The deviation from an integral value found corresponds to a packing fraction of -14 ($\times 10^{-4}$), which is much greater than would be indicated by Aston's curve, provided that cesium is a simple element. Another unexpectedly large packing fraction was recently found by Baxter and Butler[19] for titanium, although in this case doubtful indications of another mass line have been reported and the element may not be simple. It may well be that further investigation will prove that cesium is also complex.

Acknowledgment for financial assistance is made to an anonymous benefactor of this Laboratory, and to the Carnegie Institution of Washington.

Summary

An analysis of cesium chloride, prepared by the recrystallization of alums of cesium, by comparison with silver confirmed the atomic weight of cesium to be 132.81.

CAMBRIDGE, MASSACHUSETTS

THE VAPOR DENSITY AND SOME OTHER PROPERTIES OF FORMIC ACID

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Introduction

In connection with some work on the adsorption of formic acid vapor, it became necessary to know the density of the vapor at ordinary temperatures and at pressures below the vapor pressure of the liquid. The only measurements seem to be those of Bineau;[1] Peterson and Ekstrand[2] give fragmentary data at higher temperatures and pressures. It seemed necessary to undertake direct determination of the vapor density. The acid prepared for this purpose appeared to be of exceptional purity, and certain other properties were determined for purposes of comparison.

Purification and Preservation of Formic Acid

Even at room temperature, formic acid slowly decomposes into water and carbon monoxide. Bulbs of Kahlbaum's best acid, which had presumably been stored for some time, were found to contain high pressures of the latter, while freshly imported bulbs did not. After fruitless attempts to remove the water by distillation over phosphorus pentoxide, acid sodium sulfate and magnesium perchlorate trihydrate (the first two decomposed the vapor, while the third absorbed it copiously), it was

[19] Baxter and Butler, THIS JOURNAL, **50**, 408 (1928).

[1] Bineau, *Ann. chim. phys.*, [3] **18**, 228 (1846).

[2] Peterson and Ekstrand, *Ber.*, **13**, 1194 (1880).

decided to fall back on vacuum distillation, crystallization and sublimation. (That is, these processes were carried out in a vacuum apparatus, constantly pumped free of all gases other than the vapor of the acid.) As a test of the purity of the acid, the vapor pressure at 0° was observed. This is more than 8 degrees below the freezing point, but no difficulty was encountered in preventing crystallization, provided that the liquid (if formed by recent melting of the solid) was previously heated to about 20° for a minute or two. If this precaution was neglected, the liquid invariably froze upon applying the ice-bath, even though the solid previously present had first been entirely melted.

Distillation was carried out at room temperature, the distillate being condensed in a bulb packed in ice. Heating was avoided, both in order to prevent decomposition, and because the effectiveness of the separation is greater at low temperatures.[3] Five fractional distillations yielded a volatile fraction having a vapor pressure of 11.15 mm. Crystallization was carried out in an apparatus similar to a small ice calorimeter, connected to the source of acid by a mercury trap at the bottom. The inner tube was first filled with solid carbon dioxide, and allowed to collect a sheath of solid formic acid. The mercury trap being closed, the acid was melted and the major portion again frozen out on the inner tube. The mercury was then lowered to allow the mother liquor to be blown out into the evacuated system beyond. The vapor pressure of samples prepared in this way approached the same value, but the method was cumbersome and slow. The most effective procedure was found to be to freeze the whole sample with an ice-bath, and then to pump off about a tenth of it without allowing the rest to melt. The water came off with the volatile fraction, the residue being nearly pure. The vapor pressure of the residue (after fusion, of course) rose rapidly on successive sublimations to the value 11.16 mm., which was repeatedly attained, but never exceeded, in purifying different portions. This may therefore be taken as the value for pure formic acid.

In order to estimate the degree of purity attained, an isolated portion of the acid was successively diluted with known amounts of water, and the vapor pressures observed. The water was weighed into thin glass sealed bulbs, which it nearly filled, and which were placed in fingers depending from the apparatus near the manometer. The bulbs were broken one at a time, by causing their contents to freeze, and the water completely transferred to the sample of acid by immersing the bulb containing the latter in carbon dioxide. At the same time, any air which might have been introduced in sealing the water into the bulbs was pumped off, the volatility of both water and formic acid being negligible at −79°. The acid was then melted, the bulb well shaken to ensure thorough mixing,

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[3] Jones, *J. Soc. Chem. Ind.*, **38**, 362T (1919).

and the pressure determined. At the conclusion of the series, the diluted acid was sealed off and weighed. No correction was required for the amount of acid existing as vapor in the free space, which was of the same order of magnitude as that occupied by the liquid.

The vapor pressures of the pure acid, as solid and liquid, and of the diluted acids as liquids, are given in Table I. The temperatures other than 0° were read on a tenth-degree thermometer with Bureau of Standards certificate. The values given in International Critical Tables[4] are included for comparison. My values are consistently higher, which is presumably an indication of greater purity. It will be observed that at 0° the vapor pressure is depressed 0.01 mm. by about 0.02% of water. Since the purifying process was repeated twice, even after the vapor pressure had reached a value constant within this limit, it seems probable that the final product was of the order of 99.99% pure.

TABLE I

VAPOR PRESSURES OF PURE AND AQUEOUS FORMIC ACID IN MM. OF HG

		Pressures			Pressure lowering per 1% of H_2O	
Water, %		0°	10°	20°	0°	20°
0.00	(solid)	8.67				
.00	I. C. T.	8.0				
.00	(liquid)	11.16	19.88	33.54		
.00	I. C. T.		18.9	33.1		
.29		11.08		33.19	0.28	1.20
.59		10.92		32.85	.41	1.17
1.30		10.62		31.99	.42	1.19
4.09		9.47		28.83	.41	1.15
7.96		8.00		25.01	.40	1.09
10.47	I. C. T.		12.4	22.1		1.05

It is of interest to compare the lowering of the vapor pressure produced by water with the theoretical value for an involatile solute of molecular weight 18. Assuming that sufficiently dilute solutions obey van't Hoff's law, the osmotic pressure of such a solute would be $RT\delta m/18$, where δ is the density of the liquid solvent and m the weight fraction of the solute. The lowering of the vapor pressure bears to the osmotic pressure the ratio which the density of the vapor of the solvent bears to that of the liquid. Now, at 20° and 33 mm. pressure, as will appear later, the density of formic acid vapor can be calculated from the gas law on the basis of an apparent molecular weight of 83. We have, then, for the lowering of the vapor pressure

$$\Delta p = \frac{83p}{RT\delta} \times \frac{RT\delta m}{18} = 4.6\,pm = 155\,m$$

The limiting value of the observed ratio is about 120. The discrepancy is doubtless due primarily to the volatility of the dissolved water. If

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[4] Volume III, p. 209 (solid, extrapolated), 215 (liquid), 364 (aqueous).

the water polymerized, an effect in the same direction would be produced; but the degree of polymerization should change with dilution, whereas the observed lowering bears a nearly constant ratio to the concentration over the four lowest values. (The observation on the most dilute solution at 0° is plainly in error.)

It was noticed that the pressure in a bulb half full of pure acid rose at the rate of about a millimeter per day. The actual fraction decomposed must have been very small, but the carbon monoxide evolved greatly hindered the manipulation of the apparatus. It was found that decomposition could be entirely prevented by keeping the acid frozen. The main supply of purified acid was accordingly kept constantly frozen, the ice-pack never being removed except during the process of drawing off a sample for use, during which the high latent heat of evaporation prevented fusion.

The freezing point of the pure acid was determined in a double-walled tube. The inside tube contained the bulb and stem of the thermometer, while the space between the walls was occupied by partly frozen acid under its own vapor pressure. The whole was surrounded by air at about 8°. The thermometer was constant at 8.26°, even when the proportions of solid and liquid were varied.

The density of the acid was found to be 1.2456 at 0° and 1.2206 at 20°, both at atmospheric pressure.

The Vapor Density Measurements

In order to determine the vapor density, the method adopted was to transfer known quantities of acid (measured volumetrically in the liquid state) to containers of known volume, and observe the pressure developed at a series of temperatures. The apparatus is outlined in Fig. 1. It was necessary to make allowance for possible adsorption on the glass, which would cause the results to be too high. This was accomplished by comparison of the results obtained with two different containers having very different ratios of surface to volume. The first, called the globe (G, Fig. 1), was a 5-liter spherical Pyrex flask, and had, together with its connecting tubing, a volume of 5218 cc. and a wall surface estimated at 1500 cm.^{2}, giving a surface-volume ratio of 0.287 cm.$^{-1}$. The second container took the form of 13 meters of tubing arranged in a coil (C, Fig. 1) containing 324 cc., and having a wall surface of 2284 cm.^{2}, bearing to the volume the ratio 7.05 cm.$^{-1}$. Each container was connected to one arm of its own manometer (M, M, Fig. 1), which was of 2cm. diameter, and could be read to 0.02 mm. by means of a micrometer microscope sliding on parallel ways. The mercury level was adjustable by tube and leveling bulb (not shown in the figure), care being taken always to bring the mercury to the calibration mark for each reading.

By lowering the mercury, the manometers could be made to serve as valves, giving communication to the rest of the apparatus. The containers and manometers were mounted in a large iron tank, fitted with a powerful stirrer, and filled with water (or brine) which could be heated rapidly by running in live steam, or held at any desired temperature during a reading, within 0.05°, by adjustable gas burners. A plate glass window permitted reading of the manometers and also of a tenth-degree thermometer which had been compared with one standardized by the Bureau of Standards.

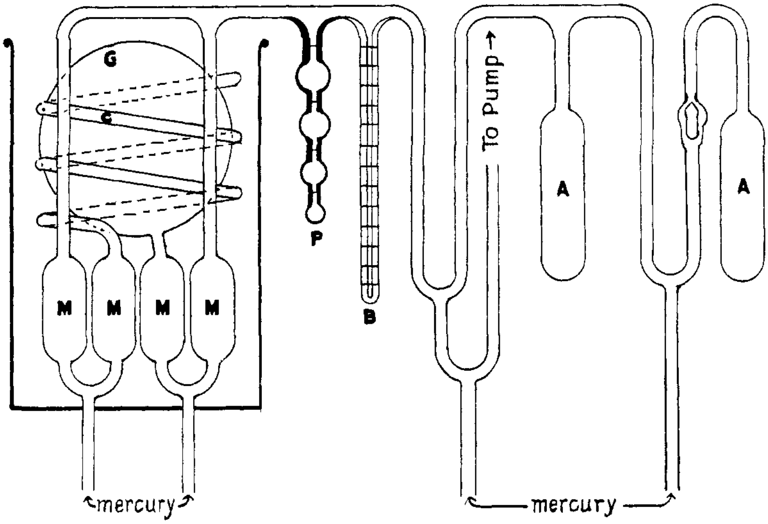

Fig. 1.

Outside the tank were located a series of little bulbs (P, Fig. 1), accurately calibrated, and a capillary buret (B) which could be read to 0.1 mg. of liquid. Other mercury valves, operated by leveling bulbs not shown in Fig. 1, gave communication to a mercury diffusion pump, and to several appendixes (two, A, A, are shown in Fig. 1) which were useful in subliming the acid during purification, in storing the final product, and in testing the vapor pressure. (For this purpose, the globe was first exhausted and its manometer closed. The sample was then placed in one of the appendixes A, an ice-pack applied, and communication established with the outside arm of the manometer M, upon which the pressure was read. In order to eliminate the possibility of traces of air or carbon monoxide being present, a series of readings was made on each sample, separated by intervals of pumping. When the acid was pure no diminution in pressure could be detected.) The appendix used for storage was fitted with a glass valve, which prevented mercury from being forced over when the pressure in the rest of the apparatus rose, either accidentally or by design.

The diffusion pump was backed by a Hyvac oil pump. In spite of the intermediate presence of a soda-lime tube, a great deal of trouble was caused by corrosion of this pump. It was finally replaced by a 3-stage rotary pump, which was not affected by the acid, even when the protecting tube was removed.

In use, the globe and coil were first evacuated for an hour at about 70° or higher. At the conclusion of the evacuation, the manometers were tested and any required corrections determined. It was anticipated that at temperatures above 70° there might be a correction due to the fact that the inside arms were exposed to the full pressure of saturated mercury vapor, while from the outside arms mercury vapor must have been constantly escaping into the cold connecting tubing. Evidently the rate of escape was small in comparison to the rate of evaporation from the relatively large mercury surface, for no significant difference in levels was observed. The apparatus was then allowed to cool, the manometer valves were closed and a suitable quantity of acid was condensed into one of the measuring devices. The buret was read, or the liquid meniscus adjusted to the mark, keeping the liquid at 0°, and the pressure in the connecting tubing at 11.2 mm. As much as possible of the measured sample was then distilled into the globe or coil, with the aid of a freezing mixture if necessary. The remainder was condensed in the capillary buret and measured, great care being taken that the volume, temperature and pressure of the vapor remaining in the connecting tubing (a small fraction of the whole charge) were exactly as before.

The manometers and connections were then exhausted, and the pressures in globe or coil determined at 10° intervals. The stirring was momentarily interrupted during the final adjustment of the micrometer. An idea of the reproducibility obtained will be given by comparison of the following figures, obtained entirely independently (except, of course, for the fundamental calibrations).

Volume of liquid used, cc.	0.1962	0.1960
Weight, mg.	0.2432	0.2429
Pressure at 10°, mm.	10.10	10.08
Pressure at 20°, mm.	11.02	11.02
Pressure at 30°, mm.	12.14	12.13
Pressure at 40°, mm.	13.44	13.42
Pressure at 50°, mm.	14.92	14.90
Pressure at 60°, mm.	16.52	16.50
Pressure at 70°, mm.	18.10	18.10

While the data obtained in this manner were sufficient for the original purpose for which the work was undertaken, it seemed worth while to extend the range to somewhat higher temperatures, in order to make possible a comparison with the data of Peterson and Ekstrand. In order to secure a favorable degree of dissociation, it was necessary to work at higher pressures. Therefore, in order to economize material, the apparatus was altered by the substitution of a bulb of 500cc. capacity in place of the 5-liter globe. The work already completed showed that the correction for wall adsorption is negligible above 40°, so that no control with the coil would be required. The bulb contained a pocket in which a standardized Anschutz thermometer was entirely contained. The bulb and manometer valve were heated by a large vapor-jacket, in which was boiled water, toluene, chlorobenzene or bromobenzene. The exact temperature of each determination was noted and the observations corrected to the nearest whole degree (100°, 111°, 132°, 156°) by means of a small correction readily determined from the observed temperature coefficients. In order to reduce the length of the manometer inside the vapor jacket, and to compensate the vapor pressure of mercury, both arms of this manometer were kept at the same pressure by admitting air to the outside arm when the bulb was being heated and the inside pressure was increasing, until a steady state was reached. The pressures were adjusted to equality within 0.1 mm. by small variations in the volume of the system outside the vapor jacket, accomplished by slightly changing the position of the mercury in one of the valves. The reading was finally taken on an outside manometer by the aid of a cathetometer.

In order to determine whether significant decomposition occurred, during the determination at the highest temperature (156°), in one experiment the acid was cooled to 100° at the completion of the series and its pressure compared with that initially determined at the same temperature. No significant difference was detected.

Reduction of Experimental Data

It is convenient to express gas densities in terms of apparent molecular weight; that is, the weight which 22.41 liters of the gas would possess if, in passing from the observed conditions of temperature and pressure to standard conditions, it expanded and contracted as a perfect gas. Changes in M, the apparent molecular weight, are a measure of the departure from the gas laws.

The results are set forth in Table II. The first column gives the pressures at which determinations were made with the globe or bulb and the second gives the calculated values of M. These data are represented by circles on Fig. 2, in which the logarithm of the pressure serves as abscissa. The data obtained with the coil are not tabulated, but are entered as crosses on Fig. 2. As was anticipated, they are somewhat higher than those yielded by the globe at the same temperatures and pressures; the difference, however, is negligible except below 50°. Since the pressures in the two series were not identical, it was necessary to interpolate the coil values to the same pressures as the globe values. This was done with the aid of smooth curves, drawn dashed in Fig. 2. The results so obtained are entered in the third column for the five lowest temperatures in Table II. Now, the differences between corresponding globe and coil values are due to surface condensation, the error in each value due to this cause being proportional to the surface-volume ratio of the container in question. The error in the coil values must therefore be about 25 times that in the globe values. The values in the fourth column, marked "corrected," were computed by subtracting from each globe value one-twenty-fourth of the difference between it and the corresponding coil value. It will be seen that in order to determine this correction with an absolute accuracy equal to that of the globe values, comparatively rough coil values will suffice.

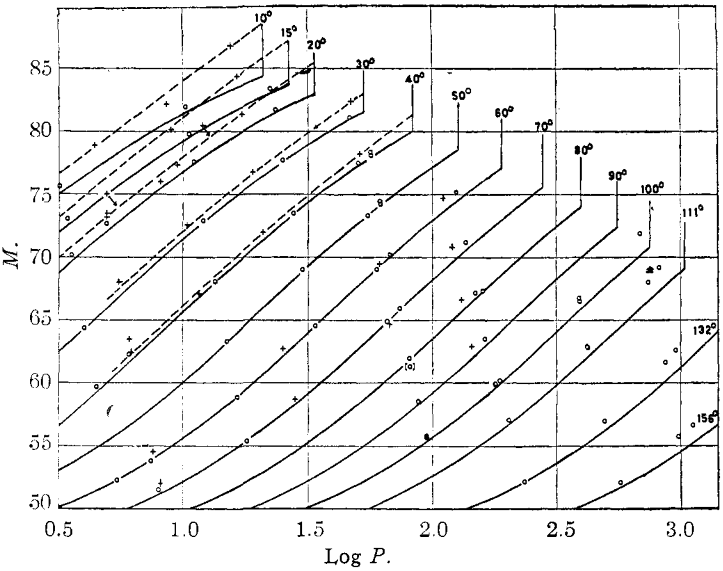

Fig. 2.—Circles represent experiments with globe or bulb. Crosses represent experiments with coil. Triangles represent experiments of Peterson and Ekstrand. Solid lines are solutions of Equations (2) and (3). The vertical portions at the upper ends show the pressures at which condensation occurs. Dashed lines are smooth curves drawn through the crosses.

TABLE II

REDUCTION OF EXPERIMENTAL DATA

	Press., mm. of Hg	Apparent molecular weight				
		Globe	Coil	Corr.	Calcd.	Difference
	3.19	75.7	76.5	75.7	75.1	+0.6
10°	10.08	81.92	83.5	81.85	81.55	+ .30
	10.10	81.92	83.5	81.85	81.55	+ .30

TABLE II (*Concluded*)

	Press., mm. of Hg	Apparent molecular weight				
		Globe	Coil	Corr.	Calcd.	Difference
	3.36	73.1	74.0	73.1	72.5	+ .6
15°	10.53	79.76	81.0	79.72	79.63	+ .09
	10.54	79.84	81.0	79.80	79.63	+ .17
	22.56	83.38	86.0	83.25	83.16	+ .09
	3.56	70.2	71.0	70.2	69.7	+ .5
	4.87	72.7	73.5	72.7	72.1	+ .6
20°	11.02	77.65	78.8	77.60	77.52	+ .08
	11.02	77.71	78.8	77.66	77.52	+ .14
	23.41	81.75	83.2	81.69	81.57	+ .12
	23.48	81.50	83.2	81.43	81.57	− .14
	4.01	64.4	65.3	64.4	64.4	.0
	12.13	72.92	74.0	72.87	72.93	− .06
30°	12.14	72.92	74.0	72.87	72.93	− .06
	25.44	77.79	79.0	77.74	77.79	− .05
	25.46	77.73	79.0	77.68	77.79	− .11
	46.24	81.14	82.3	81.09	81.10	− .01
	4.47	59.7	60.0	59.7	59.5	+ .2
	6.07	62.3	62.4	62.3	61.8	+ .5
	13.42	68.07	68.5	68.05	68.07	− .02
	13.44	68.05	68.5	68.03	68.07	− .04
40°	27.78	73.59	74.0	73.57	73.56	+ .01
	27.85	73.41	74.0	73.39	73.56	− .17
	50.06	77.43	78.0	77.41	77.48	− .07
	56.81	78.37	78.7	78.36	78.27	+ .09
	56.88	78.27	78.7	78.25	78.27	− .02

	Press., mm. of Hg	Molecular weight		Difference
		Obs.	Calcd.	
	14.90	63.28	63.36	− .08
	14.92	63.27	63.36	− .09
	30.55	69.06	69.02	− .04
50°	30.61	68.92	69.02	− .10
	54.52	73.36	73.41	− .05
	61.76	74.39	74.33	+ .06
	61.85	74.28	74.33	− .05
	5.43	52.3	52.2	+ .1
	7.48	53.8	53.9	− .1
	16.50	58.90	59.09	− .19
	16.52	58.89	59.09	− .20
60°	33.68	64.58	64.60	− .02
	59.70	69.07	69.21	− .14
	67.51	70.16	70.16	.00
	67.56	70.11	70.16	− .05
	126.1	75.11	74.88	+ .23
	5.83	50.2	50.0	+ .2
	8.05	51.5	51.3	+ .2
	18.10	55.32	55.50	− .18
70°	18.10	55.36	55.50	− .14
	65.50	64.84	65.08	− .24
	74.04	65.86	66.09	− .23
	74.11	65.80	66.10	− .30
	137.0	71.21	71.16	+ .05
	81.04	61.99	62.14	− .05
80°	81.87	(61.33)	62.20	(− .87)
	149.4	67.20	67.14	+ .06
	160.6	67.32	67.73	− .41

	Press., mm. of Hg	Molecular weight		Difference
		Obs.	Calcd.	
	88.28	58.49	58.57	−0.08
90°	88.30	58.47	58.57	− .10
	162.6	63.51	63.34	+ .17
	95.22	55.71	55.55	+ .16
	95.41	55.60	55.55	+ .05
	177.1	59.91	59.98	− .07
100°	189.3	60.21	60.48	− .27
	389.5	66.80	66.57	+ .23
	391.6	66.54	66.62	− .08
	688.2	71.87	71.80	+ .07
	205.2	57.05	57.11	− .06
	424.4	62.90	62.91	− .01
111°	424.4	62.90	62.91	− .01
	745.5	68.10	68.06	+ .04
	824.2	69.20	69.01	+ .19
	236.9	52.15	52.40	− .25
132°	495.3	56.92	56.92	.00
	869.0	61.65	61.48	+ .17
	961.0	62.66	62.41	+ .25
	573.1	52.21	52.24	− .03
156°	574.0	52.10	52.24	− .14
	1018	55.81	55.70	+ .11
	1127	56.64	56.48	+ .16

Adsorption

The amount of adsorption on the glass walls, in mg. per square meter, was calculated by interpolation from the curves in Fig. 2 and is shown in Table III. Being obtained as the differences between much larger numbers, these values have no claim to accuracy, but indicate the order of magnitude of the effect.

Table III

Adsorption of Formic Acid on Glass, Mg. per Square Meter. at Different Temperatures and Pressures

Press., mm.	10°	15°	20°	30°	40°
50	0.74	0.57	0.44	0.31	0.18
100	2.00	1.45	.96	.66	.35
200		4.1	2.5	1.2	.75
500				5.0	2.9

Theory of the Vapor Density

The simplest assumption concerning the density of the vapor of formic acid is that it is the weighted mean of the densities of two perfect gases having molecular weights 46.02 and 92.03, and present in proportions given by the mass law, the equilibrium constant being an exponential function of the temperature. Thus, if δ be the density of the vapor in grams per liter, we have for the apparent molecular weight

$$M = \frac{\delta \times 22.41 \times 760 \times T}{273 \times P} \tag{1}$$

and for the dissociation constant (in terms of partial pressures, and having the physical dimensions of pressure, in millimeters of mercury)

$$K = \frac{P \times (92.03 - M)^2}{46.02(M - 46.02)} \tag{2}$$

In Fig. 2 the curves represent the values of M which satisfy this equation, when K is calculated from the equation

$$\text{Log } K = 10.755 - 3090/T \tag{3}$$

Inspection shows that this formula satisfactorily reproduces the observed densities at low temperatures and pressures, but that at higher temperatures and pressures the observed densities are systematically greater. There appear to be three directions in which the explanation of this discrepancy may be sought. In the first place, the individual gases supposed to constitute the mixture may not be perfect gases, but may have densities greater than that calculated from their molecular weights. In the second place, the mixture of the two gases may not obey the laws of ideal solutions. Finally, it is possible that the dissociation constant does not increase with rising temperature strictly according to Equation (3), but that at higher temperatures its temperature coefficient is somewhat smaller. Since the whole discrepancy is small, it will obviously be impossible to determine with certainty the degree in which the three factors contribute; the best that can be done is to show that reasonable assumptions can be made, by the aid of which the observed densities can be reproduced.

It is certain that some allowance must be made for the departure of the individual gases from the gas law. We can advantageously follow the treatment of Lewis and Randall.[5] We suppose that, for each single gas, were it capable of independent existence, the equation of state would be reducible, within the range of temperature and pressure here considered, to the form

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

where α is a function of temperature only, and is small, so that $1 - \alpha P$ may be considered equal to $1/(1 + \alpha P)$. We shall assume provisionally that the mixture of gases is an ideal solution. This means that the single molecules behave, not as if the double molecules were absent, but as if their places were taken by equal numbers of single molecules, and *vice versa*, since only in this way can the necessary condition be fulfilled that when the two pure gases at the same pressure are allowed to interdiffuse, there will be no expansion or cooling. Now, the apparent molecular weights of the pure gases would be $M_1 = 46.02(1 + \alpha_1 P)$ and $M_2 = 92.03(1 + \alpha_2 P)$, respectively, and that of the mixture $M = n_1M_1 + n_2M_2 = 46.02[n_1(1 + \alpha_1 P) + 2n_2(1 + \alpha_2 P)]$, where n_1 and n_2 are the mole fractions of single and double molecules, respectively. Solving for n_1 and n_2, we obtain

$$n_1 = \frac{92.03(1 + \alpha_2 P) - M}{46.02[1 + (2\alpha_2 - \alpha_1)P]} \text{ and } n_2 = \frac{M - 46.02(1 + \alpha_1 P)}{46.02[1 + (2\alpha_2 - \alpha_1)P]} \tag{5}$$

The degree of dissociation is

$$x = \frac{92.03(1 + \alpha_2 P) - M}{M + 92.03(\alpha_2 - \alpha_1)P} \tag{6}$$

To calculate the equilibrium, we use the relations advocated by Lewis and Randall, namely, that the fugacity of a pure gas whose pressure is only slightly less than the ideal pressure is itself less than the actual pressure by the same ratio, and that in a mixture of gases the fugacity of each component is to be found by multiplying its fugacity in the pure state at the same total pressure by its mole fraction. We therefore write, for the fugacities in the mixture, $f_1 = n_1P(1 - \alpha_1 P)$ and $f_2 = n_2P(1 - \alpha_2 P)$.

The condition for equilibrium is

$$K = \frac{f_1^2}{f_2} = \frac{n_1^2}{n_2}P[1 + (\alpha_2 - 2\alpha_1)P] = \frac{P[92.03(1 + \alpha_2 P) - M]^2}{46.02[M - 46.02(1 + \alpha_1 P)]}[1 - (\alpha_1 + \alpha_2)P] \tag{7}$$

It will be seen that the departure from the gas law affects the observed apparent molecular weight not only directly, by increasing the densities

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[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 198, 226.

of the components, but indirectly, by displacing the equilibrium; the latter effect is represented by the factor $1 + (\alpha_2 - 2\alpha_1)P$. As would be expected, this vanishes in case the mutual attractive energy of two single molecules is equal to that of one double molecule.

In order to see how far the observations can be accounted for by thus modifying the original simple Equation (2), it is necessary to assume values for α_1 and α_2, reasoning by analogy from observations on vapors of molecular weight of the same order of magnitude, which are known to be monomolecular. Such observations seem to be lacking, except in the cases of saturated vapors or superheated vapors under several atmospheres' pressure. Inspection of the orthobaric densities of several organic vapors, as given in Volume 3 of International Critical Tables, indicates that at 100° these densities exceed those calculated from the gas law by 2 or 3% per atmosphere, as a rule. The deviation is greater than that calculated by van der Waals' equation with the usual values of the constants computed from critical data. It should decrease with rising temperature, and, in general, would be expected to be greater for heavy than for light molecules. For a first trial, the following values for α_1 and α_2 in % per atm. were arbitrarily assumed:

T	10°	15°	20°	30°	40°	50°	60°	70°	80°	90°	100°	111°	132°	156°
α_1	4.5	4.2	4.0	3.6	3.3	3.0	2.8	2.6	2.4	2.2	2.0	1.8	1.5	1.3
α_2	6.7	6.3	6.0	5.5	5.0	4.5	4.2	3.9	3.6	3.3	3.0	2.7	2.3	2.0
K	0.684	1.060	1.618	3.605	7.64	15.41	29.90	56.60	100.2	175.0	296.0	511.0	1336	3573

The values of K, given by Equation (3), are also included.

The apparent molecular weights which satisfy Equation (7) for the experimental temperatures and pressures, and with the numerical constants just given, are tabulated in Table II under the heading "Calcd." It will be seen that the discrepancies remaining are very small, except in the case of experiments at pressures below 10 mm., where an error of 0.01 mm. would suffice to cause a discrepancy of 0.2 unit in M. The agreement is so satisfactory that it seems needless to seek to improve upon the original, supposedly preliminary, assumptions.

Equation (3) indicates that the heat of dissociation at constant pressure is 14,125 calories per mole, and does not vary within the temperature range covered by the experiments. This range, however, is too small to permit drawing reliable conclusions about the temperature coefficient of the dissociation heat, which depends on the difference in the specific heats of the two forms. The customary assumption[6] is that a reaction which produces one new gas molecule involves an increase of 3.5 in the molecular heat. The equation

$$\text{Log } K = 5.542 + 1.75 \log T - 2827/T \qquad (8)$$

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[6] See A. Eucken, "Fundamentals of Physical Chemistry," First English Edition, McGraw-Hill Book Co., New York, 1925, p. 417.

has been adjusted to take this increase into account, and to reproduce as well as possible the results of experiment. It leads to values for M which exceed those calculated from Equation (3) by about 0.1 unit at 10° and 156°, fall below them by the same amount at 70°, and are indistinguishable at 40° and 111°.

It seems to be by no means certain that an increase in specific heat is theoretically necessary. True, it is always found to accompany the dissociation of gas molecules which are held together by primary valence, presumably because in such molecules certain possible modes of vibration are not developed at the temperatures in question. But when liquids evaporate without breaking primary valence bonds, a decrease of specific heat ensues, in spite of the increase in the number of gas molecules. It is conceivable that the dissociation of a double molecule of formic acid is a process of intermediate character and really involves very little change in specific heat. Unfortunately, the chemical instability of the single molecules prevents the extension of the temperature range which would be necessary to decide the question.

Summary

Formic acid probably 99.99% pure has been prepared by vacuum sublimation and some of its physical properties have been determined.

The density of the vapor has been determined at temperatures between 10 and 156°, and at pressures favorable to partial dissociation. A correction for wall adsorption has been determined and applied.

The results can be satisfactorily interpreted by assuming that the vapor is an ideal mixture of two gases, having single and double molecules, respectively, each of which deviates from the perfect gas laws in the same way as would a monomolecular vapor of similar molecular weight.

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