stant increases gradually from 4° K. to room temperature. This increase may be attributed to increased orbital contribution. The value of 3.07 at 292° K., given by Jackson,[1a] is 65% above the spin-only value, but still below the value calculated for complete spin-orbit coupling.

The magnetic and thermal data indicate that $CoSO_4\cdot 7H_2O$ behaves approximately as an ideal paramagnetic substance in the region near 1° K. There is essentially no hysteresis or remanent magnetic moment in zero field. The separation between the magnetic levels in the absence of an applied magnetic field is quite small. This is in marked contrast to the behavior of the closely analogous salts $NiSO_4\cdot 7H_2O$ and $FeSO_4\cdot 7H_2O$. In the former case the three lowest magnetic states are separated by about 2.5 cm.$^{-1}$ from each other. In the latter case the over-all separation of five states has been estimated[14] at about 25 cm.$^{-1}$. The crystal structures and molar volumes of the three salts are quite similar, and the "dilution" of the magnetic ions by diamagnetic atoms should be about the same in each case. Apparently the ideal behavior observed with $CoSO_4\cdot 7H_2O$ is characteristic of the nature of the cobalt ion itself.

The entropy associated with the population of the four low-lying magnetic levels is $R \ln 4 = 2.74$ cal. deg.$^{-1}$ mole^{-1}. It has been found possible to remove 0.8 cal. deg.$^{-1}$ mole^{-1} of this by a field of 8400 oersteds at 1.22° K.

We thank D. N. Lyon, T. H. Geballe, R. H. Busey and J. E. Kunzler for assistance with the experimental measurements and Mrs. B. J. Hurd for making the spectroscopic examination of the cobaltous sulfate.

Summary

The magnetic susceptibility and heat capacity of $CoSO_4\cdot 7H_2O$, together with associated thermodynamic data, have been measured between about 0.2 and 15° K. The thermodynamic temperature has been estimated for measurements in zero field to 0.25° K.

The magnetic data and heat capacities agree with the assumption of a set of low-lying levels of the ground state multiplet with an over-all spacing of the order of a few tenths of a wave number. The data on intensity of magnetization can be explained at the lower temperatures by the assumption of four magnetic levels of very small separation, such as could arise from the electron spins alone, with the orbital contribution "quenched."

The residual magnetism after demagnetization to temperatures as low as 0.16° K., from magnetic fields sufficient to produce about 25% saturation, is at most 1 part in 40,000 of the "spin-only" saturation value. The energy absorbed due to magnetic hysteresis is no more than 1 part in 8000 at about 0.2° K. for a. c. fields up to 14 oersteds, 60 cycles, and 29 oersteds, 550 cycles.

The entropy of $CoSO_4\cdot 7H_2O$ at 1° K. is 2.73, and at 15° K. is 3.16 cal. deg.$^{-1}$ mole.$^{-1}$.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 13, 1948

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

The Entropy of Ethylene Oxide. Heat Capacity from 14 to 285°K. Vapor Pressure. Heats of Fusion and Vaporization

BY W. F. GIAUQUE AND JOSEPH GORDON

This paper presents the results of a low temperature calorimetric investigation on ethylene oxide. The purpose of the measurements was the determination of the entropy of ethylene oxide gas from the third law of thermodynamics and the comparison of this value with one calculated from molecular data.

The measurements were made in a calorimeter which has previously been given the laboratory designation Gold Calorimeter II. References to its description and a discussion of the temperature scale are given by Gordon and Giauque.[1] The results in the previous paper were based on 0° C. = 273.10° K.; however, the values given here have been corrected to the basis 0° C. = 273.16° K.

Ethylene Oxide.—Ethylene oxide better than 99.5% pure was obtained from the Matheson Chemical Company. It was transferred from the cylinder in which it was received to a glass purification system by means of a connecting line containing rubber pressure tubing. The material was dried with phosphorus pentoxide and condensed as a solid by liquid air. The glass bulb in which it was condensed was protected from the liquid air by means of a removable metal sheath to prevent mixing in case of breakage. The system containing the solid was evacuated by means of a mercury diffusion pump to a pressure of 10^{-6} mm., followed by several repetitions of melting, freezing and pumping to remove any volatile impurities. The complete removal of all inert gas was desirable since very small amounts would have interfered with condenser operation during subsequent purification by fractionation.

The material was distilled in a silvered, vacuum jacketed, column with an ice-cooled condenser. Heat was supplied to the boiler of the column electrically by means of wire wound on its outer surface. The column which was about 1.3 cm. i. d.

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(1) Gordon and Giauque, THIS JOURNAL, 70, 1506 (1948).

was packed for a length of 50 cm. with small glass helices. A reflux ratio of about 30 to 1 was used, and the rate of removal was controlled by the pressure drop through a suitable capillary tubing. The gas issuing from the capillary was condensed as a solid by means of liquid air. The distillation required no attention except replenishing ice in the condenser. An initial volume of 500 cc. of liquid was distilled in two lots of which about 80% was discarded. The middle fractions totalling 110 cc. were used for the low temperature measurements.

The purified ethylene oxide was weighed in a glass bulb fitted with a ground-glass joint and a stopcock. Apiezon grease was used as a lubricant. At the conclusion of the measurements the material was again condensed in the weighing bulb and the initial and final weights were found to be in agreement to 0.01%.

The ethylene oxide was condensed in the calorimeter as a liquid by admitting helium to the vacuum space surrounding it and maintaining the temperature of the apparatus somewhat above the melting point of ethylene oxide. When the distillation was completed an atmosphere of helium was suddenly admitted to the line leading to the calorimeter. The line contained only a small amount of ethylene oxide due to the small vapor pressure near the melting point; however, the helium swept all of the material into the calorimeter which was then cooled to liquid air temperature. Most of the helium was pumped out but several centimeters were left to improve the rate of attaining thermal equilibrium in the solid.

From the small heat effect due to premelting which is superimposed on heat capacity in the region below the melting point the liquid-soluble, solid-insoluble impurity was estimated to be about 0.02 mole per cent.

Heat Capacity of Ethylene Oxide.—The heat capacity was measured by introducing energy by means of a resistance thermometer-heater as described previously.[1] In calculating energy, the value 4.1833 international joules = 1 calorie was used. The molecular weight of ethylene oxide was taken as 44.052. 96.821 g., equivalent to 2.1979 moles, was used in the measurements.

The liquid heat capacity measurements were corrected for the small heat effect due to vaporization into the gas space above the liquid. The vapor pressure and heat of vaporization data to be given below were used in making this correction. The density of liquid ethylene oxide was obtained from the "International Critical Tables."[2]

It is estimated that the smooth curve through the observations represents the heat capacity to within 0.2% above 35° K., within 1% at 20° K., and within 3% at 15° K. The larger error at the lower temperatures is principally due to the rapidly decreasing temperature coefficient of the resistance thermometer at these temperatures. The observations are given in Table I and heat capacity values read from a smooth curve through the data are given in Table II.

TABLE I

MOLAL HEAT CAPACITY OF ETHYLENE OXIDE

0°C. = 273.17°K.; Mol. wt. = 44.052; 2.1979 moles in calorimeter

T, °K.	Approx. ΔT	C_P, cal. deg.$^{-1}$ mole^{-1}	T, °K.	Approx. ΔT	C_P, cal. deg.$^{-1}$ mole^{-1}	Series
15.33	2.3	0.65	140.64	5.744	14.62	
17.66	2.0	1.01	146.19	5.313	15.37[a]	
20.00	2.3	1.43	151.40	4.927	16.12[a]	
22.51	2.6	1.88	160.65	Melting point		
25.45	3.0	2.42	165.97	6.0	19.72	I
28.43	2.9	3.00	172.02	5.8	19.64	I
32.13	4.3	3.70	177.79	5.3	19.56	I
36.13	3.2	4.47	183.71	6.2	19.53	I
39.67	3.8	5.16	187.01	5.9	19.49	II
43.96	4.6	5.85	190.42	5.9	19.52	I
48.83	4.3	6.57	196.79	5.8	19.42	I
53.47	4.9	7.26	203.61	5.6	19.46	I
58.24	4.3	7.91	208.85	5.0	19.50	II
62.88	4.9	8.51	215.42	4.9	19.56	II
67.71	4.7	9.00	220.67	4.8	19.53	II
72.80	5.5	9.46	226.89	5.6	19.64	II
78.13	5.0	9.91	233.20	6.1	19.72	II
83.61	6.0	10.31	240.57	5.8	19.85	II
89.47	5.7	10.72	247.09	6.6	19.96	II
95.68	6.7	11.15	253.49	5.5	20.07	II
101.96	5.9	11.55	259.73	5.3	20.17	II
108.42	7.1	11.96	265.61	5.2	20.34	II
115.00	6.1	12.38	271.59	5.0	20.51	II
121.50	6.8	12.88	275.68	4.0	20.58	III
128.02	5.7	13.45	280.31	4.0	20.68	III
134.14	6.585	13.94	283.93	2.0	20.74	III

[a] Premelting.

TABLE II

MOLAL HEAT CAPACITY OF ETHYLENE OXIDE

Values taken from smooth curve through observations: 0°C. = 273.16°K.; mol. wt. = 44.052; C_P = cal. deg.$^{-1}$ mole^{-1}

T, °K.	C_P	T, °K.	C_P	T, °K.	C_P
15	0.60	100	11.43	190	19.49
20	1.43	110	12.06	200	19.47
25	2.34	120	12.77	210	19.50
30	3.30	130	13.58	220	19.56
35	4.26	140	14.47	230	19.67
40	5.21	150	15.39	240	19.82
45	6.02	160	16.30	250	20.00
50	6.77	160.65	16.35	260	20.21
60	8.16	Melting point		270	20.46
70	9.22	160.65	19.80	280	20.67
80	10.06	170	19.66	285	20.77
90	10.76	180	19.55		

Vapor Pressure of Ethylene Oxide.—The vapor pressure was measured by means of a mercury manometer, 1.6 cm. i. d. which could be connected directly to the calorimeter which provided almost ideal temperature control. A Société Génévoise cathetometer, with a precision of 0.002 cm., was used as a comparison instrument

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(2) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926, Vol. 3.

for a standard meter suspended between the arms of the manometer. The measurements were corrected to international cm. The correction for capillary depression was taken from Cawood and Patterson.[3] Thermal expansion data for correcting the value to 0° C. were obtained from the "International Critical Tables."[2] The standard acceleration of gravity was taken as 980.665 cm. sec.$^{-2}$ and the value for this location[4] was taken as 979.973 cm. sec.$^{-2}$.

The vapor pressure observations can be represented by the equation

$$\log_{10} P_{(\text{inter.cm.Hg})} = -(2045.70/T) - 0.021507T + 2.3328 \times 10^{-5}T^2 + 13.3163$$

which is applicable over the range 224–285° K.

The boiling point, calculated from the equation, was found to be 283.66° K.

TABLE III

VAPOR PRESSURE OF ETHYLENE OXIDE

0°C. = 273.16°K.

Series	T, °K.	P obsd. (inter. cm.)	P obsd. $-P$ calcd.	T obsd. $-T$ calcd.
	223.788	3.394	+0.003	−0.013
	229.849	5.070	− .002	+ .008
	234.918	6.968	− .001	+ .001
	239.887	9.373	+ .008	− .009
	244.991	12.493	− .016	+ .023
	251.313	17.558	.000	.000
	256.204	22.528	+ .004	− .003
II	258.335	25.014	− .003	+ .002
	263.332	31.768	+ .006	− .006
	268.256	39.777	+ .001	− .001
	273.354	49.741	+ .011	− .007
III	278.804	62.507	+ .004	− .002
	282.370	72.195	− .007	+ .003
	285.094	80.401	+ .006	− .002

dP/dT = 3.0012 cm./deg. at 1 atmosphere

The vapor pressure observations are given in Table III which also includes a comparison with values calculated from the above equation. The high precision of the resistance thermometer gives a high relative accuracy for the temperatures; thus these are given to thousandths of a degree because of the interest in the temperature coefficient of vapor pressure. The absolute accuracy of the temperatures is ±0.05°. Near the boiling point the precision of the temperature measurements is the limiting factor and at low temperatures the measurement of pressure is the principal inaccuracy.

The Melting Point of Ethylene Oxide.—The melting point was measured by melting certain fractions of the solid and reading the standard thermocouple and the resistance thermometer after long periods for the attainment of equilibrium after each energy input. The observations given in Table IV were made over a period of twenty-seven hours during which energy was added four times.

TABLE IV

THE MELTING POINT OF ETHYLENE OXIDE

0°C. = 273.11°K.

Per cent. melted	T, °K. thermocouple	T, °K. resistance thermometer
6	160.58	160.573
30	160.61	160.639
70	160.66	160.646
85	160.66	160.653

Accepted value 160.65 ± 0.05°K.

The value chosen was 160.65 rather than 160.66° K. because with most of the material melted the average temperature of the resistance thermometer can read slightly high due to the cumulative effect of heat leak into the upper portions of the calorimeter.

Heat of Fusion of Ethylene Oxide.—The heat of fusion was measured in the usual manner. Energy input was started at a temperature several degrees below the melting point and ended somewhat above. Correction was applied for the small amount of premelting which had occurred at the starting temperature due to impurity. The corrections and results are given in Table V.

TABLE V

HEAT OF FUSION OF ETHYLENE OXIDE

	Calories mole^{-1}		Melting point, 160.65°K.		
Run	$T_1 - T_2$, °K.	Heat input	$\int C_p dT$	Pre-melting	ΔH Fusion
1	157.761–166.205	1401.9	156.6	2.7	1236.6
2	158.272–164.298	1343.8	110.7	3.3	1236.4
3	158.455–162.795	1310.9	78.1	3.5	1236.3
				Average	1236.4

A comparison of the melting and boiling points with those of other observers is given in Table VI.

TABLE VI

MELTING AND BOILING POINTS OF ETHYLENE OXIDE

0°C. = 273.16°K.

Melting point T, °K.	Boiling point T, °K.	Observer
161.8	283.89 ± 0.03	Maass and Boomer[5] (1922)
161.4	283.9	Timmermans and Hennaut–Roland[6] (1937)
160.65 ± 0.05	283.66 ± .05	This research

Heat of Vaporization of Ethylene Oxide.—The heat of vaporization was determined by vaporizing ethylene oxide from the calorimeter and absorbing it in a bulb containing concentrated sulfuric acid. The ethylene oxide had all been removed from the calorimeter for a check on the weight, following the heat capacity measurements, after which the same material was recondensed into the calorimeter for use in the determination of the heat of vaporization.

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(3) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).

(4) Landolt, Bornstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

(5) Maass and Boomer, THIS JOURNAL, **44**, 1709 (1922).

(6) Timmermans and Hennaut-Roland, *J. Chim. Phys.*, **34**, (1937)

TABLE VII

HEAT OF VAPORIZATION OF ETHYLENE OXIDE

Boiling point 283.66°K.; mol. wt. 44.052

Run	Moles evapd.	Time of energy input, min.	ΔH cal./mole at 1 atm.
1	0.14004	40	6095
2	.20258	50	6100
3	.23198	55	6100
4	.23368	55	6101
5	.22977	55	6111
		Average	6101 ± 6
From vapor pressure equation ΔH =			6082

The calculation of the heat of vaporization from the vapor pressure equation assumed that ethylene oxide gas at its boiling point obeyed the Berthelot equation of state using the critical constants given below. In conjunction with the thermodynamic equation $dP/dT = \Delta H/T\Delta V$ and the liquid density, the heat of vaporization was calculated at the boiling point. The agreement is reasonably good although the calculated value cannot be given any weight compared to the calorimetric value, because of the assumption involved and the magnitude of the correction.

The Entropy of Ethylene Oxide.—The calculation of the entropy from the calorimetric data is summarized in Table VII. The correction for gas imperfection was made on the assumption that the Berthelot equation of state represents the gas imperfection at the boiling point. The critical point[5] was taken as 465.1° K. and the critical pressure was taken as 49 atmospheres as estimated by Kistiakowsky and Rice.[7] It is interesting to note that if dP/dT from the vapor pressure measurements is combined with the directly measured heat of vaporization and the known critical temperature, Berthelot's equation gives 45 atmospheres for the critical pressure.

$$S_{\text{ideal}} - S_{\text{actual}} = \frac{27RT_c^3P}{32T^3P_c} = 0.15 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

at the boiling point.

TABLE VIII

CALCULATION OF THE ENTROPY OF ETHYLENE OXIDE.

	Cal. Deg.$^{-1}$ Mole^{-1}
0–15°K., Debye extrapolation	0.22
15–160.65°K., graphical	16.55
Fusion, 1236.4/160.65	7.70
160.65–283.60°K., graphical	11.25
Vaporization, 6101/283.66	21.51
Entropy of actual gas at boiling point	57.23
Correction for gas imperfection	0.15
Entropy of ideal gas at boiling point	57.38

Linnett[8] investigated the infrared and Raman spectra of liquid ethylene oxide and assigned provisional values to the fundamental frequencies. Kistiakowsky and Rice[7] have calculated the heat capacity of ethylene oxide gas from their very accurate adiabatic expansion measurements. They found that Linnett's choice of frequencies led to values of the heat capacity which were higher than those observed. Accordingly they suggested the substitution of a frequency corresponding to 1100 cm.$^{-1}$ in place of one at 811 cm.$^{-1}$ in order to bring the observed and calculated values of the heat capacity into agreement. The revised assignment was 673, 807, 868, 1100, 1122, 1163, 1172, 1270, 1350, 1453, 1494, 3000(2) and 3062(2).

The moments of inertia of ethylene oxide have been very accurately determined by Cunningham, Le Van and Gwinn.[9] They find by microwave measurement $I_1 = 32.921 \times 10^{-40}$, $I_2 = 37.926 \times 10^{-40}$ and $I_3 = 59.510 \times 10^{-40}$ g. cm.^{2}, from which $I_1I_2I_3 = 7.430 \times 10^{-116}$ g.^{3} cm.^{6}.

The entropy of the ideal gas has been calculated from these data. The constants used in the calculation are those given by Du Mond and Cohen[10] in their Report to the National Research Council.

$h = 6.6234 \times 10^{-27}$ erg sec.
$c = 2.99776 \times 10^{10}$ cm. sec.$^{-1}$
$k = 1.38032 \times 10^{-16}$ ergs deg.$^{-1}$
$N = 6.0235 \times 10^{23}$ molecules mole^{-1}
$R = 1.98718$ cal. deg.$^{-1}$ mole^{-1}

$$S_{\text{Translation}} = \frac{3R}{2}\ln M + \frac{5}{2}R\ln T - R\ln P - 2.314 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

where M represents the molecular weight, 44.052, and P is the pressure in atmospheres.

$$S_{\text{Rotation}} = \frac{R}{2}\ln I_1I_2I_3 + \frac{3}{2}R\ln T - R\ln\sigma + 267.643 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

where σ = symmetry number = 2 for ethylene oxide.

No correction has been made for rotational stretching. This effect will probably add an amount of the order of 0.01 cal. deg.$^{-1}$ mole^{-1}. The entropy calculation is summarized in Table IX.

TABLE IX

ENTROPY OF ETHYLENE OXIDE CALCULATED FROM MOLECULAR DATA

	Cal. Deg.$^{-1}$ Mole^{-1} 283.66°K.	298.16°K.
Translation	37.027	37.274
Rotation	19.705	19.854
Vibration	0.830	0.994
Total	57.56	58.12
Experimental	57.38	57.94

The "experimental" value given for 298.16° K. was obtained by adding the difference in the calculated values at 298.16° K. and 283.66° K. to the observed value at the boiling point.

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(7) Kistiakowsky and Rice, *J. Chem. Phys.*, **8**, 618 (1940).

(8) Linnett, *J. Chem. Phys.*, **6**, 692 (1938).

(9) Cunningham, Le Van and Gwinn, *Phys. Rev.*, **74** [2], 1537 (1948).

(10) Du Mond and Cohen, *Rev. Mod. Phys.*, **20**, 82 (1948).

The discrepancy of 0.18 cal. deg.$^{-1}$ mole^{-1} between the two values is outside the limit of error of the calorimetric work. The correction for the effect of gas imperfection on the entropy was made with the assistance of Berthelot's equation and an estimated critical pressure as mentioned above.

The critical temperature is known and it seems unlikely that the estimated critical pressure could be inaccurate enough to produce much effect in the above estimate. The entropy of vaporization of ethylene oxide shows it to be an approximately normal substance and thus Berthelot's equation should be applicable for this correction as has been shown by many similar calculations for other substances.

Although the total entropy contribution due to vibration is small it would appear to be the most open to question of any of the data used. For this reason we have examined with considerable care the basis used by Kistiakowsky and Rice in the frequency assignment.

In order to reduce the 0.18 cal. deg.$^{-1}$ mole^{-1} discrepancy mentioned above, at least one low lying frequency must be increased, and if the heat capacity results of Kistiakowsky and Rice are to be accepted, then at least one relatively high frequency must be reduced in order to hold C_p constant while the entropy is reduced.

We have checked the calculation of C_p^0 using the frequency assignment of Kistiakowsky and Rice and do not quite agree with their calculated results but since we obtain smaller values this is in the wrong direction to explain the above discrepancy. The comparison of the calculations is as follows:

ETHYLENE OXIDE

	Cal. Deg.$^{-1}$ Mole^{-1}		
T	C_p^0 (K. and R.)	C_p^0 (G. and G.)	C_p^0 (expt. K. and R.)
307.18	11.80	11.76	11.80
337.04	12.79	12.74	12.78
371.23	13.96	13.89	13.95

K. and R. used $R = 1.9864$ and G. and G. used $R = 1.9872$ which would make the C_p^0 values of K. and R. too low rather than too high.

However, the real difficulty as has been stated by Kistiakowsky and Rice is due to the necessity of evaluating the first and second temperature derivatives of the second virial coefficient in correcting their observations to the ideal gas state. The equations applicable to their experiment may be stated as

$$C_p = C_p' \frac{P}{R}\left(\frac{\partial V}{\partial T}\right)_P = C_p'\left[1 + \frac{P}{R}\left(\frac{\partial B}{\partial T}\right)_P\right]$$

and

$$C_p^0 - C_p = -T\int_P^0 \left(\frac{\partial^2 V}{\partial T^2}\right)_P \mathrm{d}P = TP\left(\frac{\partial^2 B}{\partial T^2}\right)_P$$

where

$$PV = RT + BP$$

C_p^0 is the heat capacity of the ideal gas, C_p the heat capacity of the actual gas and C_p' the approximate heat capacity obtained when the ideal gas formula is applied to an adiabatic expansion of an imperfect gas.

They show[11] that when Keyes' equation of state is used for propylene, the terms arising from the first and second derivatives given above are "almost completely compensated." Keyes[12] has tested his equation by use of a summary of gas imperfection data prepared by Beattie and Bridgman. He finds that it stands up well with general constants for a number of simple gases, including the term concerned in obtaining $(\mathrm{d}^2B/\mathrm{d}T^2)_p$. However, it did not hold for the few other gases tested such as ethylene, diethyl ether and polar gases such as water and ammonia. The ethylene oxide molecule may well be somewhat unusual because of bond angle strain and appreciable polarity. We feel that the use of an empirical equation of state to obtain $(\partial^2B/\partial T^2)_P$ is a questionable assumption especially in the present case. On the basis of this assumption these authors have eliminated values of C_p for the actual gas from their paper, although this requires the use only of $(\partial V/\partial T)_P$, whereas the second step requires the use of the derivative $(\partial^2 V/\partial T^2)_P$. Despite the fact that the correction depending on $(\partial V/\partial T)_P$ appears to be about twice that depending on $(\partial^2 V/\partial T^2)$, we consider that the latter step is much more questionable with any equation of state. Kistiakowsky and Rice[7] say of their assignment: "The agreement with the experimental data (C_p gas) is seen to be good but until heat capacity data over a larger range of temperature are available, one cannot be sure that the new assignment is substantially correct."

In view of this statement, and our above comments, it seems futile to try to adjust the several fundamental frequencies, or question that the observations include all of the fundamental frequencies, in order to bring the selection into agreement with the entropy. The accurate experimental determination of the heat capacity of the ideal gas is a much more powerful tool than entropy in making frequency assignments when there are numerous unknowns. The correction for gas imperfection is a sufficiently important part in work of that kind so that the actual dependence of C_p on pressure should be made a part of such experimental work. This can obviously be done without the use of empirical equations by making measurements at more than one pressure with any of the usual heat capacity methods.

Until the frequency assignment of ethylene oxide is made definite the most reliable value of the entropy of the ideal gas at the boiling point, 283.66° K., is 57.38 cal. deg.$^{-1}$ mole^{-1}. The heat capacity of the ideal gas is known well enough so that the value 57.94 cal. deg.$^{-1}$ mole.$^{-1}$ may be calculated for 298.16° K. These values do not include the entropy due to the nuclear spins of the

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(11) Kistiakowsky and Rice, *J. Chem. Phys.*, **8**, 610 (1940).

(12) Keyes, THIS JOURNAL, **60**, 1761 (1938).

protons since this effect cancels in chemical reactions.

NOTE.—A letter by Shulman, Dailey and Townes[13] gives moments of inertia of ethylene oxide which are considerably different from those given by Cunningham, Le Van and Gwinn.[9] S., D. and T. give the values 31.9×10^{-40}, 36.7×10^{-40} and 56.7×10^{-40} from microwave data. The entropy calculated from these values agrees with the calorimetric result to within 0.07 cal. deg.$^{-1}$ mole.$^{-1}$. Unfortunately this agreement must be considered to be spurious since the interpretation given by Cunningham, Le Van and Gwinn appears to be unambiguous.

We thank Dr. W. M. Jones for assistance with the experimental measurements.

Summary

The heat capacity of solid and liquid ethylene oxide has been determined from 14 to 285° K.

The melting point is 160.65° K. (0° C. = 273.16° K.). The boiling point is 283.66° K.

The heat of fusion is 1236.4 cal. mole^{-1} and the directly measured heat of vaporization at the normal boiling point is 6101 cal. mole^{-1}.

The vapor pressure of ethylene oxide has been measured from 224 to 285° K. The data are represented by the equation

$$\log_{10}(P_{\text{inter. cm.}}) = -(2045.70/T) - 0.021507T + 2.3328 \times 10^{-5}T^2 + 13.3163$$

which is applicable over the above range.

The calorimetric measurements have been used to calculate the entropy of the ideal gas at the boiling point, 57.38 cal. deg.$^{-1}$ mole^{-1}.

The entropy at this temperature has also been calculated from molecular data, leading to a result of 57.56 cal. deg.$^{-1}$ mole. The assignment of the fundamental frequencies of ethylene oxide is uncertain and the discrepancy of 0.18 cal. deg.$^{-1}$ mole^{-1} may be due to this cause.

The most reliable value of the entropy of ideal ethylene oxide gas at 298.16° K. and 1 atmosphere is 57.94 cal. deg.$^{-1}$ mole.

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(13) Shulman, Dailey and Townes, *Phys. Rev.*, **74**, 846 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Supported Oxides of Iron[1]

BY P. W. SELWOOD, MARYLINN ELLIS AND KATHRYN WETHINGTON

In this paper we describe applications of the susceptibility isotherm method to supported iron oxides.[2]

Experimental Part

Magnetic susceptibility and other measurements have been described in earlier papers. The preparation of high area *gamma*-alumina has also been given. The preparation and analysis of the supported iron oxides are described below.

Following the procedure used for supported manganese, and other oxides, the first preparative attempts consisted simply of impregnation of *gamma*-alumina (~200 m.^{2} g.$^{-1}$, BET nitrogen) with ferric nitrate solution, followed by drying and ignition at about 200°. In most cases this procedure resulted in a sample which possessed an appreciable degree of ferromagnetism. Small traces of ferromagnetism are commonly encountered in work of this kind and their effects are eliminated by measuring the susceptibility over a range of field strength and extrapolating to $1/H = 0$. This procedure is, however, not very accurate if the ferromagnetism becomes appreciable. It should be pointed out that a trace of ferromagnetism may be quite negligible so far as the analytical results are concerned, but may completely mask the magnetic data.

It was thought that the trace of ferromagnetism might be related to the colloidal hydrous oxide commonly said to be responsible for the brown color of ferric nitrate solutions. It was obviously impractical to correct this situation by raising the nitric acid concentration. The problem was solved by using for impregnation a solution of ferrous ammonium nitrate.

Ferrous ammonium nitrate solution was prepared as follows: equimolecular weights of ferrous ammonium sulfate and barium nitrate were ground together, and then treated with a rather small amount of water. The resulting solution of ferrous ammonium nitrate was poured through a filter, and then quickly used for impregnating the alumina. The impregnation was carried out in an atmosphere of carbon dioxide. It was found necessary to discard samples in which any change of color, indicating oxidation, took place at this stage. The filtered but undried impregnated samples were bright green in color. They were dried and then ignited by raising the temperature to 200° for forty-eight hours, in a partial vacuum. The finished samples were bright orange. These samples were used in obtaining the data given below.

Samples were also prepared by the use of high area *rutile*[3] (129 m.^{2} g.$^{-1}$). The first method used with this support was the same as for the alumina support. The hoped for result, of iron with an oxidation state of four, was not obtained. It was then felt that the combination of ferrous ion and ammonium ion prevented the iron from being oxidized beyond the ferric stage during the ignition step. A return was, therefore, made to ferric nitrate solution as an impregnating agent in the knowledge that this method might give erroneous magnetic results but that it would give reliable analytical results. By some perversity of nature the ferric nitrate turned out to give excellent magnetic data on the *rutile*.

A single magnetic measurement was made on an iron-alumina sample which had been reduced in hydrogen for six hours at 300°.

In all samples total iron was determined by the Zimmer-

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[1] This paper describes, in part, work performed under contract with the Squier Signal Laboratory, Signal Corps Engineering Laboratories, as part of their program for the improvement of dry cells.

[2] This is the sixth paper on the susceptibility isotherm from this laboratory. The fifth appeared in THIS JOURNAL, **71**, 693 (1949).

[3] Obtained from the National Lead Company, Titanium Division.