THE ENERGY HUMP IN CHEMISTRY. I.

BY

WILDER D. BANCROFT AND JAMES E. MAGOFFIN,

Cornell University.

INTRODUCTION.

There are a great many reduction-oxidation systems which do not fit into the orthodox picture. Potassium nitrate and nitrobenzene are readily reduced; but neither one gives an oxidizing potential with a platinum electrode. Alcohols and many other organic compounds are readily oxidized; but give no reducing potentials. An overwhelming majority of organic compounds cannot be rated electromotively as oxidizing or reducing agents, although they can be reduced or oxidized at fairly definite potentials. Even here there are discrepancies. Dimethyl acrylic acid can be reduced readily in acid solution at a platinum cathode but not by a chromous chloride solution which is approximately 0.4 volt less noble than the platinum cathode. Sulphurous acid and sodium sulphite can be oxidized electrolytically without any difficulty; but aqueous sodium sulphate cannot be reduced under any experimental conditions that have yet been realized. Concentrated sulphuric acid was reduced electrolytically by Faraday; but ordinary solutions of sulphuric acid cannot be reduced electrolytically.

Metallic oxides, such as those of manganese, are stronger oxidizing agents and less stable thermally the more oxygen they contain. No such relation holds for potassium hypochlorite, chlorite, chlorate and perchlorate. The thermal decomposition of potassium chlorate into chloride and oxygen has never been reversed experimentally, indicating that potassium chlorate is a metastable compound; and yet there is no experimental evidence that either potassium chlorate or perchlorate will revert to chloride to any appreciable extent in any reasonable time. While a potassium chlorate solution can be boiled with hydrazine without any reduction taking place, the presence of pulverulent copper causes quantitative reduction apparently at ordinary temperatures.

All these difficulties and many others disappear if one introduces, at first as a working hypothesis, the concept of the energy hump. We postulate that systems exist which will not react unless some of the molecules of one or more of the substances, which should react from the free energy relations, are raised to an energy level or to energy levels higher than those reached by any of the molecules under ordinary conditions. In the case of the energy of activation it is assumed that relatively few molecules reach the reactive energy levels under ordinary conditions. As stated, we are assuming that in certain systems none of the molecules reach the reacting energy levels under ordinary conditions. The concept of the energy hump is, therefore, the concept of the energy of activation carried to its logical conclusion. From the experimental behavior of systems in which we postulate the occurrence of energy humps, we deduce that the energy hump tends to disappear with increasing concentration, rising temperature, and the presence of suitable catalytic agents. When a reaction can be made to take place electrolytically, the energy hump is defined as the difference between the free energy and the voltage necessary to produce the reaction.

The concept of the energy hump as we are developing it is new to everybody and has not yet been received with enthusiasm by anybody to whom it has been presented. It carries with it the corollary that certain reactions which are permitted by the free energy relations will not take place to any extent even in infinite time. In other words, it postulates a zero reaction velocity in certain cases, whereas all other physical chemists postulate nowadays a finite, though often incredibly small, reaction velocity. On the other hand, if we are right it means that the physical chemists can deal with organic chemistry as a whole instead of being limited to special chapters as at present. Of course the concept of the energy hump is not limited to reduction-oxidation reactions. They are, however, the best systems with which to start, because we can determine certain chemical potentials by means of electromotive force measurements.

The question at issue is not whether the concept of the energy hump is right or wrong; but whether it is a helpful working hypothesis We shall now present a few of the reasons that make us believe that the concept satisfies this criterion.

ELECTROMOTIVE FORCES.

When electrolyzing a solution, the products set free at the electrodes are those requiring the lowest voltage under the conditions of the experiment. Consequently, we know that other products which might have appeared require a higher voltage to produce them. When we charge a storage battery and convert lead sulphate into lead peroxide, we know that it takes a higher voltage to set free oxygen; that conclusion is verified experimentally when we reach the end of the charging period. If we electrolyze aqueous caustic soda, we get hydrogen at the cathode and we conclude that the discharge of sodium ions require a higher voltage. We can check this experimentally by lowering the voltage at which sodium ions discharge. With a mercury cathode we get primary discharge of sodium ions and the formation of sodium amalgam. That is elementary now; but people opposed bitterly the concept of primary decomposition of water when it was introduced by LeBlanc forty-five years ago.

When we electrolyze dilute sulphuric acid, we get hydrogen at the cathode and we conclude that the voltage necessary to reduce sulphuric acid to sulphurous acid is higher than that necessary to set free hydrogen. We can check this experimentally by increasing the concentration of sulphuric acid and by raising the temperature, in which case we get reduction to sulphurous acid and then to hydrogen sulphide.[1] If we raise the voltage necessary to set free hydrogen, by using a zinc or mercury cathode, we can reduce sulphuric acid at a somewhat lower concentration or at a somewhat lower temperature.

A sulphur dioxide electrode[2] in molar sulphuric acid is roughly 0.4 volt more noble than a hydrogen electrode. At ordinary concentrations and temperatures a cathode over-

---

[1] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2561 (1935).

[2] Lewis, Randall and Bichowsky, *J. Am. Chem. Soc.*, **40**, 356 (1918).

voltage of one volt is not sufficient to reduce sulphuric acid. Consequently, to pass electrolytically from $H_2SO_4 + H_2$ to $H_2SO_3 + H_2O$ in molar solution means passing through an energy level at least 1.4 volts higher than the final level. Nobody has determined whether a sulphur dioxide electrode in concentrated sulphuric acid is strictly reversible or not. Assuming it to be reversible or nearly so, the energy hump for aqueous sulphuric acid can be varied, by changing the concentration, from approximately zero to a value which is certainly not less than two volts and may be a good deal more. We have no method at present for determining the theoretical voltage necessary to reduce dilute sulphuric acid. One could make determinations at a zinc or mercury cathode with fairly concentrated sulphuric acid solutions and then plot the observed figures against the concentrations; but the extrapolation would probably be so excessive even at 100° as to make the result worthless.

People have become so used to speaking of electromotive forces of reversible reactions that most physical chemists believe that an irreversible reaction cannot give a definite electromotive force. This is wrong both theoretically and experimentally. A given solution of sodium sulphite is at a definite energy level and changes to another energy level when it is oxidized to sodium sulphate. Since this change can be made to take place electrolytically under practically constant conditions, it must and does give a definite electromotive force. Schaum, G. N. Lewis and A. A. Noyes have each studied the sulphite-sulphate electrode and have had no difficulty in getting measurements which they were willing to publish. Dry cells are not reversible but hundreds of millions of them are sold.

We have shown [3] elsewhere that, at constant temperature and constant pH, the potential difference at a sulphite-sulphate electrode should be a function of the concentration of the sulphite and independent of the concentration of the sulphate as a reaction product. Schaum [4] and von der Linde [5] found that the electromotive force of a sodium sul-

---

[3] Bancroft and Magoffin, *J. Am. Chem. Soc.*, 57, 2561 (1935); 58, 2187 (1936).

[4] Schaum, *Z. Elektrochemie*, 7, 483 (1901).

[5] Von der Linde, Inaugural Dissertation, Marburg (1902).

phite-sulphate electrode varies with the concentration of the sulphite as it should, and that it makes no difference whether one dilutes with water or with sodium sulphate. Lewis, Randall and Bichowsky[6] found that at constant temperature and constant pH the change of electromotive force with change of concentration of sulphurous acid was described very well by the theoretical formula. They did not find that the sulphate concentration had no effect; but that was because they varied the pH at the same time. This gap was filled by Noyes and Steinour[7] who showed that when the hydrogen-ion concentration is nearly the same, addition of hydrochloric acid or of sulphuric acid to a sulphurous acid electrode gives substantially the same electromotive force. We have shown that adding sodium sulphate to a sodium sulphite electrode gave a slight increase in electromotive force instead of a decrease.

Although cystine can be reduced to cysteine by tin and hydrochloric acid, the reduction apparently does not take place reversibly because the electromotive force of a cysteine electrode varies with the concentration of cysteine as it should and is independent of the cystine concentration.[8] Michaelis and Flexner report, p. 721, that "a solution of cysteine in absence of oxygen establishes a definite potential at an indifferent non-attackable electrode. This potential is independent of the concentration of cystine and depends logarithmically on the concentration of cysteine [over the range from 0.1 M 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 five millivolts. 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."

The question whether a given substance, which can be oxidized or reduced, will function as a reduction or an oxida-

---

[6] Lewis, Randall and Bichowsky, *J. Am. Chem. Soc.*, 40, 356 (1918).

[7] Noyes and Steinour, *J. Am. Chem. Soc.*, 51, 1418 (1929).

[8] Dixon and Quastel, *J. Chem. Soc.*, 123, 2943 (1923); Dixon, *Proc. Roy. Soc.*, 101 B, 57 (1927); Michaelis and Flexner, *J. Biol. Chem.*, 79, 689 (1928).

tion electrode is a simple one from our point of view.[9] If a substance does not pass through a more strongly reducing stage while being oxidized, it will give an electromotive force with a non-attackable 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 reduction 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 true for an oxidizing agent.

Any given reduction-oxidation 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.

The concept of the energy hump accounts for potassium nitrate, nitrobenzene, and acetic acid not giving oxidation potentials, and for ammonia, aniline and alcohol not giving reduction potentials. The energy humps for these cases have not yet been measured; but they will be determined as soon as possible. Phenylhydroxylamine and nitroso benzene is a completely reversible system and likewise hydroquinone and quinone.[10]

If enzymes or bacteria convert an irreversible oxidation-reduction system into a reversible one, the system will then give an electromotive force with a platinum electrode. This was realized by Cannan, Cohen and Clark [11] more than ten years ago. The only thing that they lacked was the concept of the energy hump.

"[Cell] suspensions act as if there were present very small quantities of active poising material fed from a large reserve which is mobilized slowly but decidedly. Thus a reasonable interpretation of the potentiometric observations we have reported with cell catalysts would seem to be that the catalyst affects the mobilization. The full import of such an effect cannot be appreciated until the electrochemical formulation

---

[9] Bancroft and Magoffin, *J. Am. Chem. Soc.*, 58, 2187 (1936).

[10] Glasstone and Hickling, "Electrolytic Oxidation and Reduction," 159 (1936).

[11] Cannan, Cohen and Clark, U. S. Public Health Reports, Suppl. **55** (1926).

of oxidation-reduction can be extended to the so-called irreversible systems which comprise the greater part of organic chemistry," p. 24.

"It would seem that there exist catalysts whose function is an activation of a sort that would result in making a substance electromotively active. Indeed, this is partially implied in certain theories of the function of polar catalysts. Perhaps our experiments indicate that it would be worth while to search for evidence of this sort of activation," p. 25.

"Upon platinized electrodes the potential of a hydrogen electrode is induced in sugar media by cultures such as *Bact. coli* which may liberate hydrogen under proper conditions. Perhaps this might be expected as a natural and insignificant consequence of the juxtaposition of hydrogen and platinum black. But, in the present state of our knowledge, it is equally legitimate to suggest that the appearance of hydrogen harmonizes with the attainment of that reduction intensity at which hydrogen should be liberated. Indeed, it seems to require this more comprehensive point of view to maintain perspective when, on the one hand, certain cultures induce a definite over-voltage with the hydrogen which is liberated at considerably less than one atmosphere pressure and when, on the other hand, certain other cultures induce various potentials more positive than that of the hydrogen electrode but no less distinctive," p. 27.

Borsook and Schott [12] have improved on the earlier work of Thunberg [13] and of Lehmann [14] and have shown that the succinic-fumaric system gives a measurable electromotive force in presence of a suitable enzyme. We had not read these papers when we made the prediction [15] that such a phenomenon must occur.

Barron and Hastings [16] showed that electromotive forces can also be obtained for the lactate-pyruvate system, though they did not actually wait for equilibrium to be reached, preferring to add dyes to the system. They say: "There

---

[12] Borsook and Schott, *J. Biol. Chem*, **92**, 535 (1931).

[13] Thunberg, *Skand. Arch. Physiol.*, **46**, 339 (1925).

[14] Lehmann, *Skand. Arch. Physiol.*, **58**, 173 (1929).

[15] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **58** (1936).

[16] Barron and Hastings, *J. Biol. Chem.*, **107**, 567 (1934).

exist in the cell two kinds of reversible oxidation-reduction systems. The first group is made up of electromotively active oxidation-reduction systems, which will play the rôle of oxidizing catalysts if reduced by the oxidizable metabolites of the cell and then reoxidized by atmospheric oxygen. . . . The second group is made up of a number of irreversible oxidation-reduction systems which become reversible when activated by the activating coenzymes (Wieland's dehydrogenases). These reversible systems are quite different from the first group. They are sluggish reversible systems, which do not readily transfer electrons to the electrode and whose equilibrium potentials are determined only by the aid of electromotively active mediators. These systems undoubtedly play an important rôle in those studies in which the reducing intensity of cells has been determined by the aid of reversible dyes," p. 575.

The Helmholtz formula for the relation between electromotive force, heat effect and temperature coefficient was deduced for reversible cells and has hitherto been applied only to them. There seems to be no reason why this limitation should not be dropped, provided we do not do it blindly. Since an electromotive force measures a drop from one energy level to another, it is immaterial whether the operation is reversible or not. We may therefore consider the heat of reaction of an irreversible cell as consisting of a theoretically reversible part and a practically irreversible part, the latter of which may be infinitely small at times, though it probably rarely is. If we calculate a heat effect from the electromotive force and the temperature coefficient, we shall determine the heat effect of the theoretically reversible reaction. The difference between that and the observed heat effect gives the heat effect of the practically irreversible reaction.

If the reaction sulphite to sulphate is theoretically reversible and if the whole irreversibility is in the sulphate to sulphite reaction, the Helmholtz equation will apply without change. It is possible, however, that the change from sulphite to sulphate may consist of a reversible electrolytic portion and a non-electrolytic portion, which would therefore be irreversible electrolytically. This possibility was suggested by Conant and Lutz.[17] In this case the Helmholtz formula will not apply to the whole reaction and we shall have to determine what the electrolytically reversible and the electrolytically irreversible reactions are. Experiments along this line will be started in the Cornell Laboratory as soon as possible. Such a treatment of the Helmholtz equation is legitimate in a formal way. Whether it will be helpful is yet to be determined.

NITRATES.

Erich Müller[18] has studied the electrolytic reduction of weakly alkaline potassium nitrate solutions at different cathodes. With a normal potassium nitrate solution and a cathode current density of 0.1 amp./cm.^{2} at 15°–20°, and following the reaction gas analytically, he obtained percentage reductions of 14.8, 76.5, 97.6 and 96.8 at cathodes of platinized platinum, smooth platinum, iron, and zinc respectively. The low percentage reduction at a platinized platinum cathode must be a case of the misleading experiment,[19] because Gladstone and Tribe[20] had shown, twenty-three years earlier, that platinum black and molecular hydrogen reduce a potassium nitrate solution to ammonia and caustic potash. Consequently, one must get 100 per cent. current efficiency and not 15 per cent. if one electrolyzes a normal potassium nitrate solution at a platinized platinum cathode with a sufficiently low current density. Müller's own experiments are not consistent. He determined decomposition voltage curves for normal potassium nitrate plus twentieth-normal caustic potash and found that the value at a platinized platinum cathode is a little less than at a smooth platinum cathode, and that both values are a little less than the hydrogen value.

It seemed probable that Müller's abnormal value of 14.8 per cent. current efficiency was due to an adsorption of ammonia by the platinum black, poisoning the cathode to a considerable extent. We, therefore, determined decom-

---

[17] Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1047 (1923); Conant, *Chem. Reviews*, **3**, 4 (1926).

[18] E. Müller, *Z. anorg. Chem.*, **26**, 1 (1901).

[19] Bancroft, *The Rice Institute Pamphlet*, **15**, 224 (1928).

[20] Gladstone and Tribe, *J. Chem. Soc.*, **33**, 309 (1878).

position-voltage curves for different cathodes with neutral solutions of sodium nitrate saturated at room temperature. In all runs the anode was a smooth platinum foil, 1.7 × 2.5 cm. The platinized platinum foil cathode was also 1.7 × 2.5 cm. The zinc, amalgamated zinc, and iron strip cathodes were 1.3 × 2.5 cm., while the mercury cathode had a diameter of 0.6 cm. In all runs the electrodes were 3.5 cm. apart.

The break-point for a saturated sodium sulphate solution was 2.15 volts and 0.002 amp. with a platinized cathode, 2.80 volts and 0.003 amp. with a zinc cathode, both at 25°. In Table I are given condensed data for neutral and slightly alkaline solutions of sodium nitrate with cathodes of platinized platinum, smooth platinum, iron, zinc, amalgamated zinc, and mercury.

TABLE I.

Break-points for Saturated Sodium Nitrate.

The first figures indicate the point at which oxygen begins to come off; the second figures indicate the point at which hydrogen begins to come off.

Platinized Platinum				Iron	
25°		80°		25°	
Volts	Amps.	Volts	Amps.	Volts	Amps.
2.15	0.002	1.34	0.001	2.12	0.004
2.70	0.018	2.60	0.057	4.20	0.680

Zinc		Amalgamated Zinc		Mercury	
25°		25°		25°	
Volts	Amps.	Volts	Amps.	Volts	Amps.
2.40	0.005	2.80	0.004	2.90	0.002
4.40	0.640	3.60	0.180	5.20	0.230

Break-points for Saturated Sodium Nitrate, N/100 with Respect to NaOH.

Platinized Platinum		Zinc	
25°		25°	
Volts	Amps.	Volts	Amps.
1.28	0.001	2.18	0.002
2.45	0.005	4.25	0.530

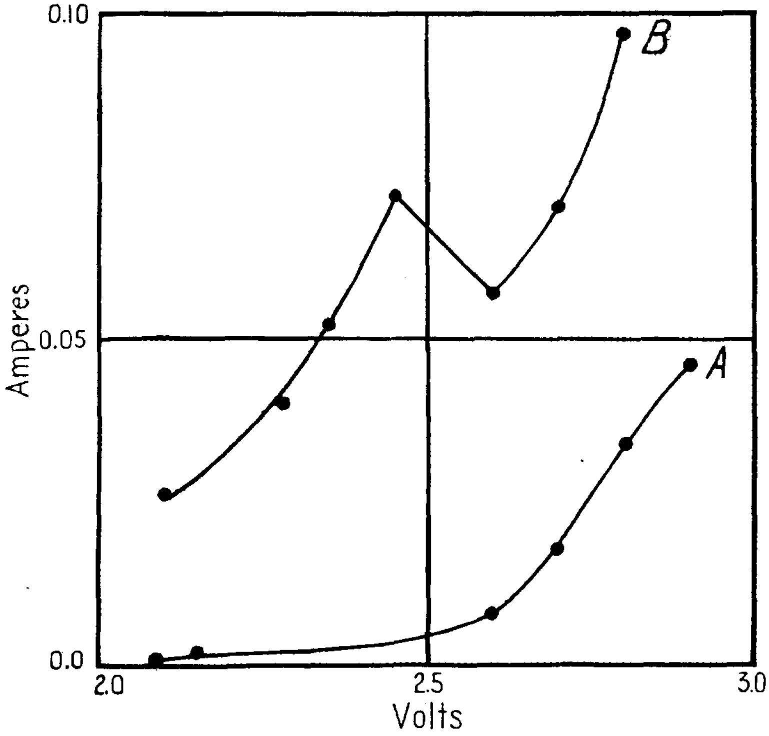
Examination of the decomposition-voltage curves, Fig. 1, for the neutral sodium nitrate solution with platinized-platinum cathodes shows that we have a system behaving like the sodium chlorate one.[21] At 25° there is no downward break in the curve; but one is quite clear at 80°. The first part of the curve at 80° represents the reduction of nitrate,

---

[21] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2563 (1935).

while evolution of hydrogen takes place as well over the latter part. The apparent passivity is caused by the impoverishment of sodium nitrate in the pores of the platinized cathode. Müller should have been on his guard in regard to this, because Gladstone and Tribe had shown that platinum black adsorbs ammonia.

FIG. 1.



Current-voltage curve for sodium nitrate. *A* = *25°*, *B* = *80°*.

Though the showy thing is the break in the 80° curve, the really important one is the very small difference in the current necessary to set free hydrogen in the 25° curve, two to eighteen milliamperes. The current density would have to be held very low in order to keep the current efficiency high and that is what Müller found without knowing it. In the slightly alkaline sodium nitrate solution a current of only five milliamperes sets free hydrogen.

Another interesting thing, which also appears from Müller's data, is that the voltage at which the reduction starts varies with the nature of the cathode. It is 2.15 volts for platinized platinum, 2.12 volts for iron, 2.40 volts for zinc, 2.80 volts with amalgamated zinc, and 2.90 volts with mercury. Amalgamating the zinc makes it behave more like mercury, changing it a good deal although this has no effect on the electromotive force of a zinc electrode. Making the solution slightly alkaline lowers the voltage somewhat.

The difference in voltage due to varying the cathode means a variation in activation of the nitrate or an existence of over-voltage in the solution, just as one prefers to word it. Although the voltage necessary to reduce sodium nitrate at a mercury cathode is higher than that necessary to set free hydrogen at a platinum cathode, the voltage necessary to set free hydrogen at a mercury cathode is relatively greater still and consequently a mercury cathode is more efficient than a platinized platinum one. Although the iron cathode does not seem to lower the initial voltage of reduction much over that of a platinized platinum one, the current that passes is so much greater at an iron cathode at any given voltage that the iron cathode is the most efficient practically. Müller found another form of the same thing. Taking three cells in series so as to get the same current through each, and using smooth platinum, zinc and iron as cathodes, Müller found 42, 181 and 187 milligrams of ammonia respectively in the three cells, although the voltage drop across the terminals was least in the cell with the iron cathode. The depolarizing effect of a nitrate solution was greatest at the iron cathode.

Müller has made a series of determinations of cathode potentials during electrolysis at different cathodes in solutions normal with respect to sodium nitrate or sodium nitrite and hundredth-normal with respect to sodium hydroxide. He gives no directly observed figures, only what he calls absolute cathode potentials. This should mean the Ostwald zero; but he takes the tenth-normal calomel electrode as − 0.59 volts, which is not what Richards made it. We shall follow the example of Foerster[22] and of Kremann and Müller,[23] adding 0.26 volts to Müller's figures and reversing the sign. This gives data which are, as near as may be, in terms of the hydrogen electrode as zero. As there are apparently very marked differences in the evolution of hydrogen from potassium sulphate solutions at iron cathodes, the data may be considerably in error.

Müller found approximately − 0.65, − 0.70, − 0.86 and − 1.10 volts respectively for the initial reduction of weakly alkaline nitrate to nitrite at cathodes of platinum, iron, zinc, and mercury respectively. Since the corresponding values for hydrogen are approximately − 0.68, − 0.90, − 1.01 and − 1.30 volts, it is evident that nitrate will be reduced to some extent to nitrite at all these cathodes, and this is true experimentally.

If we know what electromotive force a nitrate-nitrite electrode should give, supposing one could be made to function, we should be able to calculate the energy hump for nitrate with some degree of approximation. Pick[24] has calculated a value of + 0.01 volt for a nitrate-nitrite electrode in alkaline solution. This value is not strictly comparable with that of − 0.65 volt found by Müller because the alkalinity is not the same. Subject to an unknown correction for this, the energy hump for nitrate in alkaline solution is the algebraical difference of these two values, or about 0.7 volt at platinum. If the platinum cathode activates nitrate to any extent—as it undoubtedly does—the true energy hump in the absence of the electrode is still larger. It is apparently about 0.9 volt at a zinc cathode and about 1.1 volts at a mercury cathode. This shows an activation of sodium nitrate by platinum over mercury of about 0.4 volt.

Another striking case of adsorption and activation was studied fifteen years ago by Conant and Cutter[25] who did not, however, recognize it as such. Dimethylacrylic acid is reduced readily by hydrogen at a platinum cathode in an acid

---

[22] Foerster, "Elektrochemie wässeriger Lösungen," 585 (1922).

[23] Kremann and Müller, Ostwald's Handbuch der allgemeinen Chemie, **8** II, 333 (1931).

[24] Pick, *Z. Elektrochemie*, **26**, 186 (1920).

[25] Conant and Cutter, *J. Am. Chem. Soc.*, **44**, 2651 (1922).

solution. It is not reduced by a chromous chloride solution, even though this is a stronger reducing agent than platinum and hydrogen by about 0.3 volt. Evidently the platinum activates the dimethylacrylic acid.[26] This could be tested easily but has not yet been done. If platinum is held in a suitable chromous chloride or acetate solution until all the hydrogen is given off that will come off in a reasonable time, we predict that the solution will reduce dimethylacrylic acid in the presence of platinum. It is not yet necessary to differentiate in principle between hydrogenation and reduction.

CHLORATES.

Chloric acid is a fairly powerful oxidizing agent, at least as strong as chromic acid; but neutral chlorates have little or no oxidizing power at ordinary temperatures—much less than hypochlorite solutions in spite of the higher oxygen content. We explain the relative inertness of the neutral and alkaline solutions by postulating an energy hump. Since this explanation can be used to account for anything, we must show independently the existence and magnitude of the hump. Fortunately this can be done very satisfactorily in the case of the chlorates.

In a previous paper[27] it was shown that pulverulent copper activates neutral chlorate so much that hydrazine[28] reduces it quantitatively to chloride, whereas even boiling hydrazine does not reduce chlorates in the absence of copper. Hofmann[29] showed that osmium tetroxide activates sodium chlorate so much that one gets a potential difference of + 0.34 volt for a platinum-foil electrode in a solution containing 1 g. $NaHCO_3$, 0.5 g. NaCl, 5.0 g. $NaClO_3$ and 0.02 g. OsO_4 per 100 cc. when measured against a tenth-normal calomel electrode. This would correspond to about + 0.39 volt against a normal calomel electrode and means that we have approximately $E_h = +0.69$ volt. Not realizing that this was an irreversible reaction Hofmann had no difficulty in measuring this electromotive force. Chlorate can be reduced

---

[26] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2563 (1935).

[27] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2563 (1935).

[28] Hodgkinson, *J. Soc. Chem. Ind.*, **33**, 815 (1914).

[29] Hofmann, Ber. **46**, 1662 (1913).

electrolytically at a platinum cathode; but we know that the platinum activates the chlorate. Consequently we are undoubtedly justified in saying that the true value for neutral chlorate in the absence of a metal corresponds to $E_h > -0.36$ volt. Since alkaline sodium hydrosulphite reduces chlorate, the activation by platinum is not much.

The decomposition voltage for chlorate at an iron cathode is apparently about $E_h = 0.46$ volt. Consequently the energy hump for chlorate is at least 1.05 volts $(0.36 + 0.69)$, a trifle less at platinum, and about 0.8 volts $(0.36 + 0.46)$ at iron.

Osmium tetroxide vapor has only a very slight effect on the temperature at which potassium chlorate breaks down when heated and Hofmann believes that the activation is due to compound formation between chlorate and osmium tetroxide. The combination sets free iodine from potassium iodide as it should, but not bromine from potassium bromide. The so-called mercurous oxide—really mercuric oxide and mercury—is converted into mercuric oxide. Soot is oxidized readily to carbon dioxide, mellitic acid and other substances. Ethylene is converted into ethylene glycol; but hydrogen is apparently not attacked. Allyl alcohol is oxidized at 50° to glycerol. Fumaric acid is oxidized to racemic acid and maleic acid to mesotartaric acid; sodium formate to oxalate and carbonate.

While activated chlorate is called by Hofmann a pretty strong oxidizing agent, nobody calls potassium ferricyanide that, and yet molar potassium ferricyanide with platinum gives $E_h = +0.71$ volt. The reason that it does not appear to be so strong an oxidizing agent as activated chlorate is that ferricyanide is a reversible oxidizing agent and chlorate an irreversible one. If one converted ferricyanide into an irreversible oxidizing agent by removing the ferrocyanide as fast as formed, ferricyanide should do all the stunts that activated chlorate will do. Ferric chloride seemed to be the ideal thing for this purpose.

Potassium ferricyanide in molar solution gave a value of $E_c = +0.407$ volt. Addition of 0.1 cc. of a molar solution of ferric chloride to 30 cc. of the potassium ferricyanide solution caused a change to $E_h = +0.881$ volt. We therefore predicted that a solution of potassium ferricyanide alone would not oxidize sodium formate appreciably; but would do so in presence of ferric chloride.

Twenty-five cubic centimeters of a molar solution of potassium ferricyanide were mixed with an equal volume of molar ferric chloride and one gram of sodium formate added. The control had no ferric chloride. These mixtures were allowed to stand for twenty-four hours. The solution containing the ferric chloride became deep blue, and pasty, while no change in the control tube could be noticed. Both mixtures were filtered and calcium chloride added to the filtrates to determine whether oxalate or carbonate were present. Both tests were negative, which was something of a shock. The blue residue from the solution containing ferric chloride was washed with ammonium hydroxide to remove any carbonate or oxalate which might have been adsorbed. The washings were made acid with acetic acid and tested with calcium chloride. A precipitate of calcium oxalate was obtained.

The experiments were repeated, keeping the solutions in the dark and again a test for oxalate was obtained in the solution to which ferric chloride had been added. Ferric chloride and sodium formate without the ferricyanide gave no test for oxalate or carbonate.

Tommasi[30] reports that potassium perchlorate can be reduced quantitatively to chloride by sodium hydrosulphite, $Na_2S_2O_4$. We have not been able to confirm this statement. Solutions of sodium chlorate and of perchlorate were treated in the cold with sodium hydrosulphite. The excess hydrosulphite was then destroyed with sodium peroxide, the solution made acid with an excess of nitric acid and then tested with silver nitrate. No test for chloride was obtained in either case. The same runs were then made at boiling temperature. This time a test for chloride was obtained in the chlorate solution but not in the perchlorate.

Since the solutions of the sodium hydrosulphite were slightly acid, runs were made in which alkali was added. It was found that sodium chlorate was reduced at room temperature if the solution was neutral or slightly alkaline, and that

---

[30] Bull. (2) 38, 148 (1882).

perchlorate was reduced somewhat at boiling temperature if the solution was slightly alkaline. If the perchlorate solution was alkaline enough, quantitative reduction was obtained at boiling temperature.

A dilute solution of potassium perchlorate made alkaline with sodium hydroxide was electrolyzed at 99° with a plain-platinum anode and a zinc cathode. A good test for chloride was obtained, although the reduction was not quantitative. These experiments show that sodium hydrosulphite is a strong enough reducing agent to reduce both chlorate and perchlorate if the pH and the temperature of the solution are adjusted correctly. The reduction is quantitative in both cases if the conditions are controlled properly. Also, boiling solutions of perchlorate can be reduced electrolytically in alkaline solution.

When potassium chlorate is heated by itself in the air, nothing appears to happen until the temperature gets above the melting-point of the chlorate. Oxygen is then set free and some potassium perchlorate is formed. People have adopted [31] the view that two reactions take place independently and simultaneously:

$$(1)\ 2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2,$$
$$(2)\ 4\,KClO_3 \rightarrow KCl + 3\,KClO_4.$$

Equation 1 can be made to take place, one hundred per cent., by adding manganese dioxide. Nobody has yet been able to catalyze Equation 2 or to poison Equation 1 sufficiently to give a one hundred per cent. yield of Equation 2.

In Equation 2 we postulate that all three oxygens are effective in oxidizing potassium chlorate to perchlorate. Fowler and Grant [32] heated potassium chlorate with silver oxide, obtaining potassium perchlorate and metallic silver with practically no evolution of oxygen.

Since no perchlorate [33] is formed when potassium chlorate is heated in contact with manganese dioxide, it seemed to us that this was the way to start studying the phenomenon of the instability of potassium chlorate. When one solid catalyzes

---

[31] Scobai, *Z. physik. Chem.*, **44**, 319 (1903).

[32] Fowler and Grant, *J. Chem. Soc.*, **57**, 279 (1890).

[33] Eccles, *J. Chem. Soc.*, **29**, 857 (1876).

the decomposition of another solid, the reaction must take place at the solid-solid interface provided we exclude, by definition, the possibility of any appreciable vapor-phase catalysis. Consequently manganese dioxide can only decompose those particles of solid potassium chlorate with which it is in actual physical contact. Since this hypothesis seems not to be covered adequately in the literature, we have made a few preliminary experiments.

The apparatus consisted of a hard-glass test-tube closed air-tight with a stopper which connected by a capillary tube with a Hempel gas-burette. The glass test-tube was immersed in a Wood's-metal bath and the uncorrected temperature was read on a thermometer placed in the bath immediately next to the test-tube. Before oxygen starts to come off, the contents of the test-tube are somewhat cooler than the bath. When oxygen is coming off, the heat of decomposition may easily make the contents of the test-tube somewhat hotter than the bath. Such an error is of no importance so far as general principles are concerned. After each run the test-tube was allowed to cool and all measurements of gas volumes were made at room conditions of pressure and temperature. It was consequently not necessary to know the volume of the test-tube, the exact temperature to which it had been heated, or the temperature gradient.

Anhydrous potassium chlorate, potassium perchlorate and manganese dioxide were ground separately in a mortar to approximately the same particle size. Equal mixtures of potassium chlorate and manganese dioxide or of potassium perchlorate and manganese dioxide were used in all runs. The heating was continued at approximately constant temperature until practically no more gas was evolved.

With potassium chlorate and manganese dioxide at about 225° no more oxygen was evolved after forty-five minutes heating. Ten per cent. of the theoretical amount of oxygen was evolved. At 300° heating was continued for three and one-third hours before evolution of gas ceased. At 330° 96.5 per cent. decomposition was accomplished in twenty minutes and at 335° 98.1 per cent. of the oxygen was evolved in about one minute. Sodeau[34] reports that in his experi-

---

[34] Sodeau, *J. Chem. Soc.*, 81, 1074 (1902).

ments "the decomposition became rapid and beyond control when the temperature of the bath had risen to about 340°." In our runs made at 330° and 335° the residue in the test-tube sintered together as though there had been partial fusion. Nothing of this sort was observed at lower temperatures. To check this, a rough determination was made of the eutectic temperature for potassium chloride and chlorate (no manganese dioxide) with the thermometer bulb in the salt mixture. The value was approximately 338°. A mixture of potassium perchlorate and manganese dioxide was heated at 340° for a period of forty-five minutes with only a very slight evolution of gas. The apparent decomposition was about three per cent., which may have been due to traces of potassium chlorate in the perchlorate.

From the experiments it is clear that only that chlorate is decomposed which comes in contact with manganese dioxide. At any temperature below the actual fusion point of the mixture only the surface of the chlorate crystals is decomposed. The remainder of the chlorate crystals is kept from contact with the manganese dioxide by the film of potassium chloride that is formed on the surface of the potassium chlorate crystals. When the temperature is reached at which the mixture melts, the manganese dioxide can then come in contact with all of the potassium chlorate and thus complete decomposition occurs. This temperature is about 335° ± 5°, whereas the initial temperature of decomposition is about 210°. Balarew[35] found the eutectic at about 340°.

Balarew found no trace of chloride formation after the mixture had stood for a year at room temperature; but new chloride could be detected after an hour's heating at 140°. Balarew believes, however, that "only softened or molten potassium chlorate decomposes catalytically with measurable velocity."

Balarew[36] claims to have found that the presence of an unspecified amount of water vapor lowers the temperature at which oxygen begins coming off by about 12°. It does not seem probable that the mixture of potassium chlorate

---

[35] Balarew, *Z. anorg. allgem. Chem.*, **143**, 89 (1925).

[36] Balarew, *Z. anorg. allgem. Chem.*, **145**, 121 (1925).

and manganese dioxide can take up much water at high temperatures. It is more likely, therefore, that the effect, if real, is due to a change in dispersion of the potassium chlorate or of the manganese dioxide by water adsorbed at the lower temperatures.

The catalytic decomposition of potassium chlorate is similar in principle to the decomposition of alcohol at the surface of heated nickel or alumina, except that the alcohol is a vapor under the conditions of the experiment, whereas the potassium chlorate is a solid or a liquid, depending on the temperature. It is precisely similar to the case of silver oxide, the decomposition of which is accelerated by contact with metallic silver. There is no justification at present for postulating higher oxides or intermediate compounds, real or otherwise. It is a plain case of adsorption with activation. Marc[37] showed that solid silver selenide catalyzes the conversion of Selenium B into Selenium A. He considered that this was the first case of heterogeneous catalysis in solid systems. Marc had forgotten that one can get oxygen from potassium chlorate in presence of manganese dioxide without fusing any portion of the mass.

We know that hydrogen is activated when adsorbed by platinum or nickel, and that silver oxide is activated when adsorbed by silver; we know that FeO_3 is stabilized when adsorbed by iron. We cannot predict whether we shall get activation or stabilization by adsorption. Contact catalysis is mysterious; but we wish to stress the fact that the catalytic action of manganese dioxide on potassium chlorate does not differ in principle from hundreds of other cases of contact catalysis. It is the general case that is mysterious and not the special cases. The catalytic decomposition of potassium chlorate is no more mysterious—and no less mysterious—than the hydrogen electrode; but it is very difficult to convince people of that.

Since the oxygen is given off at the manganese dioxide interface, there can be no potassium perchlorate formed and actually none is formed. Since manganese dioxide does not decompose perchlorate appreciably at 340°, the catalytic

---

[37] Marc, *Z. anorg. Chem.*, **85**, 65; Berger, 75 (1914).

decomposition of potassium chlorate by manganese dioxide below 340° does not involve the formation of potassium perchlorate as a transitory stage.

OVER-VOLTAGES.

In 1916 Bancroft[38] wrote: "Peters[39] showed that platinum accelerated the evolution of hydrogen from a chromous chloride solution and Jablczynski[40] showed that mercury had no such action. It was considered that platinum catalyzed the reaction and that mercury did not. To-day we say that hydrogen is set free at the platinum because of the low over-voltage and is not set free at the mercury because of the high over-voltage. The advantage of the latter point of view is that it shows the desirability of trying other metals with chromous chloride solution so as to find out at what degree of over-voltage the hydrogen ceases to be evolved rapidly."

The next year Forbes and Richter[41] published a paper on the chromic-chromous potential at mercury electrodes. They point out the importance of using pure mercury. "Lewis[42] has shown the vital necessity of the highest degree of purity in mercury if evolution of hydrogen is to be avoided at potentials comparable with those measured by us. Peters and Mazzuchelli[43] both noted such an evolution on mercury in contrast to our own experience when using pure mercury. McBain[44] also states that pure mercury does not decompose solutions of chromous chloride."

Forbes and Richter found that "referred to normal hydrogen electrode as zero, with correction for junction potentials,

$$\pi = -0.400 + 0.065 \log \mathrm{Cr^{III}/Cr^{II}}.$$

On platinum, potentials reached a maximum about 0.16 volt lower, with evolution of hydrogen." This difference cannot be due to the same cause as the difference studied by Mi-

---

[38] Bancroft, *J. Phys. Chem.*, **20**, 399 (1916).

[39] Peters, *Z. physik. Chem.*, **26**, 217 (1898).

[40] Jablczynski, *Z. physik. Chem.*, **26**, 117 (1898).

[41] Forbes and Richter, *J. Am. Chem. Soc.*, **39**, 1140 (1917).

[42] Lewis, *Proc. Am. Acad.*, **41**, 399 (1906).

[43] Mazzuchelli, *Gazz.*, **31**, II, 374 (1901); **35**, I, 417 (1905).

[44] McBain, Inaugural Dissertation, Heidelberg (1909).

chaelis[45] with the cysteine electrode. Forbes and Richter apparently observed all due precautions in regard to the absence of oxygen.

In order to determine the maximum reducing power of chromous chloride we have made electromotive force measurements similar to those of Forbes and Richter but not with the very specially purified mercury that they used. It is only necessary that the over-voltage at the mercury be larger than the potential difference due to the chromous salt. Because of the ease with which chromous chloride is oxidized, these determinations had to be made in the absence of air. The apparatus consisted of a 250 cc. cylinder fitted with a rubber stopper, the connection being made air-tight. The stopper had three holes bored in it: one for the salt bridge leading to the calomel electrode; one for the second electrode; and one for an escape tube for any gases that might be formed in the cell. The other end of the escape tube was kept beneath water to keep any air from diffusing back into the cell. The cell was charged with chromic chloride, hydrochloric acid and zinc. The zinc reduced the chromic chloride as far as might be to chromous chloride, the electromotive force of which was then measured. In all runs the hydrochloric acid concentration was molar. Measurements were made with 1 M and 0.1 M chromous chloride with platinum and mercury electrodes, and with M/10 chromous chloride at a copper electrode. The data are given in Table II. The electromotive forces have been converted from the calomel to the normal hydrogen as zero by subtracting 0.3 volt.

TABLE II.

Electromotive Forces of Chromous Chloride Cells.

The calomel electrode is always cathode.

Cell.	E_c.	E_h.
Hg | M $CrCl_2$ + M HCl | Calomel	−0.728	−0.428
Hg | M/10 $CrCl_2$ + M HCl | Calomel	−0.663	−0.363
Cu | M/10 $CrCl_2$ + M HCl | Calomel At beginning of run	−0.634	−0.334
After 5 days (no more H_2 being evolved)	−0.569	−0.269
Pt | M/10 $CrCl_2$ + M HCl | Calomel At beginning of run	−0.456	−0.156
After 3 days (no more H_2 being evolved)	−0.363	−0.063
Pt | M $CrCl_2$ + M HCl | Calomel	−0.694	−0.394

---

[45] Michaelis and Flexner, *J. Biol. Chem.*, **79**, 689 (1928).

The measurements indicate that chromous chloride is a stronger reducing agent than hydrogen by 0.36 and 0.42 volt in 0.1 M and M solutions. With platinum and copper electrodes such a difference cannot be realized because both platinum and copper catalyze the reaction between hydrochloric acid and chromous chloride.

The fact that the electromotive force measured at a mercury electrode remains constant for a long time, while that measured at platinum or copper falls off gradually, indicates that the mercury does not catalyze the reaction between hydrochloric acid and chromous chloride to amount to anything, whereas platinum and copper do catalyze the reaction appreciably. Furthermore, since the evolution of hydrogen ceases at the copper electrode and at the platinum electrode when the electromotive forces have dropped approximately to those of the hydrogen over-voltages at copper and platinum respectively, we draw the important conclusion that the catalytic action of metals on the reaction between chromous chloride and acids or water depends on the hydrogen over-voltage of the metal in question. If the hydrogen over-voltage of the metal being used is lower than the electromotive force of the chromous salt solution in which it is immersed, hydrogen will be liberated at the surface of the metal. The liberation of hydrogen will continue practically until the electromotive force of the chromous chloride is just equal to the hydrogen over-voltage of the metal, at which point it will cease in the ordinary sense of the term. If the hydrogen over-voltage of the metal being used is greater than the electromotive force of the chromous chloride solution in which it is immersed, practically no hydrogen will be liberated and the electromotive force of the solution will remain constant, provided no air is admitted.

Practically, things will happen as described; but, theoretically, the matter is probably somewhat different. We say ordinarily that no hydrogen is set free at a mercury cathode at a voltage below that of the over-voltage of hydrogen defined. If, however, one were to polarize a mercury electrode for a long time to less than the value at which we ordinarily speak of hydrogen being evolved, it is probable that some hydrogen would actually be evolved. If we consider the surface as polarized with monatomic hydrogen, that monatomic hydrogen will undoubtedly polymerize at some rate. Since hydrogen at a mercury electrode does not give an electromotive force corresponding to the over-voltage, there can be no reverse reaction under these conditions.

We do not know whether this reasoning would or would not apply to the theory of over-voltage developed by Gurney,[46] using the concepts of quantum mechanics.[47] "It is supposed that for an ion to be discharged at a cathode, electrons must pass over, or through, an energy barrier from the metal into a vacant quantum level of *equal* energy in the ion to be discharged. If the energy of the vacant level in the ion happens to be higher than the highest occupied level in the atom, then the transfer cannot occur and the ion cannot be discharged."

Since the chromous-chromic chloride solution is relatively stable in contact with mercury and by itself, there must be what amounts to an over-voltage for hydrogen even in the absence of an electrode. It seems to us that this value must be higher than that obtained at any metal. If this were not so, the setting-free of hydrogen would be catalyzed by the solution in contact with the electrode. Stone and Beeson [48] state that chromous sulphate solutions are practically stable in the absence of platinum. This brings up a question which has never been studied experimentally. To what extent is the over-voltage at any metal a function of the other ions and constituents of the solution?

We know that some titanous solutions [49] will break down in contact with platinum, setting free hydrogen. Experiments were therefore made with titanous chloride solutions, using the same apparatus as in the chromous chloride solutions. The titanous chloride solutions were molar with respect to hydrochloric acid. The results are given in Table III. The E_h values are obtained by subtracting 0.3 volt from the E_c values.

---

[46] Gurney, *Proc. Roy. Soc.*, 134 A, 137 (1931).

[47] Glasstone and Hickling, "Electrolytic Oxidation and Reduction," 61 (1936).

[48] Stone and Beeson, *Ind. Eng. Chem. Anal. Ed.*, 8, 188 (1936).

[49] Diethelm and Foerster, *Z. physik. Chem.*, 62, 129 (1908); Denham, 72, 641 (1910).

TABLE III.

Electromotive Forces of Chromous Chloride Cells.

The calomel electrode is always cathode.

Cell.	E_c.	E_h.
Hg | M/10 $TiCl_3$ + M HCl | Calomel	−0.384	−0.084
Pt | M/10 $TiCl_3$ + M HCl | Calomel	−0.381	−0.081

It is apparent from the values in Table II that the highest electromotive force obtained with this titanous chloride solution is barely above the hydrogen value at platinum and consequently there will be very little change with the time. The difference of three millivolts in favor of the mercury electrode is probably real. Diethelm and Foerster obtained a value of $E_h = -0.023$ volt for N/2 titanous oxide in 4 N sulphuric acid, a result which agrees satisfactorily with ours when one remembers the lower concentration of titanium salt, the higher concentration of sulphuric acid, and the 98 per cent. reduction of TiO_2. Time did not permit of a study of copper electrodes. This must be made some time, because the decomposition-voltage curves for copper cathodes, as found by Diethelm and Foerster are a bit puzzling.

Similar experiments were made with sodium hydrosulphite, $Na_2S_2O_4$, in solutions 0.08 M with respect to sodium hydroxide. The data are given in Table IV.

TABLE IV.

Electromotive Forces of Sodium Hydrosulphite Cells.

The calomel electrode is always cathode.

Cell.	E_c.	E_h.
Cu | M/10 $Na_2S_2O_4$ + 0.08M NaOH | Calomel	−0.988	−0.688
Pt | M/10 $Na_2S_2O_4$ + 0.08M NaOH | Calomel	−0.922	−0.622

Since the hydrogen electrode in 0.1 M NaOH has a value of about $E_h = -0.734$ volt, neither solution can set free hydrogen and consequently sodium hydrosulphite in this solution is not as good a reducing agent as hydrogen. We have no data on more concentrated and more alkaline solutions. We also offer no explanation at present for the different voltage with a copper electrode.

SUMMARY.

1. When a reaction is permitted by the free energy relations but cannot take place unless and until some molecules

of the reactants are raised to an energy level higher than that attained by any molecules of the reactants under ordinary conditions, we say that the system has to pass an energy hump for the reaction to take place.

2. The concept of the energy hump is a normal extension of the concept of the energy of activation and includes this latter as a special case.

3. When a reaction can be made to take place electrolytically, the height of the energy hump is defined as the difference between the free energy of the system and the voltage energy necessary to produce the reaction. With a glass of water standing on a table the energy hump which keeps the water from running on the floor is given by the distance between the surface of the water and the top of the glass.

4. An energy hump tends to disappear with increasing concentration or rise of temperature as in the case of a sulphuric acid solution. The energy hump may be eliminated by a suitable catalytic agent, as in the case of osmic acid and potassium chlorate or in the case of platinum and molecular hydrogen.

5. A one-way electrode, such as the cysteine-cystine one, gives an electromotive force which, at constant temperature and constant pH, is a function of the concentration of cysteine but independent of the concentration of cystine. The sulphite-sulphate electrode is another of the same type.

6. If an electron transfer between an inert metal and an oxidizable or reducible substance involves an energy hump under the conditions of the experiment, no reduction or oxidation potential will be set up; otherwise one will. A nitrate, sulphate or nitrobenzene electrode gives no oxidation potential. A lead peroxide, permanganate or nitrosobenzene electrode gives one. A cysteine or a sulphite electrode gives a reduction potential, while an alcohol electrode does not.

7. The energy hump for the sulphate-sulphite reaction is at least two volts and may be much more. The energy hump for the nitrate-nitrite reaction in alkaline solution is approximately 0.66 volt at a platinum cathode, 0.7 volt at an iron cathode, 0.9 volt at a zinc cathode, and 1.1 volts at a mercury cathode. It will be higher still in the absence of a cathode. The energy hump in a chlorate solution appears to be at least

1.05 volts at a platinum cathode, at least 0.8 volt at an iron cathode, and zero at a platinum cathode in presence of osmium tetroxide.

8. Potassium chlorate is adsorbed and activated by manganese dioxide just as silver oxide is adsorbed and activated by silver. There is no justification at present for postulating any higher oxides of manganese, real or hypothetical, as taking part in the reaction. Only the potassium chlorate in actual physical contact with the manganese dioxide reacts. When the eutectic temperature is reached, 335° ± 5°, the manganese dioxide can come in contact with all the potassium chlorate and the reaction runs to an end.

9. When the electromotive force of a chromous chloride solution is higher than the over-voltage of hydrogen at the immersed metal, the chromous chloride will oxidize until approximate equilibrium is reached. A chromous chloride solution which is 0.4 volt negative to hydrogen will stay practically constant with mercury, will drop somewhat with copper, and will drop more with platinum. The fact that a chromous chloride solution decomposes slowly or not at all in the absence of a metal catalyst proves that there is an over-voltage for hydrogen even in the absence of a metal.

10. The reduction of dimethylacrylic acid by platinum and hydrogen when it is not reduced by a chromous chloride solution is due to the fact that platinum activates the dimethylacrylic acid. It is not a question of a difference between reduction and hydrogenation.