

Summary

By a colorimetric method the rate of bromination of the ketone *m*-nitroacetophenone has been measured in solutions of sulfuric acid in acetic acid of concentration varying from 0.016 to 0.15 molal. Measurements to establish the effect of sodium bisulfate upon the rate of the reaction in these solutions and a limited series of measure-

ments in solutions in a mixed acetic acid-water solvent have also been made.

It has been found that in the acetic acid solution the rate of reaction increases with increasing sulfuric acid concentration more rapidly than does either the acidity function H_0 , the stoichiometric concentration of sulfuric acid, or the activity of sulfuric acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Energy Levels in Electrochemistry. II

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In aqueous solutions sulfuric acid can only be reduced electrolytically when the concentration is very high. Raising the temperature is equivalent to increasing the concentration. Sodium sulfate and ammonium sulfate solutions cannot be reduced electrolytically at any concentrations and temperatures that can be reached in open vessels.

On the other hand sulfurous acid and sodium sulfite can easily be oxidized electrolytically to sulfuric acid and sodium sulfate. A sulfite-sulfate electrode is therefore a one-way electrode, the reaction being irreversible electrolytically.¹ It was shown in our previous paper² that at constant temperature and constant pH , the potential difference at a sulfite-sulfate electrode should be a function of the concentration of the sulfite and independent of the concentration of the sulfate as an oxidation product. Lewis, Randall and Bichowsky³ found that at constant temperature and constant pH the change of electromotive force with change of concentration of sulfurous acid was described very well by the theoretical formula. They did not find that sulfate concentration had no effect because they varied the pH at the same time. This gap was filled by Noyes and Steinour⁴ who showed that, "provided the hydrogen-ion concentration is nearly the same, hydrochloric acid and sulfuric acid produce (in association with sulfurous acid) substantially the same electromotive force."

Schaum⁵ and von der Linde⁶ found that the

electromotive force of a sodium sulfite electrode varies with the concentration as it should, and that it makes no difference whether one dilutes with water or with sodium sulfate. The addition of a drop of benzyl alcohol was found to shorten the time necessary to reach equilibrium. We have not been able to confirm this effect of benzyl alcohol; but our experiments were made with smooth platinum electrodes and not with platinized electrodes.

The case of the cysteine-cystine electrode is more striking, because the same general results have been obtained by all workers. Dixon and Quastel⁷ found that the electromotive force of this electrode at constant temperature and constant pH is a function of the concentration of cysteine and is independent of the concentration of cystine. This is the more interesting because cystine can be reduced to cysteine with tin and hydrochloric acid. The discrepancy between the potential difference generated by cysteine and that necessary to reduce cystine to cysteine is therefore not very large; but it is sufficient to change the electrode from the reversible to the irreversible class. Dixon thought that cysteine was a stronger reducing agent at a mercury electrode by about 200 mv. than at a gold electrode. He ascribed this, apparently erroneously, to the high hydrogen over-voltage which can be observed at a mercury electrode.

Dixon found that glutathione behaved like cysteine. Michaelis and Flexner⁸ have confirmed Dixon on the important points; but they offer a different and apparently better explanation for

(1) Conant, *Chem. Rev.*, **3**, 4 (1926).

(2) Bancroft and Magoffin, *THIS JOURNAL*, **57**, 2561 (1935).

(3) Lewis, Randall and Bichowsky, *ibid.*, **40**, 356 (1918).

(4) Noyes and Steinour, *ibid.*, **51**, 1418 (1929).

(5) Schaum, *Z. Elektrochem.*, **7**, 483 (1901).

(6) Von der Linde, Inaugural Dissertation, Marburg, 1902.

(7) Dixon and Quastel, *J. Chem. Soc.*, **123**, 2943 (1923); Dixon, *Proc. Roy. Soc. (London)*, **B101**, 57 (1927).

(8) Michaelis and Flexner, *J. Biol. Chem.*, **79**, 689 (1928).

the behavior of a mercury electrode. They report, p. 721, that "a solution of cysteine in absence of oxygen establishes a definite potential at an indifferent electrode. This potential is independent of the concentration of cystine and depends logarithmically on the concentration of cysteine [over the range from 0.1 to 0.002 *M* at a *pH* of 4.6] and of hydrogen ions. The potential is identical at electrodes of blank platinum, gold-plated platinum, and mercury, and reproducible to within 5 mv. Slight traces of oxygen displace the potential to the positive side. Mercury is much less sensitive to oxygen than platinum or gold-plated platinum and has the advantage of yielding final values in a relatively short time."

If the explanation offered by Michaelis and Flexner for the behavior of mercury electrodes is right, it should be general and should apply to all reducing agents. This is the more important because many measurements of the electromotive forces of reducing agents are made in the presence of air. The measurements given in our previous paper in Table II were repeated, using mercury electrodes instead of smooth platinum ones. The results are given in Table I.

TABLE I

Pt | *M* Na₂SO₄ + A | Calomel electrode: A = concentration of other salt; B = *E*, with smooth platinum electrode; C = *E*, with mercury electrode. The calomel electrode is always cathode

A	B	C
Zero	0.146	0.313
<i>M</i> /10 Na ₂ SO ₄	.153	.320
<i>M</i> NaSO ₄	.149	.310
<i>M</i> NaCl	.182	.323
<i>M</i> NaBr	.188	.341
<i>M</i> NaCNS	.228	.347
<i>M</i> NaOH	.271	.278
<i>M</i> NaI	.302	.499

The electromotive forces obtained with the mercury electrodes, with the exception of the cell containing sodium hydroxide, are 120–200 mv. higher than the corresponding ones with platinum electrodes. This agrees with the results of Dixon and of Michaelis. The constant values are reached much more quickly with mercury than with platinum, so that a mercury electrode is more convenient to use than a platinum one. Mercury electrodes should be tried in measurements of photographic developers.

It seemed desirable to know something about the temperatures at which sodium sulfate and some other salts could be reduced by so energetic a reducing agent as metallic sodium. A small

oven was constructed of asbestos board and a glow-coil heater installed. The dry salts were mixed with approximately an equal weight of metallic sodium and placed in a hard-glass test-tube which was lowered into the oven through a small aperture in the roof. The mixture was stirred thoroughly throughout the heating, and the temperature was measured by inserting the bulb of a thermometer into the salt-sodium mixture. No correction was made for emergent stem and the temperatures given are only first approximations. After heating, the apparatus was allowed to cool and the mixture was then poured into water to decompose any excess sodium. The resulting solution was made acid with nitric acid and tested for reduction products. In the case of the sulfates and sulfites the test was made for sulfides, while chlorides were tested for in the case of chlorates and perchlorates. Reduction of potassium chlorate was also attempted with a 0.7% sodium amalgam at temperatures below the melting point of sodium. The data are given in Table II.

TABLE II

Salt	Temp., °C.
Sodium sulfate	370
Sodium sulfite	300
Potassium perchlorate	280
Potassium chlorate	100 (70)

The temperatures of reduction given in Table II show that sulfites are reduced more readily than sulfates and chlorates than perchlorates. This was to be expected, because chlorates break down when heated at a lower temperature than perchlorates and because sulfates seem to go direct to sulfides when heated. It would be possible to do decomposition-voltage measurements for sodium sulfate in the presence of fused caustic soda; but this delightful task was left for somebody else. It was hoped to determine the approximate temperature at which hydrogen reduces platinized sodium sulfate; but the time at our disposal did not permit of this.

Potassium chlorate can be reduced by sodium amalgam at temperatures below the melting point of sodium; but the reduction is very slow, only traces of chloride being formed on heating for three hours at 70°. At 100° sodium amalgam reduces potassium chlorate quantitatively in a few minutes.

In the light of what we now know, Quastel,

Stephenson and Whetham⁹ were very close to the truth a dozen years ago. "It was found [by Quastel and Whetham¹⁰] that in the presence of resting bacteria succinic acid donates hydrogen to methylene blue with the production of fumaric acid. It was also found that in the presence of the bacteria fumaric acid oxidizes leucomethylene blue, so that finally an equilibrium is established between succinic acid, fumaric acid, methylene blue and leucomethylene blue."

Bernheim and Dixon¹¹ made use of the same concept in their study of the reduction of nitrates to nitrites in animal tissues. "If it is assumed that the nitrate invariably requires activation before it can be reduced in the tissues, it is clear that the catalyst responsible must be associated in a very special way with the particular oxidase systems in the cell. . . .

"Nitrates differ from methylene blue in giving no oxidation potential at a platinum electrode, in this respect resembling the aromatic nitro-compounds. The latter are nevertheless easily reduced, both *in vitro*, for example by -SH compounds (cysteine, glutathione, etc.) and also by the dehydrases. Nitrates are not reduced by cysteine unless a nitrate-activating catalyst is present (Quastel, Stephenson and Whetham)."

The colloid chemist—and still more the physical chemist—is not yet accustomed to considering "resting" bacteria, of which he has never before heard, as acting as catalytic agents to succinic acid in something the same way that platinum does to hydrogen. It is evident, however, that some day there will be an extensive study of the catalytic action of "resting" bacteria.

From our point of view the formulation of all oxidation-reduction systems is very simple. If a substance does not pass through a more strongly reducing stage while being oxidized, it will give an electromotive force with an inert electrode quite apart from any catalytic action of the electrode or of the solution. If the substance does pass through a more strongly reducing stage while being oxidized, it will not act electromotively as a reducing electrode unless the electrode metal or

the solution is a sufficiently powerful catalytic agent to eliminate the effect of the energy hump. The converse is also true. If a substance does not pass through a more strongly oxidizing stage while being reduced, it will give an electromotive force with an inert electrode quite apart from any catalytic action of the electrode or of the solution. If the substance does pass through a more strongly oxidizing stage while being reduced, it will not act electromotively as an oxidizing electrode unless the electrode metal or the solution is a sufficiently powerful catalytic agent to eliminate the effect of the energy hump.

Any given oxidation-reduction system may be reversible both ways as with the ferrous-ferric electrode; it may be reversible one way as with the cysteine-cystine electrode; or it may be irreversible both ways as with the chloride-chlorate or chlorate-perchlorate electrode.

This accounts for potassium nitrate, nitrobenzene and acetic acid not giving oxidation potentials, and for ammonia, aniline, and alcohol not giving reduction potentials. On the other hand, phenylhydroxylamine and nitrosobenzene is a completely reversible system and so is hydroquinone and quinone.¹²

Summary

The general results of this paper are:

1. Since the reduction of cystine to cysteine is not strictly reversible, the electromotive force of a cysteine-cystine electrode is theoretically a function of the temperature, the *pH* and the concentration of cysteine but not a function of the concentration of cystine.

2. If an electron transfer between an inert metal and an oxidizable or reducible substance involves passing through an energy hump under the conditions of the experiment, a reducing potential or oxidizing potential characteristic of that substance will not be set up; otherwise, it will.

3. "Resting" bacteria are catalytic agents for some systems and we shall some day have a bacterial chemistry based on this property.

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(9) Quastel, Stephenson and Whetham, *Biochem. J.*, **19**, 305 (1925).

(10) Quastel and Whetham, *ibid.*, **18**, 519 (1924).

(11) Bernheim and Dixon, *ibid.*, **22**, 132 (1928).

(12) Gladstone and Hickling, "Electrolytic Oxidation and Reduction," 1936, p. 159.