

which liquid data or heats of fusion are available a value of



may be obtained.

A summary of the apparent values of the N-N bond calculated from the various pairs, and using the three assumptions for the N-H bond is shown in Table VIII.

TABLE VIII
CALCULATED ENERGY OF N-N BOND

Compounds compared	Assumption N-H = 85.9 kcal.	Assumption N-H = 83.7 kcal.	Assumption N-H = 85.4 kcal.
Tetraphenylhydrazine	solids 14.8	(10.5)	..
Diphenylamine
Dibenzoylhydrazide	solids 22.1	(17.7)	..
Benzamide
Hydrazobenzene	solids 29.4	(25.0)	..
Aniline
Hydrazobenzene	liquid	28.4
Aniline
Phenylhydrazine	gas ..	23.3	..
Aniline
Phenylhydrazine	liquid	24.5
Aniline
Phenylhydrazine	solids 25.9
Aniline
Hydrazine—solid	22.3
Hydrazine—liquid	23.3
Hydrazine—gas	..	20.0	..

These values, calculated on any basis, support the contention of Lewis and Lipkin⁷ that the apparent strength of the N-N bond is dependent upon the substituents in the molecule. Further

work is under way in this Laboratory which it is hoped will throw additional light on this issue. By all calculations the value of the N-N bond in tetraphenylhydrazine thus obtained is considerably less than in any of the other compounds. The values for hydrazobenzene are somewhat out of line. Previous experience with the data of Swietoslowski and Bobinska indicate that their results may be on the low side.¹⁷ Upward revision of their combustion data would reduce the value assigned to the N-N bond.

Grateful acknowledgment is due to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences and the General Research Council of the College for financial assistance which made this work possible.

Summary

1. New data for isothermal heats of combustion of tetraphenylhydrazine and *sym*-dibenzoylhydrazide are reported.

2. Revisions of earlier data for the heat of combustion of aniline, benzamide, diphenylamine and phenylhydrazine are given.

3. Using certain arbitrary assumptions, values are computed for the energy of the N-N bond in tetraphenylhydrazine, *sym*-dibenzoylhydrazide, hydrazobenzene, and phenylhydrazine. The apparent value thus obtained depends on the substituents attached to the nitrogen.

(17) Corruccini and Gilbert, *THIS JOURNAL*, **61**, 2925 (1939).

CORVALLIS, OREGON

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. III. A Comparison of Flow Calorimeters

BY JAMES B. MONTGOMERY¹ AND THOMAS DE VRIES

The constant-flow calorimeter for measuring the heat capacity of vapors was devised by Callendar and adapted by Swann² to measure the specific heat of air. An improved calorimeter was described by Scheel and Heuse.³ An outstanding example of good design is the calorimeter used by Osborne, *et al.*⁴ Typical of the calorimeters used

(1) Present address: Hercules Experiment Station, Wilmington, Del. This paper is an abstract from the thesis submitted by J. B. Montgomery in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The second paper of this series appeared in *THIS JOURNAL*, **64**, 1224 (1942).

(2) Callendar and Barnes, *Trans. Roy. Soc. (London)*, **199A**, 55-263 (1902); Swann, *Proc. Roy. Soc. (London)*, **82A**, 147 (1909).

(3) Scheel and Heuse, *Ann. Physik*, (4) **37**, 79 (1912).

(4) Osborne, Stimson, Sligh and Cragoe, *U. S. Bur. of Standards, Sci. Papers*, **20**, 65-110, 119-151 (1925).

recently for measuring the heat capacity of organic vapors have been those described by Bennewitz and Rossner, De Vries and Collins, and Pitzer.⁵

In this investigation modifications of the flow calorimeter were studied as part of a general program to measure the heat capacity of organic vapors.

Experimental

Flow calorimeters may be arbitrarily classified on the basis of the method used for correcting for heat losses. In

(5) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938). De Vries and Collins, *THIS JOURNAL*, **63**, 1343 (1941); Pitzer, *ibid.*, **63**, 2413 (1941).

the calorimeters of the first class there is a direct flow of vapor over the first thermometer, the heater, the second thermometer and out of the calorimeter. The heat loss varies inversely with the rate of flow and may be corrected for by extrapolating the data to infinite rate of flow. The calorimeters described by Swann and by Pitzer belong to this class. In the second class, represented by the Scheel and Heuse design, a reversed flow of the vapor returns part of the lost heat to the calorimeter, and the heat loss varies inversely as the square of the rate of flow.

Apparatus.—The calorimeters were placed in a thermostat filled with hydrogenated vegetable oil and regulated to within 0.005°. Electrical measurements were made with a Rubicon, Type B, potentiometer. The vaporizer used in our earlier work⁵ was found to have insufficient capacity to permit attainment of equilibrium at high rates of flow. A recycling vaporizer was designed which proved to be satisfactory. It consisted of a "Pyrex" glass boiler of 600-ml. capacity with an exposed twelve-ohm internal chromel wire electrical heater at the bottom and a spray trap at the top (Fig. 1). The vaporizer was supported in a copper hypsometer in which was placed either the same type of liquid as was used in the vaporizer or a liquid having the same boiling point.

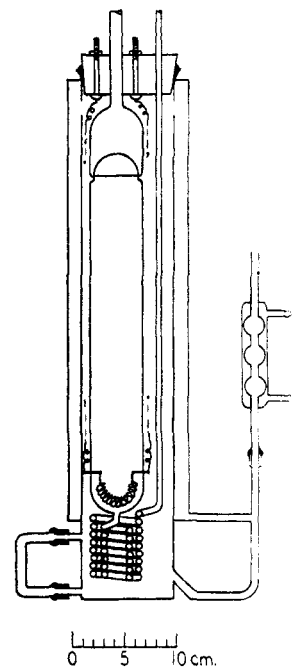


Fig. 1.—Recycling vaporizer.

Electrical heaters in the calorimeters were constructed from chromel wire and supported on glass supports. The current through the heater was computed from the potential drop across a standard resistance of 0.9339 ± 0.0003 ohm in series with the heater, and from the potential across the heater.

In the first two calorimeters platinum resistance thermometers were used. They had a resistance of approximately 60 ohms, and were constructed from no. 40 B. and S. gage platinum wire which was bifilarly wound on mica supports and fused to gold lead out wires (two at each end). The thermometers were annealed to remove strains and were found to give reproducible calibrations at the ice, steam and boiling sulfur points. In the third calorimeter a five-junction copper-constantan thermel of no. 30 gage wire was used. Measurements made with and without a heat block⁵ on the outlet end of the thermel proved the value of using the heat block.

The calorimeters were constructed from "Pyrex" glass tubing. Their jackets were silvered, evacuated with a mercury vapor pump while being slowly heated to 500°, cooled to 400°, and sealed off. The cross-sections of the three calorimeters are shown in Fig. 2.

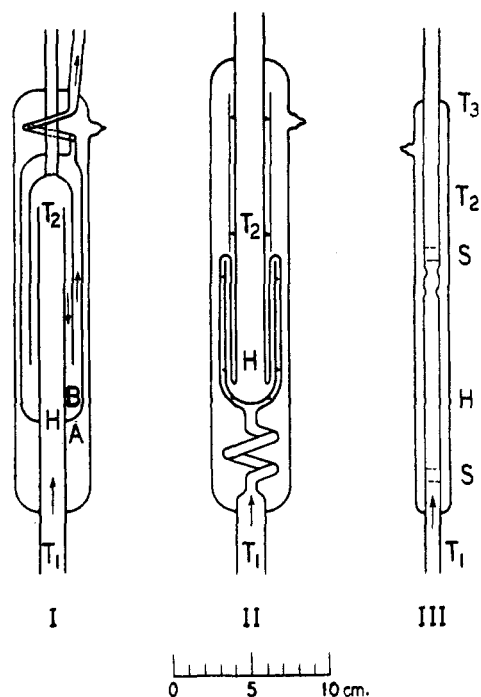


Fig. 2.—Sketch of calorimeters, details not shown.

Results.—The first calorimeter (I) was designed to provide a double layer of heated vapors around the outlet thermometer. Measurements were made upon methyl alcohol vapor at 109°. Steady state conditions were attained slowly because of the large amount of glass which had to be heated. The precision of the experimental points was excellent. The results (see Fig. 3) with the heater exposed to region A were too high because of a direct loss of heat to the surroundings which is only partially corrected for by increasing the rate of flow (F) and extrapolating the data to infinite rate of flow according to the equation, $C_p = H(1 - k/F)/F\Delta T$, which obtains for this type of calorimeter. With the heater further into the calorimeter at position B, the results were about 8% lower than those reported by De Vries and Collins.⁵ These low results were explained by assuming that heat from the hot vapors in region B was conducted along the wall of the tube to the entering vapor, thus being used twice.

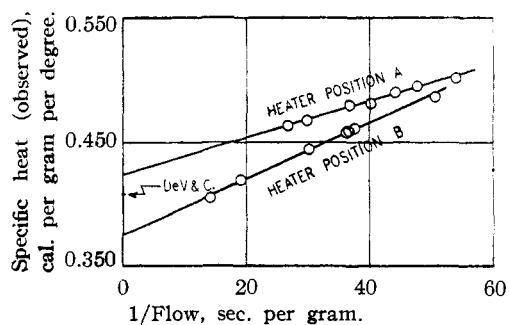


Fig. 3.—Test runs, calorimeter I: methyl alcohol at 109°.

From the results obtained with the first calorimeter it became evident that the Scheel and Heuse modification is

preferable for the arrangement which returns part of the lost heat to the incoming vapor with the result that the heat loss varies inversely as the square of the rate of flow.⁵ The second calorimeter (II) was built with a short reverse section to minimize the time required to obtain steady state conditions. Measurements were made with carbon tetrachloride at 107°. The observed specific heats gave a curved line when plotted against $1/F^2$ indicating that the heat loss, which was proportional to $1/F$ in the region around the outlet thermometer (T_2), was becoming appreciable at low rates of flow. A straight line could be obtained even at low rates of flow by plotting the results against $1/F^{1.8}$. Extrapolation to infinite rate of flow gave 0.1417 cal. per gram degree (see Fig. 4). About two hours were required to obtain steady temperatures before weighed samples of the compound were collected for five to twenty minutes.

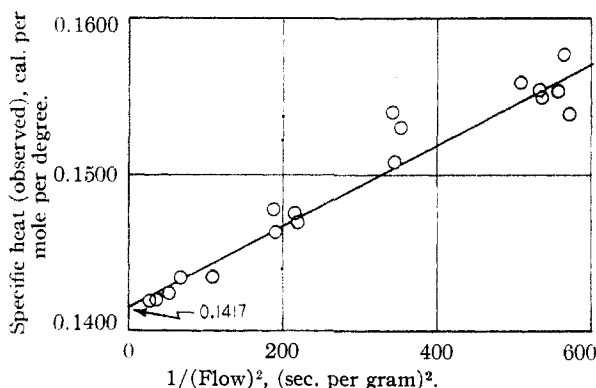


Fig. 4.—Test runs, calorimeter II: carbon tetrachloride at 107°.

A third (III) calorimeter was built in which steady temperatures were obtained in about fifteen minutes. For the first heater arrangement (not shown) the results were about 3% low. It was believed that radiation from the heater direct to the thermel junction at T_2 made ΔT too large. This belief was substantiated by the fact that higher results were obtained when the heat input was held constant and ΔT was decreased at the higher rates of flow.

Another heater arrangement (III in Fig. 2) gave satisfactory results. The method of measurement with either ΔT constant or ΔH constant had no effect on the result. It appeared that the radiation error had been eliminated. In this arrangement the heater, 4 cm. long, was supported on a glass tube, 10.5 cm. long, with two radiation shields (S) of nickel gauze at the upper end. The current carrying leads of no. 26 copper wire were in the vapor region for 5 cm., passed inside the glass tube for one cm. to avoid the radiation shields, then reappeared in the vapor space and passed the thermel junctions at T_2 . Just beyond this point the potential leads were attached to the current carrying leads. With this arrangement no heat is lost from the heater without first passing into the vapor. A failure to obtain this condition gives a positive error in the data.

The performance of the third calorimeter was checked by measuring the heat capacity of oxygen at 100°. Compressed oxygen from a tank was used and purified to remove ammonia and water vapor. At atmospheric pressure

the value 7.158 cal. per mole degree was found, based upon the use of 4.1833 joules per cal. (see Fig. 5). This value is 0.2% higher than 7.143, calculated from spectroscopic data by Johnston and Walker,⁶ and experimentally determined by Henry.⁷ The above value includes the correction from the Berthelot equation for the difference between the ideal state of zero pressure and one atmosphere.

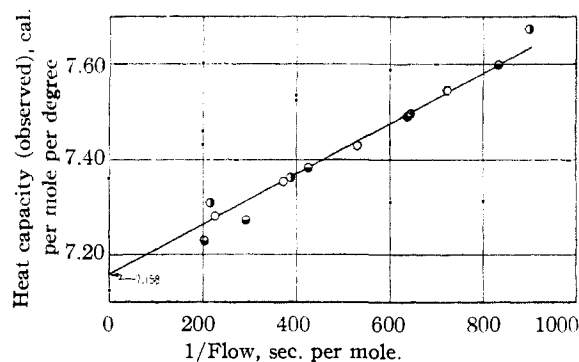


Fig. 5.—Test runs, calorimeter III, oxygen at 100°. ΔT : O, 2°; ◐, 4°; ●, 8°.

The heat capacity of carbon tetrachloride was measured at various rates of flow at 107° (Fig. 6). The result 21.82 cal. per mole degree agrees well with 21.80, measured with the second calorimeter of this investigation, and with the value 21.68, measured by Mr. Chas. F. Coleman⁸ of this Laboratory using the apparatus of De Vries and Collins.⁵ The above value is about 1% lower than 22.05 reported by Pitzer⁵ and calculated by Vold⁹ from spectroscopic data. But Pitzer's value at 107° was based upon measurements at only two rates of flow and Vold claimed an accuracy of only 3% (5% for C_p calculated to atmospheric pressure). A definite positive error may result from the use of vibrational frequencies determined in liquids, an error which may only be partially compensated by the fact that Vold used the rigid rotator-harmonic oscillator formulas.

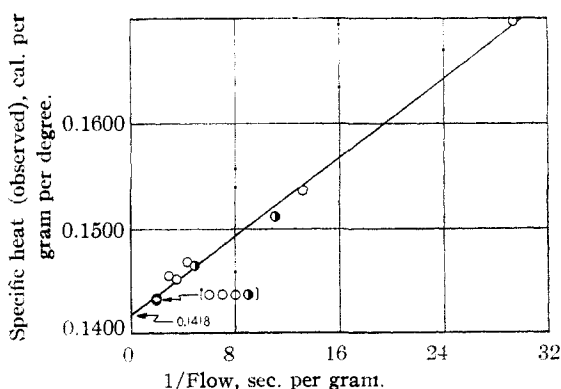


Fig. 6.—Test runs, calorimeter III, carbon tetrachloride at 107°: O, ΔT constant; ◐, ΔH constant.

This study has indicated that it is possible to construct flow calorimeters in which the results may be precise to

(6) Johnston and Walker, *THIS JOURNAL*, **55**, 172 (1933).

(7) Henry, *Proc. Roy. Soc. (London)*, **A133**, 492 (1931).

(8) Purdue Research Foundation Fellow, unpublished data.

(9) Vold, *THIS JOURNAL*, **57**, 1192 (1935).

within $\pm 0.3\%$, and to make measurements in which accidental errors are reduced to values within this limit of precision. However, the elimination of constant errors from design and the construction of flow calorimeters which will give accurate measurements of specific heat to better than a few per cent. is much more difficult. Also these results would suggest that some of the high degree of accuracy which has been claimed for published data on heat capacity might be actually a high degree of precision.

Some essentials of a properly designed flow calorimeter include: (a) a minimum rate of heat loss, obtained by reducing the radiating surface to a minimum, by evacuating the jacket space around the calorimeter, and by using properly spaced radiation shields to prevent radiated heat from being used twice; (b) a proper arrangement of the vapor heater and thermometers to eliminate constant errors due to the effect of direct radiation and conduction

from the heater; and (c) a construction which uses a minimum volume of material of low heat capacity to reduce the time-lag to temperature changes.

One of the authors (J. B. M.) is grateful to E. I. du Pont de Nemours and Co., Inc., for a fellowship which made this work possible.

Summary

A study was made of flow calorimeters for the determination of the heat capacity of organic vapors. The simpler calorimeter, following the design of Callendar, was preferred.

A recycling vaporizer for producing a constant rate of vapor flow was designed.

WEST LAFAYETTE, INDIANA RECEIVED JUNE 24, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. IV. Benzene, Fluorobenzene, Toluene, Cyclohexane, Methylcyclohexane and Cyclohexene

By JAMES B. MONTGOMERY¹ AND THOMAS DE VRIES

This paper is a continuation of a program for measuring the heat capacity of organic vapors. The heat capacities of benzene, fluorobenzene, toluene, cyclohexane, methylcyclohexane and cyclohexene vapors have been measured at atmospheric pressure at temperatures from their boiling points to 410°K. With the exception of benzene, little information is available on the heat capacity of these compounds. There are no published data for fluorobenzene and cyclohexene.

Experimental

The heat capacity of the vapor was determined by a flow-calorimeter method, using the modified Callendar direct-flow calorimeter described in the preceding paper of this series.² To correct for heat losses in the calorimeter, the observed heat capacities were plotted against the reciprocal of the rate of flow and extrapolated to infinite rate of flow. At each temperature approximately ten determinations were made at different rates of flow. The method of least squares was used to make the extrapolations. The precision of the results is within $\pm 0.3\%$.

Purification of Chemicals.—The observed boiling points and refractive indexes of the compounds are compared with reported values in Table I. The compounds were rectified in a twelve plate column, and only the middle fractions with boiling point ranges within 0.1° were used. Several compounds were distilled from a flask before rectification in a column.

(1) This paper is an abstract from the thesis submitted by J. B. Montgomery in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Montgomery and De Vries, *THIS JOURNAL*, **64**, 2372 (1942).

TABLE I
PHYSICAL CONSTANTS OF COMPOUNDS

Compound	Boiling point, °C.		Refractive index, n_D^{20}	
	Obs.	Lit.	Obs.	Lit.
Benzene	80.0	80.09 ^a	1.5004	1.5017 ^b
Fluorobenzene	84.6	84.85 ^c	1.4657	1.4677 ^b
Toluene	110.8	110.70 ^d	1.4962	1.49675 ^d
Cyclohexane	80.6	80.80 ^e	1.4262	1.4262 ^f
Methyl- cyclohexane	100.7	100.8 ^g	1.4224	1.4230 ^f
Cyclohexene	82.8	83.25 ^h	1.4465	1.44646 ⁱ

^a Smith and Matheson, *Bur. Stand. J. Research*, **20**, 641 (1938). ^b Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1939, pp. 794, 781. ^c Timmermans and Hennaut-Roland, *J. chim. phys.*, **32**, 501, 589 (1935). ^d Mathews, see ref. 4. ^e Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926). ^f Wibaut and Langedijk, *Rec. trav. chim.*, **59**, 1220 (1940). ^g Hicks-Bruun and Bruun, *Bur. Stand. J. Research*, **8**, 525 (1932). ^h Timmermans, *Bull. soc. chim. Belg.*, **30**, 62 (1921). ⁱ Vogel, *J. Chem. Soc.*, 1323 (1938).

Benzene.—Thiophene-free benzene from the Barrett Company was dried over phosphorus pentoxide, rectified and stored over sodium.

Fluorobenzene.—The fluorobenzene was prepared by the method of Flood.³ It was dried over calcium chloride, distilled through a Glinsky type column and rectified.

Toluene.—A Merck and Company purified grade of toluene was treated successively with concentrated sulfuric acid, 5% sodium hydroxide solution and water. It was dried with calcium chloride, allowed to stand over mercury

(3) Flood, "Org. Syntheses," **13**, 46 (1933).