No optical evidence has been obtained which would indicate the existence of any ternary compounds of CaO-Fe_2O_3-SiO_2 in the region studied.

Further evidence is cited tending to confirm the existence of $3CaO.SiO_2$. It has been found that the inversion of $2CaO.SiO_2$ to the gamma form takes place in cooled charges of CaO-Fe_2O_3-SiO_2 except where the concentration of $2CaO.SiO_2$ is low and the concentration of the CaO-Fe_2O_3 compounds is high.

Attention is called to the probability that only a part of the ferric oxide in Portland cement clinker is present as the crystalline $2CaO.Fe_2O_3$ or $CaO.Fe_2O_3$.

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

THE ULTRAVIOLET ABSORPTION SPECTRUM OF FORMIC ACID

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The absorption of ultraviolet light by formic acid was determined by the method developed by Porter and Iddings.[1] Formic acid vapor in a quartz cell and in a water thermostat was exposed to the radiation of a quartz mercury lamp. The light passing through the cell was photographed through a Hilger quartz prism spectrograph. On the same plate another photograph was taken of the same source of light through the same cell evacuated and through a copper gauze screen of known absorption. The blackening of the plate is the same in the two photographs at any wave length for which the particular screen and the formic acid vapor have the same absorption.

The points of equal intensities on the pairs of photographs taken for comparison could not be identified visually with greater accuracy than a range of 10 Ångström units. We resorted, therefore, to the following device. The photographic negative was placed in a lantern slide projector and an enlarged image of the spectrum was thrown on the slit of a thermopile which was connected with a galvanometer. The galvanometer deflections were read at short intervals as the plate was moved over the range selected by visual inspection. The photograph taken for comparison was then projected upon the slit of the thermopile and readings were made as before. Positions of equal intensities in the two negatives could be located within a range of 3 Å. The method is so successful that we have constructed a special holder for such negatives. The holder, which is readily attached to a Balopticon, is provided with racks and pinions that make possible very rapid and accurate adjustments.

An attempt to plot the absorption curve for formic acid vapor from meas-

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[1] Porter and Iddings, THIS JOURNAL, **48**, 40 (1926).

Table I

Points of Equal Intensities (Ångström Units) on Photographs Taken through Screens and through Formic Acid at Various Temperatures and Pressures

Screen No.	Light transmitted by screen, %	Expt. 1 40° 3.76 cm. Hg pressure	Expt. 2 40° 7.82 cm. Hg pressure	Expt. 3 75° 5.19 cm. Hg pressure	Expt. 4 75° 11.53 cm. Hg pres.	Expt. 5 75° 16.63 cm. Hg pres.
1	69.3	2348	2394	2346	2431	2470
2	48.8	2300	2361	2305	2391	2410
3	33.1	2260	2326	2265	2359	2379
4	21.2	..	2296	..	..	2370
5	11.5	..	2282	..	2296	2330
6	6.3	..	2254	..	2264	2308
7	4.4	..	..	..	2260	2301

urements made under various conditions of temperature and pressure revealed the fact that the acid exists largely in the form of associated molecules. Since the absorption was due in part to simple molecules and in part to associated molecules it became necessary for us to know the state of aggregation of the compound at each temperature and pressure used. By a vapor density method we determined the equilibrium constants, $K = (\mathrm{HCOOH})^2/(\mathrm{HCOOH})_2$, for the reaction, $(\mathrm{HCOOH})_2 = 2\mathrm{HCOOH}$ at temperatures between 25° and 80°. At higher temperatures measurements had been made by Pettersson and Ekstrand.[2] With this information available we could calculate the concentration of the unimolecular and of the bimolecular form of the acid present in the cell under the conditions of each experiment.

Attempts to plot extinction coefficients against wave lengths failed when we calculated the molal concentration on the basis of the average molecular weight of the acid. Poorer results were obtained when the calculation was based upon the assumption that the unimolecular form was exclusively responsible for the absorption, and better, but not satisfactory, relations were found when it was assumed that the bimolecular form alone was absorbing. It became necessary, therefore, to find the independent effects of the two forms.

Absorption coefficients may be calculated from the relation $I_t = I_0 10^{-ecd}$ in which e is the molecular absorption coefficient c the concentration in moles per liter, and d the length of the cell (9.13 cm.). If the absorption of light is due to both forms of formic acid we can write this relation in the form $I_t/I_0 = 10^{-(e_1c_1d + e_2c_2d)}$, in which e_1 is the absorption coefficient and c_1 is the concentration of the unimolecular form, and e_2 and c_2 are the corresponding terms for the bimolecular form. Taking the logarithm and dividing both sides of the equation by c_2d we obtain the equation

$$\frac{1}{c_2d}\log\frac{I_t}{I_0} = \frac{e_1c_1}{c_2} + e_2 \qquad (1)$$

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[2] Pettersson and Ekstrand, *Ber.*, **13**, 1191 (1880).

The values of $1/c_2d \log (I_t/I_0)$ are calculated from the data of Table I and the equilibrium constants which are given in Table III. They are plotted against wave length in Fig. 1. If there were no absorption due to the monomolecular form e_1c_1/c_2 would be equal to zero and all values of $1/c_2d \log (I_t/I_0)$ for a given temperature would fall on the same curve. This is not the case as is indicated by Fig. 1.

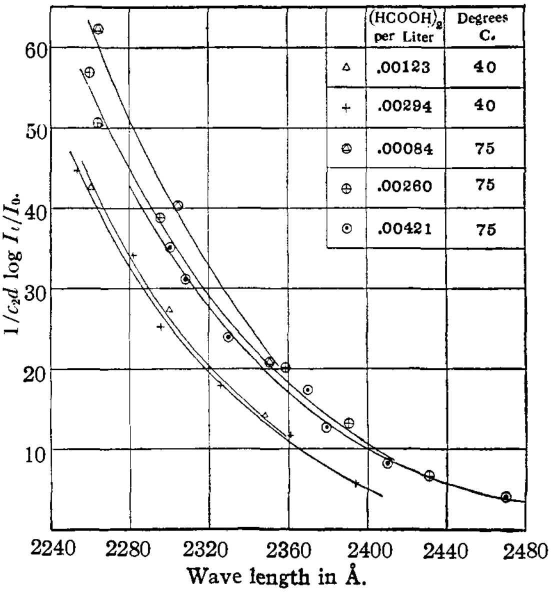

Fig. 1.

The unimolecular absorption coefficient can be calculated from the rate of change of the term $1/c_2d \log (I_t/I_0)$ with c_1/c_2. Differentiating Equation 1 we get,

$$d\left(\frac{1}{c_2d}\log\frac{I_t}{I_0}\right) \Big/ d\left(\frac{c_1}{c_2}\right) = e_1$$

The values of $1/c_2d \log (I_t/I_0)$ for a number of wave lengths are given in Table II.

TABLE II

VALUES OF $1/c_2d$ LOG (I_t/I_0) FOR VARIOUS CONCENTRATIONS AT CERTAIN POINTS IN THE SPECTRUM

		$1/c_2d \log (I_t/I_0)$				
Expt.	c_1/c_2[a]	2400 Å.	2360 Å.	2320 Å.	2280 Å.	2260 Å.
1	0.563	..	11.1	20.3	34.0	43.5
2	0.364	..	10.8	19.5	32.7	41.9
3	1.84	..	..	32.7	51.0	63.0
4	1.04	10.6	18.0	29.0	45.0	55.0
5	0.822	10.0	18.0	27.6	43.0	..

[a] The values of c_1/c_2 are calculated from the equilibrium constants, Table III, and the total pressures given in Table I.

An average value of e_1 is calculated as follows. For a wave length of 2280 Å. and for the three runs at 75 °C. we find three values of e_1 as follows: $e_1 = (51-45)/(1.84-1.04) = 7.5$; $e_1 = (45-43)/(1.04-0.822) = 9.0$; $e_1 = (51-43)/(1.84-0.822) = 8.0$. The average of these three values is 8.2. By substituting this value in Equation 1 we obtain an average value for e_2 of 36.4. In this way values for e_1 and e_2 have been calculated for all points from data obtained in the experiments at both temperatures (40° and 75°). The results are plotted in Fig. 2.

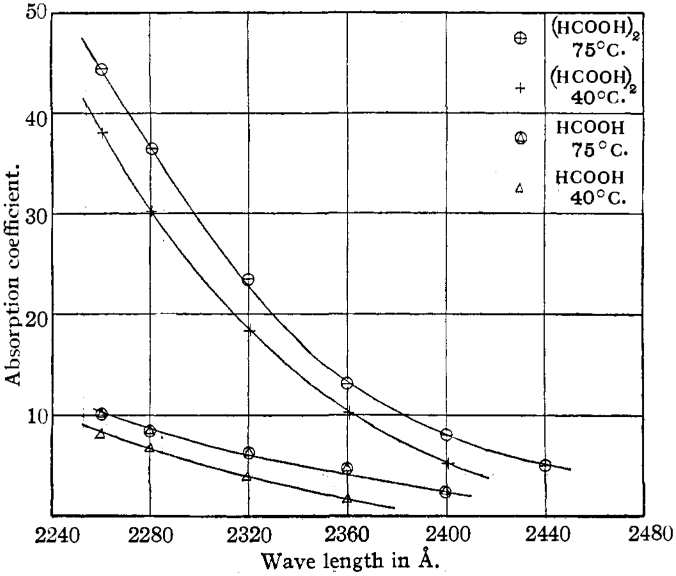

Fig. 2.

Experimental Part

Equilibrium Constants.—A 500cc. flask having an attached closed tube manometer and a capillary side tube was evacuated and then filled with the vapor of pure formic acid and sealed. The sealed flask was placed in a thermostat and the pressure of the vapor was measured. The amount of formic acid in the flask was then determined by breaking the capillary under a standard alkali solution, and then titrating the excess of the base.

The equilibrium constants, $K = p_m^2/p_b$, when p_m is the pressure, in atmospheres, due to the unimolecular form, and p_b is the pressure of the bimolecular form relate to the reaction $(HCOOH)_2 \rightleftarrows 2HCOOH$.

The assumption that no heavier molecule than $(HCOOH)_2$ exists in the vapor state is justified by the fact that at any given temperature K, as calculated from the above equation, is independent of the pressure. The value of K at the boiling point of formic acid was found by extrapola-

TABLE III

VALUES OF K AT VARIOUS TEMPERATURES

RUN 1			RUN 2		
Vol. = 546 cc.		0.0689 g. of formic acid	Vol. = 546 cc.		0.07096 g. of formic acid
T, °C.	P cm. Hg	K	T, °C.	P cm. Hg	K
25	2.91	0.00288	25	2.98	0.00291
40	3.30	.00983	40	3.40	.0103
59.5	3.92	.0342	60	4.07	.0377
66	4.16	.0505	79.5	4.86	.119
82	4.86	.143	..	..	....
RUN 3			RUN 4		
Vol. = 546 cc.		0.0762 g. formic acid	Vol. = 548.5 cc.		0.2005 g. formic acid
59.5	4.25	0.0306	50	9.45	0.01675
70.0	4.70	.0621	59.5	10.22	.0329
83.5	5.37	.152	70.0	11.10	.0603
..	..	...	84.0	12.70	.1563

tion in Fig. 4, but a check on its accuracy may be made by comparing the heat of vaporization, determined calorimetrically, and that calculated from the change of vapor pressure with temperature. From the data of Kahlbaum[3] and of Schmidt[4] we have plotted $-R\ ln\ p$ against $1/T$ (Fig. 3). The slope of this line gives the heat of vaporization per mole of gaseous formic acid as given by the equation, $d\ ln\ p/dT = \Delta H/RT^2$. The

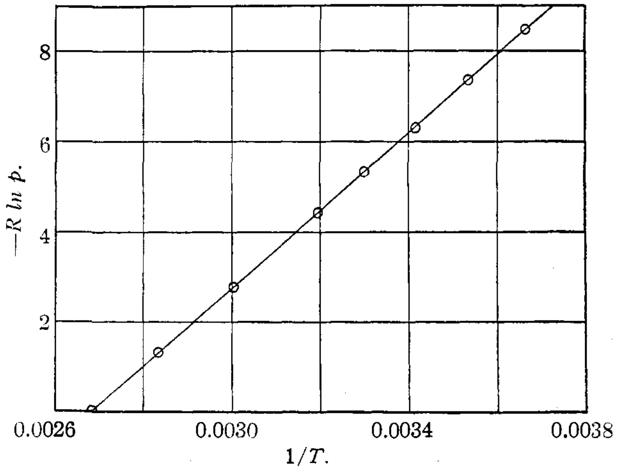

Fig. 3.

slope is constant and ΔH = 8570 cal. per mole. If at the boiling point (100.8°) the value of K is 0.404, the weight of one mole of gaseous formic acid is 70.6. The heat of vaporization is then 121.2 cal. per gram. This

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[3] Kahlbaum, *Z. physik. Chem.*, **13**, 34 (1894).

[4] Schmidt, *ibid.*, **7**, 433 (1891).

is close to the value determined calorimetrically by Brown[5] (120.4) and by Marshall[6] (120.4).

Incidentally, the data obtained in this investigation give us a means of calculating the heat of dissociation of bimolecular formic acid and afford also a check on the free energy of formation of the compound.

Heat of Dissociation.—The slope of the curve in Fig. 4 represents the heat of dissociation of bimolecular formic acid vapor from the relation: $d\,ln\,K/dT = \Delta H/RT^2$. The values at three temperatures taken from the curve are as follows: ΔH_{298} = 13,900 cal.; ΔH_{323} = 14,100 cal.; ΔH_{353} = 14,300 cal.

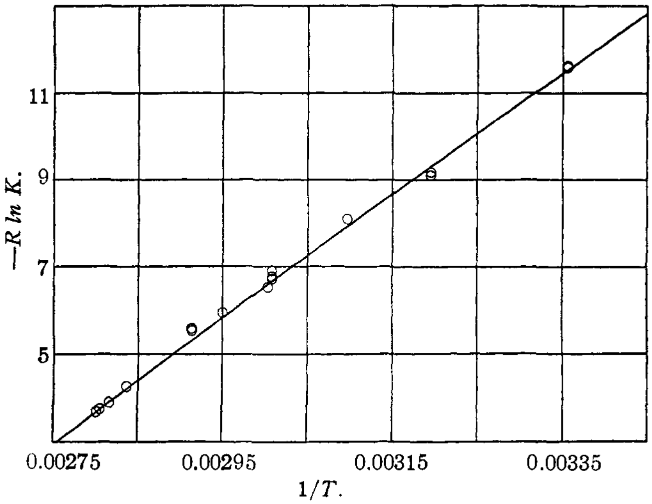

Fig. 4.

Free Energy of Formation.—From vapor-pressure measurements Branch[7] calculated the free energy of solution of formic acid and reported HCOOH (liq.) ⟶ HCOOH (1 *M*); ΔF°_{298} = —3880 cal. At 25° liquid formic acid has a vapor pressure of 0.0562 atm.[8] A molal aqueous solution has a pressure due to formic acid equal to 8.092×10^{-5} atm. Using our value of K at 25° in the equation $K = p_m^2/p_b$, where p_m is the partial pressure of the unimolecular form and p_b the pressure of the bimolecular species, we find that the pressure due to unimolecular formic acid over the pure liquid at 25° is 1.17×10^{-2} atm. The corresponding pressure due to the bimolecular form is 4.3×10^{-2}. Over the aqueous solution $p_m = 7.89 \times 10^{-5}$ atm. and $p_b = 2.03 \times 10^{-6}$ atm. The free

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[5] Brown, *J. Chem. Soc.*, **83**, 991 (1903).

[6] Marshall, *Phil. Mag.*, **43**, 29 (1897).

[7] Branch, THIS JOURNAL, **37**, 2316 (1915).

[8] Landolt-Börnstein-Roth, "Physikalisch-Chemische Tabellen," Berlin, 4th ed., p. 817.

energy of solution is, therefore, $\Delta F^\circ_{298} = RT\ ln\ (7.89 \times 10^{-5})/(1.17 \times 10^{-2})$ = —2960 cal. Lewis and Randall[9] used the value —3880 for the free energy of solution, and calculated the free energy of formation of liquid formic acid to be —84,040 cal. The corrected value becomes ΔF°_{298} = —84,960 cal.

Decomposition of Formic Acid.—The complete photochemical decomposition of formic acid vapor was accomplished by an exposure of 16 hours at a distance of 20 cm. from a 220-v. lamp at 20°. The decomposition proceeds according to the equations, (I) $HCOOH \longrightarrow CO + H_2O$; (II) $HCOOH \longrightarrow CO_2 + H_2$. Carbon monoxide and water constitute 64% of the mixed products and carbon dioxide and hydrogen 36%.

Summary

The bimolecular form of formic acid was found to be primarily responsible for the absorption of ultraviolet light between 2260 Å. and 2500 Å. But the unimolecular form has an appreciable absorption in the same range.

An approximate segregation of the effects produced by the two forms has been accomplished.

Dissociation constants of bimolecular formic acid were determined at several temperatures between 25° and 80°.

The heat of dissociation of bimolecular formic acid has been calculated; ΔH_{298} = 13,900 cal.

A revision of the free energy of solution of formic acid has been made.

The photochemical decomposition of formic acid vapor has been found to result in the formation of carbon dioxide 18%, hydrogen 18%, carbon monoxide 32% and water 32%.

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[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.