QUARTERLY REVIEWS

# DISPROPORTIONATION IN INORGANIC COMPOUNDS

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The process of disproportionation is one in which similar molecules or ions interact to give products which differ either in the magnitude of the ion charge or in the relative weights of the ionic or molecular products; the former reactions involve electron transfer, the latter atom transfer. An example of the former is $2Cu^+ = Cu + Cu^{++}$, in which the original compound is of univalent copper, but the parts into which it disproportionates are metallic copper on the one hand and cupric ions on the other. An example of atom transfer is $3NaClO = NaClO_3 + 2NaCl$, in which the hypochlorite disproportionates to chlorate and chloride, and oxygen is transferred. Such reactions have been known for very many years, in fact from almost the earliest days of inorganic chemistry; they occur quite frequently when a compound exists intermediate in valency between two others, but little has been done to systematise the detailed knowledge. No general theory has been put forward, and it is to the efforts of physical chemists to explain organic reactions that we must look for light. In this review some attempt will be made to put forward a few generalisations, and very tentative and provisional theories will be advanced which may explain some of the reactions. Some account will also be given of some of the chief cases of inorganic disproportionation, following the arrangement of the Periodic Table.*

There are two chief classes of reaction to be considered: (*A*) involves electron transfer, and consists of atomic reactions, *e.g.*,

$$2Cu^+ \rightleftharpoons Cu + Cu^{++}$$

(*B*) involves atom transfer, *e.g.*,

$$3ClO^- \rightleftharpoons ClO_3^- + 2Cl^-$$

Class (*B*) includes reactions of anions such as the above, and also reactions of uncharged compounds, such as hydrogen peroxide, carbon monoxide, etc.

Class (*A*) reactions are much the simplest and almost always the reactions concerned are one-electron transfers.

The theories of L. Michaelis [1] on the formation and equilibria of semiquinone radicals are very illuminating when applied to inorganic reactions.

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[1] *Ann. N.Y. Acad. Sci.*, 1940, **40**, 39.

* In this review, electrode potentials and equilibrium constants are related to the free energy changes by the equation $\Delta G = -nEF = -RT\log_e K$, where $K$, the equilibrium constant, has the concentrations of the products of reaction in the numerator.

If we consider the reaction when a bivalent metal is oxidised to a salt $M - 2e = M^{++}$, a bivalent oxidation, we can see that if the metal has only one state of valency, *e.g.*, magnesium, the reaction cannot proceed in any other way—there are no univalent compounds of magnesium. But if instead of magnesium we take mercury or copper which have stable univalent salts, we can see that the reaction may proceed in two steps. That the reverse process of the reduction of cupric copper proceeds stepwise can be readily demonstrated by the polarograph, for polarographic reduction of cupric salts shows two " waves ", separated (in dilute ammonia solution) by 0·28 volt. The intermediate inorganic compound is of course an " ous " salt—cuprous, mercurous, etc.; in an organic oxidation which proceeds by two one-electron steps it is a quinhydrone or similar substance, or maybe a free radical. In many cases it (the free radical or semiquinone) exists in true thermodynamic equilibrium with its oxidation and reduction products, but usually the ratio of the intermediate compound to end-products is quite small. With inorganic salts, however, there is commonly a wide range of conditions—but often not including solution in water—in which it is stable or preponderates at equilibrium. Thus, if we call the reduced form R and the oxidised form O, the total reaction will be

$$R \rightleftharpoons O + 2e \qquad (1)$$

but if it proceeds in two steps,

$$R \rightleftharpoons e + I \text{ (intermediate form)} \qquad (2)$$

$$I \rightleftharpoons e + O \qquad (3)$$

for I to be a fairly stable salt, equilibria must be such that (2) must proceed largely from left to right, and (3) from right to left. The whole equilibrium may be written

$$R + O \rightleftharpoons 2I \qquad (4)$$

and its equilibrium constant

$$[I]^2/[R][O] = K \qquad (5)$$

Michaelis, in dealing with semiquinones, called $K$ the radical formation (or semiquinone) constant, and its reciprocal the disproportionation (or dismutation) constant, because $2I \rightleftharpoons R + O$ is disproportionation. Clearly, it is the value of $K$ which shows the proportion of the compound which exists in equilibrium with the other two species. Equation (5) thus indicates many of the facts about such compounds—that if either R or O is very insoluble, and hence [R] or [O] very small, $K$ will be large and disproportionation proceed towards completion in the absence of other factors such as adverse electrical potentials, etc., whilst if [I] be made small, for example by the formation of very stable complex ions, $K$ will be very small indeed and the intermediate compound will become the stable one. For instance cuprous sulphate in water disproportionates completely to (insoluble) metallic copper and cupric sulphate, but in presence of thiocarbamide, a stable salt, $[Cu,3SC(NH_2)_2]_2SO_4$ is formed which dissolves to form a colourless solution which is also quite stable.

Commonly, electron-transfer reactions require but a small activation energy and are very rapid, whilst atom-transfer reactions, in which a covalent link is broken, need large activation energy and are slow; *e.g.*, $Fe(CN)_6^{---} + e \rightleftharpoons Fe(CN)_6^{----}$ is rapid—instantaneous—whilst such a reaction as the reduction of permanganate to manganous salt is slow unless catalysed. Thus "cationic" disproportionations rapidly reach equilibrium, in contrast to, *e.g.*, the change of sulphurous acid to sulphuric acid and sulphur, which may take weeks. But what are the criteria which indicate whether a compound of an intermediate valency state will disproportionate or not? Like all other reactions these depend on the free energies of the compounds concerned. In many cases involving cations, it is convenient to consider the electrode potentials of the metals in solutions of the two salts. The problem can be stated as follows: Let $u_1$ and $u_2$ be the charges on two ions (-ous and -ic) derived from a metal M, whose concentrations in a solution are $C_1$ and $C_2$. The disproportionation reaction may be written generally in the form

$$n_2M^{u_1} \rightleftharpoons n_1M^{u_2} + (n_2 - n_1)M$$

It comprises two individual reactions, (6) and (7), for which $n_1u_2 = n_2u_1$:

$$n_2M \rightleftharpoons n_2M^{u_1} + n_2u_1e \qquad . \quad . \quad . \quad . \quad (6)$$

$$n_1M \rightleftharpoons n_1M^{u_2} + n_1u_2e \qquad . \quad . \quad . \quad . \quad (7)$$

The free-energy change, $\Delta G$, involved in the disproportionation reaction is the difference between those for reaction (7) and for reaction (6), for which the standard electrode potentials are $E_1$ and $E_2$:

$$\Delta G = -RT\log_e K = \Delta G_2 - \Delta G_1 = -[n_1u_2E_2F - n_2u_1E_1F]$$
$$= -[n_1u_2F(E_2 - E_1)]$$

Consequently

$$K = 10^{n_1u_2F(E_2-E_1)/2\cdot3RT}$$

The equilibrium constant, $K$, may be written in terms of the ion concentrations to give equation (8), valid at room temperature,

$$K = C_2^{n_1}/C_1^{n_2} = 10^{17n_1n_2(E_2-E_1)} \qquad . \quad . \quad (8)$$

and in this form the equilibrium concentration of the ions is referred to the standard electrode potentials.

*Example* 1. If cuprous salts react, the equation will be $2Cu^+ \rightleftharpoons Cu + Cu^{++}$. Now the electrode potentials are

$$Cu/Cu^+ \quad E_1 = -0\cdot520$$
$$Cu/Cu^{++} \quad E_2 = -0\cdot340$$

and $K = 10^{+6}$ approx. Therefore the reaction will proceed from left to right.

*Example* 2. Plumbous salts might react $2Pb^{++} \rightleftharpoons Pb + Pb^{++++}$. Now $E_1$ for $Pb/Pb^{++} = 0\cdot12$ v. $Pb/Pb^{++++}$ has not been determined, but as $Pb^{++}/Pb^{++++}$ is about $-1\cdot7$, and as the free-energy change depends on the product of the electrode potential and the number of electrons involved in the cell reaction, we can derive $E_2$ of $Pb/Pb^{++++}$ as follows:

$$4E_2 = 2 \times 0{\cdot}12 - 2 \times 1{\cdot}7, \text{ hence } E_2 = -0{\cdot}79$$

Thus

$$E_1 = +0{\cdot}12 \text{ v.}, \quad E_2 = -0{\cdot}79 \text{ v.}, \quad K = 10^{17 \times 4 \times -0{\cdot}91} = \sim 10^{-61}$$

and the reaction will not proceed.

But instead of considering electrode potentials in volts, we can consider free energies in calories.* If the sum of the free energies of the compounds (ions), etc., on the left-hand side of the equation is greater than that on the right-hand side, the reaction will proceed. However, in a system where the reaction leads to heterogeneity, as in the deposition of a solid product from a liquid or gaseous system, the deposited substance, if an element, has by definition no free energy of formation; if it is a compound, there is commonly a large free-energy change in the transformation from the dissolved to the insoluble state, and in consequence the reaction is favoured.

*Examples.*

$$\text{(i)} \quad 3ClO^- \rightleftharpoons ClO_3^- + 2Cl^-$$

Free energies, k.-cals./mole:

$$\begin{array}{ccc} 3 \times (-6{\cdot}5) & -0{\cdot}25 & 2 \times (-31{\cdot}3) \\ -19{\cdot}5 & & -62{\cdot}6 \end{array}$$

and

$$\Delta G = -43{\cdot}35$$

The reaction will proceed from left to right.

$$\text{(ii)} \quad 4SO_3^{--} \rightleftharpoons 3SO_4^{--} + S$$

Free energies, k.-cals./mole:

$$\begin{array}{cc} 4 \times -116 & 3 \times -176{\cdot}5 \\ -464 & -529{\cdot}5 \end{array}$$

and

$$\Delta G = -63$$

The reaction will proceed.

Free energies do not indicate the speed of a reaction; knowledge of activation energy is also necessary. But we can generalise to some extent and say:

(1) That reactions which take place by one-electron transfers will usually be rapid.[2] The addition of a substance which can be oxidised (reduced) by one-electron transfers will be very likely to catalyse a reaction proceeding by two (or more) electron transfers; *e.g.*, the decomposition of $H_2O_2$ catalysed by ferrous or cuprous salts.

(2) Reactions involving atom-transfer (*e.g.*, $3ClO^- = 2Cl^- + ClO_3^-$) will usually be slow. As written here this reaction would be termolecular. Such reactions are rare, and usually such a reaction proceeds in steps, the slow step determining the rate. In many such reactions it is probable that

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[2] P. A. Schaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 2169; *J. Physical Chem.*, 1936, **40**, 1021.

* 1 Volt = 23,050 cals.

free radicals are involved through step-wise transfer of electrons; *e.g.*, the oxidation–reduction of sulphurous acid.

*Hydrogen Peroxide.*—We regard the decomposition of hydrogen peroxide, $2H_2O_2 = 2H_2O + O_2$, as a disproportionation, because the free oxygen is in a different state of oxidation from that of the combined oxygen. The reaction is of very great importance, recent researches having solved some of the problems which have existed for years in its susceptibility to positive and negative catalysis.

The decomposition $2H_2O_2 = 2H_2O + O_2$, $\Delta H = -46{,}120$ cals., is practically complete and irreversible. Whilst " pure " hydrogen peroxide is so unstable that shaking is sufficient to start the evolution of oxygen, yet 85 or 90% solutions can be stabilised, provided that they are kept out of contact with alkalis and certain other substances, and 30% solutions, if free from metals, can be kept almost indefinitely in waxed bottles.

In the complete absence of catalysts, fairly consistent values for the decomposition rate were obtained by B. H. Williams [3] and C. Pana;[4] in a 1M-solution the (unimolecular) velocity constant at 25° is $3{\cdot}45 \times 10^{-9}$ sec.$^{-1}$, and $E$ is 18,000 cals. per g.-mol.

The decomposition is catalysed by a great variety of substances, and it is of interest to follow some of the theories put forward to account for the catalysis. All manner of substances are catalysts—alkalis, finely divided metals, porous " inert " substances like pumice, manganese dioxide, bromides, ferrous ions, and enzymes. Their actions are not identical; they can be classified as heterogeneous or homogeneous. The stabilisers (anticatalysts) are either acids (often phosphoric or sulphuric) or organic compounds such as acetanilide, phenacetin, or esters of *p*-hydroxybenzoic acid.[5] The acid acts through suppressing the ionisation of hydrogen peroxide as a weak acid ($[H^+] \times [OOH^-] = 1{\cdot}6 \times 10^{-12}$), the ion being less stable than the undissociated compound. The other substances are " chain breakers ". They are themselves oxidised (*e.g.*, acetanilide is converted into nitrobenzene), and probably act by removing either OH or OOH radicals. Some pharmaceutical samples are so heavily stabilised as to be almost useless in laboratory operations.

The action of manganese dioxide can probably be explained by the fact that in alkaline solution hydrogen peroxide rapidly oxidises $Mn^{++}$ to $Mn^{++++}$, precipitated as hydrated manganese dioxide; in acid solution it reduces manganese dioxide to the manganese salt, with evolution of oxygen. This is not a simple reaction: by analogy with chromium, probably a per-acid is involved. In a neutral solution both reactions proceed, so that ultimately very little manganese can decompose a large quantity of hydrogen peroxide, the speed being limited by the diffusion of the molecules to the surface. Metallic mercury also decomposes hydrogen peroxide, and in very slightly alkaline solution the alternate formation and resolution of a yellow film of oxide can be observed.

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[3] *Trans. Faraday Soc.*, 1928, **24**, 245.

[4] *Ibid.*, p. 486.

[5] " The Extra Pharmacopœia ", 1941, Vol. I, p. 613.

Because of the apparent resemblance of its action to that of enzymes, colloidal platinum has been studied.[6] The mechanism is obscure; results suggest adsorption of the Freundlich type. At 25° with 1/38,000 g.-atom of Pt per l. and 1/50 g.-mol. of hydrogen peroxide, the velocity constant is $6{\cdot}1 \times 10^{-3}$ min.$^{-1}$. It can be calculated [7] that one colloid particle decomposes $1{\cdot}54 \times 10^{6}$ molecules of hydrogen peroxide per second, and that the number of activating collisions per second per particle is $7{\cdot}8 \times 10^{4}$. It thus appears possible that a chain mechanism is started.

The mechanism of several homogeneous catalysts, *e.g.*, halogen acids and ferrous salts in particular, is better understood.

Hydrobromic acid [8] reacts thus:

$$H_2O_2 + 2H^+ + 2Br^- = Br_2 + 2H_2O\,;\quad H_2O_2 + Br_2 = O_2 + 2H^+ + 2Br^-$$

both bromine ions and molecules catalysing the reaction. The second reaction is rapid, and at the "steady rate", when each of the reactions is destroying the same quantity of hydrogen peroxide, the rate equation is

$$-\,d[H_2O_2]/dt = k[H_2O_2][H^+][Br^-]$$

the formation and reduction of bromine being given by

$$d[Br_2]/dt = k_1[H_2O_2][H^+][Br^-]$$
$$-\,d[Br_2]/dt = k_2[H_2O_2][Br_2]/[H^+][Br^-]$$

and at the steady rate $[Br_2]/[H^+]^2[Br^-]^2 = k_1/k_2 = R$, a constant whose value is 1·2—1·7 (moles/l. min.$^{-1}$). As the concentration of catalyst is fixed, the reaction is *apparently* unimolecular. Bromine when formed will also react, $Br_2 + H_2O \rightleftharpoons HBrO + Br^- + H^+$, a rapid reversible reaction which introduces the further reactions

$$H_2O_2 + H^+ + Br^- = HBrO + H_2O\,;\quad H_2O_2 + HBrO = H^+ + Br^- + H_2O + O_2$$

the second having the rate $-\,d[H_2O_2]dt = k'[H_2O_2][HBrO]$, the whole being summed up by

$$-\,d[H_2O_2]/dt = -\,d[Br_2]/dt = k_2[H_2O_2][Br_2]/[H^+][Br^-]$$

which is the experimentally established relation. Chlorine behaves more or less similarly.[9] Bridge suggests that (from the high temperature coefficient of the hydrogen chloride catalysed reaction) a molecule of hydrogen peroxide in decomposing liberates more than enough energy to activate another molecule, and a chain reaction is started. Iodide reacts with hydrogen peroxide in a most complicated manner. In acid solutions (0·2N to N) the reaction

$$H_2O_2 + 3I^- + 2H^+ = I_3^- + 2H_2O$$

is stoicheiometric, but under neutral conditions other reactions occur

$$H_2O_2 + I^- = IO^- + H_2O$$
$$H_2O_2 + HIO = O_2 + I^- + H^+ + H_2O$$
$$H_2O_2 + IO^- = O_2 + I^- + H_2O$$

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[6] G. Bredig and R. M. von Bernack, *Z. physikal. Chem.*, 1899, **31**, 258.

[7] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution", p. 292.

[8] W. C. Bray and R. S. Livingstone, *J. Amer. Chem. Soc.*, 1923, **45**, 1251; 1928, **50**, 1654.

[9] E. A. Budge, *ibid.*, 1932, **54**, 1769.

the gross effect being the catalytic decomposition of hydrogen peroxide. E. Abel[10] and W. C. Bray[11] deal fully with the subject.

The effect of ferrous and ferric ions has been considered by F. Haber and J. Weiss,[12] who show that free radicals and chains are involved, and that variations in concentration of catalyst, etc., alter the length of the chains, offering different means of terminating them. The main stages in the reaction with ferrous salts in neutral solution are summarised in four equations, of which (10) and (11) show the chain mechanism, and (12) indicates its termination.

$$\mathrm{Fe^{++} + H_2O_2 = Fe^{+++} + OH^- + OH} \quad (9)$$

$$\mathrm{OH + H_2O_2 = H_2O + HO_2} \quad (10)$$

$$\mathrm{HO_2 + H_2O_2 = O_2 + H_2O + OH} \quad (11)$$

$$\mathrm{OH + Fe^{++} = Fe^{+++} + OH^-} \quad (12)$$

The radicals which take part are OH and $O_2H$. By considering the various rate equations and the reaction whereby ferrous ions can be oxidised without evolution of oxygen, namely, $H_2O_2 + 2Fe^{++} = 2Fe^{+++} + 2OH^-$, the consumption ratios of the substances are found to be

$$n = \frac{d[H_2O_2]}{d[Fe^{++}]} = 0{\cdot}5 + \frac{k_{10}[H_2O_2]}{k_{12}[Fe^{++}]}$$

until, when $[Fe^{++}]$ becomes very small, chains are no longer broken by reaction (12). As no terms for $[H^+]$ or $[OH^-]$ enter into the irreversible velocity expressions, the velocity is independent of acid concentration, and from reactions (11) and (12) the lengths of the chains also appear independent. $k_9$ is independent of acidity, but chain length is not quite independent because the concentration of $HO_2^-$ is conditioned by $HO_2^- + H^+ \rightleftharpoons H_2O_2$, and at low concentrations of $Fe^{++}$ ions, such reactions as

$$\mathrm{Fe^{++} + HO_2 = Fe^{+++} + HO_2^-} \quad (13)$$

become important. Also when $[Fe^{++}]$ is quite small, reciprocal destruction of two OH radicals is important—a process, favoured by $H^+$ ions, which may be connected with the greater stability of acid solutions. But until $[Fe^{++}]$ is very small, equations (9)—(12) explain the process.

Ferric ions also catalyse the decompositions, at a different rate from ferrous ions, but Haber and Weiss can find no evidence to support the theory that iron may be oxidised to a higher valency than 3. In neutral or alkaline solutions almost no $Fe^{+++}$ can be present. In acid solution the rate of decomposition is directly proportional to $Fe^{+++}$ concentration, and inversely proportional to the acid concentration, according to the equation

$$-\,d[H_2O_2]/dt = k[Fe^{+++}][H_2O_2]/[H^+]$$

though the reactive substance is really $HO_2^-$. The primary process for

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[10] *Z. physikal. Chem.*, 1928, **136**, 161.

[11] *Chem. Reviews*, 1932, **10**, 161.

[12] *Proc. Roy. Soc.*, 1934, *A*, **147**, 332.

ferric ion is $Fe^{+++} + HO_2^- = Fe^{++} + HO_2$, with a velocity constant of $6 \times 10^7$ at 20°. The production of oxygen proceeds through

$$Fe^{+++} + HO_2 = Fe^{++} + O_2 + H^+ \qquad . \quad . \ (14)$$

and when the speed of this reaction is greater than that of (11) above, the chain reaction swings over to this reaction of radicals not involving chains. Thus, in presence of $Fe^{+++}$, increase of $H_2O_2$ or decrease of $Fe^{+++}$ will cause a chain reaction to start. When reactions (11), (13), and (14) all proceed with maximum velocity ($H_2O_2$ 1 g.-mol./l.; $Fe^{+++}$ small, and $Fe^{++}$ also small) very long chains are formed and oxygen production rate increases about 100-fold.

The promoting effect of copper salts on iron catalysts of this decomposition is explained by the single-electron transfer process

$$Cu^+ + Fe^{+++} = Cu^{++} + Fe^{++}$$

It may be seen that in all the above reactions hydrogen peroxide is never simultaneously attacked by two " univalent " (single-electron) changes, or by a two-electron change, but always by single-electron steps involving $HO_2$ or HO radicals.

*Cuprous Compounds.*—Unless the cuprous state is stabilised by powerful complexing agents, most cuprous compounds are unstable with regard to copper and cupric ions. According to F. Fenwick[13] $Cu = Cu^+ + e$ has a standard potential of — 0·522 v., the free energy of cuprous ion is 12,040 cals., and for the reaction $Cu^{++} + Cu \rightleftharpoons 2Cu^+$, $K = 10^{-6}$. Many cuprous salts instantly decompose in contact with water, as the given data would lead one to expect, but such cuprous salts as are very insoluble or in which free cuprous ions are not present, are stable. The fundamental equilibria, and influence of complex ions, are treated by F. G. Donnan at length in R. Abegg's " Handbuch ".[14]

Cuprous chloride is a representative cuprous salt, sparingly soluble in water (solubility product $1{\cdot}02 \times 10^{-6}$). In hydrochloric acid it is fairly soluble, because of the formation of complex ions, giving a colourless solution, but in presence of water two reactions take place: (1) hydrolysis to a basic salt or cuprous oxide and free hydrochloric acid, (2) disproportionation. Thus at equilibrium the solid will contain metal, cuprous oxide or hydroxide, and unchanged cuprous chloride; the liquid will contain cuprous ions, cupric ions, free hydrochloric acid and complex anions. By measurement of the potentials of such cells as Cu | CuCl (solid), 0·1M-KCl | | 0·1M-KBr, CuBr (solid) | Cu, and knowing the total cupric, total cuprous, and total copper content of saturated solutions of CuBr and CuCl, it can be shown that cuprous ions are univalent, *i.e.* $Cu^+$, not $Cu_2^{++}$. At room temperature the equilibrium constant $K$ ($[Cu^{++}]/[Cu^+]^2$) is about $10^6$. Hence a solution which contains cupric and cuprous ions cannot have more than 1/500,000 of the copper present as cuprous ions. Thus if we have a solution in which

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[13] *J. Amer. Chem. Soc.*, 1920, **48**, 861.

[14] Group I, Band I, Part 2, pp. 504 *et seq.*

$Cu^{++}$ is kept sensibly constant, and produce $Cu^+$ ions by adding a reducing agent (in absence of excess of complex-forming anions) they will reach the concentration indicated by $Cu^+ = \sqrt{Cu^{++}} \times 10^{-3}$, after which metallic copper may be deposited.

Thus it is not possible to prepare every cuprous salt from aqueous solution. Let $S_1$ and $S_2$ be the solubility products of cupric and cuprous salts of a bivalent anion. Then in a solution saturated with respect to $Cu^+$, $Cu^{++}$, and metallic copper, $[Cu^{++}]/[Cu^+]^2 = S_1/S_2$, and the relation $[Cu^{++}]/[Cu^+]^2 = K$ must also be satisfied, and only when $S_1/S_2 = K$ can this be fulfilled. If $S_1/S_2 < K$, the solid cuprous salt must change into cupric salt and metal ; *e.g.*, cuprous sulphate cannot be prepared from aqueous solution.

The effect of the formation of complex anions is seen in the enhancement of the solubility of cuprous halides by other halides. G. Bodländer and O. Storbeck [15] were unable to detect cupric ions in a solution of cuprous chloride in 0·2N-potassium chloride, so no free $Cu^+$ ions were present. In dilute ($<$ 0·2N) solutions of potassium chloride, the cuprous ion was exclusively present as $CuCl_2^-$, but at higher halide concentrations, it became $CuCl_3^{--}$. A. A. Noyes and Ming Chow [16] showed that for the reaction $CuCl_2^- = Cu^+ + 2Cl^-$, $K = 2{\cdot}9 \times 10^{-6}$. Cuprous iodide is so insoluble (solubility product $5{\cdot}1 \times 10^{-12}$) that it is the stable copper iodide, and results always from the reaction of cupric salts with alkali iodide solution. Cuprous bromide is intermediate in properties, and because of its lower solubility is more stable than cuprous chloride in presence of water. Such ions as $Cu(CN)_2^{--}$ are stable and Latimer [16a] calculated that for $Cu(CN)_2^- = Cu^+ + 2CN^-$, $K$ is $10^{-16}$ ; hence cuprous cyanide very readily dissolves without any disproportionation in cyanide solution.

Until 1909 cuprous sulphate had never been isolated, though its presence in concentrated sulphuric acid solution was known to result from the reaction of the acid on the metal. The colourless solution obtained on pouring this solution into water deposits metallic copper, and cupric sulphate remains in solution. A. Recoura [17] prepared the solid salt by reaction between cuprous oxide and methyl sulphate : $Cu_2O + (CH_3)_2SO_4 = Cu_2SO_4 + (CH_3)_2O$. The salt is greyish, stable in dry air, but immediately decomposed by moisture into cupric sulphate, metallic copper, and a supposed $Cu_4O$. Carbon monoxide can act as a stabiliser for $Cu^+$ salts : if a solution of cupric sulphate in contact with metallic copper is treated with carbon monoxide, a solid, not very stable, with the formula $Cu_2SO_4,2CO$ can be obtained.[18]

*Mercurous Compounds.*—Superficially the reaction $Hg_2^{++} = Hg + Hg^{++}$ strongly resembles $2Cu^+ = Cu^{++} + Cu$, but the differences are marked. Even at very low concentrations, the aqueous mercurous ion is not $Hg^+$

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[15] *Z. anorg. Chem.*, 1902, **31**, 458.

[16] *J. Amer. Chem. Soc.*, 1918, **40**, 739.

[16a] W. M. Latimer, "Oxidation Potentials", p. 172.

[17] *Compt. rend.*, 1909, **148**, 1105.

[18] W. Manchot and J. N. Friend, *Annalen*, 1908, **359**, 100.

but $Hg_2^{++}$. G. H. Cartledge [19] obtained results summarised in the following equations :

$$Hg(metal) \rightleftharpoons Hg^{+}(aqueous) + e\,;\ E_0 = -1{\cdot}70,\ \Delta G = 39{,}100 \text{ cals.} \qquad (15)$$

$$2Hg^{+} \rightleftharpoons Hg_2^{++}\,;\ \Delta G^{\circ} = -42{,}000 \text{ cals.} \qquad (16)$$

$$2Hg^{+} \rightleftharpoons Hg(metal) + Hg^{++}\,;\ \Delta G^{\circ} = -39{,}000 \text{ cals.} \qquad (17)$$

Hence mercuric ion is a weak oxidising agent if it has to go through the $Hg^{+}$ stage. $Hg^{+}$ is very unstable as regards processes (16) and (17). The very high energy of the $Hg^{+}$–$Hg^{+}$ bond is shown by (16), and from this can be calculated the equilibrium $[Hg_2^{++}]/[Hg^{+}]^2 = 10^{+31}$. Thus in a saturated solution of, *e.g.*, calomel, $Hg^{+}$ ions are practically absent.

A further difference from copper is that mercuric chloride is practically un-ionised in solution, which makes a profound difference to its behaviour. It has a very great tendency to form complex anions such as $HgCl_4^{--}$. Thus in the reaction $Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$ not only is mercury removed from solution as insoluble metallic mercury, but in presence of quite small amounts of halide ions, the mercuric chloride itself rapidly disappears, through formation of complex anions, and it is to these circumstances that the disproportionation of calomel in contact with water is due, and also the acceleration of this reaction by chlorides or hydrochloric acid. S. R. Carter and R. Robinson [20] measured the potential of the mercurous–mercuric couple in perchloric acid solution. By extrapolation to infinite dilution, we obtain $Hg_2^{++} = 2Hg^{++} + 2e$ ; $E_0 = -0{\cdot}910$ ; the free energy of $Hg^{++}$ is 39,000 cals., and from other measurements $2Hg = Hg_2^{++} + 2e$ ; $E_0 = -0{\cdot}799$, and consequently the free energy of mercurous ions is $\sim$ 36,850 cals. Thus for the reaction $Hg + Hg^{++} = Hg_2^{++}$, $\Delta G = -2565$ cals., and hence one would expect mercurous salts to be stable. Indeed, mercurous nitrate and perchlorate are stable, as the factor of complex anion formation is absent.

The properties of calomel vapour have been extensively studied, as it has long been known that it tends to decompose into mercury and mercuric chloride. Thus, gold was amalgamated in its vapour, which was taken as proof of the presence of metallic mercury, and diffusion through a porous membrane [21] showed that it had dissociated to some extent.

H. B. Baker [22] showed that the density of damp calomel vapour was 8·2 (when air = 1) at 400°, corresponding to either HgCl or $Hg + HgCl_2$, but the vapour density of dry calomel was 15 at 448°, corresponding almost exactly to $Hg_2Cl_2$. His experiments have recently been extended by F. T. Gucker and R. H. Munch,[23] who were unable entirely to confirm Baker's work. By volatilising carefully dried calomel at 200° and condensing it on a cold surface they could find no evidence of metallic mercury. By means of ultra-violet spectroscopy (the absorption of the mercury resonance line 2537 A.) it was further shown that, whilst the vapour of damp calomel is

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[19] *J. Amer. Chem. Soc.*, 1941, **63**, 906.

[20] *J.*, 1927, 267.

[21] W. Harris and V. Meyer, *Ber.*, 1894, **27**, 1482.

[22] *J.*, 1900, **77**, 646.

[23] *J. Amer. Chem. Soc.*, 1927, **59**, 1275.

appreciably decomposed at 100° and completely so at 450°, dry calomel vapour is free from mercury up to 250°, but above this temperature, mercury begins to appear. Vapour-pressure measurements between 375° and 425° show that $Hg_2Cl_2$ is absent—it is either HgCl or $Hg + HgCl_2$.

The solid substance slowly becomes grey in moist air, but even warming the solid with water for some time does not appreciably decompose it. In presence of alkali chlorides, or hydrochloric acid, its solubility is much greater than in water, but it very rapidly blackens, owing to formation of metallic mercury. Chloride ions are the effective agents, through formation of $HgCl_3^-$ or $HgCl_4^{--}$ (cadmium chloride, which is hardly ionised at all, does not produce this reaction). Chlorides vary in their effect on calomel, increasing in activity in this order : Li, Ca, Ba, Na, H, K, Cs. Except for H, which looks anomalous, this is the order of increase in electropositiveness, which encourages complex-anion formation. All these solutions react much more rapidly with rise in temperature. When calomel is dissolved in, *e.g.*, potassium chloride, although mercury is rapidly produced, mercuric chloride as such is not present : it cannot be extracted by ether, although F. Mylius and K. Huttner [24] observed that ether will extract it from its solution in water. Thus the reaction must be represented as $Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$ ; $HgCl_2 + Cl^- = HgCl_3^-$. From the data of M. S. Sherrill [25] the constant of the equilibrium is $[HgCl_4^{--}]/[Hg^{++}][Cl^-]^4 = 9 \times 10^{15}$ ; the behaviour of the bromides and iodides is similar. According to E. Montignie,[26] mercurous fluoride is a yellow crystalline salt, which in water begins to decompose at 15° : it darkens in light and in general behaves like the chloride.

Mercurous sulphate is decomposed somewhat by light, but is stable in water ; its solubility is depressed by a moderate amount of sulphate ions.

Mercurous oxide is, however, unstable and has never been prepared free from metallic mercury. H. C. Freche and M. C. Sneed [27] have shown that when dilute ammonia reacts with calomel, the first product of reaction is $Hg_2O$, which further reacts to produce Hg and $HgNH_2Cl$. In concentrated ammonia reaction is too rapid for $Hg_2O$ to be isolated. The whole reaction may be summed up as

$$2Hg_2Cl_2 + 4NH_4OH = Hg + Hg_2O + NH_2HgCl + 3NH_4Cl + 3H_2O$$

*Carbon.*—The reaction $2CO \rightleftharpoons C + CO_2$ is of very great importance, and exact knowledge of its equilibria at different temperatures is essential. It was investigated by O. Boudouard [28] and very thoroughly by T. F. E. Rhead and R. V. Wheeler.[29] These authors stated that the reaction $CO_2 + C \rightharpoonup 2CO$ should be appreciable at temperatures as low as 315°, at which about 0·1% of monoxide should be formed. Rhead and Wheeler used a quartz apparatus, and highly purified wood charcoal, and found that at lower temperatures than 800°, equilibrium was only attained

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[24] *Ber.*, 1911, **44**, 1315.

[25] Quoted by W. M. Latimer, " Oxidation Potentials ", p. 166.

[26] *Bull. Soc. chim.*, 1937, **4**, 342.

[27] *J. Amer. Chem. Soc.*, 1938, **60**, 518.

[28] *Ann. Chim. Phys.*, 1901, **24**, 5.

[29] *J.*, 1911, **99**, 1140.

after several days. They found that at 850° the reaction $C + CO_2 \rightharpoonup 2CO$ was 166 times as fast as the (apparently homogeneous) reaction $2CO \rightharpoonup CO_2 + C$, a fact of great practical importance. Their values for the equilibrium constant at various temperatures have only recently been superseded by those of F. D. Rossini *et al.*[30] A summary of their figures is given here.

For the reaction $2CO \rightleftharpoons CO_2 + C$ (graphite), $\Delta H^\circ_{298} = -41{,}220$ cals. The equation at equilibrium may be written as

$$\begin{array}{lccc} & 2CO & \rightleftharpoons CO_2 & + C \\ \text{or} & 2 - 2x & x & \end{array}$$

where $x$ represents the "pass conversion", and the per cent. of $CO_2 = 100x/(2 - x)$.

The following tables summarise at various temperatures and pressures the pass conversion, % $CO_2$ and heat of reaction.

*Pass Conversion* ($100x$).

| Temp., °K.:<br>Press., atm. | 700°. | 800°. | 900°. | 1000°. | 1100°. | 1200°. | 1300°. | 1400°. |
|---|---|---|---|---|---|---|---|---|
| ½ . . . . . | 98 | 85 | 47 | 10 | 2 | < 0·5 | | |
| 1. . . . . . | 98·5 | 89·5 | 60 | 18·5 | 4 | 1 | < 0·5 | |
| 3. . . . . . | 99·5 | 94 | 76·5 | 38 | 10 | 3 | 0·5 | < 0·5 |
| 5. . . . . . | 99·5 | 95·5 | 81 | 47·5 | 15 | 4·5 | 1 | < 0·5 |

$CO_2$, % *at Equilibrium*

| Temp., °K.:<br>Press., atm. | 700°. | 800°. | 900°. | 1000°. | 1100°. | 1200°. | 1300°. | 1400°. |
|---|---|---|---|---|---|---|---|---|
| ½ . . . . . | 96 | 74·5 | 31 | 5·5 | 1·0 | < 0·25 | | |
| 1. . . . . . | 97·04 | 81 | 42·8 | 10·5 | 2·0 | 0·5 | < 0·25 | |
| 3. . . . . . | 99 | 88·6 | 62 | 23·5 | 5·3 | 1·5 | 0·25 | < 0·25 |
| 5. . . . . . | 99·8 | 91·3 | 68 | 31·1 | 8·1 | 2·3 | 0·63 | < 0·25 |

*Reaction Heat* (*calories*)

| Temp., °K.: | 700°. | 800°. | 900°. | 1000°. | 1100°. | 1200°. | 1300°. | 1400°. |
|---|---|---|---|---|---|---|---|---|
| | −41,353 | −41,193 | −40,997 | −40,781 | −40,545 | −40,031 | −39,754 | −39,484 |

The reaction is heterogeneous, and is catalysed by a variety of substances, including the deposited carbon, and also by metallic cobalt, nickel, and iron, metals which are noteworthy for forming carbonyls. Many

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[30] *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

authorities, *e.g.*, F. Ephraim,[31] stated that iron carbide, $Fe_3C$, is the effective catalyst, and that until it is formed the reaction proceeds slowly. On the other hand, Bone and his collaborators (see below) are of the opinion that iron carbide is of little, if any, importance. However it functions, iron is of immense importance in this reaction in industry. Thus at temperatures as low as 300° the effect may be appreciable, and $Fe_2O_3$ in firebricks accelerates the decomposition of carbon monoxide to such an extent that the deposited carbon can disintegrate the bricks.[32]

The reactions of carbon monoxide in the blast furnace are of critical economic importance. A classical series of investigations on a very large scale was made by Sir Lothian Bell.[33] He noted that some reduction of $Fe_2O_3$ is necessary " to induce the reaction ", which then proceeds irrespective of the presence of free iron in the charge. He considered the optimum temperature for the reaction to be 400—450°. W. A. Bone, L. Reeve, and H. L. Saunders [34] made a series of investigations into the reactions of carbon monoxide with iron oxides. They used dry ores and dry CO, to avoid the catalytic effects of water or hydrogen. The important reactions are

$$\begin{aligned}
&(1)\quad 3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \quad \text{irreversible}\\
&\left.\begin{aligned}
&(2)\quad FeO + CO \rightleftharpoons Fe + CO_2\\
&(3)\quad Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2\\
&(4)\quad 2CO \rightleftharpoons CO_2 + C
\end{aligned}\right\}\text{reversible}
\end{aligned}$$

The " carbon deposition " sets in at about 380°, and ceases at about 650°. With dry carbon monoxide reactions (1)—(3) predominate in the earlier stages, (4) when an amount of reduction which varies with the temperature has taken place. Once (4) has started, it becomes more rapid as the ore is reduced until practically all the available monoxide is converted into carbon and its dioxide. At 380° when—roughly—all the $Fe_2O_3$ has been reduced to $Fe_3O_4$, reaction (4) rapidly reaches predominance. At 550° a similar state of affairs is reached, the monoxide being converted into carbon and dioxide instead of reducing iron oxide. Above 650° reaction (4) has relatively little influence on blast-furnace reactions. According to Bone and his co-workers,[35] perhaps 20% of the total carbon in the gases formed by the combustion of the coke in the furnace is redeposited at the upper levels. The large volume of the carbon breaks up the ore, but may ultimately block up the furnace. At 450° there seems to be no limit to the process, which begins to be appreciable at 275°. At 750° the deposited carbon is a much more powerful reducing agent than is carbon monoxide. Both hydrogen and steam accelerate the reaction to a marked extent.

*Nitrogen.*—Nitrogen, having compounds in which the element appears in a variety of oxidation states, would be expected to form some intermediate compounds unstable with respect to those of a higher or a lower

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[31] " Inorganic Chemistry ", 1934, English Ed., p. 714.

[32] D. W. Hubbard and W. J. Rees, *Trans. Ceram. Soc.*, 1929, **28**, 277.

[33] *J.*, 1869, **22**, 219.

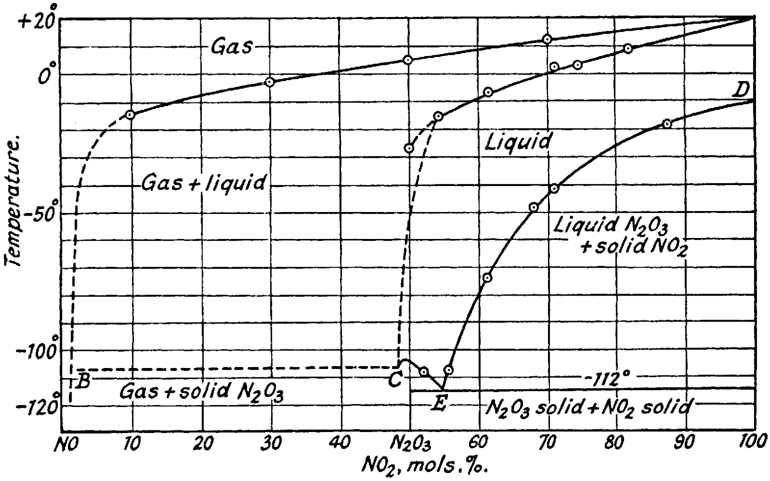
[34] *J. Iron Steel Inst.*, 1927, **115**, No. 1, 127.

[35] *Ibid.*, 1930, **121**, No. 1, 35.

valency state; this is well displayed in nitrous acid and its anhydride, dinitrogen trioxide, $N_2O_3$. The latter as a pure gas is unknown; it is always more or less disproportionated: $N_2O_3 \rightleftharpoons NO + NO_2$. From the work of E. Abel and J. Proisl[36] the following data are taken:

| Press., atm. | % $N_2O_3$ undissociated at various temperatures, in a stoicheiometric mixture of NO and $NO_2$. | | |
|---|---|---|---|
| | 0°. | 25°. | 100°. |
| 0·01 | 1·2 | 0·35 | (0·03) |
| 0·10 | 5·5 | 2·4 | 0·15 |
| 1·0 | — | 10·5 | 1·2 |

The gas is said to "boil with decomposition" at + 3·5°; its relation to the monoxide and the dioxide are well shown in the accompanying phase diagram, redrafted from Gmelin's "Handbuch der Anorganischen Chemie", Part 4, Stickstoff, p. 742, from which it appears that although solid $N_2O_3$ can exist as a pure compound, in the liquid phase it very soon begins to disproportionate, and only exists at a low temperature, under an atmosphere containing free nitrogen oxide. At temperatures above − 100° dissociation has commenced, and the gaseous phase is enriched with nitrogen oxide, the liquid with the dioxide. Thus the "blue-green liquid" commonly described as $N_2O_3$ is a solution of more or less $NO_2$ in $N_2O_3$.



*The System* $NO$–$NO_2$ *at* 1 *atmosphere pressure.*

Nitrous acid is a weak acid (dissociation constant $6 \times 10^{-4}$), so its ionisation into H ions and stable $NO_2$ ions is small. Instead of ionising, it disproportionates, a reaction of very great industrial importance, as the

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[36] *Z. Elektrochem.*, 1929, **35**, 712.

whole process of nitric acid manufacture (from ammonia) depends on this reaction.[37] Several reactions take place, and may be summed up in the equation

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \quad . \quad . \quad . \quad (1)$$

(which neglects a small side reaction, whereby a small amount of nitrogen is always produced).[38] The free-energy change $\Delta G^\circ_{298}$ of this reaction is $-$ 2120 cals., hence its equilibrium constant is 36; equilibrium is quite rapidly attained. In the nitric acid process, the first reaction is oxidation of ammonia to nitric oxide over a catalyst, the nitric oxide being oxidised to nitrogen dioxide by excess of air. The nitrogen oxides produced are scrubbed with water. If some NO is still present, stoicheiometric proportions of the two oxides react:

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \quad . \quad . \quad . \quad . \quad (2)$$

the nitrous acid formed decomposing at once according to equation (1). Nitrogen dioxide itself also dissolves in water:

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \quad . \quad . \quad . \quad (3)$$

the immediate decomposition of the nitrous acid formed yielding an overall equation

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \quad . \quad . \quad . \quad . \quad (4)$$

Of these reactions (2) is rapid, (3) is slow and rate-limiting in normal circumstances, and is of importance when the solution is dilute with respect to nitric acid, (4) is important particularly in the reverse direction, when fairly concentrated nitric acid may be reduced by NO in excess of that required for equilibrium. The free-energy change $\Delta G^\circ_{298}$ for equation (4) is $-$ 11,330, and for equation (3) $-$ 5650 cals. (without allowance for the immediate decomposition of the nitrous acid to nitrogen monoxide and dioxide and water). The newly formed monoxide is oxidised to dioxide by air, $2NO + O_2 \rightleftharpoons 2NO_2$, to be absorbed in water as before.

It was shown by B. Holmesland[39] that the mechanism of (4) is

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3$$
$$2HNO_2 \rightleftharpoons H_2O + NO + NO_2$$
$$HNO_2 + NO_2 \rightleftharpoons HNO_3 + NO$$

so that nitrous acid is an intermediate in reaction (4).

Our understanding of (1) is largely due to E. Abel and his collaborators[40] and also to W. C. Bray.[41] The equilibrium constant

$$K = \frac{[H^+][NO_3^-]p^2_{NO}}{[HNO_2]^3}$$

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[37] A. J. Prince and K. G. Denbigh, *J.*, 1947, 790.

[38] H. N. Wilson and A. E. Heron, *Analyst*, 1945, **70**, 40.

[39] *Tids. Kjemi*, 1926, **6**, 107.

[40] *Z. physikal Chem.*, 1930, *A*, **148**, 337.

[41] *Chem. Reviews*, 1932, **10**, 161.

(concns. in moles/l., pressure in atm.) has the following values :

| Temp. : | 12·5°. | 15°. | 24·9°. | 30°. |
|---|---|---|---|---|
| $K$ . . . | 13·3 | 14·1 | 28·7 | 39·6 |

The mechanism suggested was

$$2HNO_2 \rightleftharpoons NO_2 + NO + H_2O \quad \text{(rapid)}$$

$$2NO_2 + H_2O \rightleftharpoons H^+ + NO_3^- + HNO_2 \quad \text{(rate-determining)}$$

The fact that a stoicheiometric mixture of nitrogen mon- and di-oxide is much more rapidly dissolved in water or sodium hydroxide solution (with, in the second case, production of but minor amounts of nitrate) than is the dioxide, is qualitative evidence of the greater rapidity of the first reaction.

Amongst other compounds of nitrogen, hydroxylamine and hydrazine tend to disproportionate. Hydroxylamine can act as an oxidising agent, *e.g.*, in alkaline solution it oxidises ferrous iron to ferric, being itself reduced to ammonia, or it can itself readily be oxidised, *e.g.*, by ferric iron in acid solution, to nitrous oxide or by noble metals to a mixture of nitrogen and oxides of nitrogen. The salts are fairly stable in acid solution, but the free base, especially in presence of excess of alkali, slowly disproportionates into ammonia, nitrogen, and minor quantities of nitric oxide. For instance, a 0·1N-solution of free hydroxylamine, on standing for 24 hours at room temperature, is unchanged : after 4 hours' boiling under reflux, 4% of the hydroxylamine is decomposed. A solution 0·1N with respect to both hydroxylamine and sodium hydroxide, after 24 hours at room temperature, is 10·9% decomposed ; after 4 hours' boiling under reflux it is 10·3% decomposed.[41a]

Hydrazine, though usually regarded as a reducing agent, has oxidising properties under some conditions (compare hydrogen peroxide). The hydrate very slowly decomposes spontaneously into ammonia, nitrogen (and hydrogen), the decomposition being accelerated by platinum.[42] The anhydrous substance appears to be more stable. In acid solution its disproportionation is seen in such a reaction as

$$N_2H_5^+ + Fe^{+++} = Fe^{++} + \tfrac{1}{2}N_2 + NH_4^+ + H^+$$

*Phosphorus.*—The resemblance between phosphorus and nitrogen is sufficiently great to render it not surprising that phosphorus compounds of an intermediate state of valency will be unstable with respect to higher and lower states. The parallelism is not very marked ; the intermediate diphosphorus trioxide $P_2O_3$ does not disproportionate to PO and $PO_2$ but to the element and phosphoric oxide, and the lower acids of phosphorus in aqueous solution behave similarly to the anhydride, but the similarity is disguised through further reactions in water yielding phosphine, presumably

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[41a] H. N. Wilson, unpublished experiments.

[42] S. Tanatar, *Z. physikal. Chem.*, 1902, **40**, 475.

formed by reduction of water by the elementary phosphorus, and phosphoric acid.

So-called " phosphorus trioxide " $P_4O_6$ is an intermediate formed in the oxidation of phosphorus. L. Wolf and H. Schmager,[43] in separating it from $P_2O_5$ by distillation at 175° (its b.p. at atmospheric pressure), found that the distillate always contained elementary phosphorus. This is because the oxide slowly disproportionates on heating to form the " tetroxide " $P_4O_8$ and elementary phosphorus. When the trioxide is stirred into a large excess of *cold* water, only phosphorous acid is formed, but with hot water the products of reaction are phosphine, elementary phosphorus, and phosphoric acid.[44] Under certain conditions water and diphosphorus trioxide form two layers, which slowly react to give phosphorous acid, small amounts of phosphorus, and phosphoric acid.

" Phosphoric tetroxide ", although stable on heating, reacts with water as if it were a mixture of diphosphorus pentoxide and trioxide.

(i) Hypophosphorous acid and its salts are unstable, the decomposition products including phosphine and phosphoric acid, and—usually—hydrogen. The reactions are $3H_3PO_2 = PH_3 + 2H_3PO_3$ ; $\Delta G^\circ_{298} = -53{,}200$ cals. (the phosphorous acid formed will eventually disproportionate), and $H_3PO_2 + H_2O = H_3PO_3 + H_2$ ; $\Delta G^\circ_{298} = -27{,}300$ cals. The free acid and its solutions are the more stable and only decompose to any marked extent above 140°. In alkaline or neutral solution hydrogen is formed at 100°, the reaction being catalysed by finely divided metals such as palladium and copper. In alkaline solution[45] the first reaction is $H_2PO_2^- + OH^- = HPO_3^{--} + H_2$, the complete rate equation is

$$-\,d[H_2PO_2^-]/dt = k[H_2PO_2^-][OH^-]^2$$

and the suggested mechanism is

$$H_2PO_2^- + 2OH^- = H_2PO_3^- + O^{--} + H_2 \text{ (slow)}$$
$$O^{--} + H_2O = 2OH^- \text{ (fast)}$$

(ii) Phosphorous acid and its concentrated solutions decompose if strongly heated : $4H_3PO_3 = 3H_3PO_4 + PH_3$ ; $\Delta G^\circ_{298} = \sim 8800$ cals. Although the free-energy change is positive, decomposition of phosphorous acid occurs because of the volatility of phosphine. The mechanism of the reaction does not seem to have been elucidated ; it seems reasonable to suppose that the first reaction is again the formation of the element, which reacts with water by the hypothetical reaction

$$4P \text{ (red)} + 6H_2O = PH_3 \text{ (gas)} + 3H_3PO_2 \text{ ; } \Delta G^\circ_{298} = -17{,}000 \text{ cals.}$$

(iii) The sulphides of phosphorus are not similar to the oxides, *e.g.*, $P_4S_5$ can be prepared by slowly cooling a molten mixture of 2P and 3S : the chief product is $P_4S_7$, but $P_4S_5$ can be extracted from the cooled melt by carbon disulphide. W. D. Treadwell and C. Beeli[46] consider that an

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[43] *Ber.*, 1929, **62**, 771.

[44] L. Wolf, W. Juny, and M. Tschiednowsky, *ibid.*, 1932, **65**, 488.

[45] A. Sieverts and F. Lessner, *Z. anorg. Chem.*, 1912, **76**, 10.

[46] *Helv. Chim. Acta*, 1935, **18**, 1161.

equilibrium is set up: $2P_4S_5 \rightleftharpoons P_4S_3 + P_4S_7$. $P_4S_7$ is apparently stable, it boils at 523° to give a gas which only at 700° begins to dissociate.[47] When the "pentasulphide" $P_4S_{10}$ is dissolved in water, the products of hydrolysis always include hypophosphorous acid, showing that in the act of hydrolysis the compound breaks down into sulphur and a lower sulphide.[46]

*Sulphur.*—Almost all oxy-acids of sulphur tend to disproportionate, the only truly stable oxy-acid being sulphuric acid.

(i) Sulphur monoxide is not an acid anhydride, as the products of its reaction with water include both sulphur and hyposulphurous (dithionous) acid, $H_2S_2O_4$; it is a typical "sub"-oxide, and very readily breaks up into sulphur and the dioxide (cf. SiO and BiO). "Many supposed solid sub-compounds have been identified as intimate mixtures of elements with compounds exhibiting more normal valencies, but these mixtures may be disproportionation products of true sub-compounds stable at high temperatures or under special conditions." [48] Sulphur monoxide is obtained by subjecting a mixture of sulphur vapour and the dioxide under reduced pressure to a high-voltage discharge: $SO_2 + S \rightleftharpoons 2SO$. At liquid-air temperature the gas condenses to an orange-red solid, but as the temperature rises decomposition is rapid.[49]

(ii) "Sulphurous acid", the solution of the dioxide in water, very slowly decomposes, yielding ultimately free sulphur and sulphuric acid: $3H_2SO_3 = 2H_2SO_4 + S + H_2O$; $\Delta G^\circ_{298} = -22{,}600$ cals. Various sulphur acids are also produced, partly through interaction of the sulphur with sulphurous acid. The acid is either an oxidising or a reducing agent; in fairly acid solution it will oxidise ferrous salts to ferric, or iodides to iodine, being itself reduced to sulphur; in neutral or faintly acid solution it is a reducing agent. That is, sulphurous acid is oxidising, the sulphite ion is reducing:

$$3H_2O + S = H_2SO_3 + 4H^+ + 4e;\quad E_0 = -0{\cdot}45$$
$$6OH^- + S^{--} = SO_3^{--} + 3H_2O + 6e;\quad E_0 = +0{\cdot}61$$

Quantitatively its disproportionation is due to both reactions proceeding simultaneously. The disproportionation is influenced by light, and very pure solutions in water are much more stable than solutions containing traces of iron, copper, manganese, arsenic, or iodine, all of which are powerful promoters of the reaction of sulphurous acid with oxygen. The catalytic action of iodine may be due to the simultaneous occurrence of two reactions

$$4HI + H_2SO_3 \rightleftharpoons 2I_2 + S + 3H_2O$$

and

$$H_2SO_3 + I_2 + H_2O \rightleftharpoons H_2SO_4 + 2HI$$

the two summing up as

$$3H_2SO_3 \rightleftharpoons 2H_2SO_4 + S + H_2O$$

In reality neither of these reactions is at all simple: although the

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[47] A. Stock, *Ber.*, 1910, **43**, 415, 1223.

[48] A. J. E. Welch, *Ann. Reports*, 1945, **42**, 90.

[49] P. W. Schenk, *Z. anorg. Chem.*, 1937, **233**, 385.

second can be caused to proceed quantitatively, iodine, like all other oxidising agents can react also to produce some dithionic acid. In the aerial oxidation, a reaction much influenced by catalysts and inhibitors, a chain reaction is almost certain, and H. L. J. Bäckström[50] has suggested the following mechanism for the copper-catalysed reaction

$$Cu^{++} + SO_3^{--} \rightleftharpoons Cu^{+} + SO_3^{-}$$
$$SO_3^{-} + O_2 \rightharpoonup SO_5^{-}$$
$$SO_5^{-} + HSO_3^{-} \rightharpoonup HSO_5^{-} + SO_3^{-}$$
$$SO_3^{-} + \text{inhibitor} \rightharpoonup \text{termination of chain}$$
$$HSO_5^{-} + SO_3^{--} \rightharpoonup HSO_4^{-} + SO_4^{--}$$

As exactly the same catalysts are effective in oxidation and disproportionation, the first reaction is probably the same, whatever the subsequent steps. This would also explain the formation of dithionates ($2SO_3^{-} = S_2O_6^{--}$).

Some solid sulphites disproportionate. Sodium metabisulphite (pyrosulphite), heated in absence of air, forms sulphur dioxide and sodium sulphite, as well as some sulphur and sulphate. It is possible that SO formation may be an intermediate step.

(iii) Hyposulphurous (dithionous) acid $H_2S_2O_4$ is unstable :

$$2S_2O_4^{--} + H_2O = S_2O_3^{--} + 2HSO_3^{-} ; \quad \Delta G^\circ_{298} = -59{,}100 \text{ cals.}$$

Solutions of the free acid cannot exist for very long, and the rate of decomposition is increased by addition of strong acids, which cause the decomposition of the thiosulphate ion, so that the final result is $2S_2O_4^{--} + H_2O = 2H^{+} + 3SO_3^{--} + S$.

The rate of the first reaction was studied by K. Jellinek and E. Jellinek.[51] At 60° the rate equation was second-order, having the form $-d[S_2O_4^{--}]/dt = k[S_2O_3^{--}]^2$, but in presence of added bisulphite ion it is $-d[S_2O_4^{--}]/dt = k[S_2O_4^{--}]^2 [HSO_3^{-}]^2$.

Solutions of the alkali-metal salts are more stable, but decompose slowly.

(iv) Dithionic acid is also unstable : although dilute solutions only decompose very slowly at room temperature, concentrated solutions decompose according to the equation $H_2S_2O_6 = H_2SO_4 + SO_2$. A solution containing about 37% of the acid has been obtained by evaporation at low pressures ;[52] but if dilute solutions are heated to 60° or higher, the rate of decomposition becomes measurable. According to D. M. Yost and R. Pomeroy,[53] the rate equation is

$$-d[SO_4^{--}]/dt = k[H^{+}][S_2O_6^{--}] ; \quad k \text{ at } 50^\circ = 0{\cdot}003, \ k \text{ at } 80^\circ = 0{\cdot}16$$

(time in minutes, concns. in moles/l.). On addition of excess of other strong acid (total $H^{+} > 0{\cdot}6\text{N}$) the rate becomes much greater. The suggested mechanism is

$$H^{+} + S_2O_6^{--} \rightleftharpoons HS_2O_6^{-} \text{ (rapid)}$$
$$HS_2O_6^{-} + H_2O \rightleftharpoons H_2SO_3 + HSO_4^{-} \text{ (rate-determining)}$$

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[50] *Z. physikal Chem.*, 1934, *B*, **25**, 122.

[51] *Ibid.*, 1919, **93**, 325.

[52] H. Stam and R. Adolph, *Ber.*, 1934, **67**, 726.

[53] *J. Amer. Chem. Soc.*, 1927, **49**, 703.

This rate-determining step is also the rate-determining step when dithionates are oxidised in acid solution; *i.e.*, dithionates are not oxidised as such, *e.g.*, by potassium permanganate, but after disproportionation the $HSO_3^-$ ion is (rapidly) oxidised. Neither the acid nor its salts are readily reduced, but zinc amalgam can reduce them to sulphites and finally to hyposulphite. On being heated to > 200°, dithionates decompose: $Na_2S_2O_6 = Na_2SO_4 + SO_2$.

(v) Thiosulphates, stable in neutral or alkaline solution, decompose in dilute acid solution: $S_2O_3^{--} + 2H^+ = H_2SO_3 + S$. The two sulphur atoms are not combined similarly, as has been proved by experiments with radioactive isotopes of sulphur.[54] In a loose sort of way one could perhaps say that one sulphur atom is similar to sulphide sulphur (*e.g.*, in formation of heavy-metal sulphides) and the other has a valency similar to that of sulphur in sulphate.

It is rather difficult to explain the reaction of thiosulphates with dilute acids. It is almost certain that it is the $S_2O_3^{--}$ anion which reacts with hydrogen ions, and J. Janickis [55] believes that the free acid is fairly stable, because if sodium thiosulphate solution is added to concentrated hydrochloric acid at – 20°, and the solution warmed to 0°, no sulphur is deposited, and no yellow colour is produced in 8 hours. About half of the thiosulphuric acid remains, but some polythionic acids are formed.

All polythionates are unstable: a very good brief review is given by D. M. Yost and H. Russell.[56] It is there stated that " in spite of numerous investigations dating from 1850, not a single feature of the mechanism of reaction between $H_2S$ and $SO_2$ can be said to be firmly established ".

*Halogens.—Halogen compounds.* The oxy-acids of halogens and their salts exhibit many instances of disproportionation; it will be convenient to consider chlorine compounds first, then those of bromine and iodine.

(i) Hypochlorous acid in aqueous solution can decompose in two ways:

$$(1)\quad 2HOCl \rightleftharpoons O_2 + 2HCl$$

a reaction slow at ordinary temperatures, and much influenced by light and by such catalysts as cobalt salts,[57] and

$$(2)\quad 3HOCl = HClO_3 + 2HCl$$

It is this second reaction which is considered here. Actually, as hypochlorous acid is fairly rapidly attacked by hydrochloric acid,

$$(3)\quad HOCl + HCl \rightleftharpoons H_2O + Cl_2$$

reaction (2) does not occur, but hypochlorites behave similarly and we can write

$$(4)\quad 3ClO^- = ClO_3^- + 2Cl^-;\ \Delta G^\circ_{298} = \sim -43{,}000\ \text{cals.}$$

The reaction is very slow in dilute solutions, at room temperature, but

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[54] W. F. Libby and H. H. Voge, *J. Amer. Chem. Soc.*, 1937, **59**, 2474.

[55] *Z. anorg. Chem.*, 1937, **234**, 193.

[56] " Systematic Inorganic Chemistry ", 1946, p. 390.

[57] A. J. Allmand, P. W. Cunliffe, and R. E. Maddison, *J.*, 1927, 655.

proceeds very much more rapidly in hot concentrated solutions. It is clear that a three-body collision between anions is most unlikely, but as in many other atom-transfer reactions, the exact mechanism is uncertain. Moderate amounts of free alkali stabilise hypochlorites ; the solutions are least stable at pH 5·7, and have maximum stability at pH 13·1.[69] This supports an older theory that the reaction is between free hypochlorous acid and hypochlorite ion : [58]

$$(5)\ \mathrm{ClO^- + 2HClO = ClO_3^- + 2H^+ + 2Cl^-}$$

Owing to the small dissociation constant of hypochlorous acid ($K = 5{\cdot}8 \times 10^{-8}$),[59] some free acid will always be present ; it is known that, as is usual with weak acids, the constitution of the free acid differs from that of the ion,[60] so one might expect reaction in presence of both to be different from that of either separately. In absence of some free alkali, accumulation of hydrogen ions would cause reaction (3) to take place. Chlorites have been detected in the decomposition products (particularly from alkaline solutions) but they also disproportionate to chlorates and chlorides : [61] $\mathrm{3ClO_2^- \rightarrow 2ClO_3^- + Cl^-}$. Here again cobalt promotes decomposition to chloride and oxygen. Numerous researches [62, 63, 64, 65] have been made to clear up the kinetics, with not entirely consistent results. Ramstetter and Hantke say that at 45°, decomposition of an alkaline hypochlorite solution is bimolecular ; in acid solution the order of the reaction cannot be determined.

In considering the reaction, the possibility of hypochlorous acid dissociating in yet another way should be remembered : $\mathrm{HOCl \rightleftharpoons (HO{:})^- + Cl^+}$.[66] The cationic chlorine will be a very powerful oxidising agent, and may well play an important part in the reaction.

P. Pierron [67] pointed out that in the slow decomposition of potassium, sodium, or lithium hypochlorite the total oxidising power of the solution became less, the loss increasing with rising pH, and for potassium and sodium salts was at a minimum at pH 7. Pierron was able to detect peroxide in strongly alkaline solutions of the potassium salts after 4—8 days, and to a less extent in solutions of the corresponding sodium salt, more peroxide being present the more alkaline the solution : although addition of peroxide had no effect on the rate of decomposition, he concluded that formation of " nascent " peroxide was a rate-determining step. In approximately neutral solutions he detected chlorites, lithium solutions being richest in $\mathrm{ClO_2^-}$, but in sufficiently alkaline or acid solutions chlorites were absent.

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[58] F. Foerster and F. Jorre, *J.*, 1899, **76**, ii, 278 (abstract).
[59] A. Skrabal and A. Berger, *Monatsh.*, 1937, **70**, 168.
[60] K. Schaefer, *Z. physikal Chem.*, 1919, **93**, 312.
[61] W. Bray, *ibid.*, 1906, **54**, 576.
[62] H. Kauffman, *Z. angew. Chem.*, 1924, **37**, 364.
[63] J. J. Weiss, *Z. anorg. Chem.*, 1930, **192**, 97.
[64] A. Skrabal, *Monatsh.*, 1941, **73**, 269.
[65] H. Ramstetter and G. Hantke, *Z. physikal. Chem.*, 1941, *A*, **189**, 122.
[66] W. A. Waters, " The Chemistry of Free Radicals ", Oxford, 1946, p. 253.
[67] *Bull. Soc. chim.*, 1943, **10**, 445.

In one respect chlorine dioxide resembles nitrogen dioxide, *viz.*, in its reaction with alkalis in aqueous solution :

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O$$

This reaction hardly proceeds at all in pure water.

(ii) Chloric acid and the chlorates show striking differences in stability. Neutral or alkaline solutions of chlorates are stable with respect to decomposition into chlorides and perchlorates, but chloric acid readily decomposes, forming oxides of chlorine, oxygen, and perchloric acid. The "ideal" equation for this decomposition is $4ClO_3^- = 3ClO_4^- + Cl^-$; $\Delta G^\circ_{298} = \sim - 57,000$ cals.

Solid dry chlorates decompose on heating in two ways :

$$4KClO_3 \rightharpoonup 3KClO_4 + KCl \text{ and } 2KClO_3 \rightharpoonup 2KCl + 3O_2$$

The first is autocatalytic, as it is catalysed by chlorides,[68] and also by certain other substances, *e.g.*, baryta. The second is well known to be catalysed by manganese dioxide ; other oxides such as $Fe_2O_3$ also catalyse this reaction.

Similar reactions of bromates and iodates do not occur : perbromates are not known, periodates are not formed in this way.

(iii) Hypobromites are in general similar to hypochlorites but less stable : hypoiodites are still less stable.[69] Even in alkaline solution, hypoiodites rapidly disproportionate. The kinetics of hypobromite decomposition have been studied by C. F. Prutton and H. S. Marron,[70] and hypoiodites by W. C. Bray [71] and in alkaline solutions by C. F. White and Choh Hao Li.[72] Neither bromites nor iodites have been isolated : it is supposed that they are formed as intermediate steps in the decomposition.

*Manganese.*—The disproportionation reactions which occur among manganese compounds in aqueous solutions are much influenced by the exceedingly small solubility of "hydrated manganese dioxide", as compounds of either lower or higher states of oxidation, if they disproportionate, do so with precipitation of hydrated dioxide. Thus manganic (tervalent) compounds form manganous salts and precipitate the hydrated dioxide, manganates (sexivalent) precipitate the hydrated oxide and form permanganate. To calculate equilibria amongst these compounds is almost impossible ; the solubility product of the hydrated dioxide is not known with certainty, the substance itself is not of constant composition either as regards degree of oxidation or degree of hydration, and uncertainty also exists as to the electrode potentials of most manganese compounds, as the electrodes are irreversible. W. M. Latimer [73] has collected the best values up to 1938.

(i) Manganic compounds exhibit to a remarkable degree the stabilising effect of complex-forming anions. All "simple" manganic salts dispro-

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[68] C. E. Otto and H. S. Fry, *J. Amer. Chem. Soc.*, 1924, **46**, 269.

[69] R. M. Chapin, *ibid.*, 1934, **56**, 2211.

[70] *Ibid.*, 1935, **57**, 1652.

[71] *Z. physikal. Chem.*, 1906, **54**, 463.

[72] *J. Amer. Chem. Soc.*, 1943, **65**, 335.

[73] "Oxidation States of the Elements", New York, 1938.

portionate, but numerous more or less stable complex salts are known. Manganic oxide (hydrated) is a stable mineral, which remains unchanged in contact with water or alkaline solution, but by the action of most dilute acids, even weak acids, it is broken up into manganous salts and the hydrated dioxide, which may be of importance in soil biology.[74] Manganic acetate, however, can be prepared, and is fairly stable. It is a convenient material for the preparation of manganic sulphate. This compound can be dissolved in aqueous sulphuric acid, but on diluting the solution, manganous sulphate and the hydrated dioxide are formed. From the solution the remarkable red manganic alums, *e.g.*, $K_2SO_4,Mn_2(SO_4)_3,24H_2O$, can be prepared by crystallisation at temperatures below 40°. These compounds are salts of the acid $H[Mn(SO_4)_2]$. They disproportionate in solution on heating or excessive dilution.

Similarly double salts of $MnCl_4$ have been isolated. If chlorine is passed into solutions of manganous chloride strongly acidified with hydrochloric acid, considerable amounts are dissolved, to form a dark brown liquid, from which by addition of potassium chloride such salts as $2KCl,MnCl_3$ can be crystallised out. On considerable dilution, however, hydrated $MnO_2$ is precipitated : $2MnCl_3 + 2H_2O = MnO_2 + MnCl_2 + 4HCl$.

Manganic fluoride is more stable than the chloride : the salt is fairly easily prepared and can be dissolved in cold water without decomposition, though too great dilution causes disproportionation. If, however, the solution contains alkali fluorides in excess, stable $[MnF_6]'''$ ions are formed. Salts of $[Mn(CN)_6]'''$ are also known.

Potassium manganic oxalate can be prepared : on acidification it slowly reacts to form carbon dioxide and a manganous salt. The transient formation of the manganic–oxalate complex can be seen when permanganate solution is rapidly added to a slightly acid solution containing manganous salts and oxalate in excess. The red-brown complex anion is either reduced by excess of oxalate or disproportionates to form manganese dioxide and a manganous salt—a reaction often achieved by the less expert students of volumetric analysis.

But perhaps the most stable of manganic salts is the pyrophosphate ; it is probable that the acid solution contains the ion $MnP_2O_7^{--}$. In presence of pyrophosphates, manganous salts in acid solution can be titrated quantitatively with permanganate, manganic ions being stoicheiometrically formed : the end-point is detected potentiometrically.[75] Hydrated manganic oxide can be dissolved without disproportionation by dilute pyrophosphoric acid, and it has been shown [76] that at pH 7 pyrophosphate solutions containing manganous ions will stoicheiometrically dissolve manganese dioxide according to the equation $Mn^{++} + Mn^{++++} = 2Mn^{+++}$.

(ii) Manganates are unstable ; in alkaline solutions they have a tendency to decompose :

$$2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KOH + O_2 \qquad . \quad . \quad (1)$$

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[74] H. G. Dion and P. J. G. Mann, *J. Agric. Sci.*, 1946, **36**, 239.

[75] J. J. Lingane and R. Karplus, *Ind. Eng. Chem. Anal.*, 1946, **18**, 191.

[76] S. G. Heintze and P. J. G. Mann, *Nature*, 1946, **158**, 791.

In N-potassium hydroxide solution the oxidation potential is slightly higher than that of oxygen at 1 atm. pressure, but the stability rapidly rises with increase in alkalinity, because $p_{O_2} = K[K_2MnO_4]^2/[KOH]^4$. In neutral or acid solutions, the behaviour of manganates is quite different, and may be summarised as

$$3MnO_4^{--} + 2H_2O = MnO_2 + 2MnO_4^- + 4OH^- \quad . \quad . \quad (2)$$

Even carbon dioxide can be used to " acidify " alkaline solutions of manganates and cause this reaction to take place instead of reaction (1) ; and this is, in fact, the basis of the old method for the preparation of permanganates. Latimer [73] quotes the following as the best values for the electrode potentials concerned :

$$MnO_4^{--} = MnO_4^- + e \qquad -0{\cdot}54 \text{ v.}$$
$$4OH^- + MnO_2 = MnO_4^- + 2H_2O + 3e \qquad -0{\cdot}57 \text{ v.}$$
$$4OH^- + MnO_2 = MnO_4^{--} + 2H_2O + 2e \qquad -0{\cdot}58 \text{ v.}$$

from which $\Delta G^\circ_{298}$ for equation (2) can be calculated as $\sim -1640$ cals., but the experimental values are somewhat uncertain.

Various elements not mentioned above, *e.g.*, gold, tin, rhenium, and thallium, have compounds of an intermediate state of oxidation, which disproportionate, but they display no features not exemplified already. A more important omission is the recent work of J. Heyrovsky,[77] who has shown by polarographic studies that when zinc is electrolytically reduced, the product first formed is $Zn^+$, and that the " univalent " zinc ion (or ion radical) disproportionates, $2Zn^+ = Zn^{++} + Zn$, and the speed of the reaction is the speed of the disproportionation, zinc metal being entirely produced in this way—a conclusion of great importance in the realm of electrolytic reductions.

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[77] *Österreich. Chem. Ztg.*, 1947, **48**, 24.