$^1/_2H_2 + ^1/_2N_2 + O_2 = HNO_2(aq)$.—Combining Equations 21 and 19, and taking once more the free energy of formation of H^+ equal to zero, $\Delta F°_{298} = —11980$. (22)

It is to be noted that Equations 20, 21 and 22 all depend upon Equations 18 and 19, which are open to some question. It seems, therefore, extremely desirable to obtain by a different method an equation connecting the free energy of nitrate and nitrite ions. Experiments which we now have under way promise a more accurate determination of these free energies.

We wish to express our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the various compounds of nitrogen considered in this paper:

TABLE VI.

Substance.	$F°_{298}$.	Equation.	Substance.	$F°_{298}$.	Equation.
$NH_3(g)$	— 4740	1	$NO(g)$	20850	10
$NH_3(l)$	— 3490	3	$NO_2(g)$	13250	12
			$N_2O_4(g)$	25300	13*a*
$NH_3(aq)$	— 7130	5	NO_3^-	—23100	20
$NH_4OH(aq)$	—63750	7	NO_2^-	— 7410	21
NH_4^+	—19895	9	HNO_2	—11980	22

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF FORMATION OF FORMIC ACID.

BY GERALD E. K. BRANCH.

Received July 19, 1915.

Introduction.

As a first step toward the preparation of a set of free energy tables for organic substances it is important to determine the free energy of formation from their elements of a few typical organic compounds. This has been accomplished in the case of one important compound through the study of the reversible synthesis of urea by Lewis and Burrows.[1] Formic acid is another simple organic compound whose free energy of formation may be obtained by a similar method.

It is well known that formic acid decomposes on heating into carbon monoxide and water, and also that sodium formate is obtained by the action of carbon monoxide on sodium hydroxide. Preliminary experiments showed that formic acid is produced in small amounts on heating water and carbon monoxide together. It is therefore apparent that the synthesis of formic acid from carbon monoxide and water is reversible.

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[1] THIS JOURNAL, 34, 1515 (1912).

The most satisfactory condition for the accurate measurement of this equilibrium was obtained by heating dilute solutions of formic acid in closed vessels.

Experimental Method.

The apparatus consisted of a reaction tube, A, connected as shown in Fig. 1, to a capillary tube, B, in which a bulb, C, had been blown (both capillary tube and bulb being calibrated), in such a manner that it could be immersed in the vapor bath, D. To the reaction tube a small tube, E, was sealed. The apparatus was made of quartz.

Mercury was then introduced, so as to fill the connecting tube completely, the capillary tube to a graduation mark below the bulb, and the reaction tube to a height sufficient to prevent any of the solution from leaving it at the highest pressures reached. The tip of the capillary tube, which had been previously drawn out to a fine point, was quickly sealed, thus forming a manometer capable of measuring high pressures.

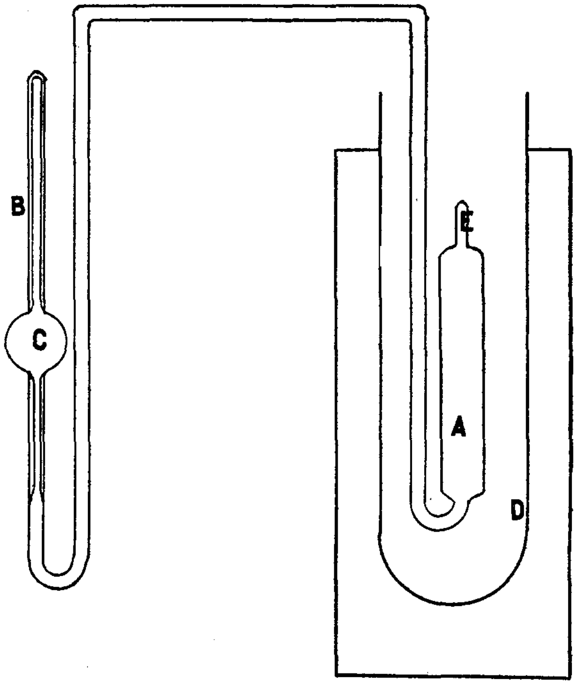

Fig. 1.

The reaction tube was filled to the top of the tube E with the reaction mixture. Some of the solution in the tube E was then rapidly boiled out, and the tube sealed off. In this way air was excluded without altering the concentration of the solution. This was tested by analyzing a sample taken from a tube which had only been sealed. It showed no detectable difference in composition from the original solution. The amount of air left could be observed as a very small bubble, and in no case could have made a measurable difference in the final pressures, as the volume of the gas space formed during the experiment was very great in comparison.

The vapor bath consisted of a large tube, well insulated on the outside with asbestos packing. The vapor at constant temperature was supplied from a pure liquid at the bottom of the tube, which was kept boiling vigorously by an electrical heater. The reaction tube was placed far down into the hot vapor, but well above the liquid. There was in no case a noticeable temperature gradient in the vapor, except at heights well above the reaction tube. Bromobenzene and naphthalene were the substances used in the bath.

The gas which was formed was collected for analysis by breaking off the point of the tube E under rubber connections.

The manometer tube was calibrated by means of a mercury thread, while the bulb was calibrated in terms of lengths of the manometer tube by weighing the mercury it could contain and comparing it to the weight of mercury contained in a known length of the manometer tube. The length of the air space was measured to a mark, and the space between this mark and the end of the tube was calibrated by means of a mercury thread. The difference in levels of the mercury column in the manometer and the reaction tube was calculated from the measured rise in the manometer tube and the fall in the reaction tube, calculated from the ratio of the diameters of the two tubes. A correction was also made for the capillary depression, which was determined by a rough experiment. The pressure of the CO was obtained by deducting the vapor pressure of the water from the total pressure.

The solutions contained known concentrations of formic acid, and in the later experiments of hydrochloric acid. These concentrations are expressed in mols per 1000 g. of solution. After the pressure was measured a weighed amount of the solution was titrated with a KOH solution, using phenolphthalein as the indicator. After each titration the KOH was titrated against a standardized solution of HCl. The difference in the concentrations of acid before and after experiment gives approximately the number of mols of CO given off per 1000 g. of solution. From this value the change in the concentration of HCl was calculated in mols per 1000 g. The concentration of the HCOOH was then obtained by difference.

Experimental Results.

Table I gives the results of an experiment in which a pure solution of formic acid was heated at 156°. It is evident that even after 14 days the reaction is still very far from equilibrium. A catalyst for the reaction was therefore sought. Hydrochloric acid was the first substance tried, with the idea that it might have the desired effect through the temporary formation of the unstable substance formylchloride. Although it is doubtful that this is the mechanism of its action, nevertheless it proved to be a very efficacious catalyst. This catalytic action is shown not only by hydrochloric acid but by all the mineral acids.

TABLE I.

Time.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 20.3°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
0	131.7	20.3°	131.65	0	75.2
10 min	24.15	19.9°	24.2	8	417
1 day	22.6	20.8°	22.6	10	448
2 days	21.8	23.0°	21.6	10	468
3 days	20.45	21.0°	20.4	12	497
4 days	19.5	18.5°	19.6	13	518
5 days	18.65	20.0°	18.65	13	543
6 days	17.95	19.6°	18.0	14	564
7 days	17.2	19.3°	17.25	15	589
8 days	16.7	23.0°	16.55	15	603
9 days	16.35	28.0°	15.95	16	627
10 days	15.75	24.8°	15.5	16	655
11 days	15.1	21.5°	15.05	17	675
14 days	13.7	19.0°	13.75	19	739

The catalytic action is shown graphically in Fig. 2, in which the two curves show the rate of development of pressure through the formation of carbon monoxide in two experiments carried out under approximately similar conditions in the presence and absence of hydrochloric acid. The curve for the reaction when HCl was absent was drawn from the data

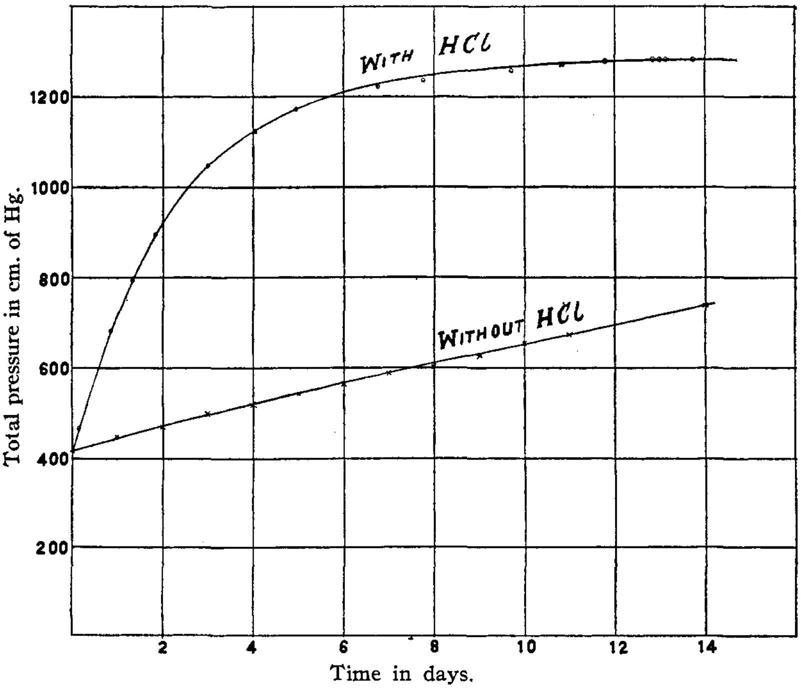

Fig. 2.

given in Table I, while the data for the other curve are given in Table II.

Tables II, III, IV, V and VI give the results obtained in the presence of HCl, and at the temperatures 156° and 218°.

Experiment 1.

TABLE II.

Temperature = 156.1°.

Time.		Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 16.9° C.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
Hrs.	Min.					
0	..	235.9	16.9°	235.9	0	74.7
3	25	40.94	16.9°	40.94	33	463
20	20	27.59	15.0°	27.77	46.5	681
31	50	23.39	13.5°	23.67	50.5	795
44	..	20.80	14.7°	20.96	53	895
72	..	17.97	20.0°	17.79	55.5	1047
119	..	15.79	17.0°	15.78	58	1175
162	30	15.04	15.5°	15.12	58.5	1224
185	..	14.87	14.8°	14.98	59	1236
233	..	14.50	13.0°	14.70	59	1258
265	..	14.99	26.2°	14.52	58.5	1272
283	..	14.52	18.0°	14.46	59	1278
308	..	14.32	14.9°	14.42	59.5	1282
312	..	14.38	16.0°	14.42	59.5	1282
315	..	14.38	16.0°	14.42	59.5	1282
330	..	14.23	13.0°	14.42	59.5	1282

The pressure at equilibrium in this experiment is taken as 1282 cm. of Hg.

The solution originally contained 0.2523 mol of formic acid and 0.4817 mol of HCl per 1000 g. of solution. After equilibrium had been reached 4.366 g. of the solution were equivalent to 58.66 cc. of a KOH solution, and 87.59 cc. of this solution were equivalent to 39.60 cc. of 0.0995 N HCl. Hence the solution contained 0.1210 mol of HCOOH and 0.4834 mol of HCl per 1000 g.

Experiment 2.

TABLE III.

Temperature = 156.1°.

Time.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 17°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
0	234.1	17°	234.1	0	75.9
6 h. 15 m.	37.81	17°	37.81	24	504
21 h. 30 m.	28.38	21.4°	27.95	43.5	680
3 d. 18 h.	17.73	16.5°	17.76	54.5	1054
4 d. 16 h.	16.88	16°	16.93	55	1105
9 d.	15.53	17°	15.53	56.5	1201
10 d.	15.16	14°	15.32	57	1217
13 d.	15.20	19°	15.10	57	1234
14 d.	15.09	17°	15.09	57	1234
15 d.	15.12	17.7°	15.08	57	1235

The pressure at equilibrium in this experiment is taken as 1234 cm. of Hg, the mean of the last three measurements.

The solution originally contained 0.3024 mol of HCOOH and 0.4801 mol of HCl per 1000 g. After the experiment 4.115 g. of the solution were equivalent to 55.07 cc. of a solution of KOH and 69.14 cc. of this solution were equivalent to 31.09 cc. of 0.0995 *N* HCl. Hence the solution contained 0.1162 mol of HCOOH and 0.4826 mol of HCl per 1000 g.

Experiment 3.

TABLE IV.

Temperature = 156.1°.

Time.	Air space in manometer in cm. in tube.	Temperature of air.	Air space calculated to 18°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
0..............	231.7	18°	231.7	0	75.65
1st day[1].........	14.91	17°	14.96	54.5	1226
2nd day.........	14.93	19°	14.88	54.5	1232
3rd day.........	14.97	20°	14.87	54.5	1233
4th day.........	14.97	20°	14.87	54.5	1233
7th day[2]........	14.51	22°	14.32	54	1278
8th day.........	14.71	21.5°	14.54	54	1260
9th day.........	14.94	22.3°	14.73	54.5	1244
11th day.........	15.16	25°	14.80	54.5	1238

The pressure at equilibrium in this experiment is taken as 1234 cm. of Hg, which is the mean of the values obtained on the 2nd, 3rd, 4th and 11th days.

The solution originally contained 0.3024 mol of HCOOH and 0.4801 mol of HCl per 1000 g. After the experiment 3.915 g. of the solution were equivalent to 45.10 cc. of a KOH solution, 38.30 cc. of which were equivalent to 20.00 cc. of 0.0995 *N* HCl. Hence the solution contained 0.1159 mol of HCOOH and 0.4826 mol of HCl per 1000 g.

Experiment 4.

TABLE V.

Temperature = 217.9°.

No. of reading.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 22.4°. Cm.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
Original.......	616.1	22.4°	616.1	0	75.2
1st[3]...........	12.03	18.4°	12.20°	44	3842
2nd...........	12.03	18.6°	12.19	44	3845
3rd...........	12.02	19°	12.16	44	3854
				Mean,	3847

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[1] The preliminary heating was done in a cumene bath boiling at 163°.

[2] The tube had been heated in the cumene bath during the 6th day so that the equilibrium might be approached from both directions in this experiment.

[3] The first reading was taken 4 hrs. after the mercury had become approximately stationary, and the three readings were taken over a period of three hours.

The solution originally contained 0.3024 mol of HCOOH and 0.4801 mol of HCl per 1000 g. After the experiment 0.6309 g. of the solution were equivalent to 26.56 cc. of a KOH solution, 85.14 cc. of which were equivalent to 11.63 cc. of 0.0995 *N* HCl. Hence the solution contained 0.0893 mol of HCOOH and 0.4829 mol of HCl per 1000 g.

Experiment 5.

TABLE VI.

Temperature = 217.9°.

No. of reading.	Air space in manometer in cm. of tube.	Temperature of air.	Air space calculated to 25°.	Difference of mercury levels in cm.	Total pressure in cm. of Hg.
Original.......	619	25°	619	0	75.2
1st...........	15.02	23.1°	15.12	46	3125
2nd...........	14.94	21.9°	15.10	46	3129
3rd...........	14.90	21.0°	15.10	46	3129
4th...........	14.89	21.2°	15.08	46	3133
5th...........	14.94	21.8°	15.10	46	3129
				Mean,	3129

In this experiment the concentration of formic acid was determined directly by oxidation in an alkaline solution with excess of $KMnO_4$.

An excess of a standard solution of sodium oxalate was then added, and the solution acidified with sulfuric acid. The excess of $KMnO_4$ was titrated with the $KMnO_4$ solution, which was standardized against the oxalate solution.

After the experiment 1.213 g. of the solution were analyzed by the above method. 68.13 cc. of the $KMnO_4$ were added when 20.03 cc. of a 0.01 *N* sodium oxalate solution were used. 38.99 cc. of the $KMnO_4$ solution were equivalent to 20.03 cc. of the 0.01 *N* sodium oxalate. Hence the concentration of the HCOOH was 0.06170 mol per 1000 g. of solution. The original concentrations of HCl and HCOOH were the same as in the previous experiment, hence the concentration of HCl is 0.483 mol per 1000 g.

The partial pressure of CO were obtained by deducting the partial pressure of water from the total pressure. The pressures of HCOOH and HCl are negligible.[1] The water vapor was considered as that of a solution containing 1 mol[2] of foreign substance in 1000 g. of water. It can then be calculated by Raoult's law, $p = p_0 N_1$, where p is the partial

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[1] The partial pressure of HCOOH calculated from its partial pressure at 25°, given in this paper, was less than 0.1 cm. at 218°. The partial pressure of HCl over a 0.4 *N* solution at 218°, calculated from experiments at 100° given by E. G. Pierce (*J. Ind. Eng. Chem.*, Vol. 7, No. 3, p. 258), is 0.4 cm.

[2] This value cannot be calculated exactly owing to the lack of data for the degree of ionization of HCl at these temperatures; but an error of 10% corresponds to errors in the pressures of only 1 and 4 cm. of Hg at the lower and higher temperatures, respectively.

pressure of water over the solution, p_0 the vapor pressure of pure water, and N_1 the molal fraction of the water. $p_0 = 419$[1] cm. of Hg at 156.1° and 1668[1] cm. of Hg at 217.9°, $N_1 = 0.982$. Hence $p = 412$ cm. and 1638 cm. at the lower and higher temperatures, respectively.

The results of these experiments are given in Table VII. K, given in the sixth column, is the equilibrium constant of the reaction $HCOOH_{1M} = H_2O_{\text{liquid}} + CO$. It is the pressure of the CO in atmospheres, divided by the concentration of the HCOOH, and multiplied by the ratio of the fugacity of the water to the fugacity of pure water.[2] The concentrations in this table are all expressed in mols per 1000 g. of water.

Table VII.

Expt.	Temperature.	Concentration of HCl in mol per 1000 g. of H_2O.	Concentration of HCOOH in mol per 1000 g. of H_2O.	Pressure of CO in atmospheres.	K.
1.........	156.1°	0.4949	0.1239	11.45	90.8
2.........	156.1°	0.4940	0.1189	10.82	89.3
3.........	156.1°	0.4940	0.1186	10.82	89.6
4.........	217.9°	0.4936	0.0913	29.06	313
5.........	217.9°	0.494	0.06299	19.62	306

Mean value of K = 89.9 at 156.1° and 310 at 217.9°.

The reaction was shown to reach true equilibrium by heating at a higher temperature and so forming a higher pressure of CO. On heating again at the original temperature the pressure returned to the original value. This is shown in Table IV.

The reaction $HCOOH = H_2O + CO$ goes with no appreciable side reactions, as the gas formed is shown by the following analyses to be almost pure CO:

One sample of the gas collected from the reaction at 156.1° measured 12.18 cc. before absorption of the CO_2, and 12.18 cc. after absorption.

Another sample measured 12.65 cc. before absorption and 12.70 cc. after absorption of the CO_2. 6.1 cc. of this gas were made up to 14.40 cc. with oxygen and exploded. After explosion the volume was 11.35 cc. After absorbing the CO_2 formed the volume was 5.35. This corresponds to 98.4% CO and 0.5% H_2. Slight admixture with air took place from the air in the rubber connections.

The gas obtained when the reaction was carried on at 217.9° also showed no decrease of volume on absorption with KOH. 36.72 cc.[3] of a mixture of the gas and air were exploded. After the explosion the volume was 33.00 cc. After absorption of the CO_2 formed, the volume was 25.62

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[1] Landolt-Börnstein-Roth, "Tabellen," 4th ed., p. 363.

[2] This ratio is taken as equal to the molal fraction, 0.982.

[3] No measurement of the original volume was made as there was considerable accidental admixture with the air during the collection of the gas.

cc. These results correspond to the theoretical values for a **mixture** of 1 mol of CO to 0.003 mol of H_2.[1]

Free Energy at 25°.

The value of K at 25° C., or 298° A, was calculated from the equation $\ln K_2/K_1 = Q/R\ (1/T_1 - 1/T_2)$, where Q is the heat absorbed at constant pressure. This equation is only approximately true, as it assumes Q to be constant over the range of temperature considered. Substituting the values for K at 156.1° and 217.9°, and 1.989 for R, and 429.2 and 491 for T_1 and T_2, respectively, we get $\ln 310/89.9 = Q/1.989\ (1/429.2 - 1/491)$. Hence $Q = 8394$.[2] Similarly, $\ln 310/K_{298} = 8394/1.989\ (1/298.1 - 1/491)$. Hence $K_{298} = 1.19$.

ΔF_{298} for the reaction HCOOH (1 *M*) = $H_2O(l) + CO(g)$ is given by the equation $\Delta F_{298} = -RT \ln K_{298}$, where $K_{298} = 1.19$. Hence $\Delta F_{298} = -1.989 \times 298.1 \times \ln 1.19 = -103$ cals. ± 40 cals.

This is the free energy when the concentration of HCOOH is an idealized one mol per 1000 g. of water, and in a solution containing about 0.49 mol of HCl per 1000 g. of water. However, an actual solution of HCOOH of such a concentration is very nearly ideal. This can be shown by its agreement with Washburn's equation for the lowering of freezing points in aqueous solutions, $N = 0.0096895(\Delta T - 0.00425\,\Delta T^2)$, where N is the molal fraction and ΔT the depression of the freezing point. This equation holds only when the solution is sufficiently dilute to be considered ideal. For formic acid when the concentration is 1.023 mols per 1000 g. of water, $\Delta T = 1.877$ and $N = 0.0181$,[3] while from the formula $N = 0.01804$.

Fugacity of the Formic Acid.

In order to obtain ΔF for the decomposition of liquid formic acid it is necessary to know the ratio of the fugacities of HCOOH in a solution of 1 mol to 1000 g. of water and in liquid formic acid. This was done by measuring the vapor pressure of formic acid over a solution identical with those used in the preceding experiments, except that the concentration of formic acid was increased in order to give a higher experimental accuracy.

The vapor pressure was obtained by bubbling a measured volume of air through a series of six tubes of the solution containing glass beads. These tubes were each connected to a larger bulb containing about 100 cc. of the solution so as to prevent any change in the concentration. The

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[1] The small amounts of hydrogen given by these analyses were neglected, as they are probably chiefly errors in the analysis.

[2] On account of the extremely contradictory values obtained calorimetrically for the heat of formation of formic acid it, seemed inadvisable to attempt to use them in this calculation.

[3] Abegg, *Z. physik. Chem.*, 15, 218 (1894).

HCOOH was absorbed in KOH and determined by oxidation with $KMnO_4$, and the excess of $KMnO_4$ determined with sodium oxalate in acid solution. A tube containing cotton wool was placed between the solution and the absorbing bulbs to keep back the spray. Two determinations were made.

The solution used contained 0.508 mol of HCl and 0.8505 mol of HCOOH per 1000 g. of water. In the first determination the volume of gas was 18330 cc. 43.57 cc. of 0.01 *N* sodium oxalate and 51.22 cc. of $KMnO_4$ were needed. 45.02 cc. of the oxalate were equivalent to 42.82 cc. of the $KMnO_4$ solution. The formic acid was therefore equivalent to 10.28 cc. of 0.01 *N* sodium oxalate. Hence 0.0000514 mol of HCOOH passed over. This represents a partial pressure of HCOOH of 0.00522 cm. of Hg. The molal fraction of HCOOH in this solution is 0.01495, while that of the solution containing 1 mol of HCOOH and 0.49 mol of HCl per 1000 g. of water is 0.01754. The partial pressure of HCOOH over the latter solution would be 0.00612 cm. of Hg.

In the second experiment, using the same solution, the volume of gas was 17540 cc. 68.75 cc. of $KMnO_4$ and 32.81 cc. of 0.01 *N* sodium oxalate were needed. 33.05 cc. of the oxalate solution were equivalent to 53.15 cc. of the $KMnO_4$ solution. This corresponds to 0.0000497 mol of HCOOH, or a partial pressure of 0.00527 cm. of Hg, corresponding to 0.00618 cm. of Hg for a solution 1 mol per 1000 g. The mean value is 0.00615 cm. of Hg.

The ratio of the fugacities of HCOOH in this solution to that in liquid HCOOH is equal to the ratio of partial pressures of HCOOH. For liquid HCOOH the partial pressure is 4.25 cm. of Hg at 298°.[1]

ΔF_{298} for the change $HCOOH(l) = HCOOH\ (1\ M)$ is therefore $-RT \ln 4.25/0.00615 = -3876 \pm 10$ cals.

Free Energy of Formation of Formic Acid.

Since for the reaction $HCOOH(l) = HCOOH(1\ M)$ $\Delta F_{298} = -3876$ cals., and for $HCOOH(1\ M) = H_2O(l) + CO$, $\Delta F_{298} = -103$ cals. For the reaction $HCOOH(l) = H_2O(l) + CO$, $\Delta F_{298} = -3979 \pm 50$ cals., or for $H_2O(l) + CO = HCOOH(l)$, $\Delta F_{298} = 3980$ cals.

The change of free energy for the formation of H_2O and for CO from their elements have been calculated by Lewis and Randall,[2] ΔF_{298} for the reaction $H_2 + {}^1/{}_2O_2 = H_2O(l)$ is -56620 cals., and for $C_{\text{graphite}} + {}^1/{}_2O_2 = CO$, $\Delta F_{298} = -32560$. Hence for the reaction $C_{\text{graphite}} + H_2 + O_2 = HCOOH(l)$, $\Delta F_{298} = -85200$ cals.

Summary.

The decomposition of formic acid into carbon monoxide and water was found to be reversible, and to be catalysed by mineral acids.

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[1] Landolt-Börnstein-Roth, "Tabellen," 4th ed., p. 817.

[2] THIS JOURNAL, **37**, 466 (1915).

The equilibrium between carbon monoxide and water on the one hand, and formic acid dissolved in water containing hydrochloric acid on the other, was measured at 218° C. and at 156° C. The partial pressure of formic acid from a similar solution was also measured.

From these data, and those given by G. N. Lewis and M. Randall for the free energies of carbon monoxide and water, the free energy of formic acid was calculated.

In conclusion, I wish to express my indebtedness to Professor G. N. Lewis for valuable suggestions and assistance in the prosecution of this research.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY. OF THE TULANE UNIVERSITY OF LOUISIANA.]

THE PHENOMENON OF PASSIVITY IN CONNECTION WITH FERROUS ALLOYS OF DIFFERENT COMPOSITION AND STRUCTURE.[1]

BY HAL WALTERS MOSELEY.

Received July 12, 1915.

Introduction.

The literature dealing with the phenomenon of passivity of iron has very little to say about the chemical composition of the samples used in the experiments and nothing to say about their physical structure. A careful examination of iron and steel from a metallographical point of view reveals the fact that there is a tremendous difference in its character, due to slight changes in chemical composition and to the method of treatment, whether mechanical or thermal or both.[2] The physical structure of a sample is dependent upon, and greatly influenced by, each of these factors. The study of its physical structure more often gives a sample's character than an ultimate chemical analysis, and it is therefore highly important that this factor be given due consideration in any study made upon commercial irons and steels. We were led to believe, therefore, that many of the apparently conflicting results recorded in experiments upon the passivity of iron and steel were due in part, at least, to the indistinct understanding of the nature of these differences, and that a study of the influence of these variables, if any, upon the phenomenon in a comparative way might lead to a more general conclusion as to its character.

The fact that iron will become passive has suggested at least a possible solution to the problem of corrosion. Cushman[3] in a comparatively

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[1] A paper read before the Section of Inorganic and Physical Chemistry, American Chemical Society, at the New Orleans meeting, April 2, 1915.

[2] Sauver, "Metallography of Iron and Steel," 1912.

[3] Cushman and Gardiner, "Corrosion and Preservation of Iron and Steel;" Cushman, U. S. Dept. Agric., *Bull.* 30, 29 (1907).