TABLE IV

PROPERTIES OF EQUIMOLAL MIXTURES

	25°	40°	70°
$100V^M/V^0$	0.010	0.039	0.088
F^E_{px} cal./mole	19.5	19.0	17.9
H^M_{px} cal./mole	30.2	30.2	30.2
E^M_{vx} cal./mole	29.4	27.1	23.8
V^M_x/β cal./mole	2.1	7.7	13.8
S^E_{px} cal./deg.	0.036	0.036	0.036
S^E_{vx} cal./deg.	0.033	0.026	0.017
a_{12}	−78.38	−74.06	−67.66
$\sqrt{a_{11}a_{22}}$	−78.84	−74.48	−68.01
$(100(a_{12} - \sqrt{a_{11}a_{22}}))/a_{12}$	0.58	0.56	0.52

free energy data are not sufficiently accurate and the heat capacity data are not consistent enough to determine H^M_{px} as a function of the temperature. Using Hirobe's value and assuming C^M_p to be zero, S^E_{vx} would be 0.004 cal. per deg. at 70°. Vold's results would make S^E_{vx} about zero at 25° and negative at 70° assuming C^M_p to be zero. V^M_x/β shows better agreement with E^M_{vx} with increasing temperature but still is only 58% of E^M_{vx} at 70°. There is a definite decrease of E^M_{vx} with temperature. In this calculation, however, the molal volume of the pure components and of the solution have increased with the temperature. The comparison with temperature should be made under conditions such that the molal volume of the components and of the solution remain identical to those at some arbitrarily chosen temperature.

The cohesive energy densities, a_{11} and a_{22}, at 25, 40, and 70° were calculated to be −73.88, −69.86, −63.86 cal. per cc. for carbon tetrachloride and −84.14, −79.40, and −72.42 cal. per cc. for benzene. The values of β in the equation of state, $V - RT/p = \beta$, at 25, 40, and 70° used in the calculation of the cohesive energy densities are −2544, −2071, and −1455 cc. for carbon tetrachloride and −2526, −2051, and −1436 cc. for benzene. The quantity a_{12} calculated from the equation

$$a_{12} = (a_{11} + a_{22} + E^M/V^0z_1z_2)/2$$

is always less than $\sqrt{a_{11}a_{22}}$, but it is interesting to note that the percentage difference is about the same at the three temperatures.

Summary

The increase of the volume on mixing benzene and carbon tetrachloride at constant pressure has been measured from 15 to 75°. From this the change of the thermodynamic functions on mixing at constant volume have been calculated from the change on mixing at constant pressure at 25, 40, and 70°. The volume of mixing increases approximately 9 fold; the excess entropy of mixing at constant volume decreases by about one-half from 25 to 70°.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Revision of the Oxidation Potentials of the Orthophenanthroline- and Dipyridyl-Ferrous Complexes

BY DAVID N. HUME AND I. M. KOLTHOFF

Walden, Hammett and Chapman[1] described the properties of the orthophenanthroline-ferrous complex as an oxidation-reduction indicator, and reported the potential of the couple to be 1.14 v. with the pronounced color change taking place at 1.20 v. An indicator with such a potential permits a very accurate titration of ferrous ions with ceric sulfate in sulfuric acid. In the presence of hydrochloric acid, however, there should be a serious titration error due to the great decrease in the cerous-ceric potential under these conditions. The oxidation potential of the cerous-ceric couple is only 1.28 v. in 1 *M* hydrochloric acid[2] which with an indicator changing color at 1.14 or 1.20 v. would result in errors of +0.4 and +2.3%, respectively. The titration of ferrous iron is frequently performed in hydrochloric acid; we have verified the accuracy of the procedure, as shown by the results in Table I. The titrations were carried out under conditions which allowed a precision of better than 0.1 of one per cent. The color change at the end-point in the hydrochloric acid medium was as sharp as that in sulfuric acid.

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[1] (a) G. H. Walden, L. P. Hammett and R. P. Chapman, THIS JOURNAL, **53**, 3908 (1931); (b) **55**, 2649 (1933).

[2] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

TABLE I

TITRATION OF FERROUS IRON WITH CERIC CERIUM IN HYDROCHLORIC AND IN SULFURIC ACIDS

Titration of 20-ml. samples of 0.1 *N* ferrous sulfate with approximately 0.1 *N* ceric sulfate, titration media being (a) 1 *M* H_2SO_4, (b) 1 *M* HCl. Two drops 0.025 *M* ferrous phenanthroline sulfate indicator present in each.

	(a)	(b)
	20.64	20.63
	20.62	20.62
	20.63	20.62
Av.	20.63	20.62 ml. of $Ce(SO_4)_2$

The discrepancy between the predicted and observed titration errors is due to an error in the original calculation of the oxidation potential of the indicator. Walden and his collaborators titrated a mixture of the indicator and ferrous sulfate potentiometrically with ceric sulfate in a medium of 1 *M* sulfuric acid. The quinhydrone half-cell in *M* sulfuric acid was used as a reference electrode. These authors found the mid-point potential of the indicator to be 0.38 v. higher than that of the ferrous–ferric system and 0.29 v. lower than that of the cerous–ceric couple in *M* sulfuric acid. They assumed 0.75 and 1.44 v. to be the standard potentials of the iron and cerium couples in *M* sulfuric acid, respectively, and obtained an average value of 1.14 v. for the standard potential of the indicator. This result is invalid for two reasons. First, the value of 0.75 v. for the iron couple is not appropriate here because it is the standard potential, applicable only to zero acidity and zero ionic strength. In sulfate solutions, the potential of the ferrous–ferric couple is considerably lower due to complex formation between ferric and sulfate ions. Second, the experimental data in the solutions containing excess ceric sulfate are in error by nearly 100 millivolts.

Experimental

We have repeated the titrations of Walden, Hammett and Chapman, using both the quinhydrone electrode in 1 *M* sulfuric acid and the mercury–mercurous sulfate electrode in 1 *M* sulfuric acid as reference electrodes. Three or four minutes were allowed for the potentials to become constant. It was found that in well-poised portions of the curve, further waiting for as long as thirty minutes resulted in values only one millivolt lower. Our experimental results were in good agreement with the data published by Walden, *et al.*, except for solutions in which an excess of ceric salt was present. In these solutions, distinctly higher potentials were obtained. The results of two such titrations are given in Part A of Table II.

TABLE II

A. Potential of a platinum electrode at various stages in the titration of solutions 0.0008 *M* in ferrous-phenanthroline sulfate and ferrous sulfate with ceric sulfate. All solutions 1.00 *M* in sulfuric acid.

B. Oxidation potential of the indicator calculated from observed potential differences and the accepted formal potentials of reference couples as indicated.

A. Observed potentials in volts *vs.* quinhydrone electrode in 1.00 *M* sulfuric acid			B. Calculated indicator potential on hydrogen scale from potential of		
$(Fe^{++}) = (Fe^{+++})$	$(In)_{OX} = (In)_{RED}$	$(Ce^{IV}) = (Ce^{III})$	Fe	Ce	QH
−0.01	0.360	0.742	1.05	1.058	1.056
−0.02	0.363	0.743	1.06	1.060	1.059

The previous investigators found a value of only 0.655 v. in a mixture in which the ratio of cerous to ceric was unity. In an effort to determine the cause of this discrepancy we first checked the reproducibility of the cerous–ceric couple. In a solution 0.002 *M* each in cerous and ceric sulfates and 1.00 *M* in sulfuric acid, the potential of a platinum electrode was found to be 0.741 v. against the quinhydrone couple. The potential was established quickly, regardless of whether the electrode had previously been anodically or cathodically polarized in sulfuric acid. Taking the potential of the quinhydrone couple to be 0.696 v. here, the value obtained for the formal potential of the cerous–ceric couple is found to be 1.437 v., in excellent agreement with the accepted value of 1.44 v.[3] The addition of enough orthophenanthroline to make the solution 0.006 *M* changed the potential by only 0.5 millivolt, which showed no change in fifteen minutes. This would make it appear to be unlikely that complex formation between ceric ions and orthophenanthroline is the cause of the discrepancy. We did note, however, that a solution of the indicator to which a 100% excess of ceric sulfate had been added, lost much of its color on standing overnight. At the same time, the potential fell from 0.743 to 0.695 v. Apparently, there is some slow irreversible oxidation of the organic matter by the excess ceric sulfate.

Discussion of Results

In the same general manner as Walden, Hammett and Chapman, we have calculated the

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(3) A. H. Kunz, THIS JOURNAL, 53, 98 (1931).

oxidation potential of the indicator from the iron and cerium potentials and obtained the results given in Part B of Table II. For the formal potential of the ferrous–ferric couple in 1 *M* sulfuric acid, the value 0.68 v. was taken.[4] The accepted value of 1.44 v. for the cerous–ceric couple also refers to 1 *M* sulfuric acid. In addition, we have calculated the indicator potential directly from the potential of the quinhydrone couple, which is known to be 0.696 v. in 1 *M* sulfuric acid.[5] It is seen that all these give a very good agreement. The use of a mercury–mercurous sulfate reference electrode in 1 *M* sulfuric acid gave potentials 20 millivolts greater than with quinhydrone. Since the formal potential of the mercurous sulfate electrode is 0.674 v. in 1 *M* sulfuric acid,[4] this constitutes an additional check. As final values, we suggest 1.06 v. for the formal oxidation potential of the indicator and 1.12 v. for the color change.

The end-point errors calculated from the new indicator potential are negligible in sulfuric acid solutions and quite small for hydrochloric acid (about 0.1% in the latter case). The potential of the indicator itself should not be greatly affected by the medium because the iron-phenanthroline complex is quite a stable one. Therefore, the use of the same potential in sulfuric and hydrochloric acids is justifiable.

The potential of the ferrous α,α'-dipyridyl complex, determined in the same manner and reported to be identical with that of the phenanthroline complex[1b] is similarly revised to 1.06 v. The potential of the nitrophenanthroline-ferrous complex, determined by a different method, was found to be approximately 1.25 v.[6] Since the observations of Smith and Getz[7] agree with this value, there seems to be no necessity for revising it.

Steigman, Birnbaum and Edmonds[8] found the potential of the ruthenium α,α'-dipyridyl complex to be 0.58 v. greater than that of the ferrous–ferric couple in *M* nitric acid. The formal potential of the latter is 0.74 v. The resulting indicator potential, 1.32 v. does not differ seriously from the value 1.33 v. calculated by them.

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Summary

The oxidation potential of ferrous-phenanthroline and of ferrous α,α'-dipyridyl in *M* sulfuric or hydrochloric acid is 1.06 v. instead of the reported value of 1.14 v.

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[4] Given in the very useful table of formal potentials compiled by C. S. Garner in E. H. Swifts' book, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1939, pp. 540–543; see also G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

[5] F. Hovorka and W. C. Dearing, THIS JOURNAL, **57**, 446 (1935).

[6] L. P. Hammett, G. H. Walden and S. M. Edmonds, *ibid.*, **56**, 1092 (1934).

[7] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 304 (1938).

[8] J. Steigman, N. Birnbaum and S. M. Edmonds, *ibid.*, **14**, 30 (1942).

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 26, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Oxidation Potential of the Chromocyanide–Chromicyanide Couple and the Polarography of the Chromium Cyanide Complexes[1]

BY DAVID N. HUME[2] AND I. M. KOLTHOFF

Although it is well known that the chromocyanide ion is a powerful reducing agent, liberating hydrogen from aqueous solutions in the presence of platinum, no determination of the oxidation potential of the chromocyanide–chromicyanide couple has ever been reported. In the present investigation, the potential has been measured in 1 *M* potassium cyanide, both polarographically and by classical methods.

Experimental

In the polarographic measurements, the conventional apparatus and technique were used.[3] Many of the experiments were made with an automatic Heyrovský polarograph, Type VIII. Others were made with the manual apparatus of Lingane and Kolthoff.[4] The temperature was kept constant at 25.00 ± 0.04° by means of a water thermostat. The polarographic cells had provision for the use of both a mercury pool and an external reference electrode. A saturated calomel electrode was used as a working and reference anode and all potentials are given

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[1] Abstracted from a thesis submitted by David N. Hume to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Du Pont Fellow in Chemistry, 1942–1943

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

[4] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939)