Beta *d*-Glucose.—The powder data for beta glucose are not capable of interpretation without the support of crystallographic data, but the observed interplanar spacings are here placed on record in Table III in order to point out a difference between the crystals of the beta and alpha forms.

Summary

The crystal structures of three forms of glucose (alpha and beta anhydrous glucose and alpha glucose monohydrate) have been studied by the x-ray powder method. The interplanar. spacings of the three forms are given. The data for anhydrous alpha glucose correspond to an orthorhombic unit cell having dimensions: $a = 10.45$ Å., $b = 14.85$ Å., $c = 4.97$ Å., and meet the requirements of space group V^4. The data for alpha glucose monohydrate agree with the requirements of a monoclinic unit cell having dimensions: $a = 8.72$ Å., $b = 5.03$ Å., $c = 9.59$ Å., $\beta = 97°59'$ and correspond to space group c_2^2.

BERKELEY, CALIFORNIA

OXIDATION–REDUCTION POTENTIALS.
IV. THE DETERMINATION FROM EQUILIBRIUM DATA.
B. FERRIC–FERROUS ELECTRODE

By STEPHEN POPOFF, VERNON B. FLEHARTY AND EDWIN L. HANSON

The determinations of oxidation–reduction potentials from equilibrium data are considered to be more reliable[1] than those from e. m. f. measurements because in the former one attains true equilibrium, while in the latter one cannot always be certain that an inert electrode will always record the true potential, especially in dilute solutions.   E. m. f. measurements are further complicated by liquid junction potentials, which cannot, theoretically at least, always be entirely eliminated.   In equilibrium data it is also possible to work with the more dilute solutions in which the principle of ionic strength can be considered to hold—thus the activity coefficients of the ions can be calculated from the limiting case of the Debye–Hückel equation.

When metallic mercury comes in contact with ferric perchlorate solution, the following reaction takes place

$$2Fe(ClO_4)_3 + 2Hg \rightleftharpoons 2Fe(ClO_4)_2 + Hg_2(ClO_4)_2$$
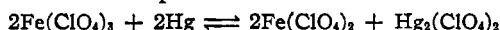
This reaction is of special interest because, at equilibrium, the substances are present in comparable amounts which can be suitably analyzed. It is therefore possible to determine the equilibrium constant by purely

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 411.

chemical means, to calculate the oxidation–reduction potential of the ferric–ferrous electrode, and to compare the latter with that obtained from e. m. f. measurements.

The equilibrium of this particular reaction has not been studied chemically, although Noyes and Brann[2] determined the equilibrium constant of the reaction

$$Ag + Fe(NO_3)_3 \rightleftharpoons AgNO_3 + Fe(NO_3)_2$$
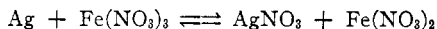
The perchlorates, mercury and perchloric acid were considered to be better suited for the determination of the equilibrium constant than the nitrates, silver and nitric acid, because in the latter case it is difficult to prepare pure metallic silver in a fine and suitable state of subdivision possessing the same energy content, and because of the possible oxidizing action of nitric acid.

In our investigation sufficiently dilute solutions were employed to be able to use the principle of ionic strength in the calculation of the equilibrium constant. The equilibrium constant was also calculated from total concentration by suitable mathematical and graphical treatments.

As a result of this experimental study the oxidation–reduction potential of the ferric–ferrous electrode was calculated to be -0.7473 v. Popoff and Kunz[3] obtained -0.7477 v. by e. m. f. measurements.

Preparation of Materials

(1) All water was redistilled from an alkaline permanganate solution.

(2) Ferric perchlorate was prepared by treating J. T. Baker c. p. ferric chloride with successive portions of G. Frederick Smith perchloric acid, and heating until no test for chloride ion was obtained. It was then recrystallized four times from 0.1 M perchloric acid.

(3) Mercury was purified by passing it through a column of dilute nitric acid six times; through redistilled water six times; distilling, filtering and passing through nitric acid and water as before.

(4) Potassium permanganate, silver nitrate, preventive, hydrochloric acid and perchloric acid solutions were made from the best chemicals obtainable.

Analytical Methods

All analyses were made using weight pipets and burets.

(1) The potassium permanganate solution was standardized electrometrically against Bureau of Standards sodium oxalate using McBride's conditions.[4]

(2) The silver nitrate solution was standardized electrometrically using a silver–silver chloride electrode with recrystallized potassium chloride as the standard.

(3) The total iron in the ferric perchlorate solution was determined electrometrically by the Zimmerman–Reinhardt method making the solution 0.5 M with respect to perchloric acid.

(4) The concentration of perchloric acid in the ferric perchloric solution was determined volumetrically using methyl orange as the indicator, by adding an excess of sodium hydroxide, filtering, and titrating the excess base with a standard acid solution.

[2] Noyes and Brann, THIS JOURNAL, **34,** 1016 (1912).

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

[4] McBride, *ibid.,* **34,** 393 (1912).

(5) and (6)   The weight ratio between the silver nitrate and sodium chloride solutions was determined electrometrically using silver–silver chloride electrodes.

(7)   The perchloric acid solution was standardized volumetrically using phenolphthalein as the indicator, against a carbonate-free solution of sodium hydroxide which had been standardized against constant boiling hydrochloric acid solution.

(8)   Analysis of the equilibrium mixture.

(a)   The ferrous iron was determined by precipitating the mercurous ion with an excess of sodium chloride, filtering, adding 20 cc. of preventive solution and enough perchloric acid to make the acid concentration approximately 0.5 M.   The solution was then titrated electrometrically with potassium permanganate.

(b)   The mercurous mercury was determined by adding an excess of sodium chloride and titrating the excess electrometrically with the silver nitrate, using a silver–silver chloride electrode.

(c)   The ferric iron was obtained by difference between the total iron and ferrous iron found.

Table I expresses the results of these analyses.   Concentration (C) is expressed in moles per thousand grams of water in vacuum in all tables.

TABLE I

ANALYTICAL METHODS

Solution	C		Solution	C
1. KMnO$_4$	0.020254	4.	HClO$_4$ in Fe(ClO$_4$)$_3$	0.079275
	.020252			.079176
	.020257			.079076
	.02025			.07918
Two months later	0.02017	5.	Concentrated NaCl	0.11058
				.11062
2. AgNO$_3$	0.027343			.11052
	.027357			.11064
	.027352			.1106
	.027352			
	.02735	6.	Dilute NaCl	0.064346
3. Fe(ClO$_4$)$_3$	0.23844			.064302
	.23826			.064316
	.23838			.064297
	.23796			.06432
	.2384	7.	HClO$_4$ Soln.	0.36087
				.36116
				.36107
				.36137
				.3611

The Relation between Equilibrium Constant and Oxidation–Reduction Potential.—The reaction

$$2Fe^{+++} + 2Hg \rightleftharpoons 2Fe^{++} + Hg_2^{++} \qquad (A)$$

occurs in the cell

$$Pt \mid Fe(ClO_4)_3, Fe(ClO_4)_2 \mid Hg_2(ClO_4)_2 \mid Hg$$

The equations for the potentials at each electrode at 25° are

$$E_{Fe} = E_{0Fe} - 0.05915 \log \frac{a_{Fe^{+++}}}{a_{Fe^{++}}}$$

$$E_{Hg} = E_{0Hg} - \frac{0.05915}{2} \log a_{Hg_2^{++}}$$

At equilibrium, the potential of the cell will be zero, and

$$E_{0Hg} - \frac{0.05915}{2} \log a_{Hg_2^{++}} = E_{0Fe} - \frac{0.05915}{2} \log \frac{a_{Fe^{+++}}^2}{a_{Fe^{++}}^2}$$

Transposing, one gets

$$E_{0Hg} - E_{0Fe} = \frac{0.05915}{2} \log a_{Hg_2^{++}} - \frac{0.05915}{2} \log \frac{a_{Fe^{+++}}^2}{a_{Fe^{++}}^2}$$

$$= \frac{0.05915}{2} \log \frac{a_{Fe^{++}}^2 \times a_{Hg_2^{++}}}{a_{Fe_2^{+++}}^2}$$

However, $a_{Fe^{++}}^2 \times a_{Hg_2^{++}}/a_{Fe^{+++}}^2$ is the equilibrium constant of reaction (A)

$$E_{0Hg} - E_{0Fe} = \frac{0.05915}{2} \log K$$

in which K is the equilibrium constant.

The value for E_{0Hg} has been determined by Lewis[5] and if the value for the equilibrium constant of the reaction shown is determined precisely, one can calculate the oxidation–reduction potential of the ferric–ferrous electrode.

Experimental Methods

(1) **Attainment of equilibrium** was accomplished by approaching the equilibrium of the reaction from both sides at a temperature of 25°. One set of runs was allowed to come to 25° in the water thermostat, approaching the equilibrium from the "cold side," so to speak. Another set of the same concentration was heated to 30–35° in an air thermostat, then brought to the equilibrium at 25° in the water-bath. This can be termed as approaching the equilibrium from the "hot side." These mixtures were continually rotated and shaken in a constant temperature bath at 25 ± 0.01°. The solutions were analyzed for the ferrous iron and the mercurous mercury by withdrawing a weighed amount of the solution, approximately 100 g. being used for each analysis.

(2) **The ease of reversibility** of the reaction was determined by varying the mercury content, the temperature and the time of rotation (for both "hot" and "cold"). It was finally decided to use 40 cc. of mercury in about 500 cc. of solution and to rotate the mixtures for both "hot" and "cold" for at least forty-eight hours at 25° before any analyses were attempted. It had been determined previously that twenty-four hours of rotation at 30–35° was more than sufficient to shift the equilibrium and that twenty-four hours of rotation at 25° was more than sufficient to obtain the same equilibrium as that established from the "cold" side. Special

⁵ Lewis and Randall, Ref. 1, p. 433.

Pyrex bottles were made (holding about 500 cc.) which could be glass sealed. Ordinary glass-stoppered bottles, which were sealed with paraffin, failed to give reproducible and identical results for both "hot" and "cold" equilibrium mixtures at 25°. At the present time no explanation will be offered.

(3) **Variation of Acid and Salt Concentrations.**—In each of the five series the acid concentration was kept constant but the concentration of the ferric perchlorate (starting mixture) was varied down to 0.001 C. The acid concentration was varied from 0.02 to 0.002 C. The latter was found to be the lowest concentration at which no hydrolysis took place when 0.001 C iron solution was used. Lower concentration of ferric perchlorate than 0.001 C was not employed because the errors in the analyses would have been too great. In the 0.003 C perchloric acid series, 0.004 C iron was the upper limit. A starting solution containing 0.001 C of iron and 0.001 C of perchloric acid hydrolyzed.

Experimental Data and Calculations

Table II gives the experimental results obtained in 0.02, 0.01, 0.005, 0.003 and 0.002 C perchloric acid concentrations, respectively, with vary-

TABLE II

EFFECT ON THE EQUILIBRIUM CONSTANT CALCULATED AS THOUGH MERCURY WAS MONOVALENT AND DIVALENT AS DESIGNATED, FROM TOTAL CONCENTRATIONS, ON VARIATION OF CONCENTRATIONS OF ACID AND SALTS

Total C_{Fe}	$C_{Fe^{++}}$	$C_{Hg_2^{++}}$ or $\frac{1}{2}C_{Hg^+}$	$C_{Fe^{+++}}$	$K'C_{Hg_2^{++}}$	$K'C_{Hg^+}$
		Series I, 0.02 C HClO₄			
0.006	0.004788	0.002456	0.001207	0.03868	0.01949
.003	.002533	.001262	.0004598	.03828	.01390
.001	.0009015	.0004588	.00009521	.04113	.008688
		Series II, 0.01 C HClO₄			
.008	.006109	.002992	.001891	.03124	.01933
.006	.004685	.002288	.001302	.02965	.01647
.003	.002513	.001244	.0004802	.03408	.01302
.002	.001731	.0008607	.0002692	.03557	.01107
		Series III, 0.005 C HClO₄			
.008	.005789	.002897	.002239	.01938	.01499
.006	.004514	.002229	.001475	.02094	.01364
.004	.003151	.001581	.0008488	.02179	.01174
.003	.002415	.001215	.0005779	.02122	.01015
.002	.001677	.0008255	.0003232	.02222	.008565
.001	.0008819	.0004526	.0001158	.02624	.006762
		Series IV, 0.003 C HClO₄			
.004	.003028	.001503	.0009720	.01459	.009365
.002	.001610	.0008053	.0003902	.01371	.006645
.001	.0008526	.0004453	.0001474	.01490	.005152
		Series V, 0.002 C HClO₄			
.002	.001546	.0007712	.0004542	.008930	.005248
.001	.0008301	.0004153	.0001698	.009920	.004060

ing concentration of iron. $K'C_{Hg_2^{++}}$ represents the equilibrium constant calculated from total concentration by the equation

$$K'C_{Hg_2^{++}} = \frac{C_{Fe^{++}}{}^2 \times C_{Hg_2^{++}}}{C_{Fe^{+++}}{}^2}$$

It was discovered that if the equilibrium constants were calculated upon the assumption that mercurous ion were monovalent, interesting results were obtained. If mercurous ion were monovalent

$$K'C_{Hg^+} = \frac{C_{Fe^{++}} \times C_{Hg^+}}{C_{Fe^{+++}}}$$

No attempt is made to draw any conclusions from the values of $K'C_{Hg^+}$.
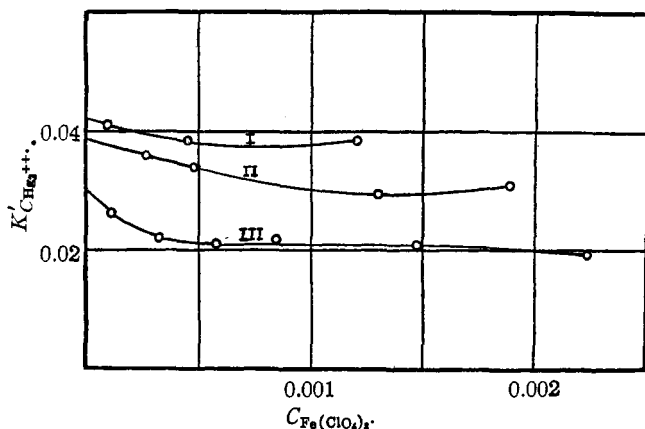
Fig. 1.—The apparent equilibrium constants from total concentration in varying acid and salt concentrations.
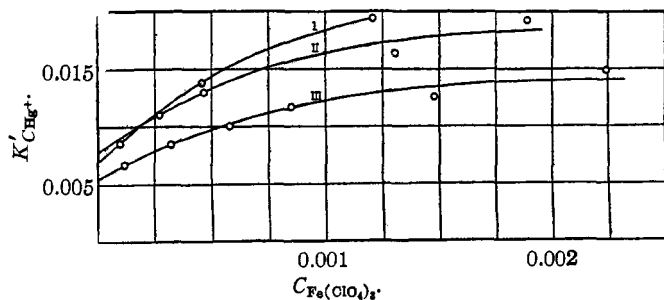

Fig. 1a.—The apparent equilibrium constants from total concentration in varying acid and salt concentrations.

In an analysis of a typical equilibrium mixture the percentage mean error was 0.1 for the determination of ferrous iron and 0.15 for mercurous mercury.

The Equilibrium Constant from Total Concentration.—The values of $K'C_{Hg_2^{++}}$ and $K'C_{Hg^+}$ in 0.02, 0.01, 0.005 (corresponding to I, II, III, respectively) C perchloric acid were plotted (Figs. 1 and 1a, respectively)

against the C of the ferric perchlorate (at equilibrium) and the curves extrapolated to zero concentration of ferric perchlorate.   The extrapolated values, Table III, were plotted (Figs. 2 and 2a, respectively) against the C of the perchloric acid and the curves again extrapolated to zero concentration of the acid.

TABLE III

EQUILIBRIUM CONSTANT IN VARYING ACID CONCENTRATION

C_{HClO_4}	$KC''_{Hg_2^{++}}$	KC''_{Hg^+}
0.020	0.0421	0.00706
.010	.0386	.00796
.005	.0310	.00556
.000	.0188	.00126

Due to the uncertainty of graphical extrapolation the data were extrapolated mathematically using the principle of moments and zero sum.   A
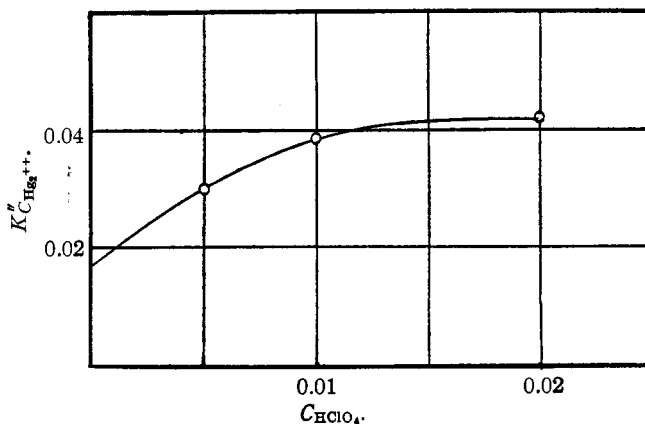

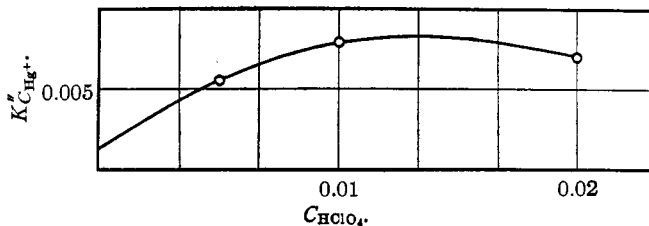Fig. 2.—The equilibrium constants in varying acid against the acid concentration.

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

value of 0.0188 was calculated for the true equilibrium constant $(K'C_{Hg_2^{++}})$ and 0.00126 for the true equilibrium constant $(K'C_{Hg^+})$ from total concentration.

The Equilibrium Constant from Ionic Strength.—It was possible in Series V, 0.002 M acid, 0.002 and 0.001 M ferric perchlorate, to calculate the activity coefficients in

$$K_f = \frac{C_{Fe^{++}} \times f_{Fe^{++}} \times C_{Hg^{++}} \times f_{Hg^{++}}}{C_{Fe^{+++}} \times f_{Fe^{+++}}}$$

by the equation[6]

$$-\log f = 0.5z^2 \sqrt{\mu}$$

The latter equation holds for most solutions whose ionic strengths are not greater than 0.01. Table IV gives the values obtained.

TABLE IV

THE EQUILIBRIUM CONSTANT FROM IONIC STRENGTH IN 0.002 M HClO₄

Total C_{Fe}	μ	f^{++}	f^{+++}	K_f
0.002	0.0117	0.608	0.326	0.01884
.001	.0068	.685	.427	.01751

Although the ionic strengths of the solutions containing 0.001 M ferric perchlorate (starting solution) and either 0.005 M or 0.003 M perchloric acid are 0.0097 and 0.0078, respectively, the equilibrium constants, using activity coefficients, calculate to be 0.0510 and 0.0274, respectively. It may be concluded that the equation used to calculate the activity coefficients does not hold for the foregoing solutions.

One may also calculate the equilibrium constants for all the solutions in Series III and IV, using activity coefficients, and then plot the values thus obtained against the square root of the ionic strength and extrapolate to zero ionic strength, assuming that the points lie on a straight line. The latter assumption, however, can hardly be justified, although the final extrapolated values agree closely among themselves and are not very far from 0.0184, the true equilibrium constant, since the equilibrium constant in each acid is different, although the ionic strengths of the solutions are the same and less than 0.01.

The true equilibrium constant may be taken as the average of the equilibrium constants obtained from total concentration and from (average) ionic strength in 0.002 M perchloric acid. The average value is 0.0184 or 0.018 ± 0.0005.

The Oxidation–Reduction Potential of the Ferric–Ferrous Electrode.— Using the equation

$$E_{0Fe} = E_{0Hg} - \frac{0.05915}{2} \log K$$

and Lewis's[5] value for E_{0Hg} (−0.7986 v.), the value for E_{0Fe} calculates to be −0.7473 v. Noyes and Brann[2] found from equilibrium data −0.7467 v., while Popoff and Kunz[3] report −0.7477 v. from e. m. f. measurements.

[6] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

Summary

1.   The following reaction was studied chemically and found to be a truly and easily reversible reaction

$$2Fe^{+++} + 2Hg \rightleftharpoons 2Fe^{++} + Hg_2^{++}$$
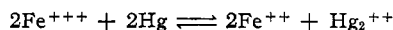
2.   The equilibrium constant of the reaction was calculated either from total concentration by suitable graphical and mathematical treatments or from ionic strength of dilute solutions, and was found to be 0.0180 ± 0.0005.

3.   The principle of ionic strength may not be considered to hold even in solutions as low as 0.01 when there is too much acid present as compared with the other salts.

4.   The oxidation–reduction potential of the ferric–ferrous electrode, calculated from the equation

$$E_{0_{Fe}} = E_{0_{Hg}} - \frac{0.05915}{2} \log K$$

was found to be -0.7473 v.   This value agrees very closely with -0.7477 v. obtained from our former e. m. f. measurements.

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METHODS OF CALCULATING AND AVERAGING RATE CONSTANTS[1]

By W. E. Roseveare

Introduction

In order to obtain a more probable value of the rate of a chemical reaction, for temperature coefficients, etc., it has been customary to take the simple arithmetical average of individual calculated values.   Due to the nature of the rate function, such an arithmetical average may possibly be as far from the true value as that calculated from the two least accurate measurements.   This applies only to the average of rate constants which are calculated from measurements made on a single sample of reacting material and not to the average of those found under identical conditions of time and concentration.   Most rates of reaction have been calculated by the interval method or the method of integrating from the zero of time using the formulas: $k = \dfrac{1}{t_n - t_{n-1}} \ln\left(\dfrac{a - x_{n-1}}{a - x_n}\right)$ and $k = \dfrac{1}{t_n} \ln \dfrac{a}{a - x_n}$.

The arithmetical averages of the rates calculated by these methods give quite different results and both are incorrect.

[1] This paper was presented in preliminary form by the author before the Mid-west Regional meeting of the American Chemical Society, May 9, 1930.