Summary

This paper describes determinations at 25° of the first and second dissociation constants of carbonic acid. The methods used involved galvanic cells without liquid junctions and glass electrodes suitable for precision measurements. The results obtained are 4.54×10^{-7} for the first and 5.61×10^{-11} for the second thermodynamic dissociation constant. The first of these figures is considerably at variance with published, and generally accepted, values of the constant obtained from conductivity measurements, but is in close accord with a redetermination by that method described in this paper. It also agrees with the potentiometric measurements of Michaelis and Rona. The second constant is in accordance, in order of magnitude, with published work based on equilibrium measurements. The new potentiometric method, however, makes much greater accuracy possible.

A study has also been made of the fugacity of carbon dioxide in mixtures with nitrogen at one atmosphere total pressure.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

A Determination of the Heat of Reaction of $2Fe(ClO_4)_3 + 2Hg = 2Fe(ClO_4)_2 + Hg_2(ClO_4)_2$ from Equilibrium Data[1]

BY VERNON B. FLEHARTY

The present investigation consists of repeating at 35° a study of the equilibrium condition of the reaction

$$2Fe(ClO_4)_3 + 2Hg = 2Fe(ClO_4)_2 + Hg_2(ClO_4)_2$$

previously made at 25° by Popoff, Fleharty and Hanson.[2] By combining the results of the two investigations the heat of reaction $2Fe^{+++}\alpha \text{ Aq} + 2Hg(l) = 2Fe^{++}\alpha \text{ Aq} + Hg_2^{++}\ \alpha \text{ Aq}$ can be computed.

Preparation of Materials.—The preparation of materials was carried out according to Popoff, Fleharty and Hanson.[2]

Analytical Methods.—The analytical methods were according to Popoff, Fleharty and Hanson[2] except that the mercurous-ion concentration was calculated from the determined concentration of ferrous ion. This was considered precise enough, since after making thirty-six mercurous ion determinations according to Popoff, Fleharty and Hanson[2] and comparing them with the corresponding ones calculated from the ferrous ion determination, it was discovered that eighteen were above and eighteen were below the calculated values.

Equilibrium was attained at 35° by a method similar to that used at 25°.[2] The reaction was allowed to take place in Pyrex glass bottles which could be glass sealed.

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[1] The problem was suggested by Dr. Stephen Popoff and the author wishes to thank Dr. Eversole for his help during Dr. Popoff's illness.

[2] Popoff, Fleharty and Hanson, THIS JOURNAL, **53**, 1643 (1931).

The three series of acid concentrations were 0.01, 0.0075 and 0.005 *C*. The three total iron concentrations used in each acid concentration were 0.004 0.002 and 0.001 *C*. All concentrations (*C*) are expressed in moles per 1000 g. of water weighed in vacuum.

Table I gives the experimental results obtained in the three series. K'_c represents the equilibrium constant calculated from total concentration by the equation

$$K'_c = \frac{C_{\text{Fe}}{}^{++2} \times C_{\text{Hg}_2}{}^{++}}{C_{\text{Fe}}{}^{+++2}}$$

μ represents the ionic strength of the equilibrium mixture.

TABLE I

THE EFFECT OF VARIATION OF CONCENTRATIONS OF ACID AND SALTS ON THE EQUILIBRIUM CONSTANT

Total C_{Fe}	$C_{\text{Fe}^{++}}$	$C_{\text{Hg}_2^{++}}$	$C_{\text{Fe}^{+++}}$	K'_c	μ
		Series I. 0.01 *C* $HClO_4$			
0.004	0.003491	0.001745	0.0005091	0.0820	0.02876
.002	.001814	.000907	.0001861	.0862	.01928
.001	.0009352	.0004676	.00006478	.0975	.01460
		Series II. 0.0075 *C* $HClO_4$			
.004	.003437	.001718	.0005641	.0638	.02635
.002	.001794	.000897	.0002061	.0680	.01681
.001	.0009279	.0004639	.00007199	.0772	.01211
		Series III. 0.005 *C* $HClO_4$			
.004	.003347	.001673	.0006531	.0439	.02398
.002	.001759	.0008794	.0002412	.0467	.01436
.001	.0009164	.0004582	.00008359	.0551	.00963

The Equilibrium Constant from Total Concentration.—The values of K'_c in 0.01, 0.0075 and 0.005 *C* (corresponding to series I, II and III,

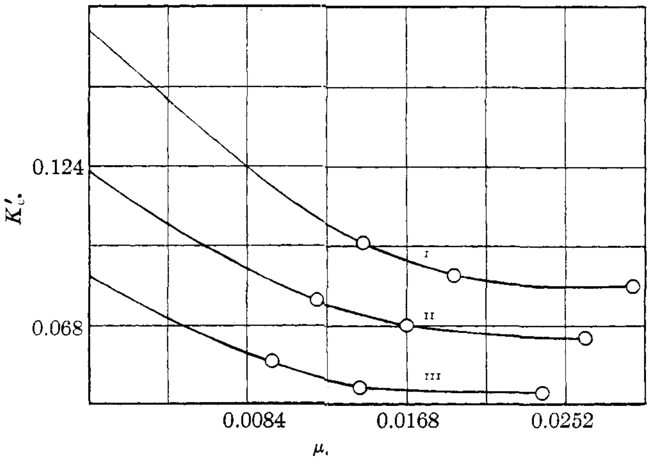

Fig. 1.—The apparent equilibrium constants from total concentration.

respectively) perchloric acid were plotted in Fig. 1 against the ionic strength of the equilibrium mixture, and the curves extrapolated to zero ionic strength. The extrapolated values K_c (Table II) were plotted in Fig. 2 against the C of perchloric acid and the curve extrapolated to infinite dilution, which gives the true equilibrium constant.

TABLE II

EQUILIBRIUM CONSTANTS IN VARYING ACID CONCENTRATIONS

C HClO$_4$	0.0100	0.0075	0.0050	0.0000
K_c	.1719	.1226	.0865	.0539

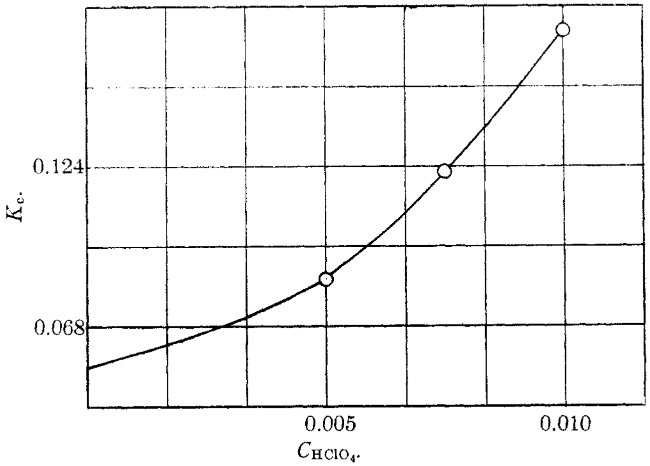

Fig. 2.—The equilibrium constants in varying acid concentrations against the acid concentrations.

The Relation of the Heat of Reaction to the Equilibrium Constant.— The relation of the heat of reaction to the equilibrium constants at two temperatures is given by the integrated form of the van't Hoff equation

$$\ln \frac{K_2}{K_1} = \frac{\Delta H\,(T_2 - T_1)}{R\,T_2 \times T_1}$$

Popoff, Fleharty and Hanson found the value of the true equilibrium constant for the reaction at 25° to be 0.0180. The present investigation finds the true equilibrium at 35° to be 0.0539 (Table II). Substituting 0.0539 for K_2 and 0.0180 for K_1 at 35° (T_2) and 25° (T_1), respectively, and the proper values for the constants, we find ΔH = 20,000 calories.

Summary

1. The following reversible reaction has been studied at 35°

$$2\text{Fe}^{+++} + 2\text{Hg} = 2\text{Fe}^{++} + \text{Hg}_2^{++}$$

2. The true equilibrium constant of the reaction was calculated from total concentration by graphical and mathematical treatments and found to be 0.539.

3. The heat of reaction was calculated from the integrated van't Hoff equation and found to be 20,000 calories.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Phenanthroline-Ferrous Ion: A Reversible Oxidation–Reduction Indicator of High Potential and its Use in Oxidimetric Titrations[1]

BY GEORGE H. WALDEN, JR., LOUIS P. HAMMETT AND RAY P. CHAPMAN

The use of oxidimetry as an analytical tool would be greatly extended by the discovery of a mobile and truly reversible oxidation potential indicator suitable for use in titrations with solutions of ceric sulfate and potassium dichromate. Such an indicator must change color at a potential at least as high as 0.93 volt if iron is to be titrated in the absence of phosphoric acid and fluorides, and should preferably change at a potential as high as 1.26 volts if the widest possible use is to be made of ceric sulfate. In addition it should possess a color change both vivid and intense, it should be stable and non-reactive with other substances likely to be present during a titration, and it should not be destroyed by irreversible oxidation when the end-point is overstepped or when it is subjected to the action of local excesses of the titrating reagent.

The phenanthroline-ferrous ion[2] satisfies all these requirements and seems to be in this respect unique.

The following properties[3] are significant for the application of phenanthroline-ferrous ion as an oxidation–reduction indicator. The base orthophenanthroline dissolves easily in solutions of ferrous salts, three molecules combining with one ferrous ion. The complex ferrous ions are intensely red in color. At room temperature they are only very slowly decomposed by strong acids or by salts of other metals (Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, Cd^{++}) which form stable complexes with the base. They do not form or form only very slowly when ferrous ion is added to a strongly acid solution of the base or to a solution containing a complex of the base with another metallic ion. Such powerful oxidants as chlorine or potassium permanganate in acid solution oxidize the ferrous complex to a ferric one, blue in color, which is remarkably resistant to further action of these reagents. The red ferrous complex is regenerated by the addition of reduc-

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(1) This article is based upon a dissertation submitted by Ray P. Chapman to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1932.

(2) Walden, Hammett and Chapman, THIS JOURNAL, **53**, 3908 (1931).

(3) These have all been known since the original article of Blau [*Monatsh.*, **19**, 647 (1898)].