[Contribution from the Chemical Laboratory of the University of California.]

THE FREE ENERGY OF NITROGEN COMPOUNDS.

By Gilbert N. Lewis and Elliot Q. Adams.

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No other forms of elementary nitrogen are known to exist except the gas N_2 and its liquid and solid modifications. As in the case of oxygen and hydrogen, we shall postpone, for the present, the calculation of the free energy of liquid and solid nitrogen. Undoubtedly, at very high temperature, nitrogen would dissociate into the monoatomic gas, but it has been shown by Langmuir[1] that at 3500° A, a temperature at which hydrogen is largely monoatomic, nitrogen at atmospheric pressure shows no sign of dissociation, although dissociaton to the extent of 5% would have been noticeable.

Concerning a large number of the important compounds of nitrogen, we have information which enables us to calculate their free energies. Of the oxides there is only one, N_2O, which enters into no known reversible reaction which permits the calculation of its free energy. In the case of N_2O_3 and N_2O_5 equilibria are known which would permit the calculation of the free energy, but these have not yet been sufficiently studied. Of the compounds of hydrogen and nitrogen only one has been sufficiently investigated, namely, ammonia.

Ammonia.

$\mathbf{{}^3/_2H_2 + {}^1/_2N_2 = NH_3(g)}$.—The equilibrium between ammonia and its elements has been fully studied, chiefly in the laboratories of Haber and of Nernst. The most recent and reliable investigations are those of Jost[2] and of Haber and Le Rossignol.[3] The data obtained by these investigators will be considered after we have obtained the general free energy equation.

From the specific heat formulae given by Lewis and Randall,[4]

$$H_2;\ C_p = 6.50 + 0.0009T$$
$$N_2;\ C_p = 6.50 + 0.0010T$$
$$NH_3;\ C_p = 7.5 + 0.0042T$$
$$\Delta\Gamma = -5.5 + 0.00235T$$

In this case the same heat of reaction was found by Thomsen and by Berthelot, namely, $\Delta H_{291} = -12200$ cal.; hence $\Delta H_0 = -10700$, and

$$\Delta F^\circ = -10700 + 5.5T \ln T - 0.001175T^2 + IT.$$

The results of the equilibrium measurements of Jost and of Haber and Le Rossignol are given in Tables I and II. Of the latter measurements

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[1] Langmuir, This Journal, 34, 860 (1912).

[2] Jost, *Z. anorg. Chem.*, 57, 414 (1908).

[3] Haber and Le Rossignol, *Z. Elektrochem.*, 14, 181 (1908).

[4] Lewis and Randall, This Journal, 34, 1128 (1912).

some were made at 30 atmos. (marked *) and the rest at atmospheric pressure. In each table the first column gives the absolute temperature; the second gives $-\log K_p$, where $K_p = [NH_3]/[H_2]^{3/2}[N_2]^{1/2}$, and the last column gives the values of I calculated from these data with the above formula.

TABLE I.
Jost.

T.	$-\log K_p$.	I.
958	3.262	—10.50
1082	3.577	—10.89
1109	3.653	—10.88
1149	3.771	—10.83
1193	3.878	—10.83
1273	4.009	—11.07
1313	4.085	—11.09

TABLE II.
Haber and Le Rossignol.

T.	$-\log K_p$.	I.
973*	3.167	—11.20
1023	3.330	—11.21
1074*	3.449	—11.37
1074	3.478	—11.24
1123	3.554	—11.51
1174*	3.672	—11.57
1203	3.699	—11.77
1273	3.830	—11.88

The agreement between the several values of I is not completely satisfactory. Both sets of measurements show a decided trend in I and it is difficult to judge whether this is due to experimental error or to errors in the values of ΔH_0 and of $\Delta\Gamma$ which we have chosen, although it is to be pointed out that the difference in one set of measurements at the extreme temperatures is no greater than the difference between the two sets at one temperature. Owing to the trend we shall choose a value of I somewhat lower than the mean and write

$$\Delta F^\circ = -10700 + 5.5T \ln T - 0.001175T^2 - 11.0T \qquad (1)$$

Hence $\Delta F^\circ_{298} = -4740$, a value which may be in error by several hundred calories.

$NH_3(g) = NH_3(l)$.—Owing to the great importance of liquid ammonia as a solvent it is desirable to calculate its free energy also. The vapor pressure of liquid ammonia at 25° is 9.8 atmos. according to the tables of Regnault and of Pictet. If ammonia were a perfect gas the increase in free energy in this reaction would be $-R'T \ln (l/p) = 1350$, but, while the deviation of ammonia from the gas law may be sufficiently small at one atmosphere to warrant our ignoring it for the present, this is not the case between 1 and 10 atmospheres. Unfortunately the compressibility data for ammonia are meagre, but we are able to make a rough estimate for $\int vdp$ between 1 and 9.8 atmos., which leads to a result about 100 cal. less than the one given above on the assumption of the gas laws. We shall therefore write $\Delta F^\circ_{298} = 1250$. (2)

$^3/_2H_2 + {}^1/_2N_2 = NH_3(l)$.—Combining (1) and (2), $\Delta F^\circ_{298} = -3490$. (3)

$NH_3(g) = NH_3(aq)$.—Ammonia solutions appear to obey Henry's Law over a wider range of concentration than might have been expected. According to the very consistent measurements of Gaus, of Abegg and

Riesenfeld, and of Locke and Forssall[1] at 25°, the constant $K = C/p$, where C is mols per liter and p is pressure in atmospheres, varies only very slightly between $C = 1$ and $C = 0.1$, and the limiting value at $C = 0$ is 56.7 with a probable error of about 1%. Hence, $\Delta F_{298} = -R'T \ln K = -2390$. (4)

$^3/_2H_2 + {}^1/_2N_2 = NH_3(aq)$.—Adding (1) and (4) gives $\Delta F^\circ_{298} = -7130$. (5)

$NH_3(aq) + H_2O(l) = NN_4OH(aq)$.—As has been pointed out in the case of carbonic acid,[2] it is entirely immaterial, from a thermodynamic point of view, whether in dilute solution we consider a substance as hydrated or unhydrated. Provided, therefore, that we neglect the difference in free energy between pure water and the water of the solution, it is evident that it is a mere matter of choice whether we write the equations involving $NH_3(aq)$ or $NH_4OH(aq)$, for in any such reaction as this we may write $\Delta F^\circ = 0$. (6)

$^5/_2H_2 + {}^1/_2N_2 + {}^1/_2O_2 = NH_4OH(aq)$.—Combining Equations 5 and 6 with Equation 54 of the paper on Oxygen and Hydrogen Compounds,[3] we find $\Delta F^\circ_{298} = -63750$. (7)

Ammonium Ion.

$NH_4OH(aq) = NH_4^+ + OH^-$.—The dissociation constant of ammonium hydroxide at 25° is given by Noyes and Kanolt[4] as 18.1×10^{-6}, whence $\Delta F^\circ_{298} = 6470$. (8)

$2H_2 + {}^1/_2N_2 + \oplus = NH_4^+$.—We may combine Equations 7 and 8 with Equation 38 of the previous paper on oxygen and hydrogen compounds. Thus,

$$\begin{aligned} {}^5/_2H_2 + {}^1/_2N_2 + {}^1/_2O_2 = NH_4OH(aq);\ \Delta F^\circ_{298} &= -63750 \\ NH_4OH(aq) = NH_4^+ + OH^-;\ \Delta F^\circ_{298} &= 6470 \\ OH^- + \oplus = {}^1/_2O_2 + {}^1/_2H_2;\ \Delta F^\circ_{298} &= 37385 \\ 2H_2 + {}^1/_2N_2 + \oplus = NH_4^+;\ \Delta F^\circ_{298} &= -19895. \qquad (9) \end{aligned}$$

Oxides of Nitrogen.

$^1/_2N_2 + {}^1/_2O_2 = NO$.—One of the most important of technical gas reactions is the direct union of oxygen and nitrogen in the electric arc. Haber has expressed the conviction that the equilibrium obtained in the arc is not a purely thermal equilibrium, but that some of the electrical energy is in some way utilized directly to produce a larger yield of nitric oxide than corresponds to the temperature. However this may be, it is evident that experiments with the electric arc alone could hardly give sufficiently accurate results for a free energy calculation. Nernst[5]

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[1] See Abegg, *Handbuch anorg. Chem.*

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

[3] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

[4] Noyes, "The Electrical Conductivity of Aqueous Solutions," *Carnegie Institution Publications*, p. 290 (1907).

[5] Nernst, *Z. anorg. Chem.*, **49**, 213 (1906).

carried out, over a wide range of temperature, measurements of the amount of NO produced by heating air at atmospheric pressure to a given temperature for a sufficient time to establish equilibrium.

The free energy equation in this case is extremely simple, since we have taken the same formula for the heat capacities of N_2, NO and O_2, $\Delta\Gamma = 0$. $\Delta F^\circ = \Delta H_0 + IT$. ΔH for this reaction is given both by Thomsen and by Berthelot as 21600 cal., which is independent of the temperature. The equilibrium measurements of Nernst are given in Table III, where the first column gives the absolute temperature, the second the percentage by volume of NO in equilibrium with air at one atmosphere, the third, $K_p = [NO]/[N_2]^{1/2}[O_2]^{1/2}$ and the fourth the constant I.

TABLE III.

T.	Per cent. NO.	K_p.	I.
1811	0.37	0.0092	—2.59
1877	0.42	0.0105	—2.55
2033	0.64	0.0161	—2.40
2195	0.97	0.0246	—2.47
2580	2.05	0.0539	—2.56
2675	2.23	0.0590	—2.44
		Mean,	—2.50

Thus $\Delta F^\circ = 21600 - 2.50T$; $\Delta F^\circ_{298} = 20850$. (10)

$NO + {}^1/_2O_2 = NO_2$.—Nitrogen dioxide, according to the density measurements of Richardson,[1] dissociates appreciably above 150° C. into nitric oxide and oxygen. Table IV gives in the first column the absolute temperatures, in the second the percentage of NO_2 dissociated, as calculated from the density, in the third $R' \ln K_p$, where $K_p = [NO_2]/[NO][O_2]^{1/2}$, and in the fourth the values of I obtained from the equation which we are about to write.

TABLE IV.

T.	Per cent. dissoc.	$R' \ln K_p$.	I.
457	5	9.58	—0.3
552	13	6.60	—1.9
767	56.5	1.01	—2.5

Assuming that the heat capacity of NO_2 obeys the same equation as that of CO_2, then for this reaction $\Delta\Gamma = -2.75 + 0.0056T - 0.00000186T^2$. The heat of this reaction calculated from Thomsen's measurements is given as 13450 cal. in Abegg's Handbuch, while the value 11000 is calculated by the equation of van't Hoff from the last two data of Table IV. We may take as a rough average 12000 cal. at ordinary temperatures, corresponding to $\Delta H_0 = -11400$. Taking the mean of the last two values of I, since the first is subject to much larger experimental error,

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[1] Richardson, *J. Chem. Soc.*, 51, 397 (1887).

$$\Delta F_0 = -11400 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 - 2.2T \quad (11)$$

and $\Delta F^\circ_{298} = -7600$. This is an illustration of a reaction which is accompanied by a comparatively small free energy change and nevertheless takes place rapidly.

$^1/_2N_2 + O_2 = NO_2$.—Adding Equations 10 and 11

$$\Delta F^\circ = 10200 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 - 4.7T \quad (12)$$

$$\Delta F^\circ_{298} = 13250.$$

$2NO_2 = N_2O_4$.—The equilibrium between nitrogen dioxide and tetroxide was one of the earliest to be studied from the thermodynamic standpoint, and has been the subject of numerous publications. This is a case where the heat of reaction can best be determined from the equilibrium measurements themselves, although the value thus obtained is in good agreement with those obtained from a study of the specific heat.[1] Schreber[2] has made a critical summary of the dissociation constant calculated from the numerous measurements of the gas density. In accordance with this work, we shall take for the average value between 0° and 100° C., $\Delta H = -13600$. The heat capacity of 2 mols of NO_2 is doubtless greater than for one mol of N_2O_4, but since this reaction can be studied only over a small range of temperature, we shall regard ΔH as constant, and write

$$\Delta F^\circ = -13600 + 41.6T; \quad \Delta F^\circ_{298} = -1200. \quad (13)$$

The value of I is obtained from the following table. The values of K_p are obtained by dividing 760 by the values of K_{p_0} given by Schreber.

TABLE V.

T.	K_p.	I.
273.0	65.0	41.5
291.3	13.8	41.4
322.9	1.25	41.7
346.6	0.296	41.6
372.8	0.075	41.6

$N_2 + 2O_2 = N_2O_4$.—Combining Equations 12 and 13 we find $\Delta F^\circ_{298} = 25300$. (13*a*)

Nitrous and Nitric Acids and Their Ions.

Neither the free energy of nitric acid nor that of nitrous acid can be determined alone from any existing measurements of chemical equilibrium, but from the series of reactions considered below we may obtain equations which permit a simultaneous solution for both of these quantities.

$2AgNO_2(s) = Ag^+ + NO_3^- + Ag + NO(g)$.—Solid silver nitrite when heated, especially in the presence of water, decomposes to form silver nitrate, metallic silver and nitric oxide, Abegg and Pick[3] showed that at 55° C. equilibrium in this reaction was established in a few days

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[1] See *Abegg's Handbuch*, III-3, p. 135.

[2] Schreber, *Z. phys. Chem.*, 24, 651 (1897).

[3] Abegg and Pick, *Z. anorg. Chem.*, 51, 1 (1906).

and that when the pressure of NO was 4.28 atmos. the concentration of silver nitrate was 0.179 *M*. The concentration was determined by a somewhat indirect method and on this account their results are subject to some uncertainty.

As a check upon their measurements we have studied briefly the equilibrium at 100° C. A glass tube containing a solution of silver nitrate and solid silver nitrite and silver was connected with a closed manometer and heated in the vapor of boiling water. The space between the solution and the manometer was swept out with pure nitric oxide before the tube was sealed, and this space was made so small that the change in concentration of the silver nitrate in the reaction was in the nature of a small correction. The apparatus was heated for three hours, the pressure reaching a constant value at the end of the second hour. After all customary corrections were made, the pressure of NO was 8.53 atmos. at 100.1° C., and the concentration of silver nitrate was 1.10 *M*.

From the data of Thomsen and Berthelot, neglecting the small heat of dilution of aqueous silver nitrate, $\Delta H = 21200$. Assuming this to be constant between 25° and 100° C., and applying the van't Hoff equation, we find the pressure of NO at 25° C. which would be in equilibrium with 0.179 *M* $AgNO_3$ to be 0.162 atmos. from the experiment of Abegg and Pick, and that in equilibrium with 1.10 *M* $AgNO_3$ to be 0.00637 atmos. We may therefore write:

$$2AgNO_2(s) = AgNO_3(0.179\,M) + Ag + NO(1\text{ atmos.});\ \Delta F_{298} = 1080.$$
$$2AgNO_2(s) = AgNO_3(1.10\,M) + Ag + NO(1\text{ atmos.});\ \Delta F_{298} = 3000.$$

We have attempted to determine the free energy of dilution of silver nitrate from the freezing-point measurements of Roth[1] and of Raoult,[2] The former extend from 0.01 *M* to 0.14 *M*, the latter, which can be given much less weight, from 0.25 *M* to 1.45 *M*. Employing the method of calculating free energy of dilution from freezing points, completely described by Lewis,[3] we find

$$AgNO_3\ (0.179\,M) = AgNO_3\ (0.1\,M);\ \Delta F_{298} = -\ \ 90$$
$$AgNO_3\ (1.10\ \ M) = AgNO_3\ (0.1\,M);\ \Delta F_{298} = -\ 1920.$$

Combining these equations with those above, $2AgNO_2(s) = AgNO_3\ (0.1\ M) + Ag + NO\ (1\text{ atmos.});\ \Delta F_{298} = 990$ (Abegg and Pick), $\Delta F_{298} = 1080$ (Lewis and Adams), average $\Delta F_{298} = 1040$. Taking, as on a previous occasion,[4] 0.67 as the corrected degree of dissociation of 0.1 *M* $AgNO_3$ we have for the change from 0.1 *M* $AgNO_3$ to hypothetical molal silver ion and nitrate ion. $\Delta F = 2R'T \ln 1/0.067 = 3210$, and therefore for the normal free energy of the reaction

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[1] Roth, *Z. physik. Chem.*, **79**, 612 (1912).

[2] Raoult, *Ibid.*, **2**, 489 (1889).

[3] Lewis, THIS JOURNAL, **34**, 1635 (1912).

[4] Lewis and Randall, *Ibid.*, **36**, 1983 (1914).

$2AgNO_2(s) = Ag^+ + NO_3^- + Ag + NO(g)$; $\Delta F^\circ_{298} = 4250$. (14)

$AgNO_2(s) = Ag^+ + NO_2^-$.—Abegg and Pick determining the solubility and the complex formation of silver nitrite obtained for the solubility product at 25° C., $(Ag^+)(NO_2^-) = 2.0 \times 10^{-4}$, whence $\Delta F^\circ_{298} = 5050$. (15)

$2NO_2^- + \oplus = NO_8^- + NO(g)$.—Combining (14), (15) and Equation 50 of a preceding paper[1] for the free energy of silver ion, $\Delta F^\circ_{298} = 12570$. (16)

$2NO_2^- + \oplus = NO_3^- + {}^1/_2N_2 + {}^1/_2O_2$.—Combining Equations 11 and 16, $\Delta F^\circ_{298} = -8280$. (17)

$H^+ + NO_3^- + 2NO(g) + H_2O = 3HNO_2(aq)$.—The reaction which occurs in the decomposition of aqueous nitrous acid is reversible. Nitric oxide at a definite pressure, in contact with a solution of nitric acid, leads to an equilibrium concentration of nitrous acid. This equilibrium was studied over a wide range of concentration by Saposhnikov[2] by passing nitric oxide through nitric acid solution and determining the amount of nitrous acid, either by analysis or by measurements of the conductivity of the solution at the beginning and end of the experiments. The latter method was also employed by Lewis and Edgar[3] with the purpose of obtaining a more exact determination of the equilibrium constant. Starting with 0.1 *M* HNO_3 and passing NO through at approximately atmospheric pressure, they were able to determine the change of conductance with unusual exactness. In five experiments the decrease in conductance, which is itself a small fraction of the total conductance, showed an average deviation from the mean of less than one-half of one per cent. There is no doubt, therefore, that a definite equilibrium is established. Unfortunately, however, it is not certain that the measured conductance is an exact criterion of the concentration of nitric acid in the mixture which contains both HNO_2 and NO. If these substances, even to a small degree, change the conductivity, the calculation of the equilibrium constant will be largely affected.

According to the measurements of Lewis and Edgar, the solution originally 0.1 *M* with respect to nitric acid becomes, in equilibrium with NO at 0.961 atmos., 0.0830 *M* with respect to nitric acid,[4] 0.0495 *M* with respect to undissociated nitrous acid. Assuming that the corrected degree of dissociation of HNO_3 at this concentration is 0.74 we find for the equilibrium constant, $K = (HNO_2)^3/(H^+)(NO_3^-)[NO]^2 = 0.0346$.

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[1] Lewis and Randall, THIS JOURNAL, 36, 1983 (1914); $Ag + \oplus = Ag^+$; $\Delta F^\circ_{298} = 18424$.

[2] Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 32, 375 (1900); 33, 506 (1901).

[3] Lewis and Edgar, THIS JOURNAL, 33, 292 (1911).

[4] *A careful reconsideration of the conductance data indicates that the value 0.0826 M* should have been chosen as the concentration. Owing to other uncertainties it does not seem necessary to make this change.

Experiments by Lewis and Edgar with 0.2 *M* nitric acid, which were regarded as incomplete, but are nevertheless significant, give a considerably lower value of K. The values found for the concentrations of nitric and nitrous acid in equilibrium with NO at 0.969 atmos. were, respectively, 0.1785 and 0.0651. In so concentrated a solution the corrected degree of dissociation is hard to estimate. Assuming it to be 0.66, K = 0.0216. Saposhnikov's constants, when recalculated in terms of the corrected degree of dissociation, were 0.0320 at 0.05 *M*, 0.0268 at 0.1 *M*, and 0.0290 at 0.2 *M*. Since Saposhnikov used both conductivity and analysis we may give more weight to his measurements than their apparent accuracy would warrant. We probably shall not be far wrong in assuming as the final value K = 0.030, whence

$$H^+ + NO_3^- + 2NO(g) + H_2O = 3HNO_2(aq); \quad \Delta F^\circ_{298} = 2080 \qquad (18)$$

$HNO_2(aq) = H^+ + NO_2^-$.—Owing to the instability of nitrous acid, its dissociation constant has not been determined with high accuracy, but there is apparently no large error in the determination of Schümann,[1] who measured the conductivities of freshly prepared mixtures of equivalent solutions of sodium nitrite and hydrochloric acid. He found $K_{298} = (NO_2^-)(H^+)/(HNO_2) = 0.00045$. Hence $\Delta F^\circ_{298} = 4570$. (19)

$^1/_2N_2 + {}^3/_2O_2 + \ominus = NO_3^-$.—From the equations which have so far been obtained it is possible to determine the free energy of formation of both nitrate and nitrite ion. Ordinarily it is possible to determine the free energies of a series of compounds one by one, but in this case it is impossible from the reactions which have been studied to obtain the free energy of either nitrate or nitrite ion without accumulating data which suffice for the determination of the other. In other words, we have equations which are to be solved simultaneously for two unknown quantities. In order to find the free energy of formation of NO_3^- we shall combine Equations 18, 19, 16 and 10 of this paper with Equations 8 and 53 of the paper on hydrogen and oxygen compounds.[2]

$$\begin{aligned}
&2H^+ + 2NO_3^- + 4NO(g) + 2H_2O(l) = 6HNO_2(aq); && \Delta F = 4160 \\
&6HNO_2(aq) = 6H^+ + 6NO_2^-; && \Delta F = 27420 \\
&6NO_2^- + 3\oplus = 3NO_3^- + 3NO(g); && \Delta F = 37710 \\
&{}^1/_2N_2 + {}^1/_2O_2 = NO(g); && \Delta F = 20850 \\
&4H^+ + 4\ominus = 2H_2; && \Delta F = 0 \\
&2H_2 + O_2 = 2H_2O(l); && \Delta F = -113240
\end{aligned}$$

Hence by addition

$$^1/_2N_2 + {}^3/_2O_2 + \ominus = NO_3^-; \quad \Delta F^\circ_{298} = -23100 \qquad (20)$$

$^1/_2N_2 + O_2 + \ominus = NO_2^-$.—Subtracting 17 from 20 and dividing by two, $\Delta F^\circ_{298} = -7410$. (21)

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[1] *Ber.*, **33**, 527 (1900).

[2] Lewis and Randall, THIS JOURNAL, **36**, 1969 (1914).

$^1/_2H_2 + {}^1/_2N_2 + O_2 = HNO_2(aq)$.—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.

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THE FREE ENERGY OF FORMATION OF FORMIC ACID.

BY GERALD E. K. BRANCH.

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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).