SOME THERMODYNAMIC PROPERTIES OF FORMIC ACID

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CONTENTS

I. INTRODUCTION

In processes involving either chemical reactions or interphase equilibria with formic acid vapor, it is useful to have tables of certain thermodynamic properties of the vapor. This paper presents such tables, based on a self-consistent treatment combining statistical calculations with thermal data. Results are given for the monomer considered as an ideal gas and for the real vapor in dimerization equilibrium at various temperatures and pressures, together with some properties of the saturated liquid and the ideal gas dimer.

II. STATISTICAL CALCULATIONS

The vibrational frequencies of the HCOOH molecule were assigned by Rasmussen (32) as follows: 668, 707, 1093, 1207, 1398, 1732, 2800, and 3650 cm.$^{-1}$ These values agree satisfactorily with the spectroscopic data and assignments of other investigators (2, 3, 6, 15, 17, 18, 20, 39, 41). The following interatomic distances and angles were used: C—H, 1.071 Å; C=O, 1.210 Å.; C—O, 1.420 Å.; O—H, 0.959 Å.; COH, 104°41′; OCO = OCH = 120°. These values agree fairly well with the results of the electron-diffraction study of Schomaker and O'Gorman (36) and seem more satisfactory than the values obtained by Williams (41) from the infrared spectrum. Other results (18, 22, 27, 28) were also considered. The product of the principal moments of inertia was calculated by the method of Hirschfelder (19) to be 1.553×10^4 in units of (atomic weight)^3 (Å.)^6 or 7.108×10^{-116} g.^{3} cm.^{6}

To the calorimetric entropy obtained by Stout and Fisher (38) for the liquid at 25°C. was added the entropy of vaporization, the entropy of transformation from equilibrium vapor to ideal gas monomer, and $\frac{1}{2} R \ln 2$ for random orientation in the crystal at absolute zero (14). The entropies of vaporization and transformation were calculated as described below. This gave for the ideal gas monomer

$$S_1^0 = 30.82 + 16.082 + 12.542 + 0.689 = 60.133 \text{ cal./degree mole} \quad (1)$$

TABLE 1

Thermodynamic functions of formic acid monomer

T	$(H^0 - H_0^0)/T$	C_p^0	$-(F^0 - H_0^0)/T$	ΔH_f^0	ΔF_f^0
°K.	*cal./degree mole*	*cal./degree mole*	*cal./degree mole*	*cal./mole*	*cal./mole*
200	8.358	9.612	47.561	−89,565	−85,566
250	8.710	10.637	49.462	−89,812	−84,627
298.16	9.102	11.636	51.029	−90,031	−83,638
300	9.118	11.674	51.086	−90,039	−83,598
350	9.555	12.674	52.524	–	–
400	10.005	13.613	53.829	−90,424	−81,388
450	10.455	14.482	55.033		
500	10.897	15.274	56.158	−90,716	−79,093
550	11.329	15.994	57.217		
600	11.745	16.648	58.220	−90,959	−76,743
650	12.146	17.243	59.176		
700	12.529	17.785	60.091	−91,141	−74,361
750	12.897	18.283	60.968		
800	13.247	18.738	61.811	−91,275	−71,955
850	13.584	19.158	62.625		
900	13.904	19.546	63.410	−91,374	−69,532
950	14.210	19.904	64.169		
1000	14.504	20.238	64.907	−91,434	−67,101
1100	15.052	20.834	66.314	−91,466	−64,667
1200	15.556	21.351	67.646	−91,474	−62,230
1300	16.020	21.800	68.911	−91,468	−59,791
1400	16.448	22.191	70.115	−91,449	−57,357
1500	16.839	22.532	71.258	−91,426	−54,919

Statistical calculations using the molecular data above, and not including the entropy from the torsional vibration of the OH group, gave

$$S_1^0 = 59.342 \text{ cal./degree mole} \quad (2)$$

Then the entropy of the OH vibration must amount to 0.791 cal./degree mole. From this the frequency 452 cm.^{-1} was calculated and was used with the other frequencies in all the statistical calculations. This agrees well with the frequency 430 cm.^{-1} found by Forsythe and Giauque (11) and 480 cm.^{-1} found by Redlich and Nielsen (33) for the torsional vibration in nitric acid. It was assumed that only vibration occurred, since a barrier of about 10 kcal. per mole is needed to give a hindered rotator the appropriate 0.791 cal./degree mole.

The presence of a small amount of the *trans* form of the monomer has been suggested (24, 41). Such isomerization is contrary to the interpretation used in this paper. An energy difference between *cis* and *trans* forms as low as even twice that suggested by Mariner and Bleakney (24) would contribute more to the entropy than present experimental and theoretical results can allow.

The tables of Pitzer and Gwinn (29) for hindered rotation and tables of Planck–Einstein functions (21, 37) were used. The usual statistical methods were applied in calculating the thermodynamic functions $(H^0 - H^0_0)/T$, C^0_p, and $-(F^0 - H^0_0)/T$ which are listed in table 1.

III. THERMODYNAMIC AND THERMOCHEMICAL DATA USED

A. Vapor pressure

Coolidge (10) measured the vapor pressure of liquid formic acid from −5° to 110°C. and fitted the data with the equation

$$\log P_{\text{mm}} = 7.8584 - (1860/T) + \theta \tag{3}$$

where θ is given by a deviation curve. The data of the *International Critical Tables* (Vol. III, page 215) scatter erratically around this. The normal boiling point then is 100.57°C. At 25°C. the calculated vapor pressure is 42.97 mm. or 0.05654 atm. Stout and Fisher (38) measured it at 25°C. as 43.1 mm., a value which is in good agreement; a difference of less than 0.1° in the temperature scale would account for this much discrepancy.

B. P–V–T behavior of the vapor

The vapor of formic acid deviates widely from ideal gas behavior, chiefly because of partial dimerization. Coolidge (10) found that at low temperatures and pressures the vapor could be treated as a mixture of ideal gases, but this was not satisfactory for the higher temperatures and pressures.

Following his treatment, it was assumed that the monomer and dimer separately obey equations of the form:

$$PV/n = RT(1 - \alpha P) \tag{4}$$

The equation of state of the mixture may be obtained by making any one of three equivalent assumptions: (*a*) linear combination of α's in the equations of state, (*b*) Amagat's law (additivity of volumes on mixing), (*c*) the mixture of gases is an ideal solution (Lewis fugacity rule). This assumption, in any of these forms, gives as the equation for the mixture

$$PV = RT(n_1 + n_2)[1 - P(y_1\alpha_1 + y_2\alpha_2)] \tag{5}$$

where V is the total volume of the mixture, and the n's, y's and α's are the numbers of moles, the mole fractions, and the deviations from ideality of each gas species. Since the n's vary with pressure (because of the dimerization equilibrium), it is inconvenient to use the extensive quantities (V, H, etc.) per total mole of mixture. All the following results (except where specified otherwise) are based on evaluating such quantities for a constant total mass equal to the gram-molecular weight of the monomer (46.026).

Besides the deviations from ideal gas behavior indicated by the α's, the vapor undergoes dissociation of the dimer; the equilibrium is described by the expression

$$RT \ln K = RT \ln \frac{f_1^2}{f_2} \tag{6}$$

where f_1 and f_2 are the fugacities of the monomer and dimer, respectively. From the equations of state,

$$RT \ln \frac{f_i}{Py_i} = -\alpha_i RTP \tag{7}$$

for either species i, so

$$\log K = \log (Py_1^2/y_2) - P(2\alpha_1 - \alpha_2)/2.3 \tag{8}$$

In practice, it is not possible to determine the mole fractions and also the α values from density measurements alone. Light absorption would permit the determination of y_1 (and y_2) if the absorption by the separate species were known. But Ramsperger and Porter (31) found that in the region of the ultraviolet spectrum which they studied apparently both monomer and dimer absorbed light, with the dimer chiefly responsible. Herman (16) determined the absorption of an infrared band of the dimer, and used Coolidge's density determinations and the assumption of ideal gas behavior for the separate species, to establish his absorption coefficient. There seem to be inadequate data at present for separating the effects of dimerization and of nonideal behavior.

Since the nonideality of behavior of the separate species is a small but necessary correction, and since there seems to be no evaluation definitely superior to Coolidge's estimates, his values were adopted. For convenience, equations were fitted to the numbers he used. The form of these equations was determined by the relation

$$-\alpha RT = B \tag{9}$$

where B is the second virial coefficient; the form for B is indicated in the discussion by Beattie and Stockmayer (4). Applying the resulting form of equation for the α's to the numerical values given by Coolidge led to the result:

$$\left.\begin{aligned} \alpha_1 &= -7.94/T + 5760/T^2 \\ \alpha_2 &= -11.80/T + 8620/T^2 \end{aligned}\right\} \tag{10}$$

From density data an "apparent" molecular weight, M', can be calculated from the relation

$$PV = \frac{g}{M'} RT \tag{11}$$

where g is the weight of the vapor in volume V. Values of M' are listed by Coolidge (10) for various values of T and P, and others may be calculated from density data such as those of Ramsperger and Porter (31).

It can be shown then that

$$y_1 = \frac{2 - \dfrac{M'}{M_1}(1 - P\alpha_2)}{1 + \dfrac{M'}{M_1}P(\alpha_2 - \alpha_1)} \tag{12}$$

Using α's calculated from equations 10 and y's calculated from equation 12, and giving equal weight to each "apparent molecular weight" experimentally determined by Coolidge and by Ramsperger and Porter, values of log K were calculated from equation 8. These values, with the pressures in atmospheres, were fitted by the equation

$$\log K = 5.62919 - 2985.33/T + 0.76044 \log T \tag{13}$$

and log K was calculated from equation 13 for all subsequent work. Some indication of the uncertainty in log K is given by the variation of the heat of dissociation derived from it.

C. Heat of dissociation of the dimer

Differentiation of equation 13 gives the standard heat of dissociation of the dimer:

$$\Delta H_d^0 = 13{,}659.83 + 1.51113T \tag{14}$$

At 25°C. the heat of dissociation is 14,110 cal./mole of dimer (92.052 g.) for the change from unit fugacity of the real gas dimer to unit fugacity of the real gas monomer. Coolidge obtained a heat of 14,125 cal. from equilibrium constants calculated on assumed ideal gas behavior; this was an average for temperatures from 10°C. to about 100°C. Ramsperger and Porter from their own data found that the heat was 13,900 cal. at 25°C. and increased to 14,300 at 80°C.; combining Coolidge's data with theirs, they found 14,100 cal. as an average over the wider temperature range. Herman calculated 12,400 cal. from his work, but this seems less certain than the other values. Halford (14) used 14,400 cal. from an equation based on Coolidge's vapor-density data from 10° to 80°C. The equation agrees fairly well at 25°C. with equation 14 above, but departs considerably at higher temperatures. The difference is due chiefly to the inclusion of higher temperature data in establishing equation 14, which is therefore considered a better representation, especially for higher temperatures.

From the equation of state and from standard thermodynamic relations,

$$\left(\frac{\partial H}{\partial P}\right)_T = n_i RT^2 \left(\frac{d\alpha_i}{dT}\right) \tag{15}$$

for n_i moles of species i. Integration gives

$$\Delta H = n_i RT^2 \left(\frac{d\alpha_i}{dT}\right)(P^* - P) \tag{16}$$

for an expansion from P to a very low pressure P^* where the species behaves as an ideal gas. When this relation is applied to each species, integration from unit fugacity ($P = 1.0405$ for the monomer, $P = 1.0629$ for the dimer) and combination with the standard heat of dissociation give the heat of dissociation for the ideal gas species. At 25°C. this is 14,140 cal./92.052 g.

D. Heat of vaporization

The heat of vaporization was calculated from the vapor pressure using the thermodynamically exact Clapeyron relation. Vapor volumes, V, were obtained from the scheme described above. Liquid volumes, v, were calculated from the equation for liquid density in the *International Critical Tables* (Vol. III, page 28); this equation represents well the more recent data of Timmermans (*Annual Tables of Constants*, 1941) and moderately well the data of Coolidge. Since v/V is small, the value of v need not be known with extreme precision. Values for $d\theta/d(1/T)$ were obtained graphically, where θ is the vapor-pressure term in equation 3.

TABLE 2

Heat of vaporization of formic acid

(calories per 46.026 g.)

t	ΔH_v	t	ΔH_v
°C.		°C.	
0	4743	75	5057
25	4782	100	5235
50	4901	125	5418

The resulting heats of vaporization at several temperatures are given in table 2. They agree well with the experimental measurements of Coolidge. The perhaps unexpected increase of the heat of vaporization with rising temperature is due to the progressively greater dissociation of the equilibrium (saturated) vapor at higher temperatures; the heat of dissociation from saturation pressure to the ideal gas monomer is not included in the heat of vaporization.

E. Heat of formation

In order to establish heats and free energies of formation, it is necessary to use some experimental data for a heat or free energy of reaction to "set the level" for the statistical calculations. Several such data are available.

(*1*) The heat of combusion of liquid formic acid is given by Bichowski and Rossini (5) as 62.8 kcal./g.-mole at 18°C. This is based on early studies (about 1880–1892) wherein values of 63.0, 62.5, and 63.0 were reported by different investigators; the uncertainty is estimated as ±300 to 1000 cal. because of the difficulties in purification (referred to by Coolidge) and calorimetric technique. Conversion of this value to 25°C. requires no significant change. Combination of this heat of combustion with heats of formation from the tables of the American

Petroleum Institute (1) or of the National Bureau of Standards (25) (see table 3) gives −99,569 cal. for the heat of formation of the liquid at 25°C. This corresponds to the value −99,750 given by Parks and Huffman (26) based on the same heat of combustion. Adding the heat of vaporization, 4782 cal. (table 2), gives −94,787 for the heat of formation of the saturated vapor. The enthalpy change in going from saturated vapor to ideal gas monomer is calculated from equations 17 and 18

TABLE 3

*Standard energies of formation at 25°C.**

SUBSTANCE	ΔH_f^0	ΔF_f^0
	cal./mole	*cal./mole*
H_2O(l)	−68,317.4	−56,689.9
CO	−26,415.7	−32,807.7
CO_2	−94,051.8	−94.259.8

* Data from the American Petroleum Institute (1, 1945).

TABLE 4

Equilibrium constants for the reaction

HCOOH(aq) = H_2O(l) + CO(g)

T	K	K_{corr}	ΔF^0
°*K.*			*cal./mole*
429.26	89.9	90.80	−3846
491.06	310	316.97	−5620

$$\Delta H = n_2 \Delta H_d(P_e) - RT^2 P_e \frac{\mathrm{d}\alpha_1}{\mathrm{d}T} \tag{17}$$

$$\Delta H_d(P_e) = \Delta H_d^0 - RT^2 \left[2 \frac{\mathrm{d}\alpha_1}{\mathrm{d}T} (P_1 - P_e) + \frac{\mathrm{d}\alpha_2}{\mathrm{d}T} (P_e - P_2) \right] \tag{18}$$

where P_e is the saturated vapor pressure, and P_1 and P_2 are the pressures of monomer and dimer at unit fugacity. At 25°C. this becomes 6245 cal./46.026 g.

Adding this to the heat of formation of the saturated vapor gives −88,542 cal. for the heat of formation of the ideal gas monomer. From the statistical calculations, $\Delta(H^0 - H_0^0)_f$ is −1631 cal. at 25°C.; therefore the heat of combustion yields a value of −86,911 cal./46.026 g. for ΔH_{0f}^0.

(*2*) Branch (7) studied the reaction

$$HCOOH(aq) = H_2O(liq) + CO(g)$$

wherein hydrochloric acid was used as catalyst. His data gave the values of K in table 4. French (13) applied fugacity corrections and obtained the values listed as K_{corr}. The activity of formic acid was taken as equal to its molality (*cf.* Redlich and Rosenfeld (34)). From the corrected K values were calculated the free-energy changes tabulated. If it is assumed that ΔH^0 for the reaction is independent of temperature from 298° to 491°K., then extrapolation gives -83.4 cal. for the free-energy change at 25°C. The uncorrected values of K give similarly a value of -103 cal.

For the dilution from pure liquid acid to unit molality with hydrochloric acid present, Ramsperger and Porter (31) calculated the free-energy change to be -2960 cal. Combining this with the -83 cal. above and the free energies of formation of water and carbon monoxide from the tables of the American Petroleum Institute or the National Bureau of Standards (see table 3) gives the free energy of formation of the pure liquid or equilibrium vapor as $-86{,}454$ cal.

TABLE 5

Equilibrium constants for the reaction

$HCOOH(aq) = H_2 + CO_2$

T	K	K_{corr}	ΔF^0
°K.			cal./mole
293.16	14×10^3	8.59×10^3	-5277
323.16	36×10^3	21.92×10^3	-6419
343.16	64×10^3	44.01×10^3	-7291
363.16	106×10^3	79.52×10^3	-8143

The change in free energy in going from saturated vapor (at P_e) to ideal gas monomer is calculated from

$$\Delta F = RTP_e\alpha_1 - RT \ln P_e y_1 \qquad (19)$$

and at 25°C. this becomes $+2629$ cal. From the statistical calculations, at 25°C.

$$\Delta F_f^0 - \Delta H_{0f}^0 = +\,4762 \qquad (20)$$

after combination with the thermodynamic functions for the elements (1); therefore for the heat of formation,

$$\Delta H_{0f}^0 = -\,88{,}587 \text{ cal.}/46.026 \text{ g.} \qquad (21)$$

(*3*) The reaction

$$HCOOH(aq) = H_2 + CO_2$$

was studied by Bredig, Carter, and Enderli (8). Table 5 presents their equilibrium constants as well as those with fugacity corrections applied by French (the gas pressures were from 30 to 70 atm. each). The concentration is again expressed in molality.

Using $\Delta C_p = -7.85$, extrapolation to 25°C. gives the free-energy change as -5429 cal. This quantity is -5764 cal. if the fugacity corrections are omitted (Parks and Huffman calculated -5810). For the dilution without hydrochloric acid present, Kaye and Parks (23) estimated a free-energy change of -2440 cal. Combining these with the other appropriate values gives

$$\Delta H^0_{0f} = -88{,}524 \text{ cal./46.026 g.} \tag{22}$$

for the ideal gas monomer.

A comparison of the values for ΔH^0_{0f} from each source shows that the one from the heat of combustion is lower than the ones from equilibrium studies, and that the latter two agree well with each other. If the heat of combustion as used were higher than the actual heat of combustion, then the resulting ΔH^0_{0f} value would be in better agreement; however, experimental errors would be expected to give too low rather than too high a heat. If part of the formic acid had decomposed to water and carbon monoxide, as Coolidge found it did unless unusual precautions were taken, then the heat of combustion found would be greater than the true value (since the heat of combustion for carbon monoxide is −67.6 kcal./mole); but quantitatively it would require decomposition of 5 to 10 mole per cent of the acid to make the difference required and this is improbably high. On the other hand, if the fugacity corrections are omitted from the equilibria, the resulting ΔH^0_{0f} values are numerically lower and in better agreement with that from the heat of combustion. But there seems no reason to omit these corrections; although uncertain in magnitude, they are presumably in the correct direction. The free energies of dilution are somewhat uncertain and may be responsible for part of this discrepancy; recalculation of them should give rather minor changes and does not seem worthwhile.

From a consideration of these results, and giving greater weight to the equilibria than to the combustion, the value of −88,400 cal./46.026 g. was selected for ΔH^0_{0f}, and this set the level for all of the other thermodynamically related values.

IV. RESULTING THERMODYNAMIC PROPERTIES OF FORMIC ACID

The final results of this work for several of the properties of formic acid are given in the preceding five sections. The following four sections give other derived properties and complete the present scheme in an internally consistent fashion.

A. Energies of formation of ideal gas monomer

The zero-temperature heat of formation found in the preceding section, −88,400 cal./46.026 g., was combined with the statistical calculations, using statistical functions for the elements from the tables of the American Petroleum Institute (1, 1949). The resulting heats and free energies of formation of the ideal gas monomer from 200°K. to 1500°K. are given in table 1. More digits are carried than are justified by the accuracy of the thermal or statistical data, but it is desirable to maintain the internal consistency of the values and of their interrelations.

B. Energies of formation of ideal gas dimer

The heat of formation of the ideal gas dimer is calculated from the expression

$$\Delta H^0_{f2} = 2\Delta H^0_{f1} - \Delta H^0_d + RT^2\left(2P_1 \frac{d\alpha_1}{dT} - P_2 \frac{d\alpha_2}{dT}\right) \tag{23}$$

where ΔH_d^0 is obtained from equation 14, the α_i's from equations 10, and the P_i's from

$$\alpha_i P_i = 2.3 \log P_i \tag{24}$$

where, as before, P_i is the pressure of the pure species i at unit fugacity.

The free energy of formation is obtained using ΔF_{f1}^0 from table 1, and equation 25:

$$\Delta F_{f2}^0 = 2\Delta F_{f1}^0 + 2.3\, RT \log K \tag{25}$$

The results, in the temperature range for which the values of α seem valid, are shown in table 6.

TABLE 6

Energies of formation of ideal gas dimer

T	ΔH_f^0	ΔF_f^0
°K.	cal./92.052 g.	cal./92.052 g.
298.16	−194,202	−170,688
300	−194,221	−170,542
400	−195,133	−162,512

C. *Energies of formation of real vapor*

The mole fractions in the real vapor at a particular temperature and pressure are calculated from equation 8, using equation 13 for log K. From the mole fractions the numbers of moles of monomer and dimer in 46.026 g. are obtained, and the heat of formation of the real vapor mixture at T and P is then

$$\Delta H_f \text{ (real vapor)} = n_1\, \Delta H_{f1}^0 + n_2\, \Delta H_{f2}^0 + RT^2P\left(n_1 \frac{d\alpha_1}{dT} + n_2 \frac{d\alpha_2}{dT}\right) \tag{26}$$

The free energy of formation is calculated from equation 27:

$$\Delta F_f \text{ (real vapor)} = \Delta F_{f1}^0 + RT\,(\ln Py_1 - P\alpha_1) \tag{27}$$

The results are shown in table 7.

D. *Energies of formation of liquid*

Combination of the heat of formation of the saturated vapor at a particular temperature with the heat of vaporization at that temperature (calculated as in Section III, D) gives the heat of formation of the saturated liquid. The free energy of formation of the liquid is, of course, the same as that for the vapor in equilibrium with it. The results are shown in table 7.

E. *Comparison with other sources*

Some calculated results are compared in table 8. The values for heats of formation of the liquid and of the ideal gas monomer given by the National Bureau of Standards (25) are numerically less than the values of this report by about 3.4

kcal. The Bureau's results, according to Rossini (35), are based on the heat of combustion given by Thomsen (40) and the vapor dissociation correlation of Halford (14). Thomsen burned the vapor of formic acid at about 93°C. (just below the boiling point) and calculated the value for 18°C. with apparently no concept of its dimerization. Besides this, the vapor was mixed with a small unspecified amount of air, and a platinum wire spiral was kept in the flame to maintain combustion; the mixing with air affects the dissociation to an unknown extent. Because of these procedures, the meaning of this heat of combustion is uncertain, and application of a dissociation relation does not establish the heats of combustion or formation with reliability. Furthermore, for the calculation of chemical equilibria, values obtained from equilibrium measurements are in general more accurate than those derived from combustion measurements,

TABLE 7

Energies of formation of real vapor and liquid

T	P	$\Delta H_f(P)$	$\Delta H_f(\mathrm{l})$	$\Delta F_f(P)$†
°K.	atm.	cal./46.026 g.	cal./46.026 g.	cal./46.026 g.
298.16	0.056536*	−96,275	−101,057	−86,266
	0.050	−96,223		−86,307
	0.030	−95,971		−86,479
	0.020	−95,726		−86,620
	0.010	−95,191		−86,873
	0.005	−94,493		−87,143
	0.002	−93,343		−87,536
	0.001	−92,408		−87,864
300	0.061786*	−96,260	−101,048	−86,174
	0.055	−96,210		−86,213
	0.030	−95,897		−86,420
	0.020	−95,635		−86,564
	0.010	−95,067		−86,821
	0.005	−94,334		−87,098
	0.002	−93,154		−87,500
	0.001	−92,227		−87,836
400	2.0753*	−94,911	−100,343	−81,306
	1.5	−94,503		−81,481
	1.0	−93,960		−81,713
	0.5	−93,002		−82,141
	0.2	−91,879		−82,765
	0.1	−91,274		−83,271
	0.05	−90,889		−83,797
	0.02	−90,621		−84,509
	0.01	−90,525		−85,054

$\Delta H_f(P)$ and $\Delta F_f(P)$ are for the equilibrium vapor mixture (real gases) at pressure P. $\Delta H_f(\mathrm{l})$ is for the liquid phase in equilibrium with the vapor.

* Saturation pressure (vapor pressure).

† $\Delta F_f(P) = \Delta F_f(\mathrm{l})$ at the saturation pressure.

which involve small differences of large numbers. Small errors of measurement in heats of combustion cause much greater differences in the calculated energy changes and equilibrium state of a given reaction than do the usual errors in careful equilibrium measurements.

The heat of dissociation as given by Halford was discussed above; his temperature coefficient is greater than that from equation 14, and the latter is believed more reliable. Foz and Morcillo (12) recently calculated 14.5 kcal., using Coolidge's data and a power series equation of state up to P^4.

The heat of vaporization established from the Clapeyron relation and the vapor behavior agrees within about 1 per cent with the experimental measurements of Coolidge at temperatures from 0°C. to 100°C. From a study of aqueous solutions of formic acid, Campbell and Campbell (9) deduced heats of vaporization for pure formic acid corresponding to 7069 cal./mole at 30°C. and 5388 cal./mole at 50°C. The latter figure is 10 per cent higher than the values presented here, and their temperature coefficient is in the reverse direction. Earlier experimental measurements of the heat of vaporization gave higher values than those of Coolidge, but involve acid of questionable purity.

TABLE 8

Comparison of results for formic acid at 298.16°K.

FORMIC ACID		ΔH_f°		ΔF_f°		S^0	
		This report	N.B.S.	This report	N.B.S.	This report	N.B.S.
		kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*	*cal./degree mole*	*cal./degree mole*
Ideal gas	Monomer	−90.03	−86.67	−83.64	−80.24	60.13	60.0
	Dimer	−194.20	−187.7	−170.69	−163.8	83.35	83.1
Liquid		−101.06	−97.8	−86.27	−82.7	30.82*	30.82*

* Not including ½ R ln 2 for random orientation in the crystal.

The mole is taken as 46.026 g. for the monomer and the liquid and as 92.052 g. for the dimer.

For the heat capacity of the liquid the experimental values 23.7 (38) and 23.88 (30) cal./degree mole have been reported. The experimental data for the vapor pressure, and the heat capacity and dissociation of the vapor, lead to a somewhat lower value. The final equation for the dissociation constant was chosen in such a manner as to give the highest value for the liquid heat capacity consistent with the vapor densities. This value, 23.57 cal./degree mole, is sufficiently close to the direct experimental results.

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V. REFERENCES

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