The enthalpy of combustion at 25° C. calculated from these data is −508.7 kcal. per mole with an estimated over-all uncertainty of ±0.7 kcal. per mole. The largest single source of error is the limited accuracy of the mercury thermometer used to measure the temperature increments.

Using the values −26.4157 and −94.0518 kcal. per mole for the standard heats of formation of CO and CO_2 (*3*), the standard heat of formation of tetranitromethane at 25° C. is calculated to be +8.8 ± 0.7 kcal. per mole, and is in agreement with the results obtained by Roth and Isecke.

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Heat of Vaporization and Vapor Pressure of 1,4-Dioxane

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The heat of vaporization and the vapor pressure of 1,4-dioxane were measured at 100.1 and 100.5° C. The heat of vaporization was compared with a value from the literature and with a value from the Clapeyron equation. All of the published vapor-pressure data were correlated with an equation which was then differentiated to obtain the slope *dP/dT* needed in the Claypeyron relation. The over-all comparison indicates the vapor pressure between 0.5 and 1.5 atm. may be slightly in error.

BECAUSE DIOXANE is a widely used solvent, it is useful to know its latent heat of vaporization and to have a correlation of the vapor pressure over a wide temperature range. Only one measurement of the latent heat of vaporization has been reported (*9*) previously, while three investigators (*1, 2, 5*) have studied the vapor pressure. The vapor pressure data have not been correlated, however, and the latent heat has not been independently corroborated.

APPARATUS AND PROCEDURE

The equipment (*10*) is a flow device with vapor generated continuously in a calorimeter which is supplied with liquid slightly below the boiling point. The calorimeter is is thermally shielded by being situated inside a second continuous vaporizer. During a determination the vapor from the calorimeter is withdrawn from the system and condensed. The weight of condensate collected in a given time is compared with the electrical power input to obtain the latent heat. A very small correction is required for the sensible heat of the liquid in being raised to the boiling point.

The accuracy of the apparatus was checked by determining the latent heat of vaporization of doubly distilled water and Baker reagent-grade methanol. The latent heat of water was found to be 540.2 cal. per gram at 741 mm. (99.3° C.), which compares favorably with the most precise literature (*7*) value of 539.9 cal. per gram. The latent heat of vaporization of methanol was measured as 263.1 cal. per gram at 744 mm., which may be compared with reported (*4, 8*) values of 264.1 and 262.9 cal. per gram at 760 mm.

The sample of 1,4-dioxane (Carbide and Carbon Chemicals Co.) was allowed to stand over calcium chloride for several weeks before use. The boiling temperature showed no rising or declining trends over several consecutive determinations, while a mass spectrometer analysis, discussed later, showed 0.04% water.

RESULTS

Of eight determinations of the latent heat of vaporization of dioxane, four at 744 mm. and 100.5° C. gave an average latent heat of 96.53 cal. per gram with a standard deviation of 0.31 cal. per gram. The other four at 736 mm. and 100.1° C. gave an average latent heat of 96.56 cal. per gram with a standard deviation of 0.23 cal. per gram. In all cases the small sensible heat correction, always less than 2%, was made using a liquid specific heat estimated from a published (*3*) value.

The above results are consistent, but differ considerably from a published (*9*) value of 105.08 cal. per gram measured at 760 mm. To determine a further independent value, all available vapor pressure data were fitted with an equation which was then used in the Clapeyron relation to calculate the latent heat. The equation of Martin, Kapoor, and Shinn (*6*) was chosen because of its ability to fit general vapor pressure behavior with a high order of precision. The equation is

$$\log_{10} P = A + \frac{B}{T} + C \log_{10} T + DT + E\left(\frac{F - T}{T}\right)\log_{10} (F - T)$$

The constants were selected to give a good fit of the average vapor pressure data of the three published investigations. With pressure (P) in atmospheres and temperature (T) in ° K., the constants are:

A = 20.776007
B = −3205.5402
C = −5.0537764
D = 0.00064574875
E = 0.39512067
F = 596

Table I shows that the equation does fit the data well and that where high deviations occur, there is great discrepancy between the investigators themselves. For example, at 529.16° K. the equation predicts a pressure 2.58% less than that reported (*2*). Temperature values just above and below this point indicate that the equation differs from another investigator's (*5*) results by −0.64 and −0.39%. The only way this situation can occur over a small temperature range is by errors in the data, not the equation.

Table I. Vapor Pressure Equation Compared with the Experimental Data

Calculated Boiling Temperature at 760 mm: 101.22° C.

Temp., ° K.	Pressure, Atm. Obsd.	Pressure, Atm. Calcd.	Deviation from Calcd., %	Source
293.16	0.0380	0.0377	0.79	(*1*)
298.16	0.0492	0.0488	0.81	(*1*)
303.16	0.0630	0.0628	0.32	(*1*)
313.16	0.1010	0.1009	0.10	(*1*)
323.16	0.1570	0.1570	0.00	(*1*)
333.16	0.2367	0.2371	−0.17	(*1*)
343.16	0.3476	0.3484	−0.23	(*1*)
353.16	0.4984	0.4995	−0.22	(*1*)
363.16	0.6990	0.7002	−0.17	(*1*)
373.16	0.9610	0.9615	−0.05	(*1*)
373.96	1.000	0.9854	1.46	(*2*)
378.16	1.119	1.1187	0.00	(*1*)
398.16	2.000	1.9632	1.84	(*2*)
415.16	3.000	3.0163	−0.55	(*2*)
427.16	4.000	3.9902	0.24	(*2*)
427.61	4.015	4.0309	−0.40	(*5*)
433.16	4.559	4.5589	0.00	(*5*)
437.16	5.000	4.9708	0.58	(*2*)
438.72	5.172	5.1389	0.63	(*5*)
444.27	5.784	5.7717	0.21	(*5*)
446.16	6.000	6.0000	0.00	(*2*)
449.83	6.464	6.4626	0.02	(*5*)
455.16	7.000	7.1813	−2.59	(*2*)
455.39	7.213	7.2135	−0.01	(*5*)
460.94	7.961	8.0260	−0.82	(*5*)
461.16	8.000	8.0596	−0.75	(*2*)
466.50	8.914	8.9061	0.09	(*5*)
467.16	9.000	9.0150	−0.17	(*2*)
472.05	9.799	9.8535	−0.56	(*5*)
473.16	10.000	10.0515	−0.52	(*2*)
477.61	10.819	10.8749	−0.52	(*5*)
483.16	11.908	11.9696	−0.52	(*2*)
483.16	12.000	11.9696	0.25	(*5*)
488.72	13.065	13.1447	−0.61	(*5*)
493.16	14.00	14.1416	−1.01	(*2*)
494.27	14.22	14.3992	−1.26	(*5*)
499.83	15.58	15.7407	−1.03	(*5*)
500.16	16.00	15.8231	1.11	(*2*)
505.39	17.01	17.1703	−0.94	(*5*)
508.16	18.00	17.9165	0.46	(*2*)
510.94	18.51	18.6886	−0.97	(*5*)
515.16	20.00	19.9060	0.47	(*2*)
516.50	20.14	20.3043	−0.82	(*5*)
522.05	21.84	22.0152	−0.80	(*5*)
527.61	23.68	23.8311	−0.64	(*5*)
529.16	25.00	24.3561	2.58	(*2*)
533.16	25.65	25.7495	−0.39	(*5*)
538.72	27.63	27.7814	−0.55	(*5*)
543.16	30.00	29.4861	1.71	(*2*)
544.27	30.14	29.9239	0.72	(*5*)
549.83	32.19	32.1901	0.00	(*5*)
555.39	34.64	34.5818	0.17	(*5*)
556.16	35.00	34.9233	0.22	(*2*)
560.94	37.08	37.1013	−0.06	(*5*)
565.16	40.00	39.1103	2.22	(*2*)
566.50	39.87	39.7658	0.26	(*5*)
572.05	42.80	42.5764	0.52	(*5*)
577.61	45.39	45.5575	−0.37	(*5*)
581.16	50.00	47.5571	4.89	(*2*)
583.16	48.72	48.7200	0.00	(*5*)
588.16	51.40	51.45	0.10	(*5*)[a]

[a] Critical point.

When the vapor pressure equation was differentiated to give the slope dP/dT, the compressibility factor of the saturated vapor estimated to be 0.98, and the saturated liquid volume estimated as 0.0937 liter per gram mole, the latent heat of vaporization at 100.5° C. was calculated as 94.32 cal. per gram. This is 2.3% less than the value determined experimentally in this study, but 10.3% less than the experimental value reported (*9*) in the literature. Latent heat determined here is concluded to be more reliable than that given in the earlier study.

There are three possible explanations for the 2.3% difference between the latent heat predicted from the Clapeyron equation and the experimental value. First, the dioxane used may have had some impurity. If the impurity were water (despite the method of drying over calcium chloride and the small amount indicated by the mass spectrometer analysis), the effect would be severe, as the latent heat of water is almost six times that of dioxane. Because water has a slightly higher vapor pressure than dioxane, any water present would be expected to raise the vapor pressure slightly. This was indeed the case, for the vapor pressure at 100.5° C. predicted by the equation was 742 mm., while the measured pressure was 744 mm. At 100.1° C. the same trend was present with the measured pressure being 736 mm., while that predicted by the equation was only 733 mm.

The second explanation lies in the selection of the compressibility factor of the saturated vapor. The 0.98 was taken after reviewing the compressibilities of many other compounds at the same low reduced pressure and temperature. It is difficult to see how the value can be any higher, through it can easily be 1% lower, which would make the discrepancy even greater.

A third explanation is that the slope of the vapor pressure with temperature may not be truly correct. If vapor pressure data are precise to 0.1%, the derivative may be precise only to about 0.5%; consequently, even though the vapor pressure equation represents the average of the experimental data, its slope may be off enough to affect the calculated latent heat by as much as 1% or so. This is particularly true in the temperature range of about 20° C. on either side of the normal boiling point, for in this region the vapor pressure data (*1, 2*) are not too concordant since they differ over 1%. Such differences can easily lead to as much as a 5% difference in slope upon which the latent heat is directly dependent. Only more accurate vapor pressures around the boiling point can settle this question. Thus, impurity, vapor compressibility, and vapor pressure slope may be responsible for the 2.3% difference between the experimental and calculated latent heat.

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