are similar and the mechanisms probably are not widely different.

Summary

1. The rates of photochemical chlorination of the three dichlorobenzenes have been investigated. Most of the measurements were made on the para compound, although little difference in behavior between the three was noted.

2. The rate of chlorination is proportional to the intensity at low intensities, but depends on some power of the intensity between 0.5 and 1.0 at higher intensities.

3. The rate is independent of the chlorine pressure, except in so far as this determines the light absorption, but is proportional to the pressure of the dichlorobenzene.

4. Various possible mechanisms of the reaction have been discussed and a brief comparison with the results for benzene and chlorobenzene has been made.

PROVIDENCE, R. I. RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Determination of the Heat Capacities and the Heat Capacity Ratios of Gaseous Hydrogen Cyanide and of Hydrogen Sulfide[1]

BY W. A. FELSING AND G. W. DRAKE

Object of the Investigation.—The purpose of this investigation was the experimental determination of the heat capacities and of the heat capacity ratios at different temperatures of gaseous hydrogen cyanide and hydrogen sulfide. Heat capacity data for gaseous hydrogen cyanide were necessary for the thermodynamic treatment of the thermal decomposition data for monomethylamine obtained in this Laboratory.[2] Hydrogen cyanide is one of the products of this decomposition, and since published data for the heat capacities of this substance are meager and discordant it was decided to measure these needed quantities. It constitutes an integral part of the study of the methylamines as refrigerating fluids in the absorption type refrigerating units as carried out in this Laboratory.[3]

Since the apparatus was available and the heat capacity data for gaseous hydrogen sulfide are rather meager, this substance was included in this investigation.

Previous Investigations.—Bryant proposed,[4] on the basis of spectroscopic measurements, the following relation for gaseous hydrogen cyanide

$$C_p(\text{cal./mole})\ \text{HCN (g)} = 7.01 + 0.006600T - 0.000001641T^2$$

This relation is claimed to apply over the region 300–2000°K. with an accuracy of about 3%. Usherwood,[5] Partington and Carroll[6] and Bredig and Teichmann[7] have determined heat capacity ratios for gaseous hydrogen cyanide at different temperatures. The latter investigators also calculated values of C_p and C_v from their heat capacity ratios.

Eastman proposed a relation for gaseous hydrogen sulfide,[8] which he based upon a review of all existing data; for the region 300–600°K. he proposed

$$C_p\ (\text{cal./mole})\ \text{H}_2\text{S (g)} = 7.2 + 0.0036T$$

for which he claimed only a 5–10% accuracy. Bryant[4] proposed a relation based upon spectroscopic measurements

$$C_p(\text{cal./mole})\ \text{H}_2\text{S (g)} = 6.48 + 0.00558T + 0.000001204T^2$$

This relation is to apply over the range 300–2000°K. with an accuracy of about 2%. Partington and Shilling[9] give a résumé of all heat capacity ratios for gaseous hydrogen sulfide as determined through 1923. Recently Giauque and Blue[10] determined the heat capacities of solid and liquid hydrogen sulfide.

The Method of this Investigation.—The method selected for the experimental determination of the heat capacities was the closed system continuous flow method of

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[1] From a thesis presented by George Wilson Drake to the Graduate Faculty of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] F. W. Jessen, Ph.D. Dissertation, University of Texas, 1933.

[3] (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); (c) Felsing and Jessen, *ibid.*, **55**, 4418 (1933); (d) Felsing and Ashby, *ibid.*, **56**, 2226 (1934).

[4] Bryant, *Ind. Eng. Chem.*, **25**, 820 (1933).

[5] Usherwood, *J. Chem. Soc.*, **121**, 1604 (1922).

[6] Partington and Carroll, *Phil. Mag.*, **49**, 1665 (1925).

[7] Bredig and Teichmann, *Z. Elektrochem.*, **31**, 449 (1925).

[8] Eastman, *Bur. Mines Tech. Paper* 445 (1929).

[9] Partington and Shilling, "The Specific Heats of Gases," Ernest Benn Limited, London, 1924, pp. 139, 199.

[10] Giauque and Blue, THIS JOURNAL, **58**, 831 (1936).

Scheel and Heuse,[11] with certain modifications suggested by Thayer and Stegeman[12] and by Haas and Stegeman.[13] Modifications dealing with calorimeter design, the heating unit, and the gas circulating pump as developed during this investigation are described in the appropriate sections following.

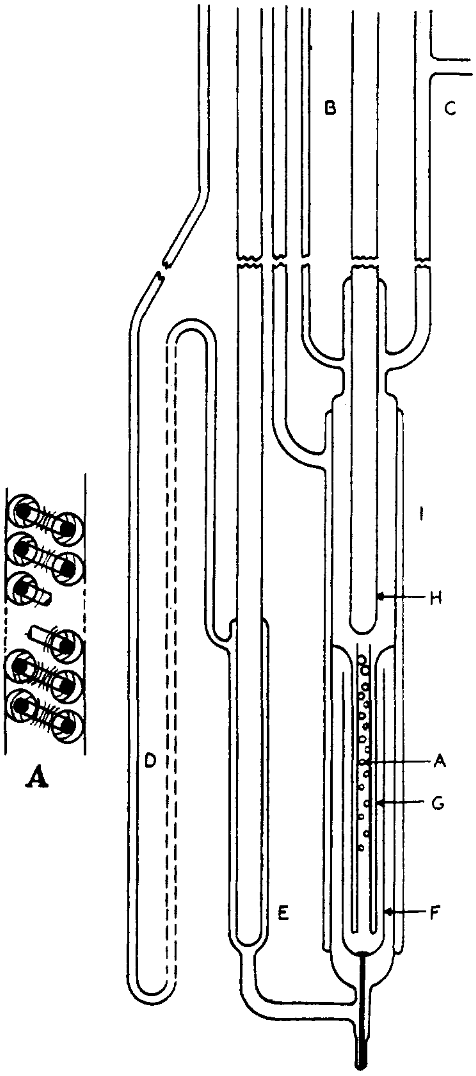

Fig. 1.

The Calorimeter.—The calorimeter is shown in Fig. 1. An enlarged section shows the heating unit design. This unit consisted of approximately 3.66 meters of No. 34 B. & S. bare manganin wire; it was wound smoothly in a lathe on 1.58 mm. diameter rod. A Pyrex rod spiral, which fitted loosely into the heater tube, was constructed; upon this the coiled heating wire was threaded. The glass spiral and its covering of coiled wire was then inserted into the heater tube; the coils fitted tightly against the walls and there was no open channel for the gas to travel through without coming in contact with the heating unit many times. The return wire from the lower end of the coil was brought through a small glass tube extending through the center of the glass spiral. Thus 3.66 meters of bare wire were placed into a tube 4.75 mm. in diameter and 7.6 cm. long.

The Thermoelement.—A 10-junction copper–constantan thermoelement, constructed with the usual precautions, was used to measure the temperature difference between the incoming and outgoing gas. In calibration, nine observations were made at each calibration point, the hot and cold junctions differing by about 3.5° as measured by calibrated Beckmann thermometers. The values of $\Delta E/\Delta t$ thus determined at a given point differed by only 2 parts in 2500 from the average.

The Circulating Pump.—The pump first used was of the type described by Scheel and Heuse,[11] by Thayer and Stegeman,[12] and by Haas and Stegeman.[13] But, since it was found impossible to prevent oscillation of the conventional mercury valves at higher rates of flow with the consequent irregularity of flow, a new design of pump was introduced. The details of this pump are shown in Fig. 2. Mercury valves were abandoned and replaced by ground glass ones, as shown at A and B of Fig. 2. The operating mechanism is shown at K; a crank was mounted on the face-plate of an ordinary speed reducer and the pin of the crank was carried on a threaded bar. This bar was supported at each end by brass blocks and the stroke was varied by turning the threaded bar; this changed, of course, the rate of flow of the gas.

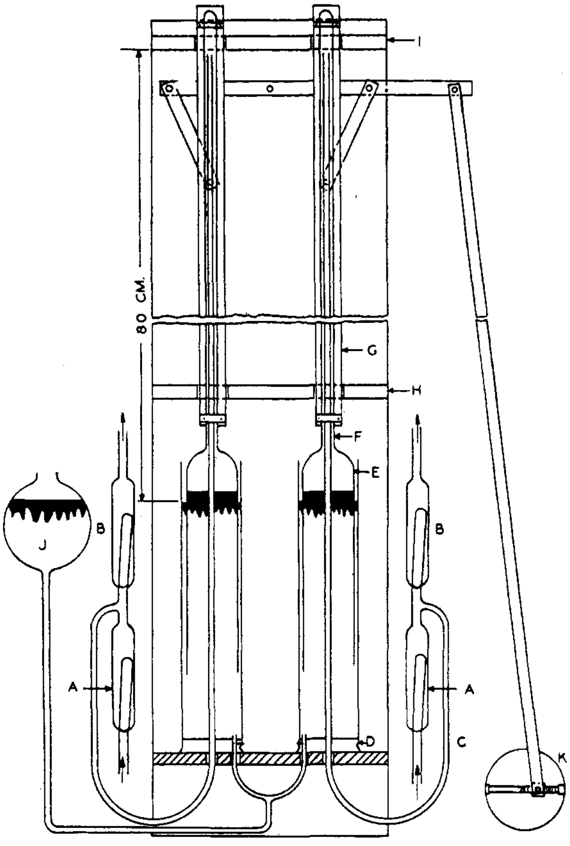

Fig. 2.

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(11) Scheel and Heuse, *Ann. Physik*, **37**, 79 (1912); **40**, 473 (1913).

(12) Thayer and Stegeman, *J. Phys. Chem.*, **35**, 1505 (1931).

(13) Haas and Stegeman, *ibid.*, **36**, 2127 (1932).

The rate of flow was determined as usual by the calibrated bulb method provided, however, with automatic timing. In addition, a flow-meter, calibrated against the bulb, was inserted in the system and the pressure drop measured with a differential manometer filled with olive oil.

The Thermostat.—The thermostat containing the calorimeter consisted of a large Dewar flask (15 × 50 cm.). It was filled with liquid paraffin and was maintained constant at each temperature to within ±0.005°.

The Kundt Tube.—This apparatus does not differ in essentials from that described by Felsing and Jessen,[3e] except in the method of sound production. A General Radio (Type 213, 1000 cycle) audio oscillator produced the current which was sent through a General Radio filter section (Type 330E, 1000 cycle, 600 ohm impedance) and a General Radio band-pass filter (Type 534-B, 1000 cycle, 2000 ohms impedance). This current, impressed upon a telephone receiver in its special housing, produced a sound wave in the tube of such a nature that the minima could be detected easily. The listening tube was closed, the sound being transmitted to a thin aluminum disk fitted into an old-style telephone receiver. The tube was approximately 4 cm. in diameter and it was accurately thermostated.

The Preparation of the Gases.—Hydrogen cyanide was prepared from potassium cyanide and sulfuric acid as recommended by Gilman.[14] The gas was freed from spray, dried by passage over calcium chloride, and condensed by an ice–salt mixture. Repeated fractional distillation under reduced pressure yielded a pure product, which was stored in a reservoir under its own vapor pressure.

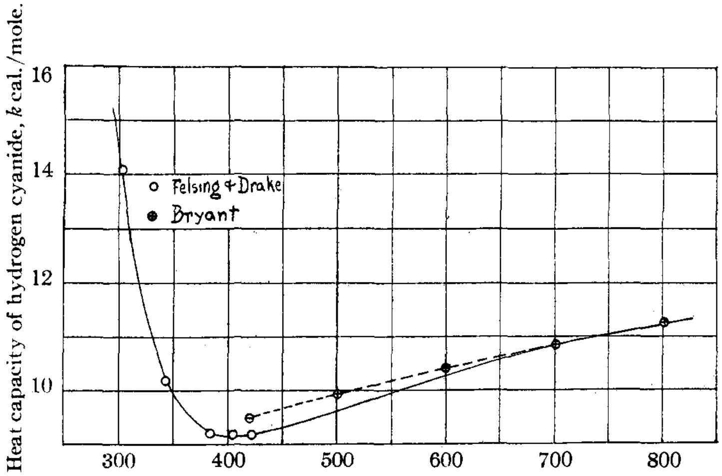

Fig. 3.—Temperature, deg. Kelvin.

Hydrogen sulfide was prepared from aluminum sulfide and water by the method of Keyes and Felsing.[15] The gas was dried by passage over aluminum sulfide.

The Heat Capacities.—The heat capacities for gaseous hydrogen cyanide were measured at 30, 70, 110, 130 and 148°; for hydrogen sulfide they were 30, 70 and 110°. The apparatus was calibrated carefully with pure air (moisture and carbon dioxide free) and the heat loss constant for the apparatus, at different rates of flow, was determined with the aid of the heat capacities listed for air in "I. C. T."[16] The loss determined for air at each temperature and given rate of flow was then assumed to be the loss for the two gases investigated under like conditions. This assumption seems justified for gases of about the same density. The following table presents the data obtained; each value listed is the average of six separate, closely agreeing determinations.

Table I

The Specific and Molecular Heat Capacities of Gaseous Hydrogen Cyanide and Hydrogen Sulfide

Hydrogen Cyanide

Temp., °C.	Heat input J./g./deg.	Heat loss J./g./deg.	Heat capacity Specific J./g.	Molecular cal./mole
30	2.697	0.513	2.185	14.107
70	2.147	.567	1.580	10.201
110	2.065	.637	1.428	9.219
130	2.085	.661	1.424	9.194
148	2.095	.667	1.422	9.181

Hydrogen Sulfide

Temp., °C.	Heat input J./g./deg.	Heat loss J./g./deg.	Heat capacity Specific J./g.	Molecular cal./mole
30	1.475	0.513	0.962	7.838
70	1.540	.567	.973	7.928
110	1.640	.637	1.003	8.172

The values for the heat capacity for hydrogen cyanide were plotted against the temperature as shown in Fig. 3; on the same plot is included the equation by Bryant.[4] The very rapid change in heat capacity at and near room temperature is due most likely to the fact that the gas is associated, as is shown in the table of densities determined during this investigation. As the temperature rises, the gas density approaches normal; Ingold[17] stated that the density of this gas becomes normal above 170°, a fact substantiated by the density measurements listed below. These were made with great care, observing every precaution for high accuracy.

Accordingly, the continuous line, representing the most probable values, does not join the Bryant line until about 700°K. It is assumed that

Table II

The Densities of Gaseous Hydrogen Cyanide

Temp., °C.	Density (1 atm.) (g./cc.)	Obsd. density/ Calcd. density
30	0.0011615	1.07050
70	.0009880	1.03013
110	.0008735	1.01699

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(14) Gilman, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, p. 307.

(15) Keyes and Felsing, This Journal, **42**, 246 (1920)

(16) "I. C. T.," Vol. V, p. 81.

(17) Ingold, *J. Chem. Soc.*, **129**, 26 (1926).

above that temperature the Bryant relation may yield values of the heat capacity. Since, however, the heat capacity changes so rapidly at or near 400°K. two relations were obtained: one for the region 280–400°K. and the other for the region 400–1000°K. These are given as follows

$$(280\text{–}400^\circ\text{K.}):\ C_p(\text{cal./mole})\ \text{HCN(g)} = 121.03 - 0.58130T + 0.00754T^2$$

$$(400\text{–}1000^\circ\text{K.}):\ C_p(\text{cal./mole})\ \text{HCN(g)} = 6.650 + 0.00675T - 0.000001257T^2$$

The relation best expressing the heat capacities of hydrogen sulfide over the temperature range investigated is

$$(273\text{–}450^\circ\text{K.}):\ C_p(\text{cal./mole})\ \text{H}_2\text{S(g)} = 12.157 - 0.02883T + 0.0000481257T^2$$

Since this relation contains rather large temperature coefficients it is not advisable to extrapolate it far past the temperature limits specified.

The Heat Capacity Ratios.—The γ values are presented in Table III; the values in the column marked "uncorrected" resulted from the relation

$$\gamma\ (\text{uncorr.}) = 1.403\ \frac{M}{28.96}\ \frac{l_2^2}{l_1^2}$$

while the values in the "corrected" column resulted from the application of the correction relation

$$\gamma\ \text{corr.} = \gamma\ (\text{uncorr.})\cdot\Phi$$

where $\Phi = 1 - {}^9/_{64}\,\pi\,\tau\,(1 - 6\tau^2)$, as suggested by Partington and Shilling[9] (p. 50). Here $\pi = p/p_c$ = actual pressure/critical pressure and $\tau = T_c/T$ = critical temperature/actual temperature. The critical data for hydrogen cyanide are those of Bredig and Teichmann,[7] while those for hydrogen sulfide are due to Pickering.[18]

The increasing values of γ for hydrogen cyanide may be explained by the apparently greater complexity, as indicated by the density; if values had been extended to higher temperatures, the γ values would most likely have gone through a maximum as is shown by the results of Bredig and Teichmann (maximum at 140°).[7]

TABLE III

VALUES OF C_p/C_v FOR HYDROGEN CYANIDE AND HYDROGEN SULFIDE

Gas	Temp., °C.	γ, uncorr.	γ, corr.
HCN	30	1.144	1.087
	50	1.252	1.201
	75	1.276	1.235
H_2S	10	1.349	1.322
	25	1.343	1.321
	50	1.330	1.313
	75	1.314	1.301

The Accuracy of the Determinations.—From a consideration of all sources of error, it is believed that the heat capacity data are accurate to within *one* per cent.; the accuracy of the heat capacity ratios is within 0.2%; and the density data for gaseous hydrogen cyanide are believed to be accurate to within 0.5%.

Summary

1. The heat capacities of gaseous hydrogen cyanide and of hydrogen sulfide have been determined over a limited temperature interval with an accuracy of approximately 1%. These have been expressed as functions of the temperature.
2. Improvements in measurement of the rate of flow in the construction of the heating unit, and in the gas circulating pump have been described.
3. The densities of gaseous hydrogen cyanide have been measured with an accuracy of approximately 0.5%.
4. The heat capacity ratios for hydrogen cyanide and sulfide have been measured over a temperature range with an accuracy of about 0.2%.

AUSTIN, TEXAS RECEIVED JUNE 19, 1936

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(18) Pickering, *J. Phys. Chem.*, **28**, 97 (1924).