

if the suggestion be accepted that the probability of Reaction 3, which was calculated to  $10^{-4}$  for excited atoms, is smaller in case of normal oxygen atoms, such as are produced in Reaction 4. But even with this assumption the excess of ozone yield over that calculated remains unexplained, since there are no reasons to assume that with normal oxygen atoms the ratio of the reaction velocities 1 and 2 is different than in case of excited atoms. This question, therefore, must be left open at present but it is hoped that further experiments now under way may bring a solution of this problem.

### Summary

1. The oxygen-hydrogen reaction has been studied in light of the two spectral regions 1719-1725 Å. and 1854-1862 Å.

2. The effect of these spectral regions is markedly different. While the longer wave lengths produce only ozone in an amount equal to that produced in similar oxygen-nitrogen mixtures, in light of shorter wave lengths the yields of ozone in the presence of hydrogen are smaller but hydrogen peroxide is formed in addition.

3. The probable reaction mechanism has been discussed. The probability of the reaction  $O + H_2 = OH + H$  has been estimated to  $10^{-4}$ , a much smaller value than that predicted theoretically.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE VAPOR PRESSURE AND HEATS OF FUSION AND VAPORIZATION OF FORMIC ACID

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### Introduction

In a recent paper<sup>1</sup> were given data on the density of formic acid vapor, together with some isolated vapor pressure data obtained in studying the process of purification. These data were obtained in order to make possible use of the Clapeyron equation in calculating heats of adsorption from equilibrium pressure data. The same equation should, of course, give the heats of evaporation of pure solid or liquid formic acid, when the corresponding vapor pressures are introduced. The case is interesting because of the wide deviation of the vapor from the perfect gas laws, produced by association. The only calorimetrically determined quantities by which the Clapeyron equation could be checked appeared to be the heat of vaporization of the boiling liquid, and the heat of fusion of the solid, which can be compared with the difference between the vaporization heats calculated for the solid and liquid at the triple point. Using

<sup>1</sup> Coolidge, *THIS JOURNAL*, 50, 2166 (1928).

the values of the vapor pressures from "International Critical Tables," it was found that in neither case did the calculated and observed values agree. It seemed worth while, therefore, to redetermine both vapor pressures and latent heats with the very pure formic acid available, in the hope of getting a thermodynamically consistent set of data.

Since the observed heat effects are to be compared with values computed by a process involving temperature differentiation of the observed pressures, it is clear that a higher order of accuracy is needed in measuring the latter than the former. Therefore, no attempt was made to surpass a precision of, say, 0.5% in the calorimetry, while no effort was spared to perfect the thermometry and manometry, and it is believed that the error does not exceed 0.1%.

### Instability of Formic Acid

It was necessary to take constant precautions against errors arising from the spontaneous decomposition of the acid into water and carbon monoxide. This reaction appears to occur in the liquid at all temperatures, and to cease only when the acid is frozen. However, at room temperature the evolution of permanent gas is very slow, and does not interfere with the measurements provided the sample is one which has been pumped free from gas while frozen, and has been melted just before the experiment. At temperatures approaching 100° decomposition is more rapid, and cannot be ignored. In one experiment, a quantity of liquid, carefully freed from gas, was confined by a column of mercury of about 30-cm. height in addition to the atmospheric pressure, and was then raised to 100°. Within five minutes bubbles began to escape through the mercury. Since the pure acid boils at 100.5°, the bubbles must have contained considerable permanent gas. Again, it was observed that when the pure acid was gently boiled under a reflux condenser, protected from atmospheric moisture, the boiling point rose a degree in ten hours, due presumably to dilution of the acid by the water resulting from its decomposition. The heat of combustion<sup>2</sup> of the acid is 62,800 calories per formula weight; that of carbon monoxide is 68,100 calories; the decomposition is, therefore, endothermic, absorbing 5300 calories per formula weight.

### Vapor Pressure Measurements

For temperatures up to 80° a static method was used to determine the vapor pressures. The acid was placed in a bulb communicating with a manometer on which pressures could be read to 0.01 mm. as high as 100 mm. For higher pressures, this instrument was used to determine the difference in pressure between the bulb and the rest of the system, in which a pressure of air nearly equal to that in the bulb was established, and could be read off another manometer by means of a cathetometer.

The bulb was maintained at the desired temperature, while the connections and

<sup>2</sup> "International Critical Tables," Vol. V, p. 165.

manometer must, of course, be kept slightly warmer to prevent distillation. A temperature of about  $-5^{\circ}$  was obtained with a sodium chromate eutectic. The salt, a c. p. product, was not further purified, and the exact temperature obtained was not always the same; in any one experiment, however, the temperature, as shown by two thermometers in different positions, was uniform and constant to  $0.01^{\circ}$ . Other temperatures up to  $20^{\circ}$  were secured with ice- and water-baths. From  $30$  to  $80^{\circ}$  an oil-bath was used. It was contained in a Dewar vessel which, together with the manometer and connecting tubing, was mounted in an air-bath with a plate-glass front. The air was maintained a degree or two hotter than the oil, which was prevented from overheating by a very slow stream of water through a coil. The temperature of mercury in manometer and exposed thread of thermometer was thus controlled, and suitable reductions applied.

The main supply of acid used had been purified in the manner described in the previous paper until it had the same vapor pressure at  $0^{\circ}$ , and was, therefore, probably 99.99% pure. It was kept continuously frozen to prevent deterioration. Samples for the measurements were distilled into the bulb, and before each reading were gently pumped to remove possible traces of permanent gas. At  $70$  and  $80^{\circ}$  constant readings were not obtained, the pressure rising steadily after each pumping, without approaching any limit. This situation was met by increasing the size of the dead space so as to dilute the evolved gas, and by making readings at definite time intervals after each pumping. By extrapolating back to zero time, satisfactory values could be obtained.

To extend the range upward, boiling points were taken at atmospheric pressure, and also at about 1000 mm. In this method no error can be produced by accumulation of carbon monoxide, since this gas is swept away by the stream of fresh vapor rising from the liquid. In order to minimize the error due to dilution with water, the boiling was reduced to the shortest possible time, and the acid was once repurified between readings. Nevertheless, it is possible that the values found may be a few hundredths of a degree too high.

Temperatures of  $20^{\circ}$  and higher were read on a thermometer certified by the Bureau of Standards. Particular care was taken with the temperatures below  $20^{\circ}$ , on which the calculation of the heat of fusion depends. The thermometer had been certified at ten degree intervals, but the correction at  $10^{\circ}$  was so different from that at either  $0$  or  $20^{\circ}$  that interpolation seemed uncertain. Therefore, the scale used below  $20^{\circ}$  was the mean of five good thermometers, including that certified by the Bureau of Standards and one certified by the Reichsanstalt, which were all carefully compared between  $-5$  and  $20^{\circ}$ . It is unlikely that the error exceeds  $0.02^{\circ}$ .

The triple point of formic acid is  $8.25^{\circ}$ , but the liquid can be cooled to  $-5^{\circ}$  without immediate solidification; attempts to go below  $-5^{\circ}$  always froze the acid. In attempting to measure the sublimation pressure, it was found that when a sample of acid having the correct vapor pressure as liquid at  $0^{\circ}$  was simply frozen and gently pumped, a pressure of about 8.7 mm. was obtained at  $0^{\circ}$ . The value given in the first paper was 8.67 mm. However, on exhaustive pumping, accompanied by occasional fusion and re-solidification, the pressure dropped to 8.22 mm., below which it failed to go even when almost all of the sample had been pumped away. Evidently traces of volatile matter which remain in solution in the liquid without perceptible effect upon the vapor pressure, are set free on crystallization, and can be removed only with difficulty. The vapor pressure of the solid thus prepared was also determined at  $-5^{\circ}$ . The pressure was also determined over a mixture of solid and liquid, at a temperature of  $8.25^{\circ}$  ( $8.26^{\circ}$  was given in the first paper). Attempts were made to detect changes in the triple point due to variations in the conditions under which the crystals were formed, or their age, but no variation was found.

TABLE I  
VAPOR PRESSURE MEASUREMENTS (MILLIMETERS OF MERCURY)

Liquid		Liquid		Solid	
T	P	T	P	T	P
-5.23°	8.12	49.93	130.1	-5.07°	4.98
0.00	11.16	59.98	192.7	0.00	8.22
8.25	17.94	70.04	280.6	8.25	17.94
12.57	22.72	79.93	395.6		
20.00	33.55	100.68	762.5		
29.96	54.36	110.62	1017.6		
39.89	85.18				

Table I gives the experimental values for the vapor pressure of solid and liquid, including the boiling points. Each entry is the mean of three closely concordant measurements, except those for the solid at -5° (two measurements) and for the liquid at 60, 80 and 110° (one measurement each).

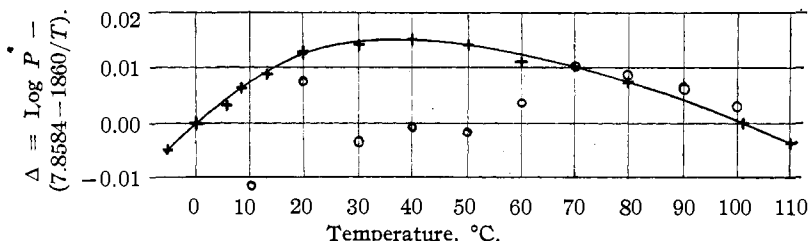


Fig. 1.—Vapor pressure of the liquid (deviation plot).

Adjustment and Comparison of Data

The three values for the vapor pressure of the solid are represented, to within 0.01 mm., by the equation

$$\text{Log } P = 12.486 - 3160/T \tag{1}$$

in which log P is the common logarithm of the pressure in mm., and T is the absolute temperature reckoned from -273.1°C. They may be compared with the values in "International Critical Tables."<sup>3</sup> These values are given only at temperatures from 1 to 8°, but may be easily extrapolated to 0 and 8.25°. The result is

Temperature.....	0°	8.25°
I. C. T.....	8.0	18.0
A. S. C.....	8.22	17.94

The experimental values for the vapor pressure of the liquid may be approximately represented by the equation

$$\text{Log } P = 7.8584 - 1860/T \tag{2}$$

but the deviations are systematic. Figure 1 shows the deviation plot, the quantity  $\Delta = \log P - (7.8584 - 1860/T)$  being plotted against the

<sup>3</sup> "International Critical Tables," Vol. III, p. 209.

temperature. The present data are represented by crosses, those of the "International Critical Tables"<sup>4</sup> by circles. A smooth curve can be drawn through the crosses so that none of them, except the single determination at 60°, falls more than 0.0005 from the curve. This corresponds to a discrepancy of 0.12%. By taking  $\Delta$  from this curve at round temperatures, values of the vapor pressure can be accurately interpolated. The results are given in Table II, which also shows the "International Critical Tables" values. The values at 0 and 20° are in excellent agreement

TABLE II  
INTERPOLATED VAPOR PRESSURES (MILLIMETERS OF MERCURY)

<i>T</i>	Liquid		<i>M</i>	Solid		
	<i>P</i> A. S. C.	<i>P</i> I. C. T.		<i>P</i> A. S. C.	<i>P</i> I. C. T.	
0°	11.16	...	85.51	8.22	[8.0]	84.45
8.25	17.94	...	84.57	17.94	[18.0]	84.57
10	19.76	18.9	84.37			
20	33.52	33.1	83.15			
30	54.55	52.2	81.88			
40	85.59	82.6	80.57			
50	130.4	125.9	79.24			
60	193.4	189.7	77.90			
70	280.2	279.6	76.56			
80	396.4	398.1	75.22			
90	549.4	552.1	73.90			
100	747.6	753.4	72.60			
100.5	...	760.0	...			
100.57	760.0	...	72.55			
110	1000	...	71.33			

with the corresponding values published in my first paper; that at 10° is a trifle lower (19.76 instead of 19.88) and is doubtless more reliable. The table also shows the apparent molecular weight of the saturated vapor, calculated as explained in the first paper.

#### Latent Heat Measurements

The latent heats directly measured were the heat of fusion at the triple point and the heat of vaporization of the liquid at temperatures from 0 to 100°.

For the former, a very simple calorimeter was used, consisting of a Dewar cylinder holding 200 cc. of water, provided with a stirrer, a Beckmann thermometer, and a heater of 44.5 ohms resistance, made of wire of negligible temperature resistance coefficient, and enclosed in a copper envelope. Current was supplied at 15 volts, being controlled by a sensitive voltmeter which could be read to 0.01 volt, and which was found actually correct to that degree by potentiometric comparison with a standard cell. The room temperature was constant within 0.5°, and it was found that

<sup>4</sup> "International Critical Tables," Vol. III, p. 215.

when the calorimeter was at room temperature, and evaporation stopped by a layer of kerosene, no detectable heat exchange occurred within twice the time required for a determination. During an experiment the calorimeter temperature fell for a few minutes to some  $2^{\circ}$  below that of the room. The rate of leak at that head was determined and the appropriate correction applied; it amounted to about 0.5% of the total heat measured.

The scheme of measurement consisted of introducing frozen acid into the calorimeter, and determining the time of current flow required to reestablish the original temperature. The acid (about 8 g.) was sealed into a vessel with five fingers, which it partially filled, thus offering a larger surface for heat transfer than a plain bulb. After freezing, it was left for some time in water at  $7^{\circ}$ , and was then quickly transferred, with a hasty wiping, to the calorimeter. The method seemed at first unpromisingly crude, but experiment showed that the errors due to the carrying over of cold water and to absorption of heat in transfer were surprisingly constant. At the same time the current was turned on and allowed to flow for a time which preliminary trial showed would nearly restore the original temperature. When equilibrium had been established, the temperature was found a few hundredths of a degree too low; the time of current flow which would have been needed to make good the deficiency was readily estimated. For example, in one experiment, the current flowed for 8.25 minutes, and the final temperature was  $0.045^{\circ}$  too low. If no thermal leak had occurred, it would have been  $0.055^{\circ}$  too low. Since 3.8 minutes of current were needed to raise the calorimeter  $1^{\circ}$  (when the acid was already at the calorimeter temperature) the extra current needed to restore exactly the original temperature would be 0.21 minutes, making the total time 8.46 minutes. Other determinations gave 8.40, 8.46 and 8.44 minutes, the average being 8.44. In some cases the acid was freshly frozen, in others it had been frozen for some hours.

What was actually measured was, of course, the heat of fusion at the triple point, plus the heat content of the solid from  $7$  to  $8.25^{\circ}$ , plus the heat content of the liquid from  $8.25^{\circ}$  to the calorimeter temperature, plus the heat content of the glass over the whole range, plus the errors of transfer. Exactly similar experiments were made (alternately with those described) in which the only difference was that the acid was not frozen. The results were 1.31, 1.34 and 1.31 minutes, average 1.32. The sum of heat quantities measured is evidently the same as before, except that the heat of fusion is absent, and the liquid, instead of the solid, has been heated from  $7$  to  $8.25^{\circ}$ . The difference between the two results, 7.12 minutes, evidently represents the heat of fusion at  $7^{\circ}$ . Similar determinations in which the original temperature was  $0^{\circ}$  gave 6.94 minutes, corresponding to the heat of fusion at  $0^{\circ}$ . The extrapolated value at  $8.25^{\circ}$  is 7.15 minutes, with a probable error of 0.03.

These values are given first in minutes, rather than in joules per gram, because an unfortunate accident prevented the exact determination of the quantity of acid used, and no more pure acid was available for a repetition. The vessel and contained acid were weighed, but when the vessel was opened to remove the acid, the liquid was thrown forcibly back by the inrush of air, and one of the fingers was broken. Almost all of the fragments were recovered and weighed, and by piecing them together it was estimated that not over 0.05 g. of glass was lost. On this basis, the acid weighed 7.85 grams. If, in reality, more glass was lost, the true weight



Fig. 2.—Device for ice calorimetry of heat of vaporization.

of the acid was less, the true heat of fusion higher than that calculated, namely 268 joules per gram at  $0^{\circ}$ , 275 joules at  $7^{\circ}$  and 276 joules at  $8.25^{\circ}$ . The value given in "International Critical Tables"<sup>5</sup> is 246.5 joules.

The temperature coefficient indicates that the liquid has, as usual, a higher specific heat than the solid. Indeed, this difference can be taken directly from the experimental data, and amounts to 1 joule per degree per gram; this figure, involving differences between four larger quantities, is subject to a large uncertainty, estimated at  $\pm 0.2$ . According to "International Critical Tables" the specific heat of the liquid is 1.83 joules<sup>6</sup> and that of the solid 1.80 joules.<sup>7</sup> The latter datum, as well as those in Landolt-Börnstein,<sup>8</sup> is based on a paper by Massol and Faucon,<sup>9</sup> an inspection of which reveals that it was lauric acid, and not formic acid, with which they were obtained. There appears to be no reliable determination of the heat capacity of crystalline formic acid. Massol and Guillot<sup>10</sup> state that they found the specific heat of the solid to exceed that of the liquid, but as they make the same statement about acetic acid, which is certainly wrong, their figures must be considered worthless.

The heat of evaporation of the liquid at  $0^{\circ}$  was obtained by allowing a known quantity to evaporate slowly out of an ice calorimeter. The acid was sealed into a device illustrated in Fig. 2. The technique used in measuring and transferring the acid to this device was the same as that which had been used in filling the globes in which the vapor density had

<sup>5</sup> "International Critical Tables," Vol. V, p. 132.

<sup>6</sup> *Ibid.*, Vol. V, p. 107.

<sup>7</sup> *Ibid.*, Vol. V, p. 101.

<sup>8</sup> Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1266.

<sup>9</sup> Massol and Faucon, *Compt. rend.*, **153**, 268 (1911) (not Vol. **154** as quoted in I. C. T.).

<sup>10</sup> Massol and Guillot, *ibid.*, **121**, 208 (1895).

been determined. The lower bulb contained a series of traps designed to hold the acid in several pools, in order to distribute the absorption of heat along the length of the calorimeter tube. In use, the acid was all collected in the lower tube, which was then inserted in the calorimeter. When equilibrium was established, the upper tube was cooled to about  $-3^{\circ}$ , causing the acid to distil over in from one to two hours. Trials with water had showed that this procedure gave values correct within 1%. In order to avoid errors in measurement and transfer, two samples of acid were used.

In determining the heats of vaporization at higher temperatures, it seemed important to use a condensation method, instead of the usual scheme in which the energy required to boil away a certain quantity of liquid is determined. For in the usual method decomposition is to be feared, especially if the boiling is produced by a hot platinum wire, and the heat absorbed by decomposition will be added to the true heat of vaporization, producing a positive error. A method was, therefore, devised in which a known amount of cold mercury was introduced into a bulb which was bathed in the saturated vapor, and the quantity of condensed liquid measured by volume. Figure 3 is a sketch of the apparatus. The vapor rises from liquid acid boiling in the bulb B, and is condensed by a reflux condenser attached at C. The pear P is heated by the vapor to the boiling point, and the condensate drips off into the calibrated tube T, where its level is read by a cathetometer. The pear is shielded from liquid running down from the condenser by the umbrella U. The rod R serves to carry the condenser liquid to the stem of the umbrella without splashing; it then runs over the surface and down the rods attached to the pointed tips, finally dropping off from the goose-neck bends just below the opening of T. It was found that when the pear had once been brought to the boiling point, no change in level in T occurred, showing that the shielding was adequate. The apparatus was constructed with a ground joint at G, but this joint was never opened in use, but was kept sealed with mercury. The acid was introduced or withdrawn by distillation through the top of the condenser, which was sealed to the main purifying and storage apparatus. Provision was made for admitting dry air at atmospheric pressure, or at a pressure controlled by a manostat.

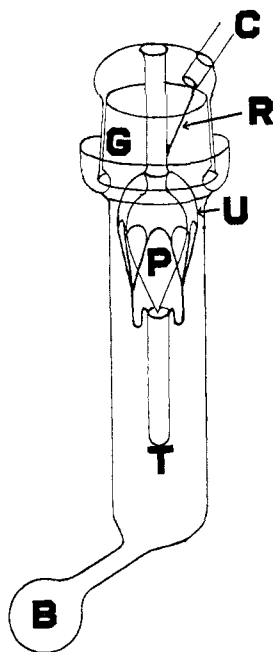


Fig. 3.—Apparatus for determining heat of vaporization.



Mercury from a water-jacketed pipet was then suddenly injected into P. The pipet was provided with a nozzle through which the mercury was forced by compressed air, the stream being so directed as not to touch the walls of the stem. As the nozzle was bathed in the water of the jacket, the only opportunity for the mercury to absorb heat prematurely was from the warm air in the stem, and the quantity so absorbed during the five or six seconds required to empty the pipet must have been very small. An obvious improvement would have been to evacuate the pear and its stem. When the level of liquid in T had again become constant, it was read, and the exact temperature of the mercury in P taken by introducing a thermometer. The weight of acid was calculated from the known volume of the tube, with the aid of the expansion formulas of Pierre and of Zander,<sup>11</sup> which agree sufficiently for the purpose.

A specimen calculation is as follows

Weight of mercury.....	268 g.
Original temperature.....	10.4°
Final (boiling) temp.....	42.2°
Heat absorbed by mercury.....	282.8 cal.
Original height in T.....	830.6 mm.
Final height.....	859.8 mm.
Corresponding volume.....	2.23 cc.
Density of acid at 42.2°.....	1.195
Weight condensed.....	2.666 g.
Heat of evap. per gram.....	106.0 cal.

In working at atmospheric pressure, a serious difficulty arose. The liquid collected in the tube T, being maintained at about 100°, began to decompose spontaneously, with escape of bubbles. This interfered with reading the level of the liquid, not only because of uncertainty as to the volume occupied by the bubbles, but because they carried away considerable acid, causing the level to fall rather rapidly. (It was at first thought that this phenomenon was caused by insufficient purification of the acid, causing a fractionation to occur, in which the more volatile fraction collected in the tube, and was actually boiled away by immersion in the hotter vapor from the less volatile residue, but repeated purification caused no diminution in the rate at which the bubbles evolved. The experiment with acid confined under mercury was then carried out in order to prove actual decomposition.) No way was found to avoid this difficulty, and the readings made at this temperature had to be corrected by admittedly uncertain estimates. They are, therefore, not as reliable as the others.

Table III contains the results of the directly determined heats of vaporization, together with the value given in "International Critical Tables."<sup>12</sup>

<sup>11</sup> Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1233.

<sup>12</sup> "International Critical Tables," Vol. V, p. 136.

TABLE III  
MEASURED HEATS OF VAPORIZATION OF THE LIQUID

	0°	42.2°	64.5°	100.5°
Observed, cal. per g.	110.6	106.0	109.3	115.5
	102.4	105.9	109.4	115.4
	103.0	106.6	109.4	
Average	102.7	106.2	109.4	115.5
Joules	430	445	458	483
"I. C. T."	...	...	...	502

Application of the Clapeyron Equation

The heat of vaporization per gram,  $\lambda$ , should be given by the equation

$$\lambda = T \Delta v (dP/dT) \tag{3}$$

Here  $\Delta v$  is essentially the volume of one gram of saturated vapor, hence we may write

$$\Delta v = (1 - \eta)RT/MP \tag{4}$$

where  $M$  is the apparent molecular weight at the particular pressure and temperature considered, and  $\eta$  is the ratio of the vapor density to that of the liquid, and constitutes a correction term which is negligible except at pressures approaching the atmospheric. The Clapeyron equation, therefore, takes the form

$$\lambda = - \frac{R d \ln P}{M d(1/T)} (1 - \eta) = -19.146 \frac{d \log P}{M d(1/T)} (1 - \eta) \text{ joules per gram} \tag{5}$$

It follows from Equation 1 that the value of  $d \log P/d(1/T)$  for the solid is  $-3160$ . At the triple point  $M$  has the value  $84.57$  and  $\eta$  is negligible. The calculated heat of sublimation is, therefore,  $716$  joules per gram.

For the liquid, we have evidently

$$d \log P/d(1/T) = -1860 - T^2 d \Delta/dT \tag{6}$$

$\Delta$  being the deviation function plotted in Fig. 1. The coefficient can be read off the smooth curve. For the four temperatures at which direct measurements were made, the calculated heats of vaporization are as shown in Table IV.

TABLE IV  
APPLICATION OF CLAPEYRON EQUATION

Temp., °C.....	0°	42.2°	64.5°	100.5°
$d \Delta/dT \times 10^4$ .....	9	-1	-2	-3.5
$d \log P/d(1/T)$ .....	-1927	-1850	-1837	-1811
$M$ .....	85.51	80.28	77.30	72.55
$\eta \times 10^4$ .....	...	...	7	20
$\lambda$ , calcd.....	432	441	455	477
$\lambda$ , obs.....	430	445	458	483

The calculated heat of vaporization of the liquid at the triple point is  $434$  joules, that of the solid  $716$  joules, and therefore, by subtraction, the calculated heat of fusion is  $282$  joules; the observed value was  $276$ , or perhaps a trifle higher. We may also calculate the heat of fusion at  $0^\circ$ ,

but the method is less simple, because in this case the vapor produced by the liquid is at a different pressure from that produced by the solid, and the joule heat has to be considered. Let  $H_s$  be the heat content of one gram of solid, and  $H_8$  that of its saturated vapor, while  $H_l$  and  $H_{11}$  are the corresponding quantities for the liquid and its vapor. Then we wish to calculate  $H_l - H_s$  (neglecting the fact that these quantities refer to slightly different pressures). We have calculated that  $H_{11} - H_l$  is 432 joules at  $0^\circ$ , and  $H_8 - H_s$  comes out 717 joules. We need to know

$$H_{11} - H_s = \int_{8.22}^{11.16} \left( \frac{\partial H}{\partial P} \right)_T dP \quad (7)$$

Now

$$\left( \frac{\partial H}{\partial P} \right)_T = v - T \left( \frac{\partial v}{\partial T} \right)_P = \left( \frac{\partial(v/T)}{\partial(1/T)} \right)_P = \frac{R}{P} \left( \frac{\partial(1/M)}{\partial(1/T)} \right)_P \quad (8)$$

and the last differential coefficient can be evaluated from the dissociation equations for the vapor, namely

$$\frac{P \times (92 - M)^2}{46(M - 46)} = K \quad (9)$$

$$\text{Log } K = 10.758 - 3092/T \quad (10)$$

(These equations are taken from the first paper. The constants of the second equation have been slightly altered in order that  $T$  may be calculated from an absolute zero of  $-273.1^\circ\text{C}$ ., instead of  $-273^\circ$ , the round number having been used in the first paper. Through an error, the value of  $K$  at  $70^\circ$  is there given as 56.60; it should be 55.72.) Logarithmic differentiation of (9) gives

$$\frac{M^3}{(92 - M)(M - 46)} \times \left( \frac{\partial(1/M)}{\partial(1/T)} \right)_P = \frac{d \ln K}{d(1/T)} = -7120 \quad (11)$$

The average value of  $M$  at  $0^\circ$  between 8 and 11-mm. may be taken approximately as 85, and, therefore, over a small range in that vicinity, we may take  $\partial(1/M)/\partial(1/T)$  as constant and equal to  $-3.2$ . Substituting in (8) and then in (7)

$$H_{11} - H_s = -23.R \int_{8.22}^{11.16} d \ln P = -8.1 \text{ joules per gram} \quad (12)$$

The calculated heat of fusion at  $0^\circ$  is, therefore,  $717 - 432 - 8 = 277$  joules, 5 joules less than at the triple point. This makes the specific heat of the liquid greater than that of the solid by 0.6 joule, a figure considerably lower than the  $1 \pm 0.2$  given by direct measurement.

### Criticism and Discussion

It will be seen that the present data are thermodynamically consistent to as good an approximation as is ordinarily obtainable in such calculations. The vapor density data were found by Ramsperger and Porter<sup>13</sup> to be in complete agreement with their own. The vapor pressure data, while

<sup>13</sup> Ramsperger and Porter, THIS JOURNAL, 50, 3036 (1928).

more regular than those of the "International Critical Tables," are not greatly different, but the directly determined heats of fusion and vaporization, if correct, require a considerable revision of the accepted values. In their favor stands the fact that they are thermodynamically consistent with the vapor density and pressure data, while the values in "International Critical Tables" are not. It is to be noted that the "International Critical Tables" value for the heat of vaporization is based upon the work of three authors, of whom one<sup>14</sup> worked long ago, while the other two<sup>15</sup> used a platinum wire to boil the acid, which may have caused error through decomposition. Neither author mentions any special precautions observed with the acid, which was merely one of several substances investigated. As for the heat of fusion, Pettersson<sup>16</sup> worked at a low temperature, and by a method which is stated by "International Critical Tables" to give low results. The paper of Guillot<sup>17</sup> is not available, but in view of his statement about the specific heat of crystalline acetic acid,<sup>10</sup> it seems more than likely that his results were vitiated by premelting, causing the specific heat of the solid to appear too great and the heat of fusion too low. The present evaluation of the difference in the specific heats of the solid and liquid must be regarded as giving an orientating value only, but leaves little doubt that it is of the ordinary sign and magnitude.

#### Interpretation

In the case of a solid or liquid emitting a vapor of constant molecular weight, a plot of  $\log P$  as ordinate against  $1/T$  as abscissa yields a curve whose slope is at every point proportional to the heat of vaporization. The temperature coefficient of the latter depends on the difference between the coefficients  $\partial H/\partial T$  for the two phases, evaluated under the restriction that the pressure shall be maintained equal to the saturation pressure. For substances which may be regarded as perfect gases or incompressible dense phases, these coefficients are equal to the specific heats at constant pressure. For solids,  $C_p$  is nearly equal to  $C_p$  of the vapor, so that the temperature coefficient is small and the vapor pressure curve is approximately straight. Liquids have higher  $C_p$ , causing their heat of evaporation to decrease with rising temperature, and the vapor pressure curves to be concave downward. The heat of vaporization of liquid formic acid has been shown to rise rapidly with the temperature, and this is due to the very high value of  $\partial H/\partial T$  for the vapor. There is no simple exact interpretation of  $\partial H/\partial T$ , but its largest term is the heat absorbed when the temperature of the vapor is raised under the prescribed conditions; and this is abnormally great with formic acid be-

<sup>14</sup> Favre and Silbermann, *Compt. rend.*, **23**, 413 (1846).

<sup>15</sup> Marshall, *Phil. Mag.*, **43**, 29 (1897); Brown, *J. Chem. Soc.*, **83**, 987 (1903).

<sup>16</sup> Pettersson, *J. prakt. Chem.*, **24**, 129, 293 (1881).

<sup>17</sup> Guillot, "Thèse," École Pharm., Montpellier, 1895.

cause the heating produces dissociation of double into single molecules with great absorption of energy.

A simple calculation will show to what extent the abnormal temperature coefficient may be accounted for by this interpretation. We may conceive of evaporation as a stepwise process, in which double molecules of vapor are first produced by evaporation, after which a certain fraction of them dissociate, absorbing heat at the rate of 14,125 calories per mole (value given in first paper) or 645 joules per gram. The whole process is conceived as isopiestic. Now, at  $0^\circ$ , only 7.6% of the saturated vapor is dissociated, so that, when 1 gram evaporates, 49 joules can be referred to dissociation. At  $100^\circ$  the figures are 30% and 194 joules, so that we might expect the heat of vaporization to be 145 joules higher at  $100^\circ$  than at  $0^\circ$ . Actually, it is only about 50 joules greater, because, superposed on the increase caused by dissociation in the vapor, we have also the normal decrease characteristic of all liquids. By adding to the actual heats of vaporization the calculated heats required to complete the dissociation of the vapor into single molecules, we may determine the heat of evaporation of single molecules from the actual liquid. The same result may be obtained by calculating the partial pressure of single molecules in the saturated vapor at various temperatures and applying the Clapeyron equation. Expressing the result in joules per mole (46 g.), we obtain 47,200 at  $0^\circ$  and 42,800 at  $100^\circ$ , a decrease of 4400. It is interesting to compare these figures with those for water, which in the liquid state is in many ways similar to formic acid, but which produces a monomolecular vapor on evaporation. For water, the heat of vaporization is 44,900 joules per mole at  $0^\circ$  and 40,700 at  $100^\circ$ , a decrease of 4200. The similarity in the figures is striking, and shows clearly how the actual temperature coefficient for formic acid is compounded of a positive term due to molecular association in the vapor, and the normal negative term. The latter may be interpreted as due to the excess of  $C_p$  for the liquid over the  $C_p$  which the vapor would possess if the equilibrium were frozen.

Although the latent heat increases with temperature, the vapor pressure curve is markedly concave downward. This is, of course, due to the variability of  $M$  in the Clapeyron equation. An inspection of Equation 5 together with Table IV shows that in determining the value of  $d \ln P / d(1/T)$  at increasing temperatures, the decrease in  $M$  outweighs the increase in  $\lambda$ .

The vapor pressure curve of the solid presents an interesting case. Let us write Equation 9 in the form

$$P \times \varphi(M) = K$$

where  $\varphi(M)$  is a function of  $M$  alone. Now, taking the value of  $K$  from Equation 10 and that of  $P$  from Equation 1, we see that they have nearly the same temperature coefficient, so that  $M$  is nearly independent of tem-

perature. As a result the curve will be of the same type obtained with other solids, and will be almost straight. The specific heat of the saturated vapor will contain only a small term due to association. This small term is of opposite sign to that which occurs in the case of the liquid, for the saturated vapor of the solid undergoes a slight increase in association when heated, due to the very rapid rise in pressure. Assuming  $C_p$  for the solid equal to  $C_p$  for the vapor with frozen equilibrium, we shall have a slight fall in the heat of sublimation with rising temperature.

While the heat of sublimation probably falls, and the heat of evaporation rises with the temperature, the heat of fusion rises, instead of falling, as it must do if it were, as in the ordinary case, the difference between the other two. We have seen already that this is due to the presence of a term  $H_{11} - H_8$ , which is usually zero. This term may also be interpreted as due to variation in the degree of dissociation. Thus, at  $0^\circ$  the liquid produces a vapor 7.6% dissociated; the vapor from the solid is 9.1%, and conversion of one into the other involves some 9 joules of dissociation heat. (The thermodynamic evaluation gave 8 joules.)

### Summary

The vapor pressure of pure formic acid, both solid and liquid, has been carefully determined between  $-5$  and  $110^\circ$ .

The heat of vaporization of the liquid, and the heat of fusion of the solid, have been determined with moderate accuracy at several temperatures.

The values so found are thermodynamically consistent among themselves, but differ, sometimes considerably, from previously accepted values.

It is shown that the differences in thermal behavior between formic acid and substances producing normal vapors, especially water, are just those to be expected when account is taken of the heat absorbed or supplied by shifting of the dissociative equilibrium in the vapor.

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