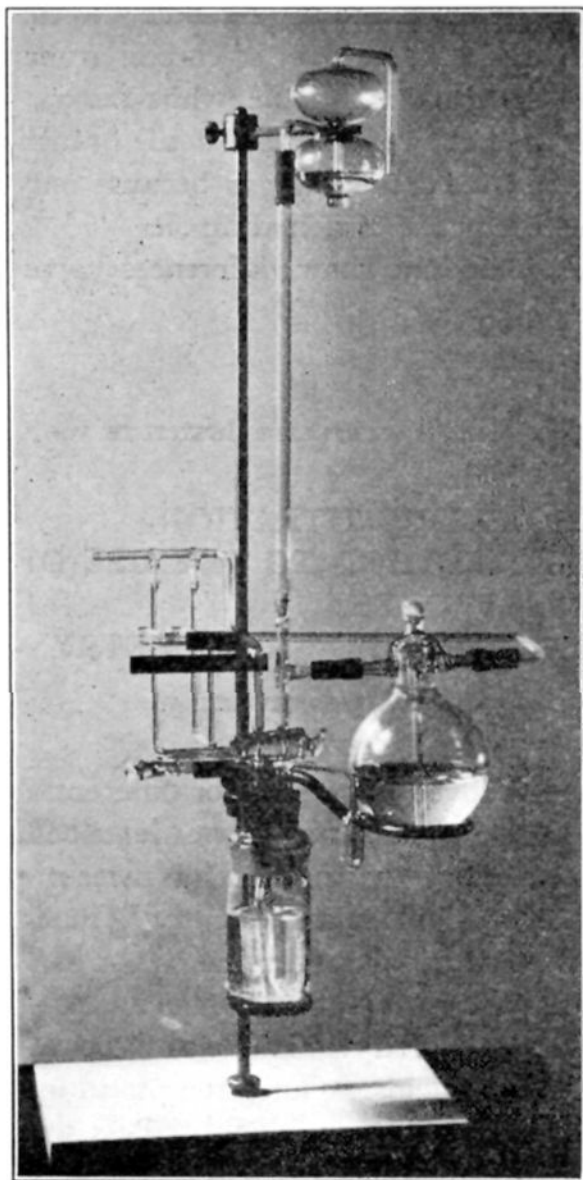


Fig. 1.

sults when using hydrogen electrodes two conditions are essential. First, the apparatus must exclude oxygen during the titration, and, second, no dissolved oxygen should be added with the titrating fluid. The apparatus as finally developed is shown in Fig. 1 and a diagrammatic sketch of the principal parts in Fig. 2. The solution to be titrated is placed in the vessel represented by A, of the latter figure. This is of about 150 cc. capacity. It is closed by a ground-glass joint a-a, into which fits a glass cover containing three openings shaped to hold rubber stoppers. These three openings are at the angles of a triangle in the actual apparatus instead of being in a line as shown. The two hydrogen electrodes E and E' are mounted in a single rubber stopper which is inserted into one of the holes in the cover. One of these electrodes, E', enters the tube G of the gas lift pump L. This pump is operated by a stream of hydrogen gas which flows through the tube h_2 , which enters through a stopper in the second hole in the cover. The other hydrogen electrode, E, is in the body of the solution in the vessel A. The solution is stirred, and at the same time saturated with hydrogen, by a stream of that gas through the tube h_1 which, in the actual apparatus, reaches to the bottom of the vessel A. The tip of the buret B and the gas exit tube leading to the trap T pass through the third rubber stopper. In operation pure hydrogen gas is passed through tubes h_1 and h_2 until no differ-

ence in potential is observed between the electrodes E and E'.² Under these conditions

² In order to cause hydrogen to flow from more than one outlet at the same time about 20 cm. of 0.5 mm. capillary tubing are inserted in the lines h_1 , h_2 and h_3 . This tubing can be seen in Fig. 1. Without this tubing bubbles will appear at only one place unless the gas pressure is very high.

both electrodes are saturated with hydrogen, and the solution in the tube G is uniform with that in the body of the solution due to circulation through this tube caused by the gas lift pump L. Now if the stopcock S is given a turn of about 45° this gas stream is stopped, causing an isolation of the solution in the tube G from the body of the solution. A further turn of the stopcock S causes the titrating fluid to flow into the solution from the tip of the buret B. On turning the stopcock back far enough to stop the flow of fluid, but not far enough to start the gas, a potential ΔE will exist between the electrodes E and E'. This potential is due to the concentration difference between the solution in the tube G and that in the body of the solution.

As already stated it has been found necessary to have all the oxygen removed from the titrating fluid. In fact, the addition of one or two drops of an oxygen-bearing solution from the buret B, after the electrodes are saturated with hydrogen, causes a very large and rapidly changing potential to develop between E and E', quite obscuring the potentials due to hydrogen and hydrogen ions. Oxygen is kept out of the titrating solution as follows. The titrating fluid (a solution of a base in these experiments) is placed in the special flask, F. This type of flask was described in a previous paper.¹⁰ With the head H turned in the direction indicated, a stream of hydrogen through tube h_2 will bubble through the liquid, displacing the oxygen in the solution in the flask and saturating it with hydrogen. From the flask the gas passes through the buret B and out of the special trap R. This is designed so that the first few cubic centimeters of the gas force the water in the lower bulb into the upper one, after which the gas bubbles through the tube J. After the air is sufficiently removed from the system, the buret may be filled from the flask by turning the head H in the reverse direction to that shown in the diagram, allowing the gas to flow through h_3 . The flow of gas and fluid may then be stopped by turning the head H through 90° . If the fluid is now run into the vessel A from the buret tip B, the volume of titrating fluid is replaced by hydrogen from the trap R. It is usually necessary to sweep gas out of the tip of the buret B and to reject some titrating fluid in order to start the buret reading at a convenient point. This rejected liquid is prevented from entering the solution in the vessel A by swinging the bent tube M under the buret tip by means of the trap T to which it is attached. In this position the rejected fluid will be forced by the gas stream from tube h_1 into the trap. The tube M may then be swung out of the way of the fluid from the buret.

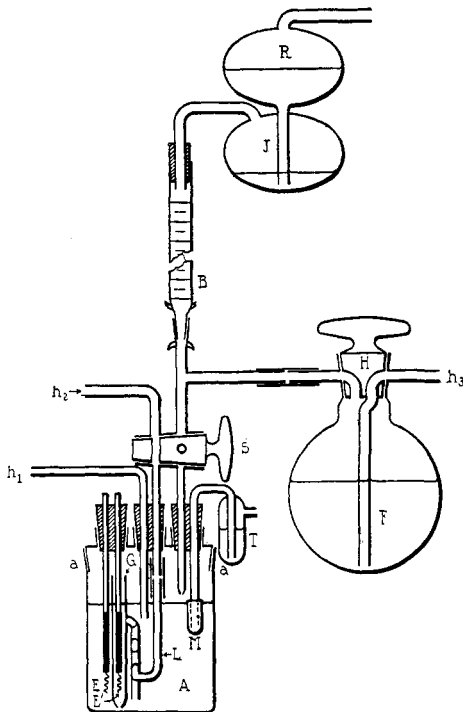


Fig. 2.

The Electrodes.—At first sight it would appear likely that, since the two electrodes are exposed to the solution under very nearly the same conditions, the readings should

be independent of the purity of the hydrogen gas, because the effect of impurities, for example oxygen, would be expected to be about the same on both electrodes. Quite the contrary was found to be true. We have found it necessary to bring the hydrogen to a very high purity before the two electrodes will have the same potential with the circulating pump operating so that both electrodes are bathed with the same solution. Ordinary tank hydrogen gave differences of potential between 5 and 50 millivolts. These conditions were but slightly improved, and occasionally were made worse by passing the gas through alkaline pyrogallol. After passing over a nickel catalyst prepared as described by Latimer, Buffington and Hoenschel³ and which, according to these authors, leaves less than 0.01% of oxygen in the gas, a difference of several millivolts between the electrodes persisted. A hot wire filament, as recommended by Lewis, Brighton and Sebastian,⁴ had no perceptible effect. However, by using a reduced copper catalyst, at a relatively high temperature (650 to 700°), the two electrodes will show a zero difference of potential. The copper catalyst used consisted of reduced copper oxide, in wire form, filling 20 cm. of a quartz tube of about 2.5 cm. diameter. To prevent channeling of this material, plugs of copper gauze were placed at the ends and at intervals in the catalyst. In order to keep out oxygen it was found necessary to avoid rubber tubing as far as possible, as the behavior of the electrodes gave definite evidence of the effect of the diffusion of oxygen through it. Such rubber connections as were unavoidable were made "glass to glass" with thick rubber tubing, impregnated with a paraffin-vaseline mixture.

The explanation of this surprising effect of very small amounts of oxygen in the hydrogen in preventing the two hydrogen electrodes from reaching the same potential is almost certainly as follows. The platinizing on the electrode tends to remove the last traces of oxygen by catalyzing its reaction with hydrogen. However, the electrode in the body of the solution in the vessel A of Fig. 2 is bathed by a constantly changing solution which is supplied with traces of oxygen from the tube h₁, and the electrode is therefore not permitted to come to equilibrium. The electrode in the tube G, on the other hand, is furnished with a relatively small portion of the solution which flows over it slowly. The catalysis of the reaction of the hydrogen with the oxygen has thus the opportunity to proceed further and the electrode thus reaches a potential nearer to the true equilibrium value than is possible with the electrode in the body of the solution.

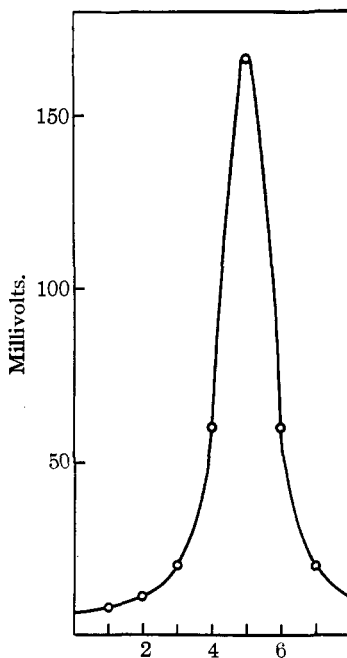
The observations just described on the effect of traces of oxygen on the potentials at the electrodes appear to be important as they indicate clearly that as ordinarily used a platinized platinum electrode has, in addition to its generally recognized function of bringing the reaction between hydrogen gas, hydrogen ions and electrons to equilibrium, the responsibility of catalyzing the reaction between hydrogen and traces of oxygen, which, as we have seen, have decided influence on the potentials observed. It seems probable, therefore, that potentials measured with hydrogen electrodes which have gas flowing over them may be in error, even if constant readings are obtained, unless extraordinary precautions are taken to make certain that the hydrogen is pure.

A Test of Standards for Precise Acidimetry.—Since, as has already been stated, it has been necessary for us to know the concentrations of acid solutions to high precision, a comparison of three different standards for

³ Latimer, Buffington and Hoenschel, *THIS JOURNAL*, **47**, 1571 (1925).

⁴ Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

acidimetry was made, employing the electrometric method in each case to find the end-point.⁵ A solution of sodium hydroxide with which the acid solutions could be titrated was prepared. The first solution of base used was calibrated, using (a) constant boiling acid, and (b) potassium acid phthalate. The constant boiling acid was prepared as described by Foulk and Hollingsworth,⁶ using the slight modification of their procedure described by MacInnes and Dole,⁷ who checked, very closely, Foulk and Hollingsworth's value for the composition of this material. A dilution of this acid was made by weight to approximately the concentration of the base. This diluted acid was then placed in a weight buret and about sixty grams was weighed out into the vessel A of the apparatus shown in Fig. 2. Then, from another weight buret, enough of the solution of the base, the titer of which was desired, was added to bring the acid within about 0.2 g. of neutralization. (To do this a preliminary rough titration, using phenolphthalein, was necessary.) The vessel A was put into place in the apparatus and the currents of hydrogen started through tubes h_1 and h_2 . When equilibrium was established (shown by a zero or nearly zero potential between electrodes E and E') the titration was completed from the buret B, using the solution of the base diluted in the proportion one to ten. This had previously been saturated with hydrogen in the flask F. The solution from B was added usually a drop at a time and the corresponding readings of the potentials between E and E' were made. One drop is, of course, equivalent to 0.1 drop of the original solution. A typical plot of the readings thus obtained is shown in Fig. 3, the e. m. f. values in millivolts appearing as ordinates and drops of solution as abscissas. The sharpness with which the end-point can be located is shown by the fact that the last drop, representing about 0.01% of the total titer, produced in this case a potential difference of 167 millivolts, whereas the previous and following



Drops of diluted base solution.

Fig. 3.

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⁵ Such comparisons, using ordinary indicators, have been made by Morey, *THIS JOURNAL*, **34**, 1027 (1912), and by Hendrixson, *ibid.*, **37**, 2352 (1915). These workers have not, however, attained quite the accuracy we have desired.

⁶ Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).

⁷ MacInnes and Dole, *ibid.*, **51**, 1119 (1929).

drops produced potentials lower than this by over 100 millivolts. The curve shown in Fig. 3 happens to be symmetrical about the maximum ordinate. In this case the drop producing this maximum potential exactly completes the titration. However, if the adjoining ordinates were of unequal heights it was possible by a simple interpolation to compute the portion of the last drop added that would have finished the titration. The interpolation was carried out with sufficient accuracy by drawing lines through the last two points on each side of the end-point, and noting the point at which they cross.

The solution of base was also standardized, using potassium acid phthalate furnished by the Bureau of Standards. We followed the directions for drying the material, and used the factor (0.9997) for its purity, as given in a circular from that Bureau. In this case the solid salt was weighed out into vessel A and the solution of the base was added from a weight buret within one or two tenths of a gram of the computed amount, after which the titration was finished as described above. The end-point was quite as definite, as in the preceding case, although the potentials were much lower. Table I, based on determinations made by the junior author, gives the results of standardizations, made by the two methods outlined above, of the solution of base. The constant boiling acid which, as collected, had a composition of 20.214% HCl was diluted in the proportion of 48.3299 grams of acid in 987.203 grams of final solution. The table is mostly self-explanatory. However, the column headed "Correction to weight of base" is computed from the weight of diluted base solution added from the buret in the final electrometric titration carried out in the apparatus shown in Figs. 1 and 2.

TABLE I

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION BY MEANS OF CONSTANT BOILING HYDROCHLORIC ACID AND POTASSIUM ACID PHTHALATE

Standard	Standard	Weight Base	Correction to weight of base	Normality of base
Constant boiling HCl	2.90026	47.2977	0.0645	0.33945
Constant boiling HCl	2.70567	44.1365	.0471	.33946
Potassium acid phthalate	4.0238	57.9822	.0990	.33948
Potassium acid phthalate	4.2204	60.7734	.1446	.33948

It will be observed that the two standards yield the same result with a high degree of accuracy. This test was repeated by an assistant, Mr. Valik, using a solution of sodium hydroxide having another strength. In this series another standard, pure benzoic acid from the Bureau of Standards, was also used. Since the addition of alcohol to dissolve this acid, as recommended by Morey,⁸ has an unfavorable effect on the hydrogen electrodes and on the end-point, the following procedure, which does not involve the

⁸ Morey, THIS JOURNAL, 34, 1027 (1912); see also Weaver, *ibid.*, 35, 1309 (1913).

use of that solvent, was adopted. About 1.4 g. of the solid acid was placed in a bottle of about 100-cc. capacity and the solution of base, the strength of which was approximately known, was added within 0.1 to 0.2 g. less than the amount necessary for neutralization and the flask was tightly stoppered. With sufficient shaking all the benzoic acid went into solution. The resulting solution, which was slightly acid and would therefore not absorb carbon dioxide, was washed into the vessel A of Fig. 2, and the titration was completed electrometrically with dilute base as already described. The results obtained for the standardization of the second solution of sodium hydroxide are given in Table II. All weights given in these tables have been reduced to vacuum standard. The weight of the potassium acid phthalate is that of the material of 0.9997% purity. The constant boiling acid in the second series of determinations contained 20.224% of HCl.

TABLE II

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION BY MEANS OF CONSTANT BOILING HYDROCHLORIC ACID, POTASSIUM ACID PHTHALATE AND BENZOIC ACID

Standard	Weight		Correction to weight of base	Normality of base
	Standard	Base		
Constant boiling acid	1.56523	41.2528	0.1483	0.20967
Constant boiling acid	1.56055	41.1483	.1364	.20963
Constant boiling acid	1.55894	41.1090	.1424	.20959
Potassium acid phthalate	2.1118	49.1500	.1833	.20963
Potassium acid phthalate	2.0194	47.0256	.1453	.20965
Potassium acid phthalate	2.0892	48.7370	.0684	.20963
Benzoic acid	1.4713	57.3510	.1538	.20963
Benzoic acid	1.4389	56.0079	.2263	.20965
Benzoic acid	1.4387	56.1074	.1271	.20962

It is evident from the data presented in Tables I and II that, in the first place, the electrometric method as outlined is capable of giving results of high precision, and, also, that the three methods tested for standardizing solutions of bases are equally accurate. Of these three methods the use of potassium acid phthalate is probably the most convenient. An empirical factor for the purity of the material must, however, be used. The constant boiling acid method involves a distillation which must be carefully carried out at a barometric pressure which must be constant and accurately known. Although it is hard to get into solution, benzoic acid is unquestionably the best material to use as a standard for precise acidimetry, since its use depends only on the stoichiometric relations, and no analytical results of other workers have to be accepted. Furthermore, it can be obtained in a state of highest purity.

A paper which will follow shortly will deal with the question of the equivalence of the electrometric and stoichiometric end-points, and with the titration of mixtures of acids.

Summary

1. The differential electrometric method for titration has been adapted to the use of hydrogen electrodes.

2. The usefulness of the method has been shown by its application to precise acidimetry. Three standards for use in acidimetry: constant boiling hydrochloric acid, potassium acid phthalate and benzoic acid, have been tested and have been shown to be suitable for accurate work (0.01% or better).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]
THE PHOTOCHEMICAL INTERACTION OF ETHYLENE AND AMMONIA

BY HUGH S. TAYLOR AND HARRY J. EMELÉUS¹

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The present work had its origin in some experiments carried out by J. R. Bates at the suggestion of one of us (H. S. T.) in December, 1926, during our studies of photosensitized decompositions by excited mercury.² In this work it was found that, in the decomposition of ammonia, both photochemically and by excited mercury, the non-condensable gas first received in a flowing system was mainly hydrogen. This suggested a primary decomposition of ammonia into NH_2 and H, and experiments were undertaken to determine whether evidence for this could be obtained from reactions initiated by such atomic hydrogen. This was readily forthcoming, since we showed that the photochemical decomposition of ammonia in presence of hydrogen and carbon monoxide led to very much larger yields of formaldehyde than were obtained under the same arc conditions in the absence of ammonia. This latter fact was also proof that we were not producing the formaldehyde by reason of the presence of excited mercury in the system. The reaction was sufficiently rapid that a solid residue was quickly laid down on the vessel walls; the solid was assumed to be hexamethylenetetramine. We have not yet examined the reaction further, and therefore confine ourselves to recording at this time the free solubility of the solid product in water.

In the following year Hill and Vernon,³ at Princeton, also showed that the illumination of ammonia in the far ultraviolet and at low partial pressures, in quartz vessels, in contact with tungstic oxide gave an immediate reduction to the blue oxide. This again pointed to atomic hydrogen, but not so directly, since hydrazine might have been the product to

¹ Commonwealth Fund Fellow.

² Bates and Taylor, *THIS JOURNAL*, **49**, 2438 (1927).

³ Unpublished experiments.