electrons. Only one structure on this basis could give zero dipole moment and that one would have the three electron pairs in a plane with the two single electron bonds at right angles to this plane. Doubt is cast on this structure from three directions. The substance is diamagnetic, and it is difficult to see how two unpaired electrons on opposite sides of the central atom could neutralize each other's magnetic fields. The molecules dissociate readily to give the trichloride and chlorine, which may indicate that, if there are two chlorine atoms held differently than the other three, they should be adjacent. Chemical reactions such as the hydrolysis with water to form the oxychloride also indicate the same. The double molecule formula, $SbCl_3 \cdot Cl_2$, is ruled out by the vapor density measurements, which show $SbCl_5$ to exist in the gas phase.

Summary

The molar polarizations of antimony pentachloride and phosphorus pentachloride have been measured in carbon tetrachloride solutions and the dipole moments concluded to be either zero or very small.

The dielectric constants of antimony pentachloride and phosphorus pentachloride have been measured for both liquid and crystalline states.

The specific conductivity of phosphorus pentachloride has been measured.

Antimony pentachloride and phosphorus pentachloride are assumed to have a symmetrical structure with a ten electron shell for the central atom.

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

THE ENTROPY AND FREE ENERGY OF METHANE[1]

BY H. H. STORCH[2]

Introduction

In a recent publication[3] C. G. Maier reported a discrepancy of about five entropy units between the entropy of methane as calculated by way of low temperature specific heat data and the third law of thermodynamics, and that obtained from Randall and Gerard's[4] and Randall and Mohammad's[5] work on equilibria in the reactions

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{I}$$
$$C + 2H_2 = CH_4 \tag{II}$$

---
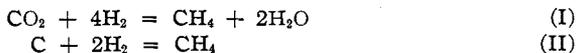
[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject, to copyright.)

[2] Physical Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station.

[3] Maier, "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," U. S. Bureau of Mines Bulletin 324 (1930).

[4] Randall and Gerard, *Ind. Eng. Chem.*, 20, 1335 (1928).

[5] Randall and Mohammad, *ibid.*, 21, 1048 (1929).

In view of the numerous reactions involving methane in which the U. S. Bureau of Mines Experiment Stations are interested, it was considered desirable to recalculate the entropy of methane using the recent measurements of Clusius[6] on the specific heat of methane in the temperature range 10.33–105.3°K.; and to revise the calculations of Randall and his collaborators, using a recent experimental value of the heat of combustion of methane, the specific heat equations given by Eastman[7] for hydrogen, carbon dioxide and water, and for methane the data given by Eucken and Lüde[8] for the temperature range 297.7–481.2°K.

Entropy of Methane from Specific Heat Data.—The entropy data given in Table I were obtained by using the data of Clusius,[6] the approximate Debye equation for the range 10.33–0.00°K., the heat of vaporization of liquid methane as calculated from the vapor pressure measurements of Keyes, Taylor and Smith,[9] and finally the equation $C_p = 5.90 + 9.60 \times 10^{-3}T$ given by Eastman[7] in the range 111.8–298.1°K.

In employing the approximate Debye equation, $C_v = 12\pi^4 N\,kT^3/5\Theta^3$, the value of Θ used was that given by Clusius. In the range 10.33–111.8°K. the specific heat curve was extrapolated to cover the region under the cusp in the vicinity of 20.4°K., the entropy of transition at the latter temperature being calculated from the value for the heat of transition as given by Clusius.

Recalculation of Entropy and Free Energy of Methane from Equilibrium Measurements.—The specific heat equations given in Table II were used in recalculating the entropy and free energy of methane, using Randall and co-workers'[4,5] data. The equations are all of the form $C_p = a + bT + CT^2$.

[6] Clusius, *Z. physik. Chem.*, [Abt. B] **3**, 41 (1929).

[7] Eastman, U. S. Bureau of Mines Technical Paper 445 (1929).

[8] Eucken and Lüde, *Z. physik. Chem.*, [Abt. B] **5**, 436 (1929).

[9] Keyes, Taylor and Smith, *J. Math. Phys., Mass. Inst. Tech.*, **1**, 191–212 (1922), determined the vapor pressure of methane and the densities of the coexisting phases, whence by use of the Clapeyron equation they calculate the heat of vaporization to be 123 cal./g. or 1968 cal./mole at the boiling point (given by them as 111.52° K.), and 2104 cal./mole at the triple point (89.98° K.). The latter figure is in excellent agreement with a calculation based on the vapor pressure of solid methane in the range 76.89–87.25°K. as obtained by Karwat, *Z. physik. Chem.*, **112**, 486 (1924)] and by Freeth and Verschoyle [*Proc. Roy. Soc.* (London), A130, 453 (1931)] in the range 64.78–90.66°K.; and on the heat of fusion as given by Clusius.[6] The heat of vaporization of solid methane calculated from Karwat's measurements is 2326 cal./mole, and combining this with 224 cal./mole for the heat of fusion (at 90.6°K.) given by Clusius, the value 2102 cal./mole is obtained for the heat of vaporization of liquid methane in the vicinity of the melting point. This figure checks that of Keyes, Taylor and Smith within 0.1%. It appears therefore that the datum 1968 cal./mole calculated by the latter authors for the heat of vaporization at the boiling point is to be preferred to 2075 cal./mole calculated from the data of Stock, Henning and Kuss [*Ber.*, **54**, 1119 (1921)]. However, it would be very desirable to obtain an accurate redetermination of the heat of vaporization.

<div align="center">TABLE I</div>
<div align="center">ENTROPY OF METHANE FROM SPECIFIC HEAT DATA</div>

Temp. range, °K.	Transition points, and form of methane	Entropy units	Authors of specific heat data
0–10.33	Solid	0.36	Debye equation
10–111.8	Solid A – Solid B at 20.4°K. ΔH = 18.1 cal./mole	0.89	Clusius
	Heat of fusion at 90.6°K. = 224.0 cal./mole	2.47	Clusius
	Specific heat 10.33–111.8°K.	14.55	Clusius
111.8	Heat of vaporization = 1968 cal./mole	17.60	Keyes, Taylor and Smith
111.8–298.1	Gas	7.52	Eastman
Total		43.39	

<div align="center">TABLE II</div>
<div align="center">C_p EQUATIONS</div>

Substance	a	$b \times 10^3$	$c \times 10^6$	Reference to authors
Graphite	1.22	4.89	−1.11	Eastman[10]
H_2	6.85	0.28	0.22	Eastman[7]
H_2O	8.22	0.15	1.34	Eastman[7]
CO_2	7.70	5.30	−0.83	Eastman[7]
CH_4	4.38	14.17	0.00	Euken and Lüde[8]

A recent determination[11] of the heat of combustion of methane yielded the value 212,728 cal. at 25°, which is in good agreement with the figure chosen by Lewis and Randall.[12] This value combined with 94,250 cal. for the heat of combustion of graphite at 25°, and 68,270 cal. for the heat of formation of liquid water at 25°, yields 18,062 cal. for the heat of formation of methane. Using this figure and the equilibrium constants determined by Randall and Gerard,[4] the following free energy equation for reaction I was obtained

$$\Delta F = -35578 + 14.28T \ln T - 4.03 \times 10^{-3}T^2 - 0.44 \times 10^{-6}T^3 - 51.0T \quad \text{(III)}$$

This equation yields $\Delta F_{298.1}$ = −26912 cal/mole. Combining this datum with the free energies of carbon dioxide and of water,[10] viz., $\Delta F_{298.1, CO_2}$ = −93,647 and $\Delta F_{298.1, H_2O_{(g)}}$ = −54,467, the free energy of methane is found to be $\Delta F_{298.1, CH_4}$ = −11,625. Hence, substituting in the equation $\Delta F = \Delta H - T\Delta S$, −11,625 for ΔF and −18,062 for ΔH, the entropy change (ΔS) at 25° is found to be −21.60 entropy units. Using the figures 1.3 and 31.23 for the entropies of graphite[12] and of hydrogen gas,[13] respectively, the entropy of methane is calculated to be 42.16 units at 25°.

[10] "The Free Energy of Water, Carbon Monoxide and Carbon Dioxide," U. S. Bureau of Mines Circular 6125, May, 1929.

[11] Frederick D. Rossini, Bur. Standards J. Research, 6, 37 (1931).

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

[13] W. F. Giauque, THIS JOURNAL, 52, 4816 (1930).

There is no scarcity of data on direct measurements of equilibrium in reaction II. These data are thoroughly reviewed by Randall and Mohammad[6] and by Egloff, Schaad and Lowry.[14] Despite the number of experimenters and the relatively large amount of data available, in no case is a sufficiently complete analysis of the equilibrium mixture described which would indicate with certainty the presence or absence of hydrocarbons other than methane. For this reason, the accuracy of the equilibrium constants reported for reaction (II) is not readily determinable. In fact, it is probable that the entropy and free energy of methane as calculated from direct equilibrium measurements are not as reliable as the figures obtained by way of low temperature specific heat measurements. Recalculating the data given by Randall and Mohammad[6] for reaction (II), using the specific heat data of Table II, and the value of $\Delta H_{298.1, \text{CH}_4} =$ $-18,062$ cal./mole, the free energy of methane is found to be $\Delta F_{298.1, \text{CH}_4} =$ $-12,542$ cal./mole; whence, using the values of the entropies of carbon and hydrogen previously cited, the entropy of methane at 298.1°K. is 45.26 units. This value is 1.87 entropy units higher than that obtained from Clusius[6] specific heat data, and 3.10 units higher than that yielded by Randall and Gerard's[4] data on reaction (I).

Using the value 43.39 units for the entropy of methane, the specific heat data of Table II, and $-18,062$ cal./mole for $\Delta H_{298.1, \text{CH}_4}$, the following free energy equation for methane is obtained

$$\Delta F = -15,313 - 10.54 T \ln T - 4.36 \times 10^{-3} T^2 - 0.11 \times 10^{-6} T^3 - 47.6 T \quad \text{(IV)}$$

Summary

The entropy of methane at 25° as calculated from Clusius' recent low temperature specific heat measurements is 43.39 units. By calculation from equilibrium measurements for the reactions $CO_2 + 4H_2 = CH_4 + 2H_2O$ and $C + 2H_2 = CH_4$, using Eastman's revision of the specific heat equations of carbon, hydrogen, water and carbon dioxide, the measurements of Eucken and Lüde of the specific heat of methane in the range 297.7–481.2°K., and a recently determined (by the U. S. Bureau of Standards) experimental value of the heat of combustion of methane, the figures 42.16 and 45.24 entropy units, respectively, were obtained. The value 43.39 entropy units as calculated from specific heat measurements is close to the average of the two data calculated from equilibrium measurements and is considered to be the most reliable estimate available at present. A free energy equation for methane based on this entropy figure is presented.

PITTSBURGH, PENNSYLVANIA

[14] Egloff, Schaad and Lowry, *J. Phys. Chem.*, **34**, 1617 (1930).