surface area and no pore volume. After reduction at 300 and 450 to 550°, respectively, both types have moderate surface areas of about 8 sq. m./g. and reasonably large pore diameters of 350 to 900 Å.

2. Thermal sintering of precipitated iron gels causes drastic changes in structure, but removal of oxygen by reduction produces an even greater effect.

3. The surface area and pore volume of an iron–synthetic-ammonia-type catalyst increased in a linear manner with extent of reduction, whereas the average pore diameter remained constant.

4. It is shown that only surface area measurements and complete chemical analysis of the raw catalyst are necessary to establish the pore structure of an iron–synthetic-ammonia-type catalyst as a function of the extent of reduction.

5. Increasing the reduction temperature of an iron–synthetic-ammonia-type catalyst from 450 to 650° produced an eightfold increase in the pore diameter.

BRUCETON, PA. RECEIVED APRIL 29, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. VII. A Flow Calorimeter Requiring Only 25 Ml. of Liquid Sample

BY ALLAN E. REYNOLDS[1] AND THOMAS DE VRIES

In the program for measuring the heat capacity of organic vapors, a calorimeter was desired when the quantity of liquid is limited to 25 ml. Since the flow method of Callendar and Barnes is capable of giving highly reliable heat capacities[2,3,4] an apparatus was developed based on this principle. The accuracy of the colorimeter was checked by measuring the heat capacity of benzene for comparison with the data of Scott, *et al.*[3] The heat capacities for the three butyl alcohols were determined at 1 atm. pressure at 135 and 160°.

Experimental

Apparatus.—The main section of the calorimeter (see Fig. 1) was about 10 cm. long and 1 cm. in diameter, drawn to a wall thickness of 0.3 mm. to permit a minimum of time lost in reaching thermal equilibrium. The heater consisted of chromel wire wound into a helix on a $^3/_{16}''$ mandrel and supported on a strip of mica. The copper lead-out wires were also wound into helices to present a greater opportunity for the incoming vapor to take up the heat energy which otherwise would be conducted out through the leads. The copper wires were brought out through short sections of 1 mm. o. d. platinum tubing sealed into the walls of the calorimeter and closed with soft solder. This method for bringing wire through the glass and maintaining vacuum tight seals was found entirely satisfactory.

The outside of the calorimeter was given a bright platinum mirror finish. A saturated solution of dry platinum chloride in 95% ethanol was dissolved in five times its volume of oil of lavender. This solution was brushed on the clean glass parts and heated over a low flame of a Bunsen burner. The operation could be repeated if a thicker mirror was desired.

A triple junction thermel of copper and constantan wire was used to measure ΔT. An extra thermocouple was used to measure the temperature of the incoming vapor.

The calorimeter was mounted inside a copper jacket which could be evacuated. A heating element was wound on the jacket as well as a temperature sensitive element to control the temperature. The grid-controlled Thyratron thermoregulator designed by Sturtevant[5] was used. The thermometer element was made of vanadium–steel wire. Jacket temperatures could be held constant within a few hundredths of a degree over long periods of time.

A flash boiler was devised to evaporate the sample injected into it at a constant rate from a 30-ml. hypodermic syringe. The boiler assembly was made by sintering ground glass in a 7 mm. Pyrex glass tube. The annular space between this tube and an outer 28 mm. tube was filled with mercury and kept about 20° above the boiling point of the liquids studied. Rapid and smooth evaporation of the sample occurred. The speed of sample injection could be varied from 0.6 to 9.1 ml. per min. by a screw drive geared to a variable speed motor. A revolution counter was geared to the screw drive to measure the volume of sample delivered. Volumes could be measured with a precision of 0.1%. The rate of flow was timed with a hand operated stop watch, which was checked against the time signals from the National Bureau of Standards.

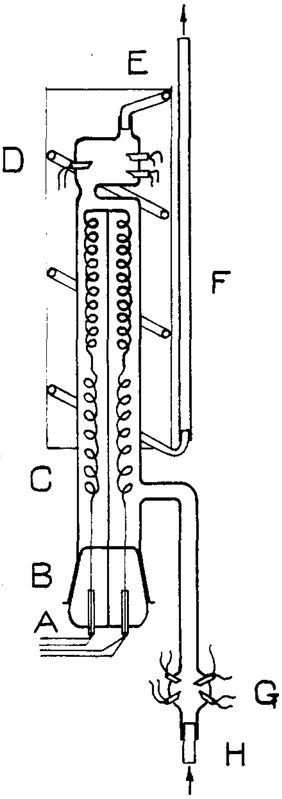

Fig. 1.—Calorimeter assembly.

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[1] This paper is an abstract from the Ph.D. thesis of A. E. Reynolds, whose present address is Hercules Experiment Station, Wilmington, Del.

[2] Callender and Barnes, *Trans. Roy. Soc.* (*London*), **199A**, 55 (1902); Swann, *ibid.*, **210**, 199 (1910); *ibid.*, **82A**, 147 (1909).

[3] Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[4] Pitzer, THIS JOURNAL, **63**, 2413 (1941); Montgomery and De Vries, *ibid.*, **64**, 2372 (1942).

[5] Sturtevant, *Rev. Sci. Instruments*, **9**, 276 (1938).

[6] Coleman and De Vries, THIS JOURNAL, **71**, 2839 (1949).

Electrical.—The heater current and potentials were measured in a manner previously described.[6]

Materials.—Best commercial grade benzene, carbon tetrachloride, primary, secondary and tertiary butyl alcohols were dried with silica gel, then rectified to ±0.1°. Refractive indices checked closely with literature values to the fourth decimal place.

Results

In the constant-flow calorimeter, vapor flowing through a thermally insulated tube is heated electrically at a known rate and the temperature rise is measured. Although Scheel and Heuse[7] introduced the reverse-flow system the modification first used by Callendar and later adapted by Swann,[2] has been found most practical.[4] In such a calorimeter heat is lost to the surroundings at a rate proportional to ΔT such that the rate of heat input, Q, equals $C_pF\Delta T + k\Delta T$, or $C_p' = C_p + k/F$. Usually the apparent value of the heat capacity, C_p', is plotted against the reciprocal of the flow rate, F, and the true value, C_p, is obtained by extrapolation to infinite rate of flow. However, if the heat lost to the surroundings is some function of ΔT, and if there is also a loss of energy, perhaps from the heater through the lead-out wires, which is more or less independent of the flow of vapor, then the heat balance equation is $Q = C_pF\Delta T + k\Delta T\mathrm{t} + \Delta q$, or $Q/F = (C_p + k\Delta T^{n-1}/F)\Delta T + \Delta q/F$.

A series of determinations were made with benzene in which the flow rate was kept constant but the heat input was varied by a sixfold factor.

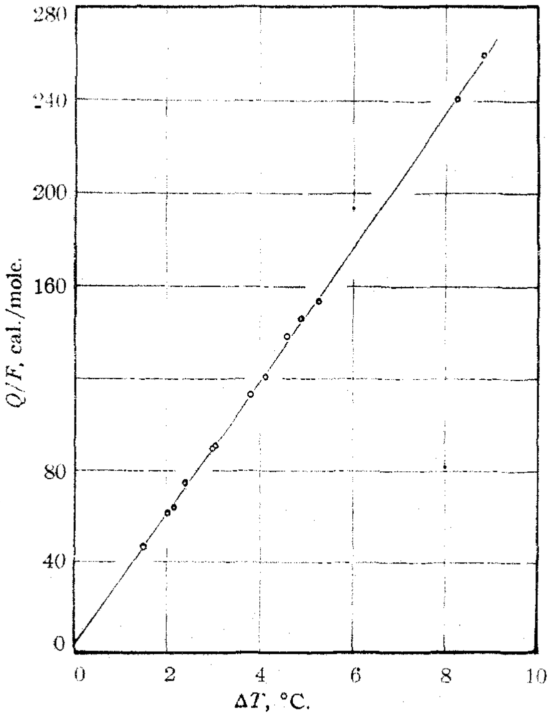

Fig. 2.—Results with benzene at 130° and a flow rate of 4.21 × 10^{-4} mole/sec.

A plot of Q/F against the temperature rise gave a straight line (see Fig. 2) thus confirming the fact that the exponent, n, of ΔT is unity. Furthermore a small, positive value for Δq was indicated. The heat capacity was calculated from the slope of the straight line from data obtained at two different flow rates. The value of $(C_p + k/F)$ was 30.17 at a flow rate of 2.02 × 10^{-4} mole/sec. and 28.85 at 4.21 × 10^{-4} mole/sec. From these data at 130° the value 27.6 cal./mole/deg. for C_p was calculated with k equal to 4.9 × 10^{-4} cal./sec./deg. The above value checks very well with the value 27.65 calculated by interpolation from the data reported by Scott, *et al.*[3]

The experiments with benzene were repeated at 161° at the two flow rates 2.03 and 4.28 × 10^{-4} mole/sec. From the corresponding values of 30.15 and 29.90 for the slopes of the lines, the value 29.6 cal./mole/deg. was calculated with k equal to 0.97 × 10^{-4}. The value reported by Scott[3] for C_p is 29.65.

The jacket and calorimeter were given at least one hour preheating to reach temperature equilibrium during which time the jacket was evacuated. The vaporizer and manometer were also preheated to about 20° above the boiling point of the sample. The syringe was loaded with liquid sample and the motor speed adjusted. When evaporation was started, temperature readings were taken with the calorimeter heater off. These readings became constant in a few minutes. The temperature of the incoming vapor was also determined in this interval. Next, the calorimeter heater was turned on. Besides the readings of the potential drop across the calorimeter heater and the standard resistor in series with it, the potential of the differential thermel was also followed. A maximum was obtained in a few minutes after the heater had been turned on. Final measurements were made of the potential across the heater. The elapsed time for a run was about fifteen minutes. Flow rates between 0.01 and 0.03 mole per minute were found most satisfactory. The heater current was of the order of 0.1 ampere and the resistance of the heater was about 16.7 ohms.

Butyl Alcohols.—A few measurements were made of the heat capacity of the three butyl alcohols at 135 and 160°. The heat loss correction found for the apparatus in the experiments with benzene was applied to the treatment of the data. This procedure was considered dependable because a determination of the heat capacity of carbon tetrachloride at 109° gave the value 22.0 cal./mole/deg. which compares well with the values 21.8 and 22.1 given in the literature.[4] The results for the three butyl alcohols are given in Table I together with values reported in the literature. Bennewitz and Rossner used a flow method. Their value is 4% lower than that found in this investigation but their value for benzene

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[7] Scheel and Heuse, *Ann. Physik*, [4] **37**, 79 (1912).

TABLE I

HEAT CAPACITY OF PRIMARY, SECONDARY AND TERTIARY BUTYL ALCOHOL AT 760 MM.

Reference	1-Butanol	2-Butanol	2-Methyl-2-propanol
This paper	34.2 (135°)	34.3 (136°)	36.2 (138°)
This paper	35.5 (162°)	36.6 (158°)	37.8 (160°)
Dobratz[a]	32.6 (135°)	32.6 (135°)	32.6 (135°)
Dobratz[a]	34.1 (160°)	34.1 (160°)	34.1 (160°)
Jatkar[b]	....	....	15.7 (134°)
Bennewitz and Rossner[c]	32.9 (137°)	....	....

[a] Dobratz, *Ind. Eng. Chem.*, **33**, 759 (1941). [b] Jatkar, *J. Indian Inst. Sci.*, **22A**, 39–58 (1939). [c] Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

is also lower than that reported by Scott by about 1.5%. Jatkar used the velocity of sound method. He was troubled with considerable absorption and pointed out that some rotational contributions to the heat capacity do not hold at supersonic frequencies. The semi-empirical method of calculation described by Dobratz included contributions to the heat capacity from free rotation about the C–C and C–O bonds. The discrepancy between the calculated and experimental values may be due to a partial association of the alcohols in the vapor state. Determination of the heat capacities at higher temperatures would indicate whether the empirically assigned values of Dobratz are in error.

Summary

A flow calorimeter was designed for measuring the heat capacity of organic vapors when the volume of liquid sample is limited. Not more than 25 ml. is needed and a determination can be made in fifteen minutes. The heat capacities of the three butyl alcohols were also determined at 135 and 160°.

WEST LAFAYETTE, INDIANA RECEIVED JUNE 1, 1950

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-temperature Heat Contents of Manganous Sulfide, Ferrous Sulfide and Pyrite[1]

BY J. P. COUGHLIN

This paper reports the results of high-temperature heat-content (enthalpy) measurements of manganous sulfide, ferrous sulfide and pyrite from 298°K. to the respective temperatures, 1814, 1488 and 980°K. Despite the wide interest in these substances, high-temperature heat content data have been available heretofore only for ferrous sulfide, which was studied in the temperature range 273 to 1473° by Bornemann and Hengstenberg.[2] Anderson[3,4] obtained heat-capacity data for all three substances in the temperature range 55 to 298°K., and Eucken and Schwers[5] studied pyrite between 21 and 84°K.

Materials and Method

Manganous sulfide[6] was prepared from reagent-grade manganous sulfate. The latter was ignited at 950°, leached with water, and reignited. The ignition product was treated for six hours at 750° in a stream of carbon disulfide and carbon dioxide, to produce the sulfide. Absence of free sulfur was proved by subsequent heating in high vacuum at 300°. The final product analyzed 63.15% Mn and 36.88% S, as compared with the theoretical 63.14 and 36.86%, respectively.

Ferrous sulfide was prepared from the pure pyrite, described below, by heating in vacuum at 1000° until sulfur evolution ceased. The product was a single-phase containing 63.04% Fe and 36.90% S, corresponding to the composition $FeS_{1.020}$. Difficulties encountered in an attempt to measure the heat content of a sample on the high iron side ($FeS_{0.970}$, which was found to be two-phase at room temperature and single-phase at higher temperatures) made it inadvisable to try to approach more closely the exact stoichiometric composition. Also it was believed that excess sulfur would help to prolong the life of the container-capsule, making it possible to reach a higher temperature in the heat-content measurements.

The pyrite was a portion of the natural mineral used previously by Anderson[4] in low-temperature heat-capacity measurements. A 20-mesh fraction was screened out, washed twice with hot 1% hydrochloric acid, washed repeatedly with cold water, and finally washed with alcohol–ether and dried in vacuum. Analysis gave 46.51% Fe, as compared with the theoretical 46.55%.

The measurements were made by the "dropping" method with previously described apparatus.[7,8] The samples of manganous sulfide and pyrite were enclosed in platinum–rhodium alloy capsules, which were sealed by platinum welding after evacuating and filling the pore space with helium. The ferrous sulfide was sealed in silica–glass capsules. The heat contents of both types of capsules had been determined in separate experiments. The furnace thermocouple, as usual, was calibrated frequently at the melting point of gold and occasionally at the melting point of palladium.

Results and Discussion

The measured heat content values are listed in Table I and shown graphically in Fig. 1.

Manganous sulfide shows normal behavior from room temperature through the melting point,[9] 1803°K. Two determinations, labeled (a) in Table I, at 1760 and 1802°K., are disturbed

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(1) Article not copyrighted.

(2) Bornemann and Hengstenberg, *Metall u. Erz*, **17**, 339 (1920).

(3) Anderson, THIS JOURNAL, **53**, 476 (1931).

(4) Anderson, *ibid.*, **59**, 486 (1937).

(5) Eucken and Schwers, *Ber.*, **15**, 582 (1913).

(6) Preparations and analyses were conducted by K. R. Bonnickson and R. E. Lorenson, Chemists, Pacific Experiment Station, Bureau of Mines.

(7) Southard, THIS JOURNAL, **63**, 3142 (1941).

(8) Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper* 686 (1946).

(9) Silverman, Morey and Rossini, *Bull. Nat. Research Council*, 107, June 1943.