Weight Ho_2O_3.	Weight $Ho_2(SO_4)_3$.	At. wt. Ho.
0.3467	0.5687	163.57
0.3400	0.5579	163.40
0.3960	0.6496	163.55
0.7631	1.2524	163.31
0.6877	1.1286	163.33
0.5378	0.8822	163.55
	Mean,	163.45

Argon.—Fischer and Froboese[1] have made numerous fractional distillations of liquid argon, and found its density as gas to be practically constant. The final result is d. 19.94–19.95, and A = 39.9.

Niton.—For the atomic weight of niton, the gaseous emanation of radium, Gray and Ramsay[2] give determinations ranging from 218–227. The mean is 223; but the value Nt = 222.4 is preferred.

Miscellaneous Notes.—Hinrichs[3] has reconsidered all the evidence relative to the atomic weight of hydrogen, and concludes that H = 1.00781. In another paper[4] he discusses the atomic weight of vanadium, which he places at 51 precisely. A brief note by Ter Gazarian[5] defends his work on the density of PH_3. C. Henry[6] has considered the proper mode of calculating atomic weights. Relations between the atomic weights are studied by Loring,[7] by Emerson[8] and by Nicholson.[9] Emerson's "helix chimica" is an arrangement of the elements on a spiral, while Nicholson develops a structural theory of their formation.

THE FREE ENERGY OF DILUTION OF HYDROCHLORIC ACID.

By Richard C. Tolman and Alfred L. Ferguson.

Received December 19, 1911.

1. Introduction.

The free energy of dilution of an electrolyte is usually obtained from measurements of the electromotive force of concentration cells. In the case of hydrochloric acid, apparently accurate measurements have been made by Jahn[10] on concentration cells of the type,

$$\text{Ag} : \text{AgCl} \quad \underset{C_1}{\text{HCl}} : \underset{C_2}{\text{HCl}} \quad \text{AgCl} : \text{Ag}.$$

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[1] *Ber.*, **44**, 92.

[2] *Proy. Roy. Soc.*, **84 A**, 536.

[3] *Rev. gén. chim.*, **13**, 351, 377 (1910).

[4] *Proc. Am. Phil. Soc.*, **50**, 191.

[5] *J. chim. phys.*, **9**, 100.

[6] *C. R. Assoc. Franc. Avance Sci.*, 269 (1909).

[7] *Phys. Z.*, **12**, 107.

[8] *Am. Chem. J.*, 45, 160 (1911).

[9] *Phil. Mag.*, [6] **22**, 864.

[10] Jahn, *Z. physik. Chem.*, **33**, 545 (1900); **35**, 1 (1900).

If E is the electromotive force of such a cell, then EF is the free energy change accompanying the passage of one faraday of electricity through the cell where F is the value of one faraday in coulombs. When one faraday passes, let us suppose that t mols of HCl are transferred from concentration C_1 to C_2, then the free energy of dilution per mol of hydrochloric acid is evidently equal to EF/t.

An objection to this ordinary method of obtaining the free energy of dilution lies in the uncertainty as to the meaning and value of t. It is customary to use for t, t_H, the Hittorf transference number for hydrogen ion in hydrochloric acid, on the assumption that t_H will be the number of mols of HCl transferred from one electrode to the other when one faraday passes through the solution, and if the solution were of uniform concentration throughout the cell, this would, of course, be the case. In the actual measurement of electromotive force, however, a very small amount of current is allowed to pass, and this is accompanied by some complicated change at the boundary between the two concentrations of acid. It is open to doubt whether this change at the boundary is really equivalent per faraday to the transfer of t_H mols of hydrogen radical from C_1 to C_2 and $(1 - t_H)$ mols of chloride radical in the opposite direction, as would be necessary if the total process including the electrode effects is to consist in the disappearance of t_H mols of HCl from the solution of concentration C_1, and their appearance at concentration C_2. The experimental fact,[1] that the potential difference between two liquids may vary with the time that they have stood in contact, certainly shows that for such cases the process accompanying the passage of electricity through the boundary is neither simple nor understood. In some cases a further uncertainty as to the value of t arises from the fact that the Hittorf transference number is different for solutions of different concentration. Moreover, in general, an exact determination of transference number is accompanied by very great experimental difficulties. Since there are these objections to the customary method of determining the free energy of dilution of an electrolyte, and since Jahn reached some rather extraordinary and much debated conclusions[2] from his measurements of electromotive force it seemed desirable to determine the free energy of dilution of hydrochloric acid without using cells with liquid boundaries. Such "concentration cells without transference" have been used or advocated by a number of investigators.[3]

In this research, the electromotive force has been measured at 18° between calomel and hydrogen electrodes of cells containing hydrochloric

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[1] Lewis and Rupert, THIS JOURNAL, **33**, 299 (1911).

[2] Arrhenius, *Z. physik. Chem.*, **36**, 28 (1901). Nernst, *Ibid.*, **36**, 596 (1901).

[3] Ostwald-Luther, "Physiko-chemische Messungen," p. 449 (1910). Lehfeldt, "Electro-Chemistry," Pt. I, p. 211.

acid at a known concentration, C. This determines the free energy change ΔF_{18° of the reaction,

$$^1/_2H_2 \text{ (1 atm.)} + HgCl(s) = Hg + HCl \text{ (Conc. C)}.$$

By making determinations with acid of different concentrations, it is obviously possible to calculate by subtraction the free energy of dilution of hydrochloric acid from one concentration to another.

2. Experimental Method.

The experiments were carried out in a thermostat at 18° in cells of the form shown diagrammatically in Fig. 1, which is drawn to scale, each cell containing as a check two hydrogen and two calomel electrodes.

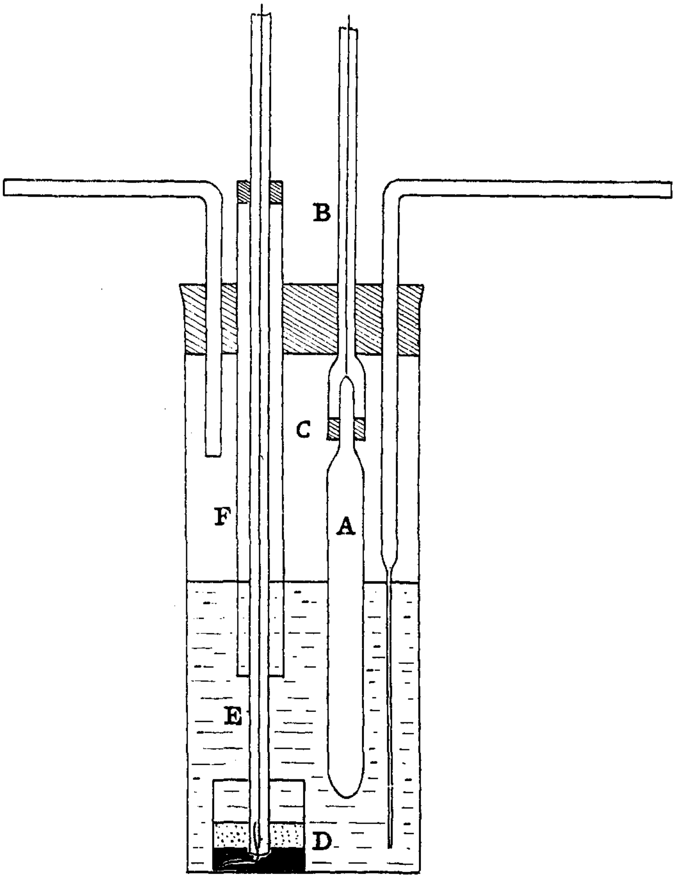

Fig. 1.

The Hydrogen Electrodes.—The hydrogen electrodes A were formed of a piece of glass tubing about 1 cm. in diameter sealed off at the lower end and drawn out above small enough to fit into the lower end of the connecting tube B. They were fastened into the connecting tube by forcing them into the central hole in the small rubber stopper C. The electrodes A were previously covered with "Glanzplatin" (W. Heraeus) and then platinized (3 grams platinum chloride, 0.025 gram lead acetate, 100 cc. H_2O, drop in potential about four volts). Connection with the electrodes was made by pouring mercury into the tube B and inserting a copper wire.

In order to obtain electrodes of sufficient constancy, it was found necessary to replatinize them at frequent intervals (after one or two runs). The platinization was continued until the electrodes had a velvety black coating (15–45 minutes). After replatinizing, the pair of electrodes were placed for purposes of cleaning in a dilute solution of sulfuric acid and made alternately anode and cathode (drop in potential four volts), the current being commutated at minute intervals for a length of time depending on the length of platinization. This treatment was completed by the commutation of the current at five-second intervals during a period of several minutes. Before use the electrodes stood at least over night in distilled water and when not in use were kept in distilled water. These electrodes were perfectly reproducible and a number of them would not vary from each other by more than 0.02–0.03 millivolts in a day.

The Hydrogen Generator.—The hydrogen used was generated electrolytically from a strong caustic solution in a generator of the type described by Bodenstein.[1] The electrodes were of nickel wire.

In order to remove possible traces of oxygen, the gas was passed before use through a tube containing a platinum wire heated to incandescence by an electric current.[2] The stream was passed through a wash bottle filled with distilled water, then bubbled from a fine capillary through acid of the same concentration and temperature as that in the cell, and finally allowed to bubble from a fine capillary through the solution surrounding the platinized electrodes and escape through a tube into the air. After the cell had been in operation for a few hours it was found advantageous to change the flow of hydrogen so as to pass over the solution instead of bubbling through it, and this was uniformly done.[3] The hydrogen entered the cell at a rate corresponding to about 40–50 bubbles, the size of a pea, per minute. When the two hydrogen electrodes in the same cell differed considerably from one another, it was sometimes possible to bring them together by shaking them or shaking the cell as a whole.

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[1] Bodenstein and Pohl, *Z. Elektrochem.*, 11, 373 (1905).

[2] In general, however, when the current was shut off from the wire, the authors were able to detect no difference in the electromotive force.

[3] Some very peculiar effects connected with the bubbling of hydrogen are now being investigated by one of the writers.

In general, when this was done attention has been called to the fact in the statement of the experimental results.

The Calomel Electrodes.—For the two calomel electrodes the materials were placed in small crystallizing dishes one inch in diameter by one inch deep (see Fig. 1, D). The electrodes for the whole series of measurements were prepared from the same batch of materials—redistilled mercury and Baker & Adamson's analyzed calomel serial No. 3772. New electrodes were prepared for each run on the day the run was started. Mercury and calomel were mixed together without grinding to form a paste with a little of the solution and then stirred with a larger amount of solution. In order to obtain constant electrodes, it was found necessary to use considerable depth of calomel especially in the more dilute solutions. Connection with the electrodes was made with the help of platinum wires sealed into a connecting tube (see Fig. 1, E) in which mercury and a copper connecting wire could be placed. The connecting tubes entered the cell inside the larger tubes F, to permit stirring without loss of hydrogen, which was found, however, to be unnecessary. Small potential differences were found between connecting tubes even when they dipped into the same mercury. This was specially noticeable if one of the platinum wires was cut off short. For use, connecting tubes were chosen which showed practically no potential difference (0.02–0.03 millivolts). The reproducibility of the calomel electrodes was nearly as good as that of the hydrogen electrodes.

The Electrical Apparatus.—The electromotive forces were measured with an Otto Wolff 15,000 ohm potentiometer and suitable galvanometer. A Weston cell No. 2041 was used as a standard and was kept in the same thermostat in which the measurements were carried out.

The Hydrochloric Acid.—An approximately fifth normal stock solution of hydrochloric acid was prepared by dilution with conductivity water from Baker & Adamson's analyzed hydrochloric acid C. P. and its concentration determined by precipitation of AgCl (five analyses, Cl_2 per 1000 grams solution 7.259, 7.265, 7.266, 7.262, 7.263).

The solutions used for measurement were 0.1 *N*, 0.02 *N*, 0.01 *N* and 0.002 *N* and were made from a weighed quantity of the stock solution by dilution at 18°, using one liter, 500 cc. and 100 cc. flasks. The flasks were carefully calibrated with standardized weights.

3. The Experimental Results.

Without a critical examination of the experimental data, it is impossible to judge of the value of a series of electromotive force measurements which pretend to more than superficial accuracy. The potentials of electrodes are always somewhat variable, and in the case of continuous-flow gas electrodes an additional complication is introduced by the possibility of a progressive change in the constitution of the solution.

TABLE I.

					0.1 *N*.		0.02 *N*.		0.01 *N*.			
No.	Date.	Time.	Temp.	Bar.	A.	B.	A.	B.	A.	B.	0.02*N*–0.1*N*.	0.01*N*–0.1*N*.
1	June 15	1.30 P.M.	....	....	39594	39600	47097	47059	50749	50[illegible]75	....	....
2		3.00	18.1	733.1	628	628	7152	7160	658	658	....	....
3		4.00	18.1	33.1	633	641	7164	7176	634	638	....	....
4		5.00	18.0	33.1	632	642	7151	7147	614	616	....	....
5		6.30	18.0	33.1	643	650	7140	7133	604	605	....	....
6		8.00	18.1	33.1	611	608	7116	7000	579	578	....	....
7		9.00	18.0	33.3	603	608	7095	7090	566	570	....	....
8		10.00	18.1	33.5	600	610	7089	7090	562	564	....	....
9	June 16	9.00 A.M.	18.1	33.5	574	585	7010	7040	521	514	7445	10938
10		10.00	18.0	33.5	577	590	7001	7032	518	513	33	34
11		11.00	18.0	33.5	579	593	7000	7039	519	519	34	33
12		11.30	....	....	573	573	7010	7022	515	505	43	37
13		12.00	18.0	33.5	578	579	7011	7012	516	506	33	32
14		1.00 P.M.	18.0	33.5	577	583	7013	7030	520	507	45	37
15		2.00	....	....	577	577	7013	7030	512	510	45	34
16		3.00	18.1	33.1	585	582	6994	7003	522	521	15	38
17		4.30	18.1	....	578	589	7000	7013	526	518	23	38
18		6.00	18.0	33.1	577	578	7039	7048	512	506	66	31
19		9.30	18.0	34.5	590	590	7036	7079	509	508	68	19
20	June 17	8.00 A.M.	18.0	33.5	588	591	6997	7040	515	506	29	21
21		5.00 P.M.	18.0	33.4	574	586	6984	7026	505	499	25	22
22		9.30	18.0	33.8	558	577	6986	7023	501	499	37	32
23	June 18	9.30 A.M.	17.9	36.2	560	558	6989	7009	469	465	40	08
24		9.30 P.M.	18.0	36.2	596	598	6994	7036	508	502	18	08
										Average,	7437	10930

Remarks:

Cell started June 15, 12 M.

Hydrogen changed to flow over the solution at 6.30 P.M.

Observation No. 11, cell containing 0.01 *N* solution was shaken after the reading had been taken.

Observation No. 14, upon shaking, the reading, B, in 0.1 *N* solution became 39577.

Observation No. 16, all the cells were shaken after the reading was taken.

TABLE II.

					0.1 *N*.		0.02 *N*.		0.01 *N*.			
No.	Date.	Time.	Temp.	Bar.	A.	B.	A.	B.	A.	B.	0.02*N*-0.1*N*.	0.01*N*-0.1*N*.
1	June 19	4.30 P.M.	18.0	735.4	39630	39622	47332	47326	50687	50634	....	....
2		5.00	18.0	35.4	619	613	270	263	620	606	....	....
3		5.45	18.1	35.4	613	611	243	243	600	588	....	....
4		8.00	17.9	35.6	585	587	214	213	521	519	....	....
5		10.00	18.0	36.0	580	583	208	207	504	509	....	....
6	June 20	9.00 A.M.	18.1	36.7	564	557	177	171	467	471	7613	10908
7		10.00	18.0	36.7	563	561	174	175	459	465	13	900
8		11.00	18.0	36.8	562	562	169	174	455	461	10	896
9		12.00	17.9	36.8	562	562	169	174	454	460	10	95
10		1.00 P.M.	18.1	36.8	553	560	167	174	453	451	14	95
11		3.00	17.9	36.8	550	556	160	164	448	436	09	89
12		4.00	17.9	36.4	554	555	152	168	446	439	05	88
13		5.30	18.1	36.4	565	565	158	174	465	451	01	93
14		8.45	18.3	38.5	563	574	165	183	471	455	....	....
15	June 21	8.30 A.M.	19.1	40.8	603	600	195	219	520	536	....	....
16		9.30	18.0	40.8	559	569	160	166	454	456	7599	91
17		10.30	18.0	40.6	556	570	161	168	459	460	7602	97
18		12.00	18.0	40.0	556	562	148	169	460	457	00	900
19		1.00 P.M.	18.0	39.6	553	563	163	167	456	448	07	894
20		2.30	18.0	39.5	553	566	167	173	458	437	10	88
21		3.30	18.0	38.9	566	566	169	169	456	456	03	90
										Average,	7607	10895

Remarks:

Cell started June 19, 2.30 P.M.

Hydrogen changed to flow over the solution at 4.30 P.M.

Observations No. 14 and No. 15, these values were omitted from the calculations, owing to the poor temperature regulation.

Observation No. 17, the hydrogen electrodes in 0.1 *N* solution were shaken after the reading and then gave the values 39546 and 39547; ten minutes later they gave the values 39554, 39554.

Observation No. 18, the hydrogen electrode, A, in the 0.02 *N* solution was shaken, changing the readings to 47160, 47160.

Observation No. 20, 0.01 *N* solution was shaken at 3.00 P.M.

TABLE III.

No.	Date.	Time.	Temp.	Bar.	0.1 *N*. A.	0.1 *N*. B.	0.02 *N*. A.	0.02 *N*. B.	0.002 *N*. A.	0.002 *N*. B.	0.02*N*–0.1*N*.	0.002*N*–0.1*N*.
1	June 21	10.30 P.M.	....	....	39595	39605	(47218)	47283	59200	58990	....	....
2	June 22	9.00 A.M.	18.2	738.4	567	555	(162)	170	58400	57752	7609	18515
3		10.15	18.	....	532	547	(137)	151	8330	7800	11	25
4		11.00	18.1	37.5	542	548	(119)	161	8310	7800	16	10
5		12.00	18.2	37.0	551	553	(139)	173	....	....	21	...
6		1.30 P.M.	18.1	36.6	552	549	(143)	167	8270	7800	16	484
7		2.30	18.1	36.4	527	536	(105)	172	....	....	40	...
8		3.30	18.1	35.7	540	550	(142)	174	....	....	29	...
9		5.00	18.0	35.4	540	550	(133)	160	8290	7850	15	525
10		8.30	18.1	35.9	551	555	(129)	156	250	877	03	11
11		9.30	18.0	35.9	551	559	(124)	166	270	865	11	13
12	June 23	8.00 A.M.	18.0	35.9	555	547	(160)	168	280	960	17	69
13		9.00	18.1	35.6	547	548	(120)	160	250	935	12	45
14		10.00	18.0	35.4	552	554	(126)	155	235	915	02	22
15		12.00	18.0	35.0	552	555	(112)	156	245	923	02	30
16		1.00 P.M.	18.0	34.5	555	555	(115)	154	215	92	99	13
17		2.00	17.9	34.3	549	552	(123)	156	220	915	05	17
18		3.00	17.9	34.4	556	556	(118)	145	220	923	589	16
19		5.30	18.0	34.4	556	555	(112)	156	220	923	600	16
20		8.45	18.0	35.3	558	552	(114)	155	235	950	00	38
21		10.30	18.1	35.3	556	551	(112)	142	150	955	588	499
22	June 24	8.30 A.M.	18.0	37.5	552	554	(153)	154	205	940	601	520
23		9.30	18.0	....	552	556	(150)	156	200	940	02	16
										Average,	7609	18520

Remarks:

Cell started June 21, 5.00 P.M.

Time when hydrogen was changed to flow over the solution not recorded.

Owing to their variability, all the observations made in the 0.02 *N* solution with electrodes A were neglected in the final averages.

TABLE IV.

					0.1 *N*.		0.02 *N*.		0.002 *N*.			
No.	Date.	Time.	Temp.	Bar.	A.	B.	A.	B.	A.	B.	0.02*N*–0.1*N*.	0.002*N*–0.1*N*.
1	June 26	8.15 P.M.	....	....	39630	39625	47338	47344	59085	59305	....	....
2	June 27	9.00 A.M.	18.1	732.6	553	560	212	227	8450	8475	7663	18906
3		10.00	18.0	32.6	569	572	217	233	453	470	54	891
4		11.00	18.0	32.6	562	575	213	225	430	453	50	73
5		12.00	18.0	32.6	575	585	217	225	442	465	41	74
6		1.00 P.M.	18.0	32.8	581	593	221	231	447	471	39	72
7		2.00	18.0	32.8	578	589	221	229	413	440	41	43
8		3.00	18.0	32.8	553	552	197	197	427	436	44	79
9		5.00	18.0	32.8	564	569	188	190	416	445	22	64
10		7.30	17.9	32.8	556	562	188	189	417	427	30	63
11		10.45	18.0	....	585	587	210	220	428	449	2[illegible]	53
12	June 28	8.30 A.M.	17.9	37.5	574	571	202	206	428	424	31	53
13		10.00	18.0	37.5	576	578	213	217	435	452	38	67
14		11.00	18.0	37.5	584	58[illegible]	208	207	420	443	24	48
15		12.00	18.0	37.5	58[illegible]	585	203	206	420	448	20	49
16		1.00 P.M.	18.0	37.5	586	591	210	211	418	45[illegible]	22	45
17		2.00	17.9	37.5	584	583	204	205	412	447	19	44
18		3.00	18.0	37.7	58[illegible]	594	209	217	422	453	22	47
19		4.00	18.0	37.9	595	59[illegible]	215	228	430	464	25	50
20		5.00	18.0	38.1	592	5[illegible]	210	214	430	455	17	48
21		10.00	17.9	39.2	596	607	224	215	427	414	18	19
22	June 29	9.00 A.M.	18.0	41.5	609	611	239	240	439	475	30	47
										Average,	7632	18859

Remarks:

Cell started June 26, 5.00 P.M.

Hydrogen changed to flow over the solution at 8.30 P.M.

TABLE V.

					0.1 N.		0.02 N.		0.002 N.			
No.	Date.	Time.	Temp.	Bar.	A.	B.	A.	B.	A.	B.	0.02N–0.1N.	0.002N–0.1N.
1	June 29	5.30 P.M.	....	....	39671	39638	47390	47390	58920	58865	....	....
2		8.00	17.	741.0	635	620	290	282	556	500	....	....
3		9.30	18.0	41.0	623	614	269	261	493	450	....	....
4	June 30	8.30 A.M.	18.0	42.5	553	542	167	150	300	320	7611	18762
5		9.30	18.1	42.5	560	553	161	162	328	315	605	65
6		10.30	17.9	42.0	560	556	158	153	317	308	598	55
7		11.45	18.0	42.0	564	562	162	163	317	317	600	54
8		1.00 P.M.	18.1	41.5	561	547	178	170	326	329	20	74
9		2.00	18.1	41.5	565	543	184	174	327	327	25	73
10		3.00	18.0	41.0	560	573	188	176	320	323	15	55
11		5.00	18.0	40.6	559	571	185	171	305	315	13	45
12		11.15	18.0	40.0	553	573	190	180	316	320	22	55
13	July 1	10.00 A.M.	17.9	40.2	(535)	(408)	183	182	296	288	....	..
14		1.00 P.M.	18.1	39.1	563	(448)	194	190	300	295	29	35
15		2.30	18.0	38.9	567	(...)	195	191	315	270	26	26
16		4.00	18.0	38.4	561	(...)	199	195	305	290	36	37
17		10.00	18.1	38.4	560	(...)	200	180	320	295	30	48
										Average,	7618	18753

Remarks:

Cell started, June 29, 3.30 P.M.

Hydrogen changed to flow over the solution at 5.30 P.M.

Observation No. 13, before this observation the temperature had been very unsteady, just before the reading the 0.1 N cell had been shaken. These readings are omitted from the final average. Also, from this time on, all the readings on electrodes, B, 0.1 N solution, have been neglected on account of their abnormality.

In the preceding tables, I–V, are presented the experimental data from which our conclusions are drawn. These tables include all the measurements which were made at 18°, except one run in which the electrical connections were wrongly made so that the different cells electrolyzed each other.

It will be seen from the tables that measurements were made at the same time on three different cells containing solutions of different concentration. In the tables the first five columns give the number of the reading, the date and time when it was taken, the temperature of the thermostat and the height of the barometer. In column A for each cell is given the electromotive force in volts $\times 10^5$ between one hydrogen and one calomel electrode, and in column B the electromotive force between the other two electrodes. In all cases the calomel electrode was positive.

In each set of measurements cell No. 1 contained 0.1 *N* acid. The last two columns of each table give the difference between the average electromotive force in the 0.1 *N* acid and the average found for the two weaker acids. The electromotive force in any one cell is dependent on the barometric height, since that determines the pressure of the hydrogen supplied to the electrodes. If, however, the different cells respond equally quickly to changes in barometric height it is evident that the differences in electromotive force recorded in the last two columns should be independent of the barometric reading.[1] These differences multiplied by the value of Faraday's equivalent in coulombs give in joules the free energies of dilution of hydrochloric acid from tenth-normal concentration to the other dilutions.

As is to be expected, it will be seen from the tables that the electromotive forces are most reproducible in the more concentrated solutions. It will also be noticed that the electromotive force of the cells tends to fall pretty rapidly for several hours after the cell is set up and then usually remains reasonably constant for two or more days. In obtaining the final averages the writers have arbitrarily started with the readings obtained on the morning of the day after the cell was set up. Any readings omitted from the final averages are indicated in the notes accompanying the tables.

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[1] Under favorable conditions, the authors have had no difficulty in observing the connection between barometric height and the electromotive force of the hydrogen electrode, the variations in electromotive force being of the calculated order of magnitude, but in general lagging somewhat behind the barometric changes. A further advantage of always measuring a cell containing 0.1 *N* acid along with the other concentrations lies in the practical elimination of errors, due to changes in the electromotive force of the standard cell. Any errors in the electromotive force of the standard cell produce an equal percentage error in each of the electromotive forces measured. Since these electromotive forces are, however, of the same order of magnitude the error from this source in their difference is negligible.

In the final averages it did not seem necessary to make any allowance for the fact that the readings were not taken at equal intervals of time.

It should be specially noticed that after the readings have become constant (*i. e.*, beginning with the day following the setting up of the cell), no systematic tendency appears for the electromotive forces to vary either upward or downward. In an extensive series of measurements which the authors had previously made at 25°, the electromotive forces showed a continued and decided tendency to decrease, especially in the more dilute solutions. In these earlier measurements, however, instead of changing the hydrogen so as to flow over the solution it was bubbled through the solution during the whole run. The cells were arranged, moreover, with the hydrogen and calomel electrodes in the separate arms of an H tube. The constancy of the measurements reported appears to be quite satisfactory.

Table VI summarizes the average values found in each set of measurements for the difference between the electromotive force in the 0.1*N* solutions and the more dilute solutions. The final averages for all the sets of measurements are also presented together with the average deviation from the mean. Owing to the wide deviation, the bracketed value has been omitted entirely from the calculations. An examination of the table will afford an idea of the reproducibility of the measurements.

Table VI.—Differences between E. M. F. in 0.1 *N* Solution and Dilute Solution.

	0.02 *N*–0.1 *N*.	0.01 *N*-0.1 *N*.	0.002 *N*–0.1 *N*.
	(0.07437)	0.10930	0.18520
	0.07607	0.10895	0.18859
	0.07609	.....	0.18753
	0.07632	.....	.....
	0.07618	.....	.....
Average,	0.07617 ±0.00009	0.10913 ±0.00018	0.18711 ±0.00127

The value in joules for the free energy of dilution, $\Delta F_{dil.}$, from 0.1 *N* to the more dilute solutions (of concentration C′) have been obtained by multiplying the final average differences in electromotive force by the value of Faraday's equivalent, 96580 coulombs. These values are represented in the second column of Table VII. The free energies of dilution are, of course, all negative.

4. The Fugacity of Hydrochloric Acid.

Accurate data on the free energy of dilution of an electrolyte are chiefly valuable for their bearing on the problem of ionic dissociation. Employing the well adapted conceptions introduced by Lewis[1] in his system

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[1] Lewis, *Proc. Amer. Acad.*, **37**, 49 (1901); *Ibid.*, **43**, 259 (1907); *Z. physik. Chem.*, **38**, 205 (1901); *Ibid.*, 61, 129 (1907). In the second of the above articles, Professor

of thermodynamic chemistry let us represent the fugacity of undissociated HCl in 0.1 *N* solution by the symbol f_{HCl}, and its fugacity in other concentrations under consideration by f'_{HCl}. Similarly, f_{H}^{+}, f_{Cl}^{-}, f'^{+}_{H} and f'^{-}_{Cl} will represent the fugacities of the ions. If $\Delta F_{\mathrm{dil.}}$ is the free energy change accompanying the transfer of one mol of hydrochloric acid from the 0.1 *N* solution to one of the more dilute solutions, we may write the following evident relation,

$$-\Delta F_{\mathrm{dil.}} = \mathrm{RT} \ln \frac{f_{\mathrm{HCl}}}{f'_{\mathrm{HCl}}} = \mathrm{RT} \ln \frac{f_{\mathrm{H}}^{+} f_{\mathrm{Cl}}^{-}}{f'^{+}_{\mathrm{H}} f'^{-}_{\mathrm{Cl}}}$$

Further, since C_{H}^{+}, the concentration of hydrogen ion in any solution, is equal to C_{Cl}^{-}, the concentration of chloride ion, we may assume $f_{\mathrm{H}}^{+} = f_{\mathrm{Cl}}^{-}$ and write

$$-\Delta F_{\mathrm{dil.}} = 2\mathrm{RT} \ln \frac{f_{\mathrm{H}}^{+}}{f'^{+}_{\mathrm{H}}}.$$

These "fugacity ratios" have been calculated from the free energy data; using the value R equals 8.3162 joules per degree, T equals 291.13°, and are given in columns four and six of Table VII. In these columns are also presented the deviations produced in the "fugacity ratios" by the average deviations from the mean electromotive forces given in Table VII.

TABLE VII.

C′.	E. M. F.	—ΔF.	$f_{\mathrm{HCl}}/f'_{\mathrm{HCl}}$.	$C_{\mathrm{HCl}}/C'_{\mathrm{HCl}}$.	$f_{\mathrm{H}^+}/f'_{\mathrm{H}^+}$.	$C_{\mathrm{H}^+}/C'_{\mathrm{H}^+}$.
0.02 *N*	0.07617	7356.5	20.9 ± 0.1	7.76	4.57 ± 0.01	4.78
0.01 *N*	0.10913	1054.0	77.7 ± 0.3	17.3	8.82 ± 0.03	9.49
0.002 *N*	0.18711	1807.1	174.4 ± 9.1	112.5	41.8 ± 1.1	46.7

In general, it has been found for dilute solutions of non-electrolytes, and weak electrolytes, that the "active mass" or fugacity of the substances present is proportional to their concentration.[1] For this reason we have calculated from conductivity measurements, and presented in Table VII for comparison the ratios of the concentration of undissociated HCl in 0.1 *N* acid to that in the more dilute solutions, as well as the ratios of the concentration of hydrogen ion in 0.1 *N* solution to that in the more dilute solutions.

In calculating these concentration ratios, we have used the conductivity measurements of Kohlrausch[2] employing for Λ_0 the value 396 obtained

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Lewis has definitly stated as a problem for research the determination of the relation between the concentration and fugacity (activity) of the components of an electrolytic solution. This article is a contribution to the quantitative solution of that problem. The fugacity of a substance and its activity, *a*, are connected by the equation $f = a\mathrm{RT}$. Hence, the ratios for the fugacities of HCl and H^+, given above, are the same as the corresponding activity ratios.

[1] See Lewis, THIS JOURNAL, 30, 673 (1908).

[2] Landolt and Börnstein.

from the work of Noyes and Sammet.[1] The ratio of the concentrations of the undissociated acid in the two solutions was calculated from the evident expression,

$$\frac{C_{HCl}}{C'_{HCl}} = \frac{\lambda_0 - \lambda}{\lambda_0 - \lambda'} \frac{n}{n'},$$

where λ and λ' are the equivalent conductances of the two solutions of normality n and n'. The ratio of hydrogen ion in the two solutions was calculated from the equation,

$$\frac{C_{\overset{+}{H}}}{C'_{\overset{+}{H}}} = \frac{\lambda}{\lambda'} \frac{n}{n'}.$$

Referring now to Table VII, we notice wide discrepancies between the fugacity ratios and the concentration ratios of the undissociated acid as well as smaller but real differences between these ratios for the ions.[2]

If we assume that calculations from conductivity measurements give true values for the degree of dissociation of a "strong" electrolyte, we can not further explain these discrepancies exhibited by the ratios in Table VII, but must merely state that for "strong" electrolytes, *even in dilute solutions*, the fugacity of the ions is not strictly proportional to their concentration, while the fugacity of the undissociated electrolyte is very far from proportional to its concentration.

The remarkable nature of this result, however, may well be emphasized, since for all ordinary solutions, including even those of "weak" electrolytes, fugacity and concentration have been found closely proportional over wide ranges of concentration.[3] In fact, this apparent deviation, for solutions of "strong" electrolytes from the laws obeyed by all other solutions, must cause us to regard with great suspicion the calculation of ionic concentration from conductivity measurements in the usual manner. Such calculations assume in general that the ions move with

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[1] Noyes and Sammet, THIS JOURNAL, 24, 944 (1902).

[2] Before doing this work at 18°, the authors carried out an extensive series of measurements at 25° with solutions of concentrations 0.2, 0.1, 0.02, 0.01 *N*. These measurements were made in cells less well adapted to the purpose than the ones described above and the electromotive forces measured were more variable. Nevertheless, the computations led in every instance to similar differences between the fugacity and concentration ratios. Jahn, using KCl, NaCl and HCl solutions, also obtained similar differences for the ions between the concentration ratios as calculated from conductivity and electromotive force measurements. His data might also have been employed for calculating the fugacity ratios for the undissociated part of the electrolyte. A result of this nature was to be expected because of the well known deviations from the Ostwald dilution law shown by strong electrolytes when their degree of dissociation is calculated from conductivity measurements. That the discrepancies for the ions should be less than for the undissociated part of the electrolyte is to be expected from the approximate validity of the principle of solubility product. See also Lewis, *loc. cit.* For other examples of such deviations see Lewis and von Ende, THIS JOURNAL, 32, 737 (1910). Bray and MacKay, THIS JOURNAL, 32, 930 (1910); 32, 1213 (1910).

[3] Lewis, THIS JOURNAL, 30, 668 (1903).

the same velocity under unit potential gradient in solutions of all different concentrations. The validity of this assumption was denied by Jahn,[1] who explained his results by assuming increased speed with increased concentration. It is greatly to be hoped that further investigation will throw light upon the actual facts.

In later articles one of the authors will present a method of calculating relative degrees of ionization from conductivity and transference data without assuming that the ions move with the same velocity at different dilutions.[2] Methods will also be presented of calculating the free energy of dilution from freezing-point and vapor-pressure data.

The experimental work described in this article was done in the chemical laboratory of the University of Michigan.

CINCINNATI. OHIO, AND ANN ARBOR. MICH.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE THERMAL DISSOCIATION OF BARIUM PEROXIDE.

BY JOEL H. HILDEBRAND.

Received January 15, 1912.

Introduction.

The equilibrium between barium oxide, peroxide and oxygen has a technical interest due to the use of barium peroxide in the preparation of hydrogen peroxide, and in the historic, though now almost abandoned, Brin process for oxygen. It must also share in the general interest given to all heterogenous equilibria by the discussion of the applicability to them of Nernst's heat theorem.[3] In addition to the researches of Boussingault and others on this equilibrium we have the measurements of Le Chatelier[4] of the dissociation pressures between 525° and 790°. In view of the discrepancies between later work and that of Le Chatelier, and the desirability of exact knowledge of this equilibrium, the following work was undertaken. Since its completion the writer has discovered a thesis by Wilhelm Becker, "Zur Frage der Erdalkaliperoxydbildung,"[5] to which reference will be made in the discussion of the results of this work.

Apparatus.

The accuracy of measurements of this sort depends greatly upon the accuracy with which the temperature can be maintained and measured.

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[1] See note, p. 245.

[2] The possibility of combining transference and conductivity measurements for calculating the degree of dissociation of electrolytes was suggested to the writer by Professor Lewis.

[3] Foote and Smith, THIS JOURNAL, **30**, 1344. Walden, *Ibid.*, 1350. Johnston, *Ibid.*, 1357.

[4] *Compt. rend.*, **115**, 655 (1892).

[5] *Prag.*, 1909. (Work done at Karlsruhe.)