alcoholic solution and digested with equivalent amounts of alkyl toluenesulfonates for two hours on a water-bath. The alkylated products were worked up in the usual way and purified in all cases but one by recrystallization of the dihydrochloride from alcohol or a mixture of alcohol and ether. *s*-Butylapocupreine was best purified by crystallization of the monosulfate from alcohol.

The bases were recovered from the purified salts. The *n*-propyl, *i*-propyl and *n*-butyl derivatives were crystallized from ether, the *i*-butyl from acetone and the *s*-butyl failed to crystallize from all the ordinary solvents.

Summary

Some alkyl ethers of apocupreine have been prepared and some of their pharmacological properties have been briefly presented.

PITTSBURGH, PENNA. RECEIVED SEPTEMBER 20, 1937

[CONTRIBUTION FROM THE SUN OIL COMPANY EXPERIMENTAL DIVISION]

Isolation of Pure Isomeric Hexanes from Natural Gas, Including the Determinations of their Physical Properties and the Phase-Equilibrium Diagram of the Condensed System *n*-Heptane-2-Methylpentane[1]

BY JOHANNES H. BRUUN, MILDRED M. HICKS-BRUUN AND W. B. MASON FAULCONER

In addition to the normal hexane there are four theoretically possible isomers of this hydrocarbon. Three of these isomeric hexanes were reported isolated from a mid-continent petroleum by two of the authors[2] while connected with the American Petroleum Institute Project No. 6 at the National Bureau of Standards. While the purity of the isolated isomeric hexanes appeared to be fairly high, and at the time of publication of the paper equal to the purest reported synthetic samples of these isomers, the authors have felt that considerable improvement could be made in their purification. Since the separating power of our present day stills is between 500 and 1000% as great as that of the stills used eight years ago, the present investigation was undertaken partly in order to determine whether it would be possible to isolate isomeric hexanes in a very much purer form than hitherto and with only a very small fraction of the effort previously required (20 to 25 distillations) for the isolation of even relatively impure compounds.

Experimental

The raw material consisted of a commercial cut from natural gas boiling between 55 and 65° and originating from the Clendenin Gas Field in West Virginia.

The preliminary distillation was done at a rate of 1 to 2 ml. per minute with a 12:1 reflux ratio in a 52-plate, all glass bubble-cap column made in 4-cm. sections. As indicated in Figs. 1 and 2, most of the other distillations were done in a 100-plate column made in 2-cm. sections at low rates of distillation (0.1 to 0.3 ml. per minute) and high reflux ratios (20:1 to 50:1). A complete description of the distillation equipment used may be found in previous publications from this Laboratory.[3,4]

The 3-methylpentane was isolated in a pure condition after two distillations (see Curve C-100 Plate). The 2-methylpentane required three distillations (see Curves B-52 Plate and E-100 Plate), and in the case of 2,3-dimethylbutane a total of five distillations was necessary to produce a compound of high purity (see Curves A-52 Plate, D-100 Plate, F-100 Plate, and G-100 Plate). As a result of these distillations three groups of fractions were obtained, each of which is represented by the flat portion of its distillation curve, G-100 Plate (pure 2,3-dimethylbutane), E-100 Plate (pure 2-methylpentane), and C-100 Plate (pure 3-methylpentane). The extreme boiling point differences found between the last and first fraction in each of these groups varied between 0.03 and 0.07° when carefully determined in the Cottrell boiler. The individual best fractions selected from each group had a boiling point spread in the 100-plate column of 0.01°, or less.

In reference to Fig. 2, it is noted that as soon as the 60% point had been passed in Curve C-100 Plate the material remaining in the still consisted largely of 3-methylpentane. Hence a constant boiling range was obtained. During the first part of the distillation (between the 5 and 35% points) the effect of the partial vapor pressure of the higher boiling 3-methylpentane, which was present in large amounts, prevented the 2-methylpentane from distilling at a constant or narrow boiling range.

Generally speaking, however, it may be stated that it is considerably easier to isolate a pure compound by distillation from a mixture containing, for instance, 10% of low boiling impurities than from a mixture containing the same amount (10%) of high boiling impurities, assuming, of course, that the difference in vapor pressure between the high boiling impurity and the compound is about the same as that between the compound and the low boiling

---

[1] Presented before the Symposium on Characteristic Properties of Hydrocarbons and their Derivatives as Related to Structure, of the 94th meeting of the American Chemical Society at Rochester, New York, Sept. 6-10, 1937.

[2] Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **5**, 933-942 (1930).

[3] Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).

[4] Bruun and Faulconer, *ibid.*, **9**, 192 (1937).

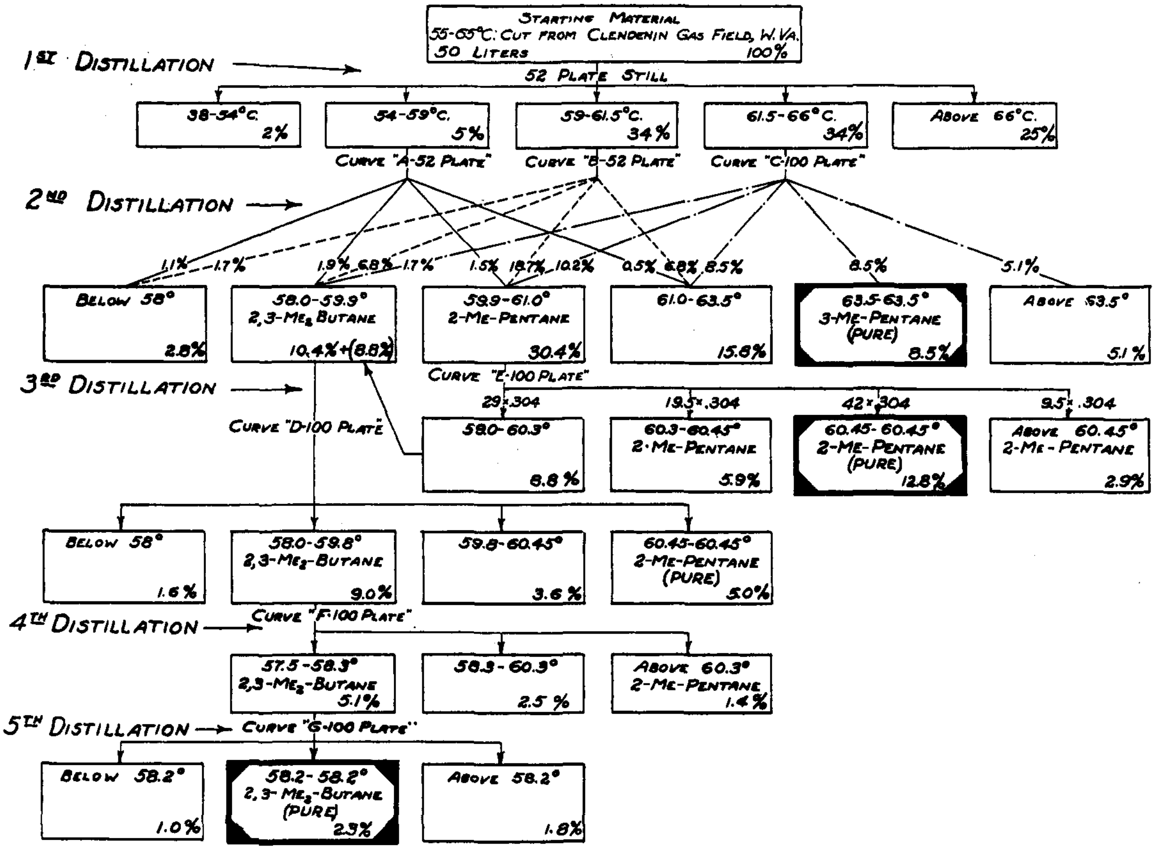

Fig. 1.—Flow chart of distillations.

impurity. This is clearly shown in Fig. 3. In dealing with low boiling impurities the concentration of the main constituent in the still pot will increase rapidly from 90 to near 100%. In the presence of a high boiling impurity, however, the concentration of the main constituent in the still pot will decrease continually from 90 to 0%, with the result that fractionation becomes increasingly more difficult.

Percentage of Isomeric Hexanes in the Natural Gas.—It is interesting to note (see Table I) that the 2-methylpentane is present in far larger quantities than the other two isomers. The figures in the table are based upon a reported yield of 935 ml. of liquid, boiling between 55 and 65°, per cubic meter of natural gas at 4.4° (7 gallons per 1000 cubic feet at 14.9 lb. pressure).

TABLE I

CALCULATED AMOUNTS OF ISOMERIC HEXANES IN THE NATURAL GAS

Amount of liquid present	2,3-Dimethylbutane	2-Methylpentane	3-Methylpentane
In the 55–65° cut, %	8	45	21
In natural gas, ml. per cu. m.	74	420	196

Physical Constants of the Isomeric Hexanes.—The boiling points were determined by means of a Cottrell boiler and the values given in Table II are corrected according to the conventional methods. The specific gravities were determined by means of a 100-ml. pycnometer, with ground-in thermometer and calibrated capillary to the fifth decimal place, and corrected for buoyancy effect, loss by evaporation through the capillary tube during weighing, etc. The values thus obtained have been rounded off to four decimal places since they were considered accurate only within ±0.0001. The refractive indices were measured on a Valentine refractometer of the Abbe type and the maximum probable error is 0.0001. For the determination of the freezing points the same apparatus and technique were employed as for propane.[5] The thermoelement was calibrated at the National Bureau of Standards and the values on the temperature scale were certified to 0.05°.

Discussion

The most significant criterion for the purity of a compound (or of a eutectic mixture) is the value for its freezing point together with the shape of its time–temperature cooling curve. No isomer of *n*-hexane has ever been synthesized or isolated which, on freezing, would yield a horizontal break in this curve. It seems that the nearest approach to this is the time–temperature freezing curve of the 3-methylpentane which was isolated from petroleum some eight years ago.[2] The difficulty in obtaining such a curve, or even an approximate

---

(5) Hicks-Bruun and Bruun, THIS JOURNAL, **58**, 810–812 (1936).

TABLE II

PHYSICAL CONSTANTS OF THE ISOMERIC HEXANES

	B. p., (760 mm.)	F. p. (in vacuum)	Specific gravity d^{15}_4	d^{20}_4	dd/dt	n^{15}_D	Refractive index n^{20}_D	n^{25}_D	dn/dt
	2,3-Dimethylbutane								
From natural gas:									
(Bruun, Hicks-Bruun, and Faulconer)	57.93 ±0.05	−129.0 ±0.5	0.6665	0.6615	0.00099	1.3776	1.3750	1.3722	0.00054
From petroleum: (Bruun and Hicks-Bruun)[a]	58.0	−135	...	.668	....	....	1.378	....	....
Synthetic: (Cramer and Mulligan)[b]	57.82–58.02	...	...	.6612	....	....	1.3750	....	....
	2-Methylpentane								
From natural gas:									
(Bruun, Hicks-Bruun, and Faulconer)	60.19 ±0.05	−154.0 ±0.05	.6575	.6527	.00097	1.3740	1.3711	1.3684	.00056
From petroleum: (Bruun and Hicks-Bruun)[a]	60.4	(−143)[c]	...	.659	....	....	1.374	....	....
Synthetic: (Cramer and Mulligan)[b]	60.22–60.26	...	...	.6532	....	....	1.3718	....	....
	3-Methylpentane								
From natural gas:									
(Bruun, Hicks-Bruun, and Faulconer)	63.20 ±0.05	...	.6690	.6640	.00099	1.3790	1.3764	1.3738	.00052
From petroleum: (Bruun and Hicks-Bruun)[a]	63.3	−118	...	.665	....	....	1.376	....	....
Synthetic: (Cramer and Mulligan)[b]	63.16–63.21	...	...	.6642	....	....	1.3775	....	....

[a] See ref. 1, or Landolt-Börnstein, Ext. Vol. III-A, p. 339 (1935 edition). [b] Cramer and Mulligan, THIS JOURNAL, **58,** 373–374 (1936). [c] This value is incorrect; see text.

freezing point of the hexane isomers, is due to their peculiar tendencies to form a viscous glassy mass upon cooling, and their pronounced resistance to any kind of crystallization. The results obtained are discussed below for each compound.

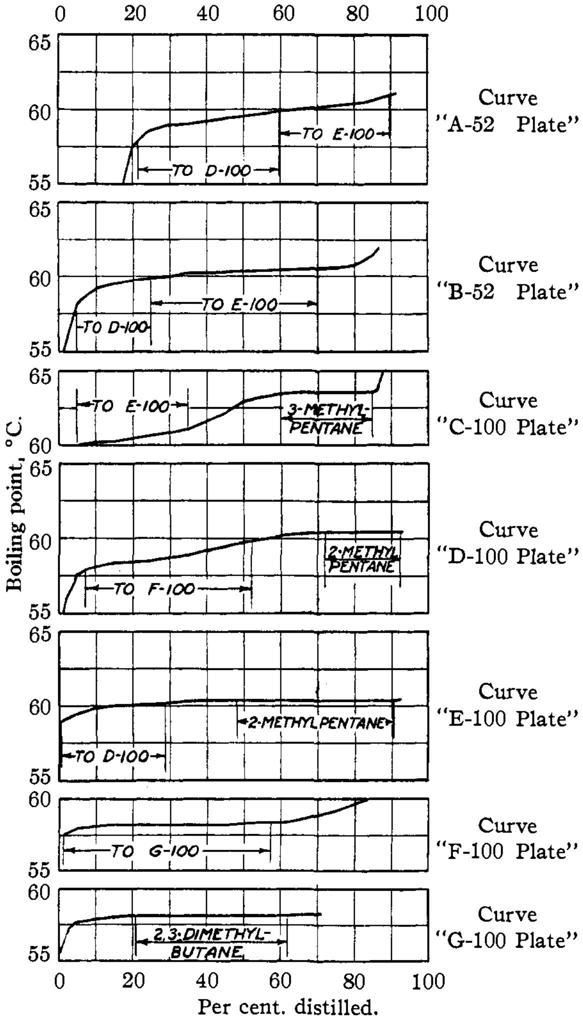

Fig. 2.—Distillation curves.

2,3-Dimethylbutane.—The values for the freezing point reported in the literature for 2,3-dimethylbutane are −135°. This same value was obtained in the present investigation when the fractionation had progressed to the 20% point of Curve F-100 Plate (Fig. 2), but by a subsequent careful distillation, Curve G-100 Plate, further purification of the 2,3-dimethylbutane was effected, with the result that the freezing point was raised by 6°. The new value thus found for the freezing point of 2,3-dimethylbutane

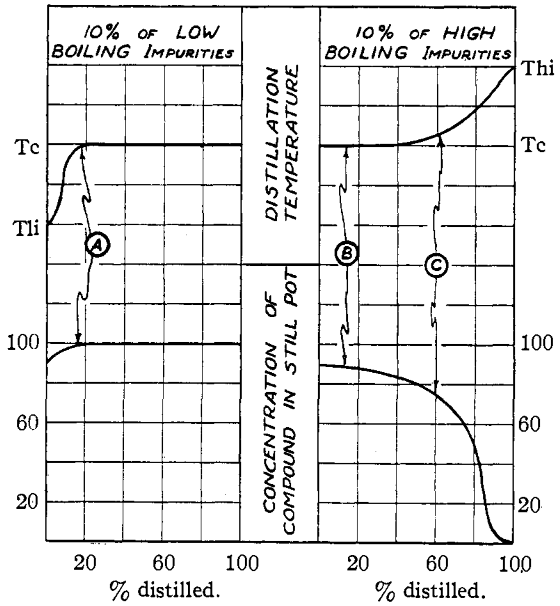

Fig. 3.—Separation of low boiling and of high boiling impurities from a compound.

is −129.0 ± 0.5°. Since this value was found for three different fractions from the flat portion of Curve G-100 Plate, it is evident that the upper limit of distillation fractionation had been reached. One of the time–temperature cooling curves obtained is given in Fig. 4. A definite break occurred at the same temperature for each fraction, but the short halting point in the curve is most unusual for a compound of exceptional purity and could be taken as an indication that this point, −129°, is the initial freezing point of a solution consisting of a constant boiling mixture of 2,3-dimethylbutane with some other compound. Since the boiling point, refractive index, and specific gravity values are identical with those of the synthetic compound, this would mean that all reported synthetic samples of this hydrocarbon would have to be mixtures with another compound. The most probable explanation, however, is that the short, horizontal portions of the curve in Fig. 4 are caused by a low heat of fusion (value unknown) of the 2,3-dimethylbutane. This explanation is further substantiated by the fact that the transition between liquid and solid was abrupt in spite of the slight halting point, which made it impossible to place the freezing point more accurately than within 1°.

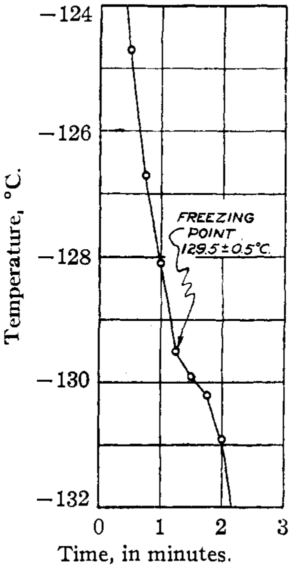

Fig. 4.—Time–temperature freezing curve for 2,3-dimethylbutane.

Contrary to the other isomers of *n*-hexane, no difficulty whatsoever was encountered in the freezing of the 2,3-dimethylbutane.

2-Methylpentane.—No data on the freezing point of 2-methylpentane are listed in the literature with the exception of those which two of the authors obtained in their earlier work.[2] Other investigators have either omitted all mention of the freezing behavior or reported that it froze to a glass. In the present investigation the 2-methylpentane also exhibited a very high viscosity in the region of its freezing point, and did not crystallize readily on cooling in spite of a variety of means which were employed to induce crystallization. As some success in crystallizing this compound had been obtained previously by adding solid carbon dioxide below −50°, it was thought probable that it might freeze as a eutectic mixture with another hydrocarbon. A search was made for a second hydrocarbon with properties such that when mixed with 2-methylpentane its eutectic composition would be a solution high in 2-methylpentane. From calculated data, *n*-heptane appeared to be such a compound and it had the advantage of being readily available in fairly pure form. The freezing point and eutectic point composition diagram for 2-methylpentane and *n*-heptane has been determined in the course of this work and is given in Fig. 5.

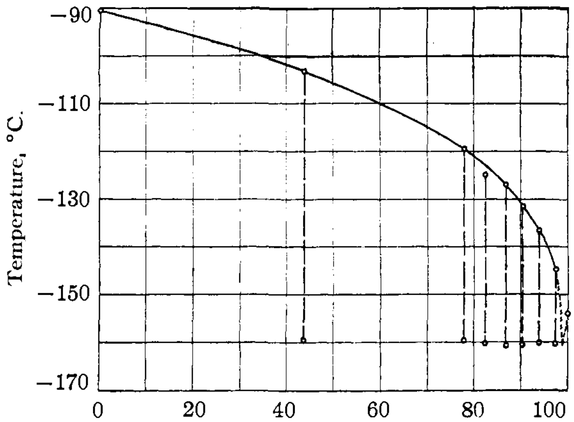

Fig. 5.—Phase equilibrium diagram for the condensed system *n*-heptane–2-methylpentane.

The initial freezing points for solutions of different concentrations of *n*-heptane in 2-methylpentane were calculated and compared with their experimental values. Very little deviation was observed in the two values until the two solutions consisted of more than 50 mole per cent. of 2-methylpentane. More concentrated solutions had their freezing points uniformly higher than the calculated values. This deviation served to bring the eutectic composition closer to the region of 2-methylpentane. The eutectic temperature which was observed for each solution was a constant value, −160.2 ± 0.5°. Solutions more concentrated than 95.7 mole per cent. of 2-methylpentane proved to be difficult to freeze, but at this concentration both the initial freezing point and the eutectic point could still be determined.

In view of this observation, the following procedure was adopted for determining the freezing point and the time–temperature freezing point curve of the 2-methylpentane: a solution containing 95.7 mole per cent. of 2-methylpentane and 4.3 mole per cent. of *n*-heptane was frozen completely and kept below its eutectic temperature. Then a sample of the pure 2-methylpentane was cooled to between −155 and −160° under constant agitation. At this point a crystal of the 95.7 mole per cent. 2-methylpentane was drawn up quickly by means of a hook and plunged into the pure 2-methylpentane. Immediate crystallization of the latter resulted. This crystalline mass was kept frozen until a second pure sample of 2-methylpentane could be cooled to about −160° while stirring constantly. Then a crystal was taken from the crystallized 2-methylpentane and introduced into the second sample, thus causing crystallization to ensue. From this chain process, it can be seen that the second crystallized mass of 2-methylpentane could contain only traces (less than 1 part in 10,000) of *n*-heptane. Time–temperature cooling data from this sample are shown in the curve in Fig. 6. The flatness of this cooling curve indicates that the 2-methylpentane had an exceptionally high degree of purity, and the freezing point was found to be −154.0 ± 0.05°. The freezing point found in the earlier work was −143.0° but this was indicated by only a slight break in the curve. Such a break can occur at the initial freezing point of a solution, or at the freezing point of a pure compound with a heat of fusion sufficiently low to be offset by the rate of cooling. It was noted that although solutions of 2-methylpentane with 3-methylpentane were found to freeze to glasses, solutions of 95–96 mole per cent. 2-methylpentane with either *n*-hexane or *n*-heptane froze at about −143° with a slight break in their time–temperature cooling curves. The long halting period and the narrow freezing range (0.05°) obtained in the present investigation and shown in Fig. 6, however, leaves no doubt regarding the purity of the 2-methylpentane, and it must therefore be concluded that the correct freezing point of this hydrocarbon is −154.0 ± 0.05°. The purity of the isolated 2-methylpentane is above 99.99 mole per cent.

3-Methylpentane.—The only value for the freezing point of the 3-methylpentane which has been reported in the literature is −118 ± 0.5°, which was recorded by two of the authors some years ago. Difficulty was experienced in attempting to freeze the present fraction of 3-methylpentane. It became viscid on cooling and could not be induced to freeze, either by the seeding method or as the main constituent of a concentrated solution with any of several hydrocarbons tried. However, as a fairly satisfactory time–temperature cooling curve had been obtained for this compound in the earlier work, no further efforts were made to freeze it at this time.

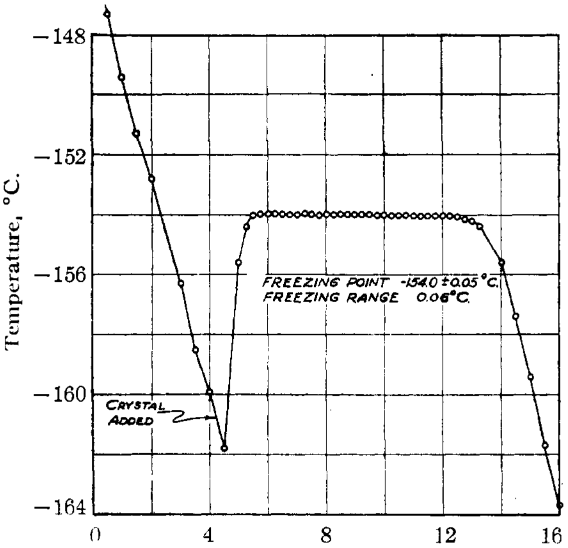

Fig. 6.—Time–temperature freezing curve for 2-methylpentane.

Summary

Three of the isomeric hexanes have been isolated from natural gas by distillation in a 100-plate still. The purity of the final fractions is believed to be equal to or higher than that of the best reported synthetic samples. Hexanes containing a single side chain in the molecule, such as 2-methylpentane and 3-methylpentane, are extremely difficult to freeze by usual methods because of their pronounced tendencies to form glasses upon cooling. The isomers containing two branch chains, such as 2,3-dimethylbutane, are readily frozen to crystalline solids.

The freezing point of 2,3-dimethylbutane was found to be −129.0 ± 0.5°, which is 6° higher than the accepted value for this hydrocarbon.

By a special method it was possible to obtain the only flat time–temperature freezing point curve on record for 2-methylpentane. The freezing point of this hydrocarbon was found to be −154.0 ± 0.05°, or 11° lower than the previously reported value. The purity of the sample used for

this determination exceeded 99.99 mole per cent.

The phase equilibrium diagram for the condensed system 2-methylpentane–*n*-heptane has been determined and the observed value for the eutectic point was −160.2 ± 0.5°.

NORWOOD, PENNA. RECEIVED JULY 1, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, NO. 61, AND THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 390, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Measurement of the Molal Ferric–Ferrous Electrode Potential

BY WALTER C. SCHUMB, MILES S. SHERRILL AND SUMNER B. SWEETSER

In a previous paper[1] the authors calculated the molal ferric–ferrous electrode potential to be −0.782 v. from equilibrium measurements of the reaction between ferric ion and silver. This value was 10 mv. higher than that calculated by Bray and Hershey[2] from the electromotive force measurements of Popoff and Kunz[3] and the equilibrium measurements of Popoff, Fleharty and Hanson[4] for the reaction between ferric ion and mercury. The latter were made in perchloric acid solution but the former were done in hydrochloric acid solution, which necessitated a correction for complex formation. The authors' previous work was done in perchloric acid solution, but because of analytical difficulties the measurements could not be carried to low ionic strengths. Thus, although equilibrium studies of this potential have been made in perchloric acid, the only electromotive force measurements in perchloric acid which appear to have been carried out are two preliminary experiments by C. G. Clear, reported by Bray and Hershey.[2] Professor Bray has kindly furnished the results of these measurements, the average value being closely in agreement with the results obtained in this investigation.

The results of measurements of the electromotive force of the following cell are given and discussed in the present paper.

$$\mathrm{Pt,H_2(g),\ HClO_4(}c_1\mathrm{),}\ \begin{array}{l}\mathrm{Fe(ClO_4)_3(}c_3\mathrm{)}\\ \mathrm{HClO_4(}c_1\mathrm{),}\\ \mathrm{Fe(ClO_4)_2(}c_2\mathrm{)}\end{array}\ \mathrm{Pt}$$

Materials and Apparatus.—Electrolytic iron with a guaranteed purity of at least 99.95% was used in the preparation of both ferrous and ferric perchlorates. The ferrous perchlorate was prepared by electrolyzing a 1:15 solution of 60% reagent grade perchloric acid, using a rod of electrolytic iron as anode and a platinum gauze as cathode. A current of 0.5 ampere was used. During the electrolysis samples of the solution were withdrawn for analysis, and more perchloric acid added when necessary to prevent hydrolysis of the iron salt. Under these conditions only a trace of chloride was formed. However, if too high a current density were used, or if the solution were heated, an appreciable reduction of perchlorate to chloride occurred.

Ferric perchlorate was prepared by oxidizing the ferrous perchlorate solution thus obtained with hot nitric acid. The solution was then evaporated three times to dense white fumes with perchloric acid to remove the excess nitric acid. No attempt was made to crystallize either the ferrous or ferric perchlorate.

Purified commercial electrolytic hydrogen was used for the hydrogen electrode. The purification train consisted of a gas washing bottle containing 10% sodium hydroxide solution, a tube containing glass wool to remove spray, and a tube containing reduced copper heated to 425°. From this the hydrogen passed through a long cooling tube, then through a bubbling tower containing perchloric acid of the same strength as that used in the cell, and finally through a 3-mm. copper tubing to the hydrogen half of the cell. There was a second saturator in the cell containing the same concentration of acid.

The cell used in this investigation was the one used by Sherrill and Haas[5] in their study of the thallic–thallous electrode potential. However, in this case only the two electrodes in the hydrogen half-cell were platinized. The two electrodes in the ferric–ferrous solution were bright platinum and were cleaned occasionally in hot chromic acid. The technique of operation was otherwise essentially the same in the two cases.

The electrical measuring apparatus consisted of a Leeds and Northrup Type K potentiometer, a Sullivan high sensitivity galvanometer, and an Eppley standard cell which was checked against a new standard cell.

Methods of Analysis.—Tenth normal potassium permanganate solution was standardized against Sörensen sodium oxalate by the method of Fowler and Bright.[6] When more dilute permanganate solutions were required, they were prepared on the day of use by diluting a standard 0.1 *N* solution with weight burets. Total iron was determined by the Zimmermann–Reinhardt method.[7] Ferrous iron was determined by diluting the sample to 400 ml., adding 25 ml. of manganous sulfate titrating

---

[1] Schumb and Sweetser, THIS JOURNAL, **57**, 871 (1935).

[2] Bray and Hershey, *ibid.*, **56**, 1889 (1934).

[3] Popoff and Kunz, *ibid.*, **51**, 382 (1929).

[4] Popoff, Fleharty, and Hanson, *ibid.*, **53**, 1643 (1931).

[5] Sherrill and Haas, *ibid.*, **58**, 952 (1936).

[6] Fowler and Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

[7] See W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 305.