

not be related to catalytic activity. There should be, however, a closer concordance between reactivity and the adsorption processes occurring with marked activation energy. Limitations of space prevent such a discussion in this place but opportunity to treat this problem separately will be taken at a later date.

Summary

A general theory of adsorption involving several forms of adsorption at surfaces has been shown to lead to a number of conclusions capable of experimental verification. It has been shown, from abundant data in the literature, that these conclusions are already experimentally verified. It seems necessary, therefore, to abandon entirely the assumption implicit in older theories that the processes of adsorption are rapid. The assumption that all processes of adsorption possess their own characteristic activation energies permits a single general treatment of adsorption inclusive of processes which hitherto have been considered separate and unrelated. It has been shown that the only essential distinction between "secondary" and "primary" adsorptions or between "reversible" and "irreversible" adsorptions is that "secondary" or reversible adsorption processes are adsorptions normally with small heats of adsorption and small activation energies and that in the so-called "primary" or "irreversible" adsorptions, moderate or large energies of activation are involved, frequently with high heats of adsorption. The velocities of these latter processes may indeed be extremely slow. In general, it is the adsorptions with the higher energies of activation which are important in catalytic change.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY
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THE QUINHYDRONE ELECTRODE. II

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. Introduction

While there have been a number of papers which included work more or less directly related to the effect of oxygen on the potential and to the use of nitrogen in the preparation of the quinhydrone half cell, we are not aware of any study having been made of the reproducibility of the electrode possible under conditions of preparation and use which excluded oxygen in acid solution. It is the object of this paper, then, to present the results of such a study made in 0.1 *N* hydrochloric acid and to compare the reproducibility of the quinhydrone electrodes prepared with nitrogen with those obtained with air and upon which we have previously reported.¹

¹ Morgan, Lammert and Campbell, *THIS JOURNAL*, 53, 454 (1931).

Preparation and Purification of Materials.—The materials used have been described in the first paper of this series with the exception of the following.

Nitrogen.—Tank nitrogen from the Air Reduction Sales Company was reduced to the desired pressure and passed successively through solutions of alkaline permanganate, alkaline pyrogallol acid, distilled water, and the electrolyte used in the cell before it was conducted to the cell.

Oxygen.—Tank oxygen supplied by the Linde Air Products Company was purified by the same method as the compressed air.

Apparatus.—The electromotive force measurements were made with the apparatus and with the precision described in the first paper, to which reference has been made; the gases were conducted through the purifying solutions, kept at the same temperature, before being conducted to the cell solution containing the quinhydrone.

The electrodes and electrode vessels were identical with those used for the experiments in air except that in the stopper of the electrode vessel a gas inlet tube replaced the stirrer.

Procedure and Results.—The procedure adopted for the determination of the reproducibility of the quinhydrone electrode under circumstances which permit the use of nitrogen was in every respect identical with the procedure adopted in the first paper of this series¹ except that the electrodes were dried with nitrogen instead of with air and the solutions stirred with nitrogen instead of by a mechanical stirrer. The procedure was carried out in such a way that no air was admitted to the electrodes after they were immersed in alcohol. Nitrogen was bubbled through the alcohol for several minutes, the alcohol was forced out of the electrode vessel with nitrogen, and the flow of nitrogen was continued while the quinhydrone solution was being poured into the electrode vessel as well as during the time the electrodes were in the thermostat. Later results obtained when the electrodes were dried in air as described in the first paper and then stirred with nitrogen indicated that the more elaborate procedure of drying with nitrogen was unnecessary; these results will be discussed presently. In some cases oxygen or compressed air was substituted for nitrogen in both drying and stirring operations, the procedure being similar.

The results obtained with nitrogen-dried electrodes and nitrogen-stirred solutions are collected in Table I. The averages and deviations were calculated by the method used for the potentials measured in air, which results were presented in Table I of the first paper of this series.

In Table II are given the percentages of the total number of cells measured in nitrogen which lie within certain ranges.

A number of conclusions are obvious from the results collected in these tables. In the first place, quinhydrone electrodes prepared with nitrogen are far more reproducible than those prepared with air. The average

TABLE I

COMPARISON OF THE REPRODUCIBILITY OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 N HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN ELECTRODES MADE OF METALS OF DIFFERENT DIMENSIONS AND COMPOSITIONS WITH DIFFERENT PRE-TREATMENTS; ELECTRODES DRIED AND SOLUTIONS STIRRED WITH NITROGEN^a

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying ops. between meas.	Average potential difference. (volt)	Ranges of difference 0.000000 to -volt	Average deviation, milli-volt	Results discarded in average
Small wires							
Shorted O, 1-6	6	54	4	0.000002	0.000008 (.000023)	0.002	1
Shorted Au, 7-12	6	16	2	.000068	.000200	.070	0
Large wires							
Shorted A, 1-6	6	63	5	.000001	.000006 (.000007)	.001	1
Unshorted A, 1-6	6	34	2	.000001	.000005 (.000008)	.001	1
Shorted B, 1-6	6	61	5	.000001	.000004	.001	0
Unshorted B, 1-6	6	33	2	.000003	.000008 (.000039)	.002	2
Large wires							
Shorted Pt, 1-6	6	116	12	.000001	.000007	.001	0
Unshorted Pt, 1-6	6	35	2	.000002	.000008 (.000031)	.001	4
Shorted Au, 1-6	6	63	7	.000003	.000012 (.000021)	.003	2
Unshorted Au, 1-6	6	35	2	.000003	.000013	.002	0
Shorted Ir, 1-6	6	51	5	.000006	.000025	.006	0
Unshorted Ir, 1-6	6	32	2	.000007	.000033	.005	0
Shorted Rh, 1-6	6	52	5	.000002	.000011 (.000053)	.002	2
Unshorted Rh, 1-6	6	34	2	.000002	.000005 (.000012)	.001	1
Shorted St, 1-6	6	60	5	.000006	.000028 (.000034)	.006	1
Unshorted St, 1-6	6	40	2	.000006	.000014 (.000053)	.002	1
Special wires							
Shorted Am. Pt, 1-6	6	27	2	.000002	.000010	.002	0
Unshorted Am. Pt, 1-6	6	35	2	.000001	.000005	.001	0
Shorted L. & N., 1-4	4	22	2	.000000	.000001	.000	0
Foils							
Shorted P ₁₁₋₁ -P ₁₁₋₄	4	20	2	.000001	.000005	.001	0
Unshorted P ₁₁₋₁ -P ₁₁₋₄	4	20	2	.000001	.000006	.001	0
Shorted G ₁₁₋₁ -G ₁₁₋₄	4	22	2	.000004	.000012	.003	0
Unshorted G ₁₁₋₁ -G ₁₁₋₄	4	18	2	.000001	.000002	.001	0

TABLE I (Concluded)

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns. between meas.	Average potential difference, (volt)	Ranges of difference 0.000000 to -volt	Average deviation, milli-volt	Results discarded in average
Shorted P ₁₂₋₁ -P ₁₂₋₄	4	31	4	0.000002	0.000006	0.002	0
Unshorted P ₁₂₋₁ -P ₁₂₋₄	4	20	2	.000001	.000007	.001	0
Shorted D-F	6	49	4	.000002	.000005	.002	0
Shorted G ₁₂₋₁ -G ₁₂₋₄	4	42	6	.000001	.000006	.001	0
Unshorted G ₁₂₋₁ -G ₁₂₋₄	4	21	2	.000001	.000005	.001	1
					(.000012)		
Shorted P ₁₃₋₁ -P ₁₃₋₄	4	46	4	.000002	.000008	.002	0
Unshorted P ₁₃₋₁ -P ₁₃₋₄	4	20	2	.000001	.000003	.001	0
Shorted G ₁₃₋₁ -G ₁₃₋₄	4	35	4	.000002	.000008	.002	0
Unshorted G ₁₃₋₁ -G ₁₃₋₄	4	20	2	.000001	.000002	.001	0
Shorted P ₂₂₋₁ -P ₂₂₋₄	4	34	4	.000001	.000004	.001	0
Shorted I-N	6	44	4	.000002	.000009	.002	0
Shorted G ₂₂₋₁ -G ₂₂₋₄	4	33	4	.000003	.000009	.002	0
Shorted P ₂₃₋₁ -P ₂₃₋₄	4	30	4	.000001	.000005	.001	0
Shorted G ₂₃₋₁ -G ₂₃₋₂	2	5	2	.000000	.000001	.000	0

^a Compare with Table I, Morgan, Lammert and Campbell, THIS JOURNAL, 53, 454 (1931).

TABLE II

SUMMARY OF RESULTS SHOWING THE PERCENTAGE VARIATION IN POTENTIAL DIFFERENCES OBTAINED WHEN METALS OF DIFFERENT COMPOSITIONS AND DIMENSIONS ARE USED IN THE PREPARATION OF THE QUINHYDRONE ELECTRODE. NITROGEN USED FOR DRYING AND STIRRING

Electrode series	Number measured	Percentage of total		
		<0.000005 volt	<0.000010 volt	>0.000010 volt
Small wires				
O, 1-6	55	85	98	2
Au, 7-12	16	6	44	56
Large wires				
A, 1-6	99	95	100	0
B, 1-6	96	88	98	2
Pt, 1-6	155	86	97	3
Au, 1-6	100	69	89	11
Ir, 1-6	83	47	80	20
Rh, 1-6	89	79	94	6
St, 1-6	102	49	74	26
Special wires				
Am. Pt, 1-6	62	84	98	2
L. & N., 1-4	22	100	100	0
Foil				
P ₁₁₋₁ -P ₁₁₋₄	40	95	100	0
G ₁₁₋₁ -G ₁₁₋₄	40	72	95	5
P ₁₂₋₁ -P ₁₂₋₄	51	90	100	0

TABLE II (Concluded)

Electrode series	Number measured	Percentage of total		
		<0.000005 volt	<0.000010 volt	>0.000010 volt
D-F	49	90	100	0
G ₁₂₋₁ -G ₁₂₋₄	64	92	98	2
P ₁₃₋₁ -P ₁₃₋₄	66	85	100	0
G ₁₃₋₁ -G ₁₃₋₄	55	87	100	0
P ₂₂₋₁ -P ₂₂₋₄	34	100	100	0
I-N	44	86	100	0
G ₂₂₋₁ -G ₂₂₋₄	33	64	100	0
P ₂₃₋₁ -P ₂₃₋₄	30	93	100	0
G ₂₃₋₁ -G ₂₃₋₄	5	100	100	0

potential differences, the range of differences, and the average deviations obtained in nitrogen are much lower than those obtained in air.

Second, and a conclusion of perhaps the greatest importance, the quinhydrone electrode when prepared with c. p. platinum dipping into 0.1 *N* hydrochloric acid solution saturated with quinhydrone and stirred with nitrogen gives a half-cell which in our experience is more easily reproduced with great precision than any of the other half-cells used for reference. Even with the very small platinum wires (O, 1-6) few potential differences (Table II) occur which are greater than 0.000010 volt; the medium sized platinum wires (A, 1-6; B, 1-6; Pt, 1-6) as well as the foils give excellent results, over 85% of the total number of cells measured giving potential differences less than 0.000005 volt and over 95% (in many cases 100%) giving differences less than 0.000010 volt. The smallest gold wires (Au, 7-12), as in the case of the results in air, gave erratic results and large differences; the two series of larger gold wires (Au, 1-6 and St, 1-6) and the gold foils were also less satisfactory than the platinum electrodes of the same dimensions. On the other hand, the gold electrodes purchased from Leeds and Northrup (L. & N. 1-4) were by far, as in the case of air, the most satisfactory electrodes we measured. The platinum-rhodium alloy, while less satisfactory than the pure platinum, was nevertheless more satisfactory than the platinum-iridium alloy.

Further, it is to be observed (Table I) that the potential differences obtained when the electrodes are short-circuited in pairs during pre-treatment and measurement are, in general, no smaller than when the electrodes are cleaned and dried singly. Moreover, the irregularity in the potential differences of the unshorted electrodes observed in air did not appear when the electrodes were measured in nitrogen.

What is not indicated in these tables is the very important point that whereas the cells composed of air-dried electrodes and mechanically-stirred solutions sometimes take as long as sixty minutes to reach an equilibrium potential difference, and unstirred solutions even longer, cells made with nitrogen-stirred solutions take up the equilibrium value almost

immediately; the initial values are almost always very nearly the final values. That this is not due to a more efficient stirring with the nitrogen is indicated by the results obtained when air or oxygen is bubbled through the solution, results which will be discussed presently.

Our next efforts were in a direction to find out whether, if the electrodes were dried in nitrogen, it was necessary to stir the solutions with nitrogen throughout the time of measurement. We found that the average potential differences, the ranges and the average deviations were not as large as they were when the electrodes were air dried as well as measured in solutions stirred in air; on the other hand, neither were they as small as when they were measured in nitrogen-stirred solutions. This is due to the fact that when the electrodes are dried with nitrogen and the solutions mechanically stirred in the presence of air, they give small initial potential differences comparable to those obtained when nitrogen is used throughout, and larger final potential differences comparable to the equilibrium potential differences obtained when the electrodes are dried with air and the solutions mechanically stirred in the presence of air. The results which we calculated are the averages of the two types of results. Apparently, then, stirring the solution with nitrogen is of importance if the better reproducibility is desired.

Our next step was to dry the electrodes with air and to stir the solution with nitrogen. The results are given in Table III.

TABLE III

SUMMARY OF RESULTS OBTAINED WHEN THE ELECTRODES WERE DRIED WITH AIR BUT MEASURED IN SOLUTIONS STIRRED WITH NITROGEN. ELECTRODES SHORT-CIRCUITED; 0.1000 *N* HYDROCHLORIC ACID SATURATED WITH QUINHYDRONE USED

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns. between meas.	Average equilibrium potential, volt	Ranges of difference, 0.000000 to -volt	Average deviation, millivolt
A, 1-6	6	31	2	0.000001	0.000006	0.001
B, 1-6	6	28	2	.000002	.000010	.002
Pt, 1-6	6	32	2	.000000	.000003	.000
Au, 1-6	6	31	2	.000001	.000004	.001
St, 1-6	6	32	2	.000001	.000005	.001

Quite apparently electrodes dried in air and measured in solutions stirred with nitrogen give results fully as satisfactory as those obtained when the electrodes are dried in nitrogen as well as measured in solutions stirred with nitrogen. Consequently the more elaborate technique of drying electrodes with nitrogen may be discarded.

Some measurements were made as in the case of air with electrodes which were not dried but which were rinsed in some of the 0.1 *N* hydrochloric acid used and then measured in solutions stirred with nitrogen.

While the results were in general very satisfactory, they were not quite as consistent as those obtained when the electrodes were dried.

Still further measurements were made when the electrodes were dried with air and the solutions stirred with compressed air and when the electrodes were dried with oxygen and the solutions stirred with oxygen.

These methods do not give the same consistently low potential differences that are observed when nitrogen is used, which fact makes it obvious that it is the inert nitrogen which is instrumental in obviating the errors present when the half-cell is prepared in air and not an improved method of stirring the solution.

In conclusion, then, it seems fairly obvious that it is highly desirable that nitrogen be passed through the solutions during the measurements to eliminate errors which seem to arise as the result of the presence of oxygen in the solution. In the case of the gold and platinum alloys the desirability is not so marked; the action of these electrodes is erratic and demands some further study. It seems probable that the differences in air are due to the oxidation of the quinone, which introduces local disturbances in the hydroquinone-quinone equilibrium, but we are not at present able to offer any theory of the part the metal of the electrode plays in this disturbance.

Up to this time the work reported has been on the reproducibility of the different metals, in the course of which work comparisons have been made between electrodes of any one series, which is to say, in most cases, comparisons between similar specimens of the same metal. While from these results we can draw conclusions as to the relative precision with which different metals and different sizes reproduce the quinhydrone half-cell when different pieces of the same sample of metal or size are used, we cannot draw any conclusions as to whether a sample of one metal will give, within the precision of its own reproducibility when another sample of the same metal is used, the same potential as a sample of another metal; the same may be said as to the comparative potentials of electrodes of two different sizes. Work is in progress to decide this point; it involves an intercomparison between the different series of electrodes. The results of this work will be published in the next paper.

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Summary

An investigation has been made of the effect of nitrogen upon the reproducibility of the quinhydrone electrode in 0.1 *N* hydrochloric acid, from which the following conclusions may be drawn.

1. The quinhydrone half-cell, when prepared with electrodes dried in nitrogen and with solutions stirred with nitrogen, or when prepared with electrodes dried with air and with solutions stirred with nitrogen, is far

more readily reproducible than when prepared with air-dried electrodes and solutions stirred either mechanically in the presence of air or with compressed air or oxygen.

2. In the preparation of the quinhydrone half-cell it is not sufficient to dry the electrodes with nitrogen; nitrogen must be passed through the solution. If, however, nitrogen is passed through the solution the electrodes need not be dried with nitrogen.

3. The 0.1 *N* hydrochloric acid quinhydrone half-cell, prepared as described in this and in the first paper of this series, is the most easily and readily reproducible electrode which the authors have used.

4. Electrodes prepared with nitrogen acquire a definite equilibrium potential much more quickly than those prepared with air.

5. Short circuiting the electrodes in pairs during pre-treatment does not affect the potential differences obtained in nitrogen.

Work is in progress which involves an inter-comparison of the electrodes of different series made up of electrodes of different metals and of different sizes of the same metal.

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THE ATOMIC WEIGHTS OF NITROGEN AND SILVER. I. THE RATIO OF AMMONIA TO SILVER

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Because accurate, simple and direct methods are lacking, until recently the atomic weight of nitrogen has been less certainly known than most of those of elements of low atomic weight. But in view of recent gravimetric evidence, as well as gas density and mass spectrograph measurements, there now seems to be little doubt that the value of this constant is very nearly 14.008.

This paper describes an investigation of the ratio $\text{Ag}:\text{NH}_3$. The ratio $\text{NO}_3:\text{Ag}$ is already known with a higher degree of precision than most gravimetric ratios.¹ By combining the two the ratio $\text{NH}_3:\text{NO}_3$ may be obtained. This with the assumption of the atomic weights of hydrogen and oxygen makes possible the calculation of the atomic weight of nitrogen. In spite of the fact that the method of calculating the atomic weight of nitrogen is indirect, the result is not particularly sensitive to experimental error, for an uncertainty in the ratio $\text{NH}_3:\text{NO}_3$ affects the atomic weight of nitrogen by a proportion only 60% greater, while a given uncertainty in

¹ 0.57479, Richards and Forbes, *Pub. Car. Inst.*, No. 69, 47 (1907); Hönlgschmid, Zintl and Thilo, *Z. anorg. allgem. Chem.*, 165, 284 (1927)