[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH CAROLINA]

Activity Coefficient Ratios of Mixed Electrolytes in Aqueous Solutions at 25°. I. Sulfuric Acid and Cupric Sulfate. II. Perchloric Acid and Cupric Perchlorate

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Activity coefficient ratios of the electrolytes in the systems sulfuric acid–cupric sulfate and perchloric acid–cupric perchlorate have been determined at 25° from electromotive force measurements on cells of the type Ag, AgCl, HCl (0.2 m)/glass/$\left\{\begin{matrix}\text{H}_2\text{SO}_4\ (m_1),\ \text{CuSO}_4\ (m_2) \\ \text{or} \\ \text{HClO}_4\ (m_1)\ \text{Cu(ClO}_4)_2\ (m_2)\end{matrix}\right\}$, Cu.

Introduction

Activity coefficient ratios of the electrolytes in each of the two aqueous systems nitric acid–silver nitrate[1] and nitric acid–mercurous nitrate[2] have been determined by electromotive force measurements of the cells

$$\text{Ag, AgCl, HCl } (0.2\ m)/\text{glass}/\text{HNO}_3\ (m_1),\ \left\{\begin{matrix}\text{AgNO}_3\ (m_2),\ \text{Ag} \\ \text{or} \\ \text{Hg}_2(\text{NO}_3)_2\ (m_2),\ \text{Hg}\end{matrix}\right\}$$

The glass electrode must be used here instead of the hydrogen electrode as the silver and mercurous ions are reduced by hydrogen in the presence of platinum.

In a similar manner, the activity coefficient ratios of the electrolytes in each of the two systems sulfuric acid–cupric sulfate and perchloric acid–cupric perchlorate may be determined from e.m.f. measurements of the cells

$$\text{Ag, AgCl, HCl } (0.2\ m)/\text{glass}/\left\{\begin{matrix}\text{H}_2\text{SO}_4\ (m_1),\ \text{CuSO}_4\ (m_2) \\ \text{or} \\ \text{HClO}_4\ (m_1),\ \text{Cu(ClO}_4)_2\ (m_2)\end{matrix}\right\},\ \text{Cu}$$

The Nernst equations for the latter two cells are

$$E = (E^0_{\text{glass}} - E^0_{\text{Cu,Cu}^{++}}) - \frac{RT}{2F} \ln \frac{a^2_{\text{H}_2\text{SO}_4}}{a_{\text{CuSO}_4}} = (E^0_{\text{glass}} - E^0_{\text{Cu, Cu}^{++}}) - \frac{RT}{2F} \ln \frac{4m^2_{\text{H}_2\text{SO}_4}}{m_{\text{CuSO}_4}} - \frac{RT}{2F} \ln \frac{\gamma^3_{\text{H}_2\text{SO}_4}}{\gamma^2_{\text{CuSO}_4}} \quad (1)$$

and

$$E = (E^0_{\text{glass}} - E^0_{\text{Cu, Cu}^{++}}) - \frac{RT}{2F} \ln \frac{m^2_{\text{HClO}_4}}{m_{\text{Cu(ClO}_4)_2}} - \frac{RT}{2F} \ln \frac{\gamma^4_{\text{HClO}_4}}{\gamma^3_{\text{Cu(ClO}_4)_2}} \quad (2)$$

The standard potential of the glass electrode is known to depend somewhat on the acid concentration. The variation of the standard potential of this electrode with acid concentration was therefore determined by comparisons with a hydrogen electrode in acid solutions ranging from 0.01 to 1.0 molal. In subsequent calculations, the E^0_{glass} values obtained were used for solutions of the same acid concentration.

Experimental

Electrodes.—Smooth surface copper electrodes have been found to be somewhat erratic in behavior due to strains and other variations in the physical state of the metal. The following procedure was carried[3] out in order to minimize these effects and obtain more reproducible electrodes:

Copper was deposited onto a platinum wire loop about 5 mm. in diameter from a solution containing 200 g. of copper sulfate per liter. The current density was such that the copper was deposited in an amorphous or "spongy" form. The electrodes were carefully washed with distilled water and placed in the solution to be measured. Electrodes prepared in this manner were reddish-brown in color and the potentials agreed to within ±0.10 millivolt. It was observed that the potentials changed slowly with time, therefore all determinations were made with freshly prepared electrodes.

The glass electrode was prepared in a manner given previously,[1] and calibrated against a hydrogen electrode in acid solutions from 0.01 to 1.0 molal.

Apparatus.—For the electromotive force measurements, a Leeds and Northrup galvanometer with a sensitivity of 5×10^{-4} microampere per mm. was used in conjunction with a Rubicon potentiometer. Because of the high resistance of the glass electrode, a Leeds and Northrup thermionic amplifier was employed in the potentiometer circuit.

Standardization of Solutions.—The copper sulfate and copper perchlorate concentrations of the mixtures were determined iodometrically by titration of the free iodine liberated upon the addition of potassium iodide with standard thiosulfate using starch as indicator. The acid concentrations were determined by titration with standard base employing brom cresol green indicator. The determinations were made on a weight basis and concentrations are expressed as molalities. All chemicals were reagent grade and were used without further purification.

Discussion

The Standard Potential of the Copper, Cupric Ion Electrode at 25°.—The different values of the copper, cupric ion electrode found in the literature cover a range of about 5 millivolts. An early value obtained by Lewis and Lacey[4] was 0.3469 v. This value has since been corrected to 0.3453 v., however, because of a more accurate value for the mercury, mercurous sulfate electrode used as the other half-cell. More recently, Tourkey and El Wakkad[5] obtained values of 0.3456 v. in the presence of hydrogen and 0.3420 v. in air. According to the authors, the higher value should be more nearly the true potential as oxide formation is not favored in this case.

It is seen from equation 1 or 2 that the activity coefficient ratios can be determined quite readily from electromotive force measurements providing the quantity $E^0_{\text{glass}} - E^0_{\text{Cu, Cu}^{++}}$ is known. If equation 2 is rearranged to the following form

$$E + \frac{RT}{2F} \ln \frac{m^2_{\text{HClO}_4}}{m_{\text{Cu(ClO}_4)_2}} + \frac{RT}{2F} \ln \frac{\gamma^4_{\text{HClO}_4}}{\gamma^3_{\text{Cu(ClO}_4)_2}} = (E^0_{\text{glass}} - E^0_{\text{Cu. Cu}^{++}})$$

it is apparent that the standard potential of the copper electrode should be found by extrapolation

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[1] O. D. Bonner, A. W. Davidson and W. J. Argersinger, Jr., THIS JOURNAL, **74**, 1047 (1952).

[2] O. D. Bonner and Francis A. Unietis, *ibid.*, **75**, 5111 (1953).

[3] F. H. Getman, *Trans. Electrochem. Soc.*, **26**, 67 (1914).

[4] G. N. Lewis and W. N. Lacey, THIS JOURNAL, **36**, 804 (1914).

[5] A. R. Tourkey and S. E. S. El Wakkad, *J. Chem. Soc.*, 740 (1948).

to infinite dilution of a plot of the left side of the equation *vs.* a function of the ionic strength, since E^0_{glass} can be determined. This extrapolation may be more conveniently accomplished if activity coefficients are assumed for the acid and salt and substituted in the above equation. Activity coefficients for perchloric acid are given by Harned and Owen[6]; however, none could be found in the literature for copper perchlorate. Zinc perchlorate, for which coefficients have been determined,[7] should be similar to the copper salt in behavior and consequently the ratio $\gamma^4_{\text{HClO}_4}/\gamma^3_{\text{Zn(ClO}_4)_2}$ was used in the extrapolation.

The results are given in Table I.

The value of −0.3439 v. for the standard potential is about mid-way of the two values given by Tourkey and El Wakkad.

TABLE I

E.M.F. DATA FOR THE CALCULATION OF THE STANDARD POTENTIAL OF THE COPPER, CUPRIC ION ELECTRODE AT 25°

$\frac{m_{H^+}}{m_{Cu^{++}}}$	μ	$E + \frac{RT}{2F}\ln\frac{m^2_{HClO_4}}{m_{Cu(ClO_4)_2}}$	$\frac{RT}{2F}\ln\frac{\gamma^4_{HClO_4}}{\gamma^3_{Zn(ClO_4)_2}}$	$E^0_{glass} - E^0_{Cu}$	$-E^0_{Cu}$
2.007	0.2134	−0.0159	0.0068	−0.0091	0.343
2.007	.1432	− .0150	.0061	− .0089	.3436
2.007	.0840	− .0138	.0050	− .0088	.3437
2.007	.0426	− .0117	.0030	− .0087	.3438
	.0000 (Extrapolated)				.3439

Activity Coefficient Ratios.—Six stock solutions of each of the two systems sulfuric acid–copper sulfate and perchloric acid–copper perchlorate were prepared and standardized. The solutions were of an ionic strength of approximately unity and ranged in ratio of hydrogen ion to salt concentration from 8.0 to 0.4. Each of the twelve stock solutions was diluted to give the data presented in Tables II and IV.

Plots of activity coefficient ratios *vs.* ionic strength were made and points taken from the smoothed curves. The results are given in Tables III and V. The activity coefficient ratios of the perchlorates exhibit the behavior expected of electrolytes of these valence types. The sulfates are of interest in that the activity coefficient ratio decreases greatly with increasing cupric sulfate concentration. This behavior is obviously due to the repression of the ionization of the sulfuric acid by the excess sulfate ion.

Argersinger[8] has shown that the activity coefficients of each electrolyte in binary mixtures may also be calculated from e.m.f. measurements. This calculation was not performed, however, since these data are primarily of interest in ion exchange work

TABLE II

E.M.F. DATA FOR THE CELLS OF THE TYPE: GLASS/H_2SO_4 (m_1), $CuSO_4$ (m_2), Cu AND THE CORRESPONDING ACTIVITY COEFFICIENT RATIOS

$\frac{m_{H^+}}{m_{Cu^{++}}}$	μ	$(E^0_{glass} - E^0_{Cu}) - E$	$\frac{\gamma^3_{H_2SO_4}}{\gamma^2_{CuSO_4}}$
7.178	1.319	0.0271	1.795
	0.897	0.0217	1.726
	.509	.0142	1.698
	.2522	.0050	1.686
	.1280	− .0048	1.547
	.0638	− .0138	1.535
	.0307	− .0253	1.304
	.0154	− .0385	0.932
5.435	1.359	.0222	1.712
	0.926	.0170	1.672
	.522	.0094	1.634
	.2637	.0003	1.596
	.1314	− .0083	1.647
	.0634	− .0181	1.610
	.0312	− .0281	1.442
	.0159	− .0405	1.009
3.294	1.309	.0122	1.634
	0.878	.0066	1.572
	.500	− .0004	1.596
	.319	− .0059	1.633
	.1409	− .0173	1.523
	.0634	− .0266	1.670
	.0312	− .0370	1.476
	.0159	− .0488	1.168
1.660	1.334	− .0024	1.466
	0.878	− .0080	1.442
	.520	− .0143	1.488
	.2353	− .0240	1.547
	.1303	− .0309	1.634
	.0652	− .0399	1.692
	.0317	− .0497	1.547
	.0159	− .0613	1.254
1.026	1.477	− .0122	1.376
	1.010	− .0173	1.355
	0.576	− .0239	1.420
	.2874	− .0319	1.523
	.1441	− .0396	1.672
	.0717	− .0483	1.698
	.0351	− .0581	1.622
	.0139	− .0727	1.314
0.361	1.401	− .0378	1.313
	0.950	− .0428	1.295
	.689	− .0465	1.356
	.344	− .0543	1.477
	.1374	− .0646	1.660
	.0693	− .0730	1.713
	.0275	− .0860	1.573
	.0160	− .0965	1.400

TABLE III

VARIATION OF ACTIVITY COEFFICIENT RATIO WITH COMPOSITION IN THE SYSTEM H_2SO_4–$CuSO_4$

$\frac{m_{H^+}}{m_{Cu^{++}}}$			μ		
	0.02	0.04	0.08	0.12	0.20
7.18	1.07	1.41	1.56	1.60	1.67
5.43	1.18	1.49	1.63	1.64	1.64
3.29	1.29	1.53	1.66	1.66	1.64
1.660	1.38	1.59	1.68	1.66	1.59
1.026	1.43	1.62	1.70	1.69	1.59
0.361	1.48	1.64	1.72	1.70	1.58
$\frac{m_{H^+}}{m_{Cu^{++}}}$			μ		
	0.40	0.80	1.00	1.20	1.30
7.18	1.69	1.71	1.73	1.77	1.80
5.43	1.64	1.64	1.65	1.69	1.71
3.29	1.61	1.57	1.58	1.61	1.64
1.660	1.51	1.45	1.44	1.45	1.45
1.026	1.48	1.38	1.35	1.35	1.36
0.361	1.45	1.32	1.29	1.29	1.30

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[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 601.

[7] Ref. 6, p. 602.

[8] W. J. Argersinger, *J. Phys. Chem.*, **58**, 792 (1954).

TABLE IV

E.M.F. DATA FOR THE CELLS OF THE TYPE: GLASS/$HClO_4$ (m_1), $Cu(ClO_4)_2$ (m_2), Cu AND THE CORRESPONDING ACTIVITY COEFFICIENT RATIOS

$\frac{m_{H^+}}{m_{Cu^{++}}}$	μ	$(E^0_{glass} - E^0_{Cu^{++}}) - E$	$\frac{\gamma^4_{HClO_4}}{\gamma^3_{Cu(ClO_4)_2}}$
8.122	1.485	0.0490	5.18
	0.986	.0424	4.64
	.558	.0331	4.03
	.279	.0223	3.42
	.1388	.0111	2.91
	.0688	− .0007	2.44
	.0338	− .0140	1.91
6.111	1.498	.0443	4.98
	0.997	.0374	4.49
	.559	.0285	3.94
	.282	.0175	3.37
	.0140	.0064	2.88
	.0695	− .0049	2.39
	.0341	− .0175	1.90
2.007	1.497	.0222	4.71
	1.008	.0160	4.29
	0.572	.0072	3.82
	.285	− .0036	3.30
	.1410	− .0144	2.86
	.0706	− .0259	2.36
	.0344	− .0379	1.89
1.011	1.489	0.0067	4.47
	0.990	.0007	4.20
	.564	− .0081	3.70
	.278	− .0189	3.35
	.1400	− .0296	2.80
	.0700	− .0412	2.27
	.0341	− .0526	1.91
0.779	1.497	.0005	4.32
	1.009	− .0051	4.16
	0.572	− .0139	3.67
	.282	− .0249	3.19
	.1420	− .0358	2.71
	.0705	− .0468	2.26
	.0345	− .0586	1.90
0.397	1.412	− .0177	4.19
	1.010	− .0230	3.90
	0.674	− .0286	3.61
	.342	− .0394	3.22
	.1356	− .0591	2.56
	.0679	− .0649	2.21
	.0263	− .0806	1.69

TABLE V

VARIATION OF ACTIVITY COEFFICIENT RATIO WITH COMPOSITION IN THE SYSTEM $HClO_4$–$Cu(ClO_4)_2$

$\frac{m_{H^+}}{m_{Cu^{++}}}$			μ		
	0.04	0.08	0.12	0.20	0.40
8.12	2.04	2.53	2.80	3.17	3.72
6.11	2.04	2.48	2.76	3.11	3.65
2.01	2.00	2.45	2.74	3.09	3.56
1.011	2.00	2.42	2.70	3.03	3.50
0.779	1.98	2.38	2.62	2.94	3.42
0.397	1.98	2.30	2.50	2.82	3.31

$\frac{m_{H^+}}{m_{Cu^{++}}}$		μ		
	0.80	1.00	1.20	1.40
8.12	4.40	4.66	4.89	5.08
6.11	4.28	4.50	4.69	4.88
2.01	4.10	4.29	4.46	4.62
1.011	4.03	4.20	4.34	4.44
0.779	3.95	4.13	4.24	4.30
0.397	2.74	3.90	4.03	4.16

where only the activity coefficient ratios are needed.

Attempts to obtain data on two additional systems involving copper salts proved unsuccessful. These systems were nitric acid–cupric nitrate and hydrochloric acid–cupric chloride. In the former case it was found that the spongy copper electrode was attached by even very dilute nitric acid. In the latter instance cupric ion, in the presence of copper, was reduced irreversibly to cuprous ion precipitating from the solution as cuprous chloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Relative Strengths of Certain Acids in Liquid Ammonia[1]

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Potentiometric titrations of urea, thiourea and guanidinium acetate and chloride with potassium amide in liquid ammonia at −36° show that the decreasing order of relative acidic strengths of the several acids involved in these systems is: $NH_4^+ > H_2NC(NH)NH_3^+ > H_2NC(S)NH_2 > H_2NC(O)NH_2 > H_2NC(NH)NH_2 > H_2NC(S)NH^- > H_2NC(O)NH^- \geqslant H_2NC(NH)NH^- > NH_2^-$. The monopotassium salts of guanidine, urea and thiourea are soluble in liquid ammonia, while the dipotassium salts are substantially insoluble. The data obtained are discussed with reference to reported properties of these compounds.

Experimental evidence in support of the concept of ammono- and aquoammonocarbonic acids[2,3] consists largely of the displacement of hydrogen from such acids upon reaction with metals in nonaqueous solvents; typical neutralization reactions also have been demonstrated. These reactions have been used in the preparation of salts such as the monosilver and dipotassium salts of guanidine,[4] the mono- and dipotassium salts of urea,[5,6] and the monopotassium salt of thiourea.[7] Despite

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[1] This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639 and the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Publ. Corp., New York, N. Y., 1935.

[3] L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953.

[4] E. C. Franklin, THIS JOURNAL, **44**, 490 (1922).

[5] J. S. Blair, *ibid.*, **48**, 97 (1926).

[6] R. A. Jacobson, *ibid.*, **58**, 1984 (1936).

[7] E. A. Werner, *J. Chem. Soc.*, **109**, 1120 (1916).