similar table covering the range 25 to 85° and 1 to 1000 bars has been compiled for water, older values of the expansions and new measurements of the compressions being used. Suitable equations for computing the first and second derivatives are given, the Tait equation always being used for the pressure–volume relations. The thermal expansibilities, the compressibilities, the pressure–temperature coefficients, the energy–volume coefficients, $(C_P - C_V)$ and other related properties have been computed.

The energy–volume coefficients of carbon tetrachloride decrease slightly with rise of temperature at constant volume. This is regarded as the normal behavior of actual liquids and is explained in terms of the effect of change in molecular distribution on the repulsive component of $(\partial E/\partial V)_T$. A pure volume function, tentatively identified with the attractive component of $(\partial E/\partial V)_T$, is obtained when $(\partial E/\partial V)_T$ is combined with the constant B of the Tait equation. The energy–volume coefficients of water behave

quite differently from those of other liquids, but all the differences may be accounted for by the addition of a term which gives the change in hydrogen bonding energy in the liquid with volume. The magnitude of the term is reasonable. Qualitatively the $(\partial E/\partial V)_T - V$ diagram for ethylene glycol resembles that of water, but the increase of $(\partial E/\partial V)_T$ with temperature at constant volume is so much less that we feel justified in assuming that distribution changes in glycol and glycol solutions have only a minor effect on the volume properties of these liquids.

The effect of temperature on the energy–volume coefficients of the liquids discussed is correlated with the variation with volume of their specific heats at constant volume. A comparison of the thermal expansibilities of the liquids at constant pressure and at constant volume is also made.

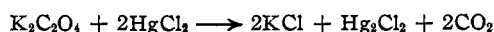Several refinements in the technique of measuring compressions by the piezometer method are described.

The Chain Carriers in Eder's Reaction

BY G. H. CARTLEDGE

The oxidation of oxalates by mercuric chloride according to the reaction

$$K_2C_2O_4 + 2HgCl_2 \longrightarrow 2KCl + Hg_2Cl_2 + 2CO_2$$

has been the subject of numerous investigations since Eder's studies on its use in actinometry.[1] The most important facts derived from these investigations may be summarized as follows. (1) The reaction proceeds at room temperature only when the solution is illuminated or supplied with a suitable chemical inductor, such as potassium permanganate. (2) The reaction occurs photochemically when the illumination contains no more ultraviolet light than is able to pass through glass (even window panes), although the reacting solution is colorless and the only components absorbing in the visible region of the spectrum are the traces of impurities remaining. The reaction occurs readily in ultraviolet light and under X-radiation.[2,3] (3) The photochemical

reaction is extremely sensitive to inhibitors and catalysts. Oxygen is a strong inhibitor to both the dark and photochemical reactions[2,4,5,6]; numerous fluorescing dyes and potassium trioxalatocobaltiate[5] are examples of positive catalysts. These appear to act as photosensitizers in the photochemical reaction. (4) The order of the reaction depends upon the conditions.[7] The reaction has a chain mechanism, Roseveare[2] having found a very large quantum yield with X-rays. The temperature coefficient of the photochemical reaction varies between 1 and 2 for different wave lengths.[8] (5) In the dark, the reaction may be induced by addition of very small amounts of strong oxidizing agents such as potassium permanganate, manganese dioxide, and the oxalato complexes of trivalent manganese or cobalt. Ferrous salts alone do not induce the reaction, but if oxygen also is present, the higher

(1) Eder. Ber.. **13**, 166 (1880).

(2) Roseveare, THIS JOURNAL, **52**, 2612 (1930).

(3) Wyckoff and Baker. Am. J. Roentgenol. Radium Therapy, [6], **22**, 551 (1929).

(4) Jodlbauer and Tappeiner, Ber., **38**, 2602 (1905).

(5) Cartledge and Djang, THIS JOURNAL, **55**, 3214 (1933).

(6) Roseveare and Olson, ibid., **51**, 1716 (1929).

(7) Cartledge and Goldheim, ibid., **55**, 3583 (1933).

(8) Padoa and Minganti, Atti accad. Lincei, **24**, II, 97 (1915).

"moloxide" of iron then formed brings about a copious precipitation of calomel. Ferric salts do not induce the dark reaction at room temperature, though the reaction proceeds readily at 100°. Certain additional characteristics of the reaction have been discussed by Kistiakowsky[9] and by Weber.[10]

The reaction is attended by a decrease in free energy of 58.7 kcal. when the solution is saturated with mercuric chloride and carbon dioxide. It appears then that the function of either the radiation or the chemical inductor is merely to produce one of the chain carriers upon which the reaction depends. In previous attempts to account for the reaction rates it has been assumed usually that the active component is some kind of complex containing both mercury and oxalate ions. The reaction rates are so susceptible to traces of oxygen and metallic salts, however, as well as to electrolytes in general, that very conflicting results have been reported in the literature. Roseveare[2] accounted for his results by assuming the reaction to depend upon the decomposition of a complex having the formula $HgCl_2C_2O_4^{--}$ From freezing-point and distribution measurements, Cartledge and Goldheim[7] concluded that within a moderate range of concentrations the weak complex $Hg_2Cl_2(C_2O_4)_2^{--}$ is formed; they further showed that the velocity constants obtained under varying conditions are in harmony with such a formulation.

The existence of a complex of some kind is shown by the change in the ultraviolet absorption which occurs when an oxalate is added to mercuric chloride; the absorption of the mixture extends to considerably longer wave lengths than that due to the separate components placed tandem in the path of light. Such complexes, however, have no measurable absorption in the visible, and it seems necessary to assume that in blue light the initiation of the reaction must originate in the photochemical decomposition of the oxalato-ferriate complex probably always present in traces. The sensitivity to blue light rapidly decreases as the purity of the materials is increased, though wave lengths below about 300 mμ remain effective. It is evident that more than one means exists for the initiation of the reaction, and the rate is most probably determined by the rate at which the chains are started.

Studies on the kinetics of the oxidation of oxalates have made it probable that the half-oxidized oxalate ion $C_2O_4^-$ is an intermediate in these reactions. This assumption was made by Berthoud and Bellenot in their work on the photochemical oxidation of oxalate ions by iodine,[11] and also by Launer[12] in order to account for the rate of oxidation of oxalic acid by potassium permanganate. It has been suggested that the same intermediate may be one of the chain carriers in Eder's reaction, though there has been no direct kinetic evidence to support the suggestion. The second necessary chain carrier has not been previously identified, so far as the author has been able to discover. The present paper is devoted to the development of the hypothesis that the second chain carrier is the unpolymerized mercurous ion Hg^+.

From the absence of any appreciable dark reaction in purified solutions at room temperature in spite of the favorable change in free energy it may be inferred that mercuric ions and oxalate ions (simple or complex) react in stages, the first of which is either thermodynamically impossible or extremely slow. The half-oxidized oxalate ion, having an odd electron, should be very reactive and no doubt would be able to reduce mercuric ions rapidly. (Throughout the discussion, it will be understood that the formula $C_2O_4^-$ is used for this oxidation product of the oxalate ion in solution only for convenience; there is no experimental ground for decision of the exact formula, which might equally well be CO_2^- or HC_2O_4, for example.) The presence of an effective reducing agent of limited life in solutions in which oxalate ions are being oxidized is shown by the experiments on the so-called "active oxalic acid."[13,14] The hydrogen peroxide formed by absorption of oxygen in such solutions also indicates the presence of a reducing agent very different from the oxalate ions or oxalic acid.[12]

Additional evidence for the participation of this active reducing agent in Eder's reaction has been obtained from the following experiments.

Anodic Induction.—An Eder mixture was prepared by mixing equal volumes of 0.2 M

(9) Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, N. Y., 1928.

(10) K. Weber, "Inhibitorwerkungen," Ferdinand Enke, Stuttgart, 1938.

(11) Berthoud and Bellenot, Helv. Chim. Acta, 7, 307 (1924).

(12) Launer, THIS JOURNAL, 54, 2597 (1932); 55, 865 (1933); Launer and Yost, ibid., 56, 2571 (1934).

(13) Oberhauser and Hensinger, Ber., 61, 521 (1928); Oberhauser and Schormüller, Ann., 470, 111 (1929).

(14) Abel and Schmidt, Naturwissenschaften, 23, 501 (1935); Abel, Z. Elektrochem., 43, 629 (1937). The second paper contains a good bibliography.

HgCl₂ and 0.2 M H₂C₂O₄. The solution was placed in a thoroughly cleaned porous porcelain cup which was surrounded by a solution of potassium oxalate. A platinum spiral was used as anode in the Eder solution and an e. m. f. of about 2.5 volts was applied to the cell, which was kept in the dark at room temperature. After thirty minutes, the anode was withdrawn and washed; it was found to be coated with calomel. This was identified by treatment with ammonia. As a control, the same spiral was left in the Eder mixture for two days; no calomel was found. The experiment was repeated twice with a mixture of 0.2 M HgCl₂ and 0.2 M K₂C₂O₄; the results were the same. In the second experiment approximately 0.1 amp. was passed through the cell, and in the third experiment, about 0.2 amp.
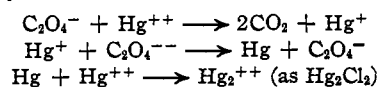
The experiment was repeated without using a porous cup in the following manner. The anode compartment consisted of a test-tube completely jacketed by a tube containing saturated potassium dichromate. So effectively did this filter absorb the blue light that a few millimeters of the solution was sufficient to protect the solution against direct sunlight; no turbidity was visible in an Eder mixture kept in such a tube after a week's exposure in a bright window. A salt bridge connected the Eder solution with potassium oxalate in the cathode chamber. An anode of platinum foil was suspended about 4 cm. from the bottom of the test-tube and current was passed. The upper part of the anode solution was stirred by the gas evolved. After electrolysis for about fifteen minutes, the upper part of the solution was very turbid, whereas the lower, unstirred portion of the solution remained clear. This arrangement is much more convenient and convincing than that in which the porous cup is used, in that the solution can be observed without difficulty through the dichromate filter, and there is no possibility of diffusion from the cathode chamber. At no time did the temperature rise above 27°.

The experiment was repeated with a carefully purified graphite anode with similar results. The anode did not induce the reaction when it stood overnight in the solution in a control test. These experiments clearly show the enhanced reducing power of some product derived from the oxalate ions by oxidation, since no chemical inductor was employed.

An additional experiment was made in the following manner. To a solution of pure potassium oxalate enough potassium permanganate was added to give an easily perceptible color. The solution was placed in a vertical tube having a stopcock at the bottom. A platinum anode was inserted at the middle of the tube and a salt bridge connected with the cathode solution. After a slow electrolysis for about fifteen minutes the solution was drawn off in three portions. In repeated experiments the lowest portion, which was below the anode, retained the original intensity of color, while the portions around and above the anode were completely or nearly decolorized. If not completely reduced, they became colorless before the portion below the anode. To eliminate possible catalytic effects of the anode itself, a piece of platinum similar to the electrode was left on the bottom of the tube during electrolysis.

A Possible Chain Mechanism.—If the half-oxidized oxalate ion is the active reducing agent in Eder's reaction, its concentration should be expected to remain very low, because of its great activity. Abel[14] estimated the concentration as 10^{-4} M in his experiments. Under these circumstances, its reaction with mercuric ions should be expected to be bimolecular, according to the reaction C₂O₄⁻ + Hg⁺⁺ → 2CO₂ + Hg⁺. It is to be expected that the ion Hg⁺ would be very active as an oxidizing agent, in view of the high ionizing potential of mercury. If its oxidation potential is sufficient to permit it to react rapidly with oxalate ions, we have the following as a possible chain mechanism for Eder's reaction, once the chain is started by formation of C₂O₄⁻ by an inductor, or otherwise

$$C_2O_4^- + Hg^{++} \longrightarrow 2CO_2 + Hg^+$$
$$Hg^+ + C_2O_4^{--} \longrightarrow Hg + C_2O_4^-$$
$$Hg + Hg^{++} \longrightarrow Hg_2^{++} \text{ (as Hg}_2Cl_2)$$

In such a mechanism the action of radiation consists in supplying the first C₂O₄⁻ by decomposition of an oxalato complex either of mercury or of iron; oxidizing inductors play the same role by starting the oxidation of the oxalate. The inhibitory action of oxygen is due presumably to its breaking the chains by reacting with one or both of the chain carriers.

Experimental evidence favoring the hypothesis has been found along two directions: it has been found possible (1) to detect free mercury in the reaction mixture and (2) to induce the production of carbon dioxide by addition of a *reducing agent* in complete absence of oxygen. Finally, theoreti-

cal calculations have been made which show that the half-reaction $Hg(l) \rightleftharpoons Hg^+ (aq) + \epsilon$ should have an electrode potential of about -1.71 volts on the hydrogen scale, and hence that Hg^+ should oxidize oxalate ions far more vigorously than mercuric ions.

The Detection of Mercury.—Although it would be reasonable to expect that little free mercury could long remain in solutions containing mercuric chloride, a test was sought for its detection in the presence of calomel. Two simple tests proved to be sufficiently sensitive and agreed in their indications. The first depended upon the reduction of ferric chloride, followed by addition of potassium ferricyanide.

Mercury has been proposed as a reducing agent in the volumetric determination of iron.[15,16,17] In a solution containing chlorides the reaction proceeds to completion, whereas it is incomplete in the absence of chlorides:

$$2Hg + 2Fe^{+++} + 2Cl^- \longrightarrow Hg_2Cl_2 + 2Fe^{++}$$
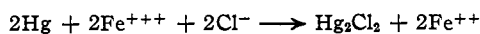
The reagent was 0.01 M Mohr salt in 0.1 N hydrochloric acid fully oxidized by addition of bromine. The excess was expelled by boiling. The suspected calomel was agitated with 2–3 ml. of this solution at room temperature for ten minutes, the mixture was centrifuged or filtered, and then one drop of a dilute solution of potassium ferricyanide was added. This solution was freshly prepared and gave a clear brown color with the ferric solution. Even traces of mercury caused the color to be green or blue, whereas it was found that no reduction of iron was caused by calomel that had been freed of mercury by long contact with mercuric chloride.

The second test consisted in the production of molybdenum blue by reduction of a phosphomolybdate solution. A stock solution of ammonium molybdate was prepared by dissolving 4 g. of the solid salt in a mixture of 137 ml. of water and 63 ml. of concentrated hydrochloric acid. The reagent itself was freshly prepared with 10 ml. of this stock solution and 5 ml. of 0.2 M Na_2HPO_4 in 50 ml. In making the test, the calomel was placed in a 15-ml. centrifuge tube with 2–3 ml. of the reagent and warmed for two minutes in a beaker of water at 50°. During this time the reagent alone developed a slight yellow color, whereas if mercury was present the color

was green or blue. After centrifuging out the calomel the color was noted most readily after addition of 3 drops of 0.1 M $H_2C_2O_4$. This bleached the yellow color of the reagent, leaving only the molybdenum blue due to free mercury. Under the conditions of the test, purified calomel gave only the faintest perceptible tint, if any, after the reagent was bleached.

In the first experiments designed to detect any free mercury formed during the progress of Eder's reaction, a piece of extremely pure gold sheet was placed in the mixture.[18] The gold was subsequently washed and agitated with one of the test reagents for ten minutes. These experiments showed the presence of mercury under certain conditions, but since it was later found unnecessary to have the gold to pick up the mercury, they will not be described in detail.

Mercury has been identified in the calomel obtained in the reduction of mercuric chloride by a large excess of potassium oxalate, the reaction being induced by either sunlight, the trioxalatocobaltiate ion, or the trioxalatomanganiate ion. In a series of experiments Eder mixtures were prepared from the 0.2 M reactants in different proportions; a trace of trioxalatocobaltiate was added and the solutions were exposed in a sunny window. The results were as follows

Molar ratio $HgCl_2:K_2C_2O_4$	Calomel	Test for Hg
0.02	Grayish	Positive
.04	Grayish	Positive
.2	White	Negative
1	White	Negative
5	White	Negative

These results alone do not establish the validity of the assumed mechanism, however, because of the well-known ease with which calomel is reduced to mercury by sufficiently active reducing agents. Such reduction is generally presumed not to occur at all in the oxalate solution, or when phosphorous acid is used in the quantitative determination of mercury as calomel. When pure calomel was suspended in potassium oxalate solution for some hours in the dark, it was found that a detectable amount of free mercury was present. A good molybdenum-blue test was also obtained on the calomel precipitated from mercuric chloride by excess phosphorous acid. It is therefore probably justifiable to conclude that free mercury is formed slowly by secondary processes

(15) Borar, *J. Chem. Soc.*, **99**, 1414 (1911).

(16) McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).

(17) Campbell and Hook, *Soc. Chem. Ind. Victoria, Proc.*, **31**, 544 (1931).

(18) The gold was obtained from the Williams Gold Refining Co. of Buffalo, and assayed 99.97%.

even in these cases where the normal reduction product is calomel, and that the mercury found arises through the intermediate formation of Hg^+.

Induction by Reducing Agents.—More convincing evidence for the proposed mechanism was obtained from experiments which consisted in the induction of Eder's reaction by addition of a reducing agent. All inductors heretofore used have been oxidizing agents which attack the oxalate ion. If the proposed mechanism is correct, it should also be possible to start the chains by producing the other assumed chain carrier, the Hg^+ ion. In carrying out these experiments it was necessary to exclude oxygen very scrupulously, since the active reducing agents used are prone to form peroxy compounds with molecular oxygen, and these would initiate chains by oxidation of oxalate ions.

Reducing agents were selected which can supply only a single electron in a bimolecular reaction with the mercuric ions. They were also used in only small amounts so as to diminish still further the likelihood of reducing the Hg^{++} ion completely to mercury. The reducing agents used were the Ti^{+++} and Cr^{++} ions.

Titanous sulfate was prepared by reduction of titanyl sulfate with a couple made of pure zinc and copper. An Eder mixture was placed in a flask in the dark and largely freed from oxygen by a stream of nitrogen which passed over copper at about 500°. After fifteen minutes of bubbling, the titanous solution was added. Immediately induction occurred, as judged from the formation of barium carbonate in an absorption tube in the effluent gas train. A parallel experiment with only the oxalate and titanous salt in the flask showed only a trace of carbon dioxide, due to incomplete removal of oxygen from the solution.

To eliminate oxygen more effectively, the experiment was repeated in the following manner. A reaction vessel was constructed consisting of two 25-ml. bulbs connected in the form of an H. Each bulb had an inner tube sealed in carrying a stopcock. The cross tube also had an outlet with a stopcock for evacuation. In one bulb was placed 10 ml. of 0.2 M potassium oxalate with a few drops of the titanous solution. The other bulb contained 5 ml. of 0.2 M mercuric chloride. The solutions were put under a vacuum through the middle stopcock with the vessel in an inclined position to facilitate boiling. The solutions were gently heated after the removal of dissolved gases

made boiling difficult. In total darkness the solutions were then mixed and shaken for two minutes. Nitrogen freed from carbon dioxide was passed over the solutions to sweep out any carbon dioxide formed. Considerable barium carbonate precipitated.

The induction by addition of chromous sulfate was carried out in flasks through which purified nitrogen was passing. The solutions of potassium oxalate and mercuric chloride were first boiled separately to expel dissolved air, and after being rapidly cooled were mixed in the flask in the dark. The nitrogen stream was continued two hours before addition of chromous sulfate. Immediate production of carbon dioxide was observed. In a repetition of the experiment, two flasks containing boiled-out Eder solutions were placed in series in the nitrogen stream. After one hour ferrous sulfate was added to the second solution to detect any residual oxygen. If any carbon dioxide at all resulted it was quite uncertain. The first solution was then connected to the barium hydroxide absorber and chromous sulfate was added. Immediate production of a considerable amount of carbon dioxide was observed. The experiments leave no doubt of the production of an effective oxidizing agent by addition of the strong reducing agents.

There is one very apparent difference between the action of the particular reduction inductors here used and that of the usual oxidation inductors. A very small amount of the trioxalatomanganiate ion, for example, is sufficient to cause complete reaction in an Eder mixture; the induction factor is very large and with the cobalt complex appears to be infinite. The exact mechanism of the action is not clear, but it is obviously related to the measureably slow decomposition of the manganic complex into a half-oxidized oxalate ion. On the contrary, the reduction inductors employed react very rapidly with mercuric ions and have a relatively small induction factor. Once these reducing agents have been oxidized to their stable states it seems that they play no further part in the reaction.

Calculation of the Hg^+ Potential.—In view of the apparently reliable hydration energies and entropies recently made available[19] it seemed worth while to make a theoretical estimate of the standard electrode potential for the reaction $Hg(1) \rightleftarrows Hg^+ (aq) + \epsilon$. The only values that

(19) Latimer, Pitzer and Slansky. J. Chem. Phys., 7, 108 (1939).

have to be obtained by approximation are the radius of the Hg^+ ion and its hydration energy. For the radius, it is sufficient to observe the variation of the known radii in the neighborhood of mercury in the periodic system. The important values may be tabulated as follows:[20]

Pt^0	1.38	Au^+	1.37
Au^0	1.44	Hg^+	(1.41)
Hg^0	1.50	Tl^+	1.44

On passing from the metal to the isoelectronic univalent ion there appears to be a slight contraction, whereas from Pt^0 to Hg^0 and from Au^+ to Tl^+ there is an increase of about 0.1 Å. Since Au^0 is midway between Pt^0 and Hg^0, it is most likely that the estimated value 1.41 Å. is very close to the correct radius of the Hg^+ ion.

For the estimation of the hydration energy, comparison has been made with the silver ion. Latimer[21] gives the sum of the heats of hydration of the gaseous silver and chloride ions as 192 kcal. per mole. Subtracting 89 kcal., the new value for the chloride ion given by Latimer, Pitzer and Slansky,[19] we obtain 103 kcal. for the silver ion. An estimate of -8 cal. as the entropy of hydration gives ΔF^0_{298} -101 kcal. for the hydration of the silver ion.

To estimate the heat of hydration of the ion Hg^+, use has been made of Latimer's observation that the Born equation gives satisfactory results for univalent cations of the rare gas type if their crystal radii are increased by 0.85 Å. The hydration energies are inversely proportional to the corrected radii. Although ions of the eighteen-electron type have higher hydration energies than are indicated by the Born formula, no serious error can be made by deriving the energy of the Hg^+ ion from that of the silver ion by use of the radius ratio. Such a calculation gives $\Delta H^0_{298} = -96$ kcal., and an estimated entropy of hydration of -6 cal. leads to a value $\Delta F^0_{298} = -94$ kcal.

The electrode potential may be derived by comparison with the theoretical and observed potentials of the silver electrode, thereby diminishing any error inherent in the hydration energies. The calculation rests on the following steps[22]:
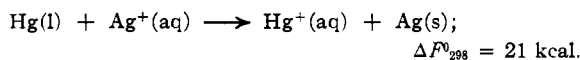
(20) Data from Stillwell, "Crystal Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938.

(21) Latimer, "Oxidation States of the Elements," Prentice-Hall, Inc., New York, N. Y., 1938.

(22) Data for steps 1, 2, 5 and 6 are from Latimer, *loc. cit.*, the ionizing potentials being corrected for the entropy of the electron gas.

ΔF^0_{298} (kcal.)

(1)	$Hg(l) \longrightarrow Hg(g)$	7.6
(2)	$Hg(g) \longrightarrow Hg^+(g) + \epsilon(g)$	239.8
(3)	$Hg^+(g) \longrightarrow Hg^+(aq)$	-94
(4)	$Hg(l) \longrightarrow Hg^+(aq) + \epsilon(g)$; $\Delta F^0_{298} = 153$ kcal.
(5)	$Ag(s) \longrightarrow Ag(g)$	58.7
(6)	$Ag(g) \longrightarrow Ag^+(g) + \epsilon(g)$	174.3
(7)	$Ag^+(g) \longrightarrow Ag^+(aq)$	-101
(8)	$Ag(s) \longrightarrow Ag^+(aq) + \epsilon(g)$; $\Delta F^0_{298} = 132$ kcal.

Combination of (4) and (8) gives

$$Hg(l) + Ag^+(aq) \longrightarrow Hg^+(aq) + Ag(s);$$
$$\Delta F^0_{298} = 21 \text{ kcal.}$$

This free-energy change corresponds to a potential of -0.91 volt, and by elimination of the silver half-reaction ($E^0 = -0.80$ volt) we obtain

$$Hg(l) \longrightarrow Hg^+(aq) + \epsilon; \quad E^0 = -1.71 \text{ volts}$$
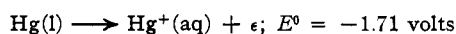
Unless this value is seriously in error for reasons that are not apparent, the Hg^+ ion should certainly be capable of oxidizing the oxalate ion even at low concentrations.

By combining this value with other standard mercury potentials the following additional data may be derived:

		E^0	ΔF^0_{298} (kcal.)
(1)	$Hg^+ \rightleftarrows Hg^{++} + \epsilon$	0.00	..
(2)	$2Hg^+ \rightleftarrows Hg(l) + Hg^{++}$	..	-39
(3)	$2Hg^+ \rightleftarrows Hg_2^{++}$	..	-42

From the first reaction it is clear that the mercuric ion is a very weak oxidizing agent if it must go through the Hg^+ stage. The Hg^+ ion itself is shown to be very unstable with respect to processes (2) and (3). Since these are both bimolecular, however, they could not be rapid in Eder's solution, where the abundant oxalate ions undoubtedly keep the Hg^+ ion at a very low concentration. Reaction (3) shows the high value of the energy of the Hg–Hg bond in the ordinary mercurous ion Hg_2^{++} (including the difference in the hydration energies). This value is qualitatively confirmed by consideration of the extensive contraction of the mercury atoms in calomel. Whereas the radius of the atoms in solid mercury is 1.50 Å., the Hg–Hg distance in calomel is only 2.55 Å.[23] This contraction of 0.45 Å. suggests that a strong covalent bond connects the atoms in calomel. It is to be noted also that the Hg–Cl distance is 2.52 Å., corresponding closely to the sum of

(23) Wyckoff, "The Structure of Crystals," Second Edition, The Chemical Catalog Co., Inc., New York, N. Y., 1931, and "Supplement," Reinhold Publishing Corp., New York, N. Y., 1935.

the covalent radii, which is 2.47 Å. The radius sum for ions would be 3.22 Å.[24]

Summary

1. From a consideration of the peculiarities of Eder's reaction the hypothesis has been developed that the chain carriers are the half-oxidized oxalate ion and the unpolymerized mercurous ion Hg^+.

(24) After the manuscript of the present paper had been almost completed, the November issue of THIS JOURNAL was received, in which Kolthoff and Barnum (**62**, 3061 (1940)) suggest that their data on the anodic behavior of cysteine can be explained only by the assumption of an unpolymerized mercurous salt HgSR. They point out that at extremely low concentrations the Hg_2^{++} ion may be considerably dissociated. From equation (3) above, the equilibrium constant for the reaction $Hg_2^{++} \rightleftarrows 2Hg^+$ is found to be 10^{-31}. Taking 10^{-18} as the solubility product constant for calomel, it may be calculated that in saturated aqueous calomel the mercurous ion is not dissociated into Hg^+ ions to an appreciable extent. The dissociation would be greater at the extremely low concentrations prevailing in the work of Kolthoff and Barnum, but could hardly account for their results except for the strong affinity of mercury for sulfur and possible specific effects of the cysteine radical.

2. Additional evidence for the formation of an active reducing agent by oxidation of oxalates has been presented.

3. Mercury has been shown to be present in the calomel formed in Eder's reaction under favorable conditions.

4. It has been shown that the reaction may be induced by addition of reducing agents.

5. Calculations have been made which indicate that the normal potential of the half-reaction $Hg(1) \rightleftarrows Hg^+ (aq) + \epsilon$ should be -1.71 volts.

6. This potential has been combined with other mercury potentials to show that the dissociation of the ordinary mercurous ion Hg_2^{++} in solution is attended by a standard free-energy change of 42 kcal.

Kinetics of Oxidation of Typical Hydrocarbons

BY R. A. DAY, JR., AND R. N. PEASE

It is generally agreed that the tendency of a hydrocarbon to knock when used as a fuel in an internal combustion engine is related in some way to the ease with which the fuel–air mixture undergoes spontaneous ignition. The experiments of Townend and his co-workers[1] with regard to the influence of pressure on the temperature required for spontaneous ignition showed the existence of a tongue, or peninsula, in a pressure–temperature plot of the ignition curve, pointing toward lower pressures at temperatures around 300–350°. Such peninsulas are generally bounded on the low pressure side by a region in which mild explosions, or so-called "cool flames" are observed, and the peninsula and cool flame regions are usually termed the "low temperature system." A comparison of the ignition curves of branched chain paraffins with those of their straight chain isomers revealed that higher temperatures and pressures are required over the whole range in order to effect the ignition of the former. This is in accord with the well-known tendency of branched chain compounds to resist knock when used as fuels.

A further comparison has now been made of the ignition and cool flame characteristics of some highly branched paraffins, and the study was extended to include two naphthenes and also benzene. The compounds studied were n-heptane, 2,2,3-trimethylbutane, 2,2,4-trimethylpentane (iso-octane), 2,2,3,3-tetramethylbutane (hexamethylethane), benzene, cyclohexane, cyclopropane, and propane. A few runs were also made with propylene, propylene oxide and ethylene oxide. Use was made of oxygen instead of air to effect combustion, so that cool flame formation and ignition occurred well below atmospheric pressure. In the slow combustion region the rates of oxidation could be measured conveniently by pressure change, and permitted a further comparison of these compounds.

Experimental Procedure

The experiments were conducted in a static apparatus previously described.[2] The only modification necessary in the case of liquid hydrocarbons was the use of Pyrex-plug stopcocks which were wound with chromel wire and heated electrically to prevent condensation. A high-temperature stopcock grease made from finely powdered bentonite and

(1) Townend and Mandlekar, *Proc. Roy. Soc.* (London), **A141**, 484 (1933); **A143**, 168 (1933); Townend, Cohen and Mandelkar, *ibid.*, **A146**, 113 (1934); Townend and Chamberlain, *ibid.*, **A154**, 95 (1936); Maccormac and Townend, *J. Chem. Soc.*, 238 (1938).

(2) Day and Pease, THIS JOURNAL, **62**, 2234 (1940); see also Newitt and Thornes, *J. Chem. Soc.*, 1656 (1937).