was positive. Horizontal dispersion with $r > v$ was clearly observed.

Summary

1. The author has been successful in separating and identifying a new purine occurring in tea.

2. This was separated from concentrated tea residues after the commercial removal of caffeine.

3. The purine has been found to be identical with 1,3,7,9-tetramethyl-2,6,8-trioxypurine.

4. This is the first methylated derivative of 2,6,8-trioxypurine (uric acid) to be found in nature.

5. The study of plant extracts containing purines will be continued.

NEW HAVEN, CONN. RECEIVED APRIL 26, 1937

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

Ethylene. The Heat Capacity from 15°K. to the Boiling Point. The Heats of Fusion and Vaporization. The Vapor Pressure of the Liquid. The Entropy from Thermal Measurements Compared with the Entropy from Spectroscopic Data

BY CLARK J. EGAN AND J. D. KEMP

There has been some uncertainty previously, due to the possible persistence of rotation in the crystal below 10°K., as to whether the third law entropies of molecules containing symmetrically placed hydrogens would be the correct ones to use in thermodynamic calculations. This has been discussed recently,[1] with the conclusion "that very probably no molecules other than hydrogen and deuterium will have any residual entropy due to the persistence of rotation in the crystal at temperatures below 10°K." The results of the present measurements on ethylene, which contains symmetrically placed hydrogens, confirm the above conclusion.

Purification of Ethylene.—Ethylene, of 99.5% purity, from a cylinder, was passed through a tube containing phosphorus pentoxide and was condensed as a liquid in a previously evacuated bulb. The ethylene was cooled to a temperature slightly above the melting point and the gaseous impurities were removed by pumping with a mercury diffusion pump. The liquid was distilled in a vacuum-jacketed fractionating column under a pressure of 10 to 20 cm., the middle third portion being collected. The above procedure was repeated twice. The three middle portions were combined and fractionated again.

Due to an unusually rapid rise in the heat capacity curve below the melting point, it was at first thought that the ethylene contained a rather large amount of impurity. A further, more careful investigation of the heat capacity curve and of the extremely small variation of the melting point with the percentage melted disclosed that the rapid rise was actually the course of the true heat capacity curve. From the premelting effect shown by the heat capacity measurements very close to the melting point, it was estimated that the liquid-soluble, solid-insoluble impurity in the ethylene was less than 0.001 mole per cent.

Apparatus and Measurement of Amount.—The calorimetric apparatus and procedure have been described previously.[2] The calorimeter of laboratory designation Gold Calorimeter IV was used for the investigation. After the completion of the measurements, the amount of ethylene was determined using the 5-liter measuring bulb described by Giauque and Johnston.[3] The expression

$$\text{Amount in moles} = PV \times \frac{d}{M} \times \frac{1}{1 + \alpha t}\,[1 - \lambda(1 - P)]$$

was used in the calculation of the amount, where V = volume in liters, P = pressure in international atmospheres, d = density of the gas in grams per liter at standard conditions, M = molecular weight, α = mean coefficient of thermal expansion for the range 0 to 25°C., λ = coefficient of deviation from Boyle's law per atmosphere, and t = the temperature in °C. The pressure measurements were made using a Société Génévoise cathetometer as a comparison instrument in connection with a steel standard meter bar, and the pressure readings were converted to international atmospheres using the data in the "I. C. T." for the thermal expansion of mercury and of the meter bar. The corrections for capillary depression were taken from the work of Cawood and Patterson,[4] and the acceleration of gravity for this location was taken as 979.973 cm./sec.^{2}.[5] The standard ac-

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[1] Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).

[2] Kemp and Giauque, *ibid.*, **59**, 79 (1937).

[3] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

[4] Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).

[5] Sternwarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

celeration of gravity was taken as 980.665 cm./sec.^{2}. The values of the constants employed were d = 1.26026 g./liter,[6] α = 0.003746,[7] $\lambda_{25°}$ = 0.00619,[8] and M = 28.051.[9]

Vapor Pressure.—The procedure used in the measurements of the vapor pressure has been described previously.[2] The same measuring instruments and corrections mentioned above were used for the vapor pressure measurements.

The observations have been represented by the equation

liquid ethylene, 123 to 170°K., (0°C. = 273.10°K.)

$$\log_{10}P_{(\text{Int. cm. Hg})} = -(962.794/T) + 9.80431 - 0.0184522\,T + 0.000030870\,T^2 \quad (1)$$

A summary of the measurements is presented in Table I. The calculated and observed values are compared in columns 3 and 4. The temperatures have been given to 0.001° because of the high relative accuracy. The absolute temperatures may be in error by several hundredths of a degree. Column 5 contains values of the rate of change of pressure with temperature calculated from equation (1).

The boiling point calculated from equation (1) is 169.40 ± 0.05°K.

Table II contains a comparison of the temperatures calculated from the vapor pressure equations of this research and of Henning and Stock.[10]

TABLE I

VAPOR PRESSURE OF LIQUID ETHYLENE
(0°C. = 273.10°K.)

T, °K.	$P_{\text{Int. cm.}}$ observed	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$T_{\text{obsd.}} - T_{\text{calcd.}}$	$\frac{dP}{dT}\,\frac{\text{Cm.}}{\text{deg.}}$
123.460	1.578	−0.001	+0.003	0.190
128.545	2.838	+ .003	− .010	.312
135.918	6.067	.000	.000	.588
140.935	9.656	− .014	+ .016	.861
145.539	14.365	.000	.000	1.190
151.002	22.175	+ .001	− .001	1.690
156.160	32.374	+ .002	− .001	2.286
161.620	46.937	+ .027	− .009	3.068
165.114	58.644	+ .016	− .004	3.654
167.752	68.900	− .002	+ .000	4.144
170.349	80.337	.000	.000	4.670

TABLE II

COMPARISON OF TEMPERATURES FROM THE VAPOR PRESSURE EQUATION OF HENNING AND STOCK

T, °K.	135	145	155	165	170
$T_{\text{This research}} - T_{\text{H. and S.}}$	−0.05	+0.03	+0.08	+0.06	0.00

Melting Point.—The melting point was observed with various percentages of the ethylene melted. The observation for 3% melted was taken later, after a series of short heat capacity measurements below the melting point. The results are summarized in Table III.

TABLE III

MELTING POINT OF ETHYLENE
(0°C. = 273.10°K.)

Time	% melted	T, °K. resistance thermometer	T, °K. thermocouple
		3/13/37	
3:05 P. M.	Stopped supply of heat		
4:33 P. M.	3	103.957	103.95
5:20 P. M.	3	103.952	103.95
6:00 P. M.	3	103.951	103.96
6:36 P. M.	3	103.953	103.96
		3/1/37	
9:40 A. M.	Stopped supply of heat		
11:00 A. M.	15	103.949	103.95
11:53 A. M.	15	103.945	103.96
12:14 P. M.	Stopped supply of heat		
1:32 P. M.	30	103.950	103.92
2:37 P. M.	30	103.950	103.95
3:10 P. M.	Stopped supply of heat		
4:35 P. M.	47	103.952	103.94
5:27 P. M.	47	103.952	103.95
5:46 P. M.	Stopped supply of heat		
7:18 P. M.	64	103.952	103.96
8:08 P. M.	64	103.952	103.96

Accepted value 103.95 ± 0.05°K.

Table IV gives a comparison of the melting and boiling points observed in this research with those observed by other experimenters.

TABLE IV

MELTING POINT AND BOILING POINT TEMPERATURES OF ETHYLENE

M. p., T, °K.	B. p., T, °K.	Observer
....	170.5	Olszewski[11]
....	170.5	Ramsay and Travers[11]
....	169.5	Wroblewski and Witkowski[11]
....	169.2	Burrell and Robertson[12] (1915)
103.7	169.2	Maass and Wright[13] (1921)
....	169.38	Henning and Stock[10] (1921)
103.95 ± 0.05	169.40 ± 0.05	This research

Heat Capacity of Ethylene.—The heat capacity measurements are given in Table V. 1.0004 absolute joules were taken equal to 1 International joule and 4.185 absolute joules equal to 1 calorie.

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(6) Stock and Ritter, *Z. physik. Chem.*, **126**, 172 (1927).

(7) Calculated from the data of Coppock and Whytlaw-Gray, *Proc. Roy. Soc.* (London), **A143**, 487 (1934).

(8) Extrapolated from the data of Cawood and Patterson, *Trans. Roy. Soc.*, **A236**, 77 (1936).

(9) Int. At. Wt. Committee, THIS JOURNAL, **59**, 219 (1937).

(10) Henning and Stock, *Z. Physik*, **4**, 226 (1921).

(11) See M. W. Travers, "The Experimental Study of Gases," 1901, p. 243.

(12) Burrell and Robertson, THIS JOURNAL, **37**, 1893 (1915).

(13) Maass and Wright, *ibid.*, **43**, 1098 (1921).

A graphical representation of the data is shown in Fig. 1. Table VI contains values of the heat capacity taken from a smooth curve, and a comparison with the results of Eucken and Hauck.[14] Previous comparisons for other substances have shown their work to be unreliable.[15,16,17]

TABLE V

HEAT CAPACITY OF ETHYLENE

Molecular weight, 28.051; 2.4570 moles in calorimeter 0 °C. = 273.10 °K.

T, °K.	C_p, cal./deg./mole	ΔT	Series
16.00	0.803	2.359	III
18.81	1.299	3.315	III
21.91	1.921	2.842	III
25.17	2.556	3.665	III
29.10	3.362	4.207	III
33.16	4.288	3.872	III
37.35	5.187	4.454	III
42.08	6.045	4.956	III
47.29	6.932	5.419	III
52.52	7.809	5.022	III
57.60	8.598	5.123	III
62.80	9.279	5.329	III
68.41	9.980	5.861	III
74.70	10.79	5.845	III
80.79	11.70	6.222	III
86.77	12.65	5.607	III
92.11	13.83	3.942	III
94.46	14.56	3.751	I
95.48	14.94	3.612	III
98.10	16.03	3.405	I
98.99	16.44	3.283	III
100.94	17.65	1.870	IV
101.39	17.97	3.051	I
101.90	18.47	2.450	III
102.28	18.59	0.759	IV
103.03	19.62	.723	IV
103.36	20.77	.896	I
103.59	20.58	.369	IV
103.81	34.96	.089[a]	IV
103.95	Melting point		
106.69	16.51	3.700	II
108.58	16.49	3.666	II
112.28	16.43	6.364	II
119.03	16.33	6.926	II
125.90	16.28	6.687	II
132.60	16.21	6.476	II
139.08	16.11	6.272	II
145.38	16.09	6.104	II
151.88	16.08	6.621	II
158.55	16.03	6.432	II
164.23	16.04	4.701	II
168.71	16.09	4.075	II
169.40	Boiling point		

[a] This point obviously includes some premelting.

TABLE VI

HEAT CAPACITY OF ETHYLENE

Molecular weight, 28.051

Values taken from smooth curve through observations

T, °K.	C_p, cal./deg./mole	Deviation E. and H.—This research, %	T, °K.	C_p, cal./deg./mole	Deviation E. and H.—This research, %
15	0.682		80	11.55	28.1
20	1.519		85	12.35	
25	2.537		90	13.29	15.5
30	3.559		95	14.73	
35	4.682		100	17.05	−6.2
40	5.665		103.95	Melting point	
45	6.542		105	16.54	
50	7.394		110	16.46	3.0
55	8.211		120	16.32	6.6
60	8.923		130	16.21	9.8
65	9.553		140	16.12	12.7
70	10.18		150	16.07	15.1
75	10.83		160	16.04	17.2
			170	16.07	17.0

An interesting feature of the heat capacity curve is the sharp rise just below the melting point. The heat capacities of Series IV were measured in order to investigate more closely the portion of the curve in this region. Only the last heat capacity point, which had a temperature rise of about 0.09°, and ended within 0.1° of the melting point, showed any observable premelting effect. The melting point was observed again for 3% of the ethylene melted, after the completion of Series IV. The constancy of the melting point shown in Table III presents strong evidence that the sharp rise is the course of the true heat capacity curve. This region of high heat capacity is similar to those preceding the transitions in solid carbon monoxide[18] and solid nitrogen[19] with the difference that ethylene melts before the heat capacity drops to a value comparable with that before the rise.

Heat of Fusion.—The measurements of the heat of fusion of ethylene are summarized in Table VII.

TABLE VII

HEAT OF FUSION OF ETHYLENE

Molecular weight, 28.051

Temperature interval, °K.	Corrected heat input/mole	$\int C_p dT$	ΔH, cal./mole
103.810–106.480	859.4	58.6	800.8
103.499–106.707	872.7	71.6	801.1
103.135–106.320	873.4	72.9	800.5
		Av. value =	800.8 ± 0.8

The value 699 cal./mole, given by Eucken and

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(14) Eucken and Hauck, *Z. physik. Chem.*, **134**, 161 (1928).

(15) Wiebe, Hubbard and Brevoort, THIS JOURNAL, **52**, 611 (1930).

(16) Witt and Kemp, *ibid.*, **59**, 273 (1937).

(17) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(18) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932).

(19) Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

Hauck, is not in agreement with the results of the present measurements.

Heat of Vaporization.—The ethylene was vaporized from the calorimeter into the 5-liter measuring bulb mentioned previously. A constant pressure regulating device described by Giauque and Johnston[3] was used. The individual measurements are summarized in Table VIII and compared with the value from the vapor pressure measurements and Berthelot's equation. The value obtained from the equation of Henning and Stock is also included.

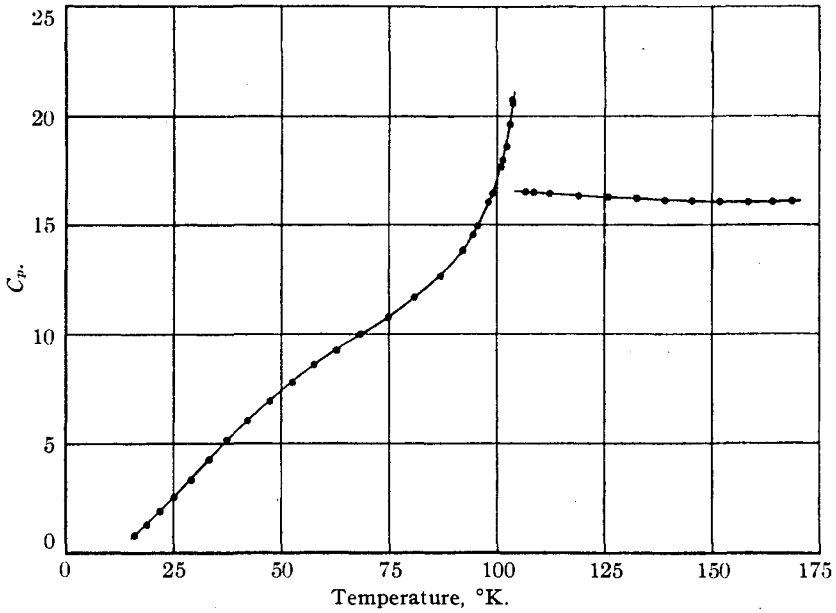

Fig. 1.—Heat capacity of ethylene in cal./deg. per mole.

Entropy from Calorimetric Data.—The calculation of the entropy of ethylene at the boiling point 169.40°K. from the calorimetric data is given in Table IX.

TABLE VIII

HEAT OF VAPORIZATION OF ETHYLENE

Boiling point, 169.40°K.; Molecular weight, 28.051

No. moles vaporized	Time of energy input, min.	ΔH at 760 mm. cal./mole
0.21949	36	3237
.21197	34	3237
.21006	34	3238
.21252	34	3237
	Av. value =	3237 ± 3
From vapor pressure equation 1. This includes a Berthelot correction of −122 cal./mole		3222
From vapor pressure equation of Henning and Stock, assuming a Berthelot gas		3175

TABLE IX

ENTROPY OF ETHYLENE FROM CALORIMETRIC DATA

0–15°K., Debye extrapolation, ($hc\nu/k$ = 128)	0.25
15–103.95°K., graphical	12.226
Fusion, 800.8/103.95	7.704
103.95–169.40°K., graphical	7.924
Vaporization, 3237/169.40	19.11
Entropy of actual gas at boiling point	47.21 ± 0.1
Correction for gas imperfection	0.15
Entropy of ideal gas at 1 atm. and 169.40°K.	47.36 cal./deg. per mole

The correction for gas imperfection was obtained from the expression $S_{\text{ideal}} - S_{\text{actual}} = (27RT^3P_c)/(32T^3P_c)$. This is obtained from Berthelot's equation and thermodynamics. The values of the critical pressure and temperature were taken as T_c = 282.8°K., P_c = 50.9 atm.[20]

Entropy from Spectroscopic Data.—The entropy of ethylene at one atmosphere has been calculated from spectroscopic data. The results are summarized in Table X. The values used for the natural constants were those given in the "I. C. T." The moments of inertia have been given by Badger[21] as 33.2×10^{-40}, 27.5×10^{-40} and 5.70×10^{-40} g./cm.^{2}. The following vibrational frequencies (in cm.$^{-1}$) given by Bonner[22] were used in the calculation

$\nu_1 = 1623.3$
$\nu_2 = 3019.3$
$\nu_3 = 1342.4$
$\nu_4 = 2988.2$
$\nu_5 = 1443.9$
$\nu_6 = 3069$
$\nu_7 = 950$
$\nu_8 = 3107.4$
$\nu_9 = 950$
$\nu_{10} = 940$
$\nu_{11} = 1100$
$\nu_{12} = 825$

The symmetry number σ was taken equal to 4. In the above calculations the nuclear spin entropy has been ignored. The absolute entropies are obtained by adding $R \ln 2$ for each hydrogen atom. ($R \ln 16$ = 5.51 entropy units.)

A comparison of the third law value of the entropy with the value calculated from spectroscopic data is given in Table XI.

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(20) "International Critical Tables," McGraw-Hill Book Co., New York, 1926.

(21) Badger, *Phys. Rev.*, **45**, 648 (1934).

(22) Bonner, THIS JOURNAL, **58**, 34 (1936).

TABLE X

ENTROPY OF ETHYLENE AT 1 ATMOSPHERE FROM SPECTROSCOPIC DATA

	$T =$ 169.40°K.	$T =$ 298.10°K.
$S_{\text{trans.}} = 3/2\, R \ln M + 5/2\, R \ln T - R \ln P - 2.300$	33.130	35.938
$S_{\text{rot.}} = R/2 \ln I_1 I_2 I_3 + 3/2\, R \ln T - R \ln \sigma + 267.649$	14.192	15.876
$S_{\text{vib.}} = R \sum\limits_{\nu_1 \text{ to } \nu_{12}} \left[\ln \frac{e^x}{e^x - 1} + \frac{x}{e^x - 1} \right]$	0.031	0.656
where $x = hc\nu/kT$		
Total entropy in cal./deg. per mole	47.35	52.47

TABLE XI

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC VALUES OF THE ENTROPY OF ETHYLENE

		$T =$ 169.40°K. Cal./deg. per mole	$T =$ 298.10°K.
	Absolute	52.86	57.98
Spectroscopic	Less nuclear spin entropy	47.35	52.47
Experimental	Actual gas	47.21 ± 0.1	...
	Ideal gas	47.36	52.48

The excellent agreement between the spectroscopic and experimental values of the entropy of ethylene indicates it is correct to use the third law value in thermodynamic calculations. It also gives more experimental substantiation to the conclusion of Kemp and Pitzer that no molecules other than hydrogen and deuterium will retain any entropy due to the persistence of rotation in the crystal below 10°K.

Summary

The heat capacity of ethylene has been measured from 15°K. to the boiling point. Evidence has been presented to indicate that the sharp rise in the heat capacity curve immediately below the melting point is the true course of the curve and is not due to premelting.

The melting point was found to be 103.95 ± 0.05°K., the boiling point 169.40 ± 0.05°K., (0°C. = 273.10°K.), the heat of fusion 800.8 ± 0.8 cal./mole, the heat of vaporization 3237 ± 3 cal./mole.

The vapor pressure of ethylene has been measured and the results have been represented by the equation

liquid ethylene, 123 to 170°K., (0°C. = 273.10°K.)

$$\log_{10} P_{(\text{Int. cm.})} = -(962.794/T) + 9.80431 - 0.0184522\, T + 0.000030870\, T^2$$

The entropy of ethylene (ideal gas) at 1 atmosphere and at the boiling point 169.40°K. has been calculated from the calorimetric data to be 47.36 cal./deg. per mole and compared with the value 47.35 obtained from spectroscopic data. These values of the entropy are the ones ordinarily used in thermodynamic calculations and do not contain the nuclear spin contribution of R ln 2 for each hydrogen atom. The close agreement of the experimental and spectroscopic values of the entropy substantiates the conclusion that no molecules, other than hydrogen and deuterium, containing symmetrically placed hydrogens will have any residual entropy due to the persistence of rotation of the molecules in the crystal below 10°K.

BERKELEY, CALIF. RECEIVED MAY 3, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,4-Dimethylphenanthrene by the Pschorr Reaction, and the Non-identity of the Product with the 1,4-Dimethylphenanthrene of Bardhan and Sengupta[1]

BY RUSSELL BLISS AKIN,[2] GELU S. STAMATOFF AND MARSTON TAYLOR BOGERT

In a recent article, Bogert and Stamatoff[3] described the synthesis of 1,3-dimethylphenanthrene by the Pschorr process and recorded the properties of their product.

After this research had been completed and the results submitted for publication, but before the article appeared, Bardhan and Sengupta[4] reported the preparation of 1,4-dimethylphenanthrene by the cyclodehydration (with phosphorus pentoxide) of ethyl 2-(beta-2′,5′-dimethylphenylethyl)-cyclohexanol-2-carboxylate (X) to the corresponding octahydrophenanthrene derivative (XI), and fusion of the latter with selenium.

Upon comparing with the Bogert and Stamatoff products the constants given by Bardhan

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[1] Presented before the Division of Organic Chemistry, at the Chapel Hill Meeting of the American Chemical Society, April 13, 1937.

[2] Ferguson Fellow, Columbia University, 1934–1935 and 1936–1937.

[3] Bogert and Stamatoff, *Rec. trav. chim.*, **52**, 583 (1933).

[4] Bardhan and Sengupta, *J. Chem. Soc.*, 2520–2526 (1932).