dence to support it, belief is held that the higher values obtained on the samples just after their receipt may reasonably be selected as more representative, and weighted preference be given them.

The results obtained on the original 3,3-dimethylpentane were seriously out of line. The b. p. was somewhat high, also. Another sample of this compound was obtained from the Ethyl Gasoline Corporation. This sample as received showed the presence of traces of unsaturated material. It was subjected to rigorous purification but final fractionation was carried out in a different still from that used for the other isomers. The results are therefore not strictly comparable.

Grateful acknowledgment is due the Standard Oil Company of California for their support of this project including a fellowship (1938–41), the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant permitting the purchase of apparatus, and to Dr. George Calingaert of the Ethyl Gasoline Corporation for a sample of 3,3-dimethylpentane.

Special thanks are due Dr. F. D. Rossini of the Bureau of Standards for assistance without which the project could not have been completed.

Summary

1. Isothermal heats of combustion at 25° have been reported for the nine isomeric heptanes.

2. From these are calculated the energies of isomerization for the heptanes in liquid form.

3. The heats of formation at 25° have been calculated and tabulated.

Corvallis, Oregon Received June 2, 1941

[Contribution from the School of Chemistry of the Institute of Technology, University of Minnesota]

Current-Voltage Curves of Mercurous and Mercuric Salts at the Dropping Mercury Electrode

By I. M. Kolthoff and C. S. Miller[1]

It is claimed[2] that the concentration of dissolved mercury salts cannot be determined polarographically. In the present paper it is shown that the concentration of both mercurous and mercuric salts can be determined with the dropping electrode, while a few experiments revealed that these salts yield well-defined diffusion currents at a platinum micro-wire electrode. It was of interest to subject the various current–voltage (c. v.) curves to a physico-chemical analysis. When in equilibrium with the surrounding mercurous ion solution the potential of a mercury electrode is given by

$$\pi = C + RT/2F \ln [\mathrm{Hg_2}]_0^{++} \qquad (1)$$

in which the subscript zero denotes the concentration (or better the activity) of the mercurous ions at the surface of the dropping electrode. The equation of the polarographic wave then should be given by[3]

$$\pi = \pi_0 + RT/2F \ln (i_d - i) \qquad (2)$$

i_d denoting the diffusion current of the mercurous ions.

When a solution of a mercuric salt is electrolyzed at the dropping electrode, the interaction between mercury and the mercuric ions has to be considered

$$\mathrm{Hg} + \mathrm{Hg^{++}} \rightleftarrows \mathrm{Hg_2^{++}} \qquad (3)$$

The equilibrium constant of this reaction $[\mathrm{Hg_2^{++}}]/[\mathrm{Hg^{++}}] = K$ was first determined by Ogg,[4] who shook solutions of mercuric nitrate with mercury until equilibrium was attained. He reported an average value for K of 120. Carter and Robinson[5] determined the oxidation potential of mercurous–mercuric perchlorate solutions at a platinum electrode. From the value obtained and the normal potential of the mercury–mercurous ion electrode they calculated a value of K of 81. In the experimental part it is shown that equilibrium between mercury and mercuric ions (eq. 3) is established very rapidly at the dropping electrode. Consequently, the c. v. curve of a mercuric salt (strong electrolyte) should practically coincide with that of an equimolecular mer-

---

(1) From the experimental part of a thesis submitted by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the Doctor's degree (1940).

(2) H. Hohn, "Chemische Analysen mit dem Polarographen," Julius Springer, Berlin, 1937.

(3) Comp. I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

(4) A. Ogg, *Z. physik. Chem.*, **27**, 293 (1898).

(5) S. R. Carter and R. Robinson, *J. Chem. Soc.*, 267 (1927).

curous salt, and the equation of the wave should be given by expression (2).

Interesting also is the behavior of mercuric chloride

$$Hg + HgCl_2 \rightleftarrows Hg_2Cl_2 \qquad (4)$$

From various complex and other equilibrium constants reported in the literature we calculate that the concentration of mercuric chloride in aqueous solution which is in equilibrium with metallic mercury and solid mercurous chloride is 1.7 × 10^{-6} *M*. At reasonable concentrations, therefore, reaction (4) will go quantitatively to the right. In the experimental part it is shown that this equilibrium is established practically instantaneously at the dropping electrode. The cathodic wave, then, of mercuric chloride corresponds to the reduction of calomel

$$Hg_2Cl_2 + 2e \rightleftarrows Hg + 2Cl^-$$

and the equation of the wave is given by

$$\pi = C + \frac{RT}{2F}\ln\frac{S_{Hg_2Cl_2}}{[Cl^-]} = C' - \frac{RT}{F}\ln\,[Cl^-]_0 = \pi_0'' - RT/F\ln i \qquad (5)$$

When the current approaches the diffusion current and there is no more solid mercurous chloride around the electrode, expression (5) does not hold any longer.

Experimental

Current–voltage curves with the dropping electrode were determined with the manual apparatus[3] at 25.00 ± 0.05°. Since mercury ions from their strongly dissociated salt solutions are discharged at fairly positive potentials, it is not necessary to remove the oxygen in analytical work. In the present work, as a rule, oxygen was removed in the usual way.

C. v. Curves of Mercurous and Mercuric Nitrate.—Solutions in 0.1 *N* nitric acid as supporting electrolyte were electrolyzed. With both mercurous and mercuric salts pronounced maxima on the c. v. curves were found before the diffusion currents were attained. These maxima were eliminated by adding small amounts of suppressors, such as tropeolin 00 (about 10^{-5} *M*), methyl red (about 10^{-5} *M*) or gelatin (0.01%). Examples of c. v. curves obtained in the presence of maximum suppressors are given in Fig. 1.

Diffusion currents of mercuric and mercurous mercury after correction for the residual current were found to be proportional to the concentration of these ions in the range studied between 2 × 10^{-4} and 2 × 10^{-3} *M*. Hence, mercurous and mercuric ions can be determined polarographically in their strongly dissociated salts.

Comparing the diffusion currents of equimolecular solutions of mercurous and mercuric nitrate revealed the unexpected result that i_d of the former was distinctly greater than that of the latter. With the aid of the Ilkovič equation[6] and the determined characteristics of the capillary used, we calculated a diffusion coefficient of mercurous ions of 0.92 × 10^{-5} cm.^{2} sec.$^{-1}$ and of mercuric ions of 0.82 × 10^{-5} cm.^{2} sec.$^{-1}$ at 25°. It is unexplained yet why dissolved Hg_2^{++} ions have a greater diffusion coefficient than Hg^{++} ions.

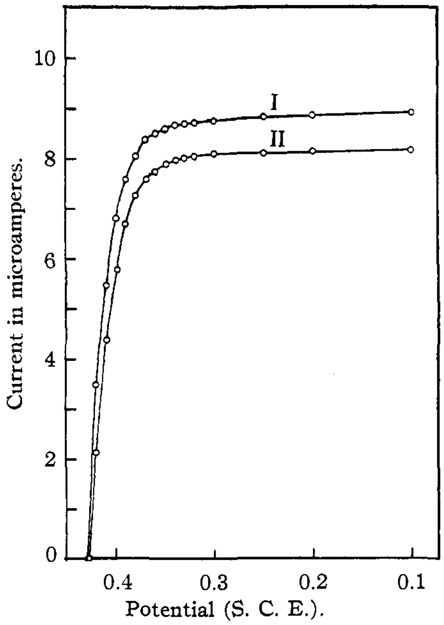

Fig. 1.—Reduction of mercurous and mercuric nitrates: I, $Hg_2(NO_3)_2$ approx. 10^{-3} *M*, HNO_3 10^{-1} *N*, Trop. 00 10^{-3} %; II, $Hg(NO_3)_2$ approx. 10^{-3} *M*, HNO_3 10^{-1} *N*, Trop. 00 10^{-3} %.

From Fig. 1 it is seen that the waves of equimolecular mercurous and mercuric nitrate solutions start at the same potential and are identical in shape, except for the difference in diffusion currents. If the mercuric nitrate did not interact with the mercury the potential of the system would be about 0.060 v. more positive than that of an equimolecular solution of mercurous nitrate. Actually, a 0.001 *M* mercurous nitrate solution in 0.1 *N* nitric acid yielded a potential of +0.4294 v. (*vs.* S. C. E.) at the dropping electrode, while the equimolecular solution of mercuric nitrate had a potential of 0.4281 v.

The waves of mercurous and mercuric nitrate were analyzed by plotting the potential after correction for the *iR* effect against log ($i_d - i$). In both cases a straight line relation was obtained which was to be expected according to eq. (2). However, the slope of the line was 0.046 instead of the theoretical value 0.030. This slope was found to remain the same, independent of the maximum suppressor used. It is possible that the deviation is due to an irregularity during the formation of the drops as a result of the interaction between mercury and the solutions. However, no stirring around the forming drops could be seen microscopically in the presence of maximum suppressors.

C. v. Curves of Mercuric Chloride at the d. e.—Typical current–voltage curves of mercuric chloride at the dropping electrode in the presence of methyl red as a maximum suppressor and 0.1 *N* potassium nitrate as supporting electrolyte are shown in Fig. 2. The diffusion current was found

---

(6) D. Ilkovič, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

to be proportional to the concentration, hence mercury in mercuric chloride can be determined polarographically. It is seen that the zero current potential and the waves until the diffusion currents were the same at concentrations between 10^{-4} and 10^{-3} M mercuric chloride. This shows conclusively that the mercuric chloride reacts practically instantaneously at the dropping mercury with the formation of mercurous chloride according to equation (4).

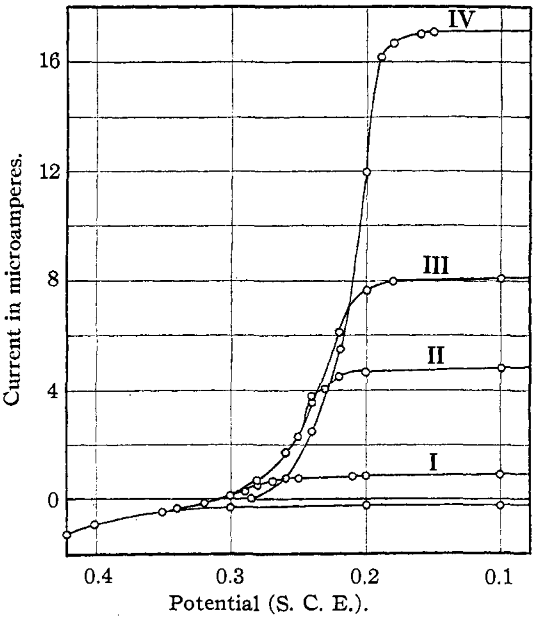

Fig. 2.—Reduction of mercuric chloride: I, KNO_3 10^{-1} N, $HgCl_2$ approx. 1 × 10^{-4} M; II, KNO_3 10^{-1} N, $HgCl_2$ approx. 5 × 10^{-4} M; III, KNO_3 10^{-1} N, $HgCl_2$ approx. 10 × 10^{-4} M; IV, KNO_3 10^{-1} N, $HgCl_2$ approx. 20 × 10^{-4} M (all in Me Red 10^{-5} M).

When the concentration of mercuric chloride was 2 × 10^{-3} M the wave started at more negative potentials and intersected with the 10^{-3} M wave at a current of about 7 microamps. This shift of the beginning of the wave undoubtedly is due to the interfering effect of the film of calomel around the dropping electrode which may be the seat of a large resistance. In a previous paper[7] it was shown that abnormalities in the shape of the anodic wave of chloride close to the diffusion current occur at chloride concentrations of 2 × 10^{-3} M. The abnormality on curve IV disappears when the current gets larger as the calomel is removed by reduction to mercury and chloride ions. From Fig. 2 it is quite apparent that the "zero current potential" at the dropping electrode is not exactly equal to that measured at a quiet mercury electrode. The curve below the zero current line gives the residual (anodic) current of the medium. At the zero current potential in mercuric chloride solutions the anodic residual (charging) current is equal to the cathodic reduction current of mercuric chloride at this potential. The same considerations also hold in solutions of other mercury salts.

In conclusion it may be mentioned that we have determined and analyzed waves obtained with solutions of complex mercuric compounds, such as of $HgI_4^{=}$ in an excess of potassium iodide, and of $Hg(S_2O_3)_2^{=}$. The equations of the waves experimentally determined agreed with those derived on the basis of reversible reduction and the existence of equilibrium conditions at the electrode. Since the results do not further contribute to the subject a detailed description is omitted.

Summary

1. At the dropping electrode the equilibrium $Hg^{++} + Hg \rightleftarrows Hg_2^{++}$ is attained practically instantaneously. The waves obtained with well dissociated mercuric and mercurous salts, therefore, are practically identical. Mercuric chloride in contact with dropping mercury yields calomel quantitatively at the surface of the electrode.

2. Mercurous and mercuric mercury in their salts can be determined polarographically, preferably in the presence of a maximum suppressor. In 0.1 N nitric acid the diffusion coefficient of Hg_2^{++} was calculated to be 0.92 × 10^{-5} cm.^{2} sec.$^{-1}$ and of Hg^{++} 0.82 × 10^{-5} cm.^{2} sec.$^{-1}$ at 25°.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 21, 1941

---

[7] I. M. Kolthoff and C. S. Miller, THIS JOURNAL, 63, 1405 (1941)