

been synthesized and from it the corresponding 1',2-diethylthia-2'- and -4'-cyanine iodides and the 2,2'-diethylthiacarbocyanine bromide.

3. In no case was a dye derived from the new base a powerful sensitizer. The thiocarbocyanine, for example, was considerably inferior even at the wave length at which it conferred maximum

sensitivity, to the corresponding dyes derived from the methyl- α - and β -naphthothiazoles.

4. In every case the dyes derived from 2-methylphenanthro-[9,10]-thiazole absorb nearer the red than the corresponding dyes derived from the methylnaphthothiazoles.

ROCHESTER, N. Y.

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

Carbonyl Sulfide. The Heat Capacity, Vapor Pressure, and Heats of Fusion and Vaporization. The Third Law of Thermodynamics and Orientation Equilibrium in the Solid

BY J. D. KEMP AND W. F. GIAUQUE

At the present time the most important problem in connection with the third law of thermodynamics relates to the circumstances under which false equilibrium complicates the practical application of this law. When either the third or the second law of thermodynamics is combined with experimental data to permit the evaluation of some desired quantity, it is implied that the observations were made under conditions of true equilibrium with respect to all processes under consideration.

Recent low temperature investigations have shown that lack of equilibrium exists in the cases of hydrogen, water and their deuterium analogs, carbon monoxide, nitric and nitrous oxides. For each of the above substances the entropy may be accurately calculated from spectroscopic data and it has been possible to give a satisfactory quantitative explanation of the discrepancy between the calorimetric and the spectroscopic values. Carbon monoxide, nitrous oxide (NNO) and nitric oxide (N_2O_2) enter the crystalline state without discrimination between the molecular orientation positions of carbon, nitrogen or oxygen in the crystal lattice. These neighboring atoms in the periodic system are very similar in size and it seems desirable to carry out experiments in which the possibility of lack of discrimination is investigated with more dissimilar atoms.

Linear, unsymmetrical, polyatomic molecules offer a particularly simple case since it is evident that only the two positions corresponding to a rotation of 180° are possible within a crystal lattice. The substance selected for investigation was the linear molecule, carbonyl sulfide (SCO).

The measurements to be presented show that the practical application of the third law gives the correct entropy. However, thermal equilibrium was obtained with great difficulty in a considerable region below the melting point, as might be expected if the molecules were beginning to acquire random orientation in the equilibrium state at these temperatures.

Carbonyl Sulfide.—Carbonyl sulfide was made by dropping c. p. concentrated sulfuric acid into a saturated water solution of c. p. potassium sulfocyanate. All solutions were boiled and the preparation line was evacuated with a mercury diffusion pump to eliminate air. The gas was bubbled through a 33% sodium hydroxide solution and collected in a bulb cooled by liquid air. The last traces of water were removed by passing the gas through a tower containing phosphorus pentoxide. Generous first and last fractions were discarded, leaving about 425 cc. of liquid carbonyl sulfide. The gas was then bubbled through some of its own liquid for further purification, a procedure similar to that employed by Gray¹ and by Johnston and Giauque.² The final purification was effected by the use of a vacuum jacketed fractionating column: 135 cc. of purified liquid carbonyl sulfide remained after these treatments.

By means of the premelting effects which are superimposed on the heat capacity just below the melting point, it was possible to estimate that the final preparation contained less than one part in twenty thousand of liquid-soluble solid-insoluble impurity.

Apparatus.—A vacuum calorimeter assembly similar to that described by Giauque and Wiebe³ was used for the measurements. A full description of a similar calorimeter has been given by Giauque and Egan.⁴ The calorimeter, which has been given the laboratory designation Gold Calorimeter IV, weighed 443 g. It was 4 cm. in

(1) Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

(2) Johnston and Giauque, *THIS JOURNAL*, **51**, 3194 (1929).

(3) Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

(4) Giauque and Egan, *J. Chem. Phys.*, January (1937).

diameter and 12.5 cm. in length. In order to assure rapid distribution of thermal energy twelve radial vanes of gold, 0.2 mm. in thickness, were welded lengthwise to the inside wall of the calorimeter. The walls of the calorimeter were 1 mm. thick. A platinum inlet tube 2 cm. long and 2 mm. in diameter was welded to the top of the calorimeter and connected to a soda glass tube by means of a cobalt glass seal. Double silk covered, B. and S. gage No. 40, gold wire was wound on the calorimeter to serve as a thermometer heater; 0.175% of silver was added to the gold to increase the heater resistance at low temperatures. Other details of apparatus and procedure including the calibration of the standard thermocouples are given by Giauque and Egan.⁴

A copper-constantan thermocouple, of laboratory designation W-21, was wound around the calorimeter and one junction soldered into the platinum thermocouple well with Wood's metal. Thermocouple W-21 previously had been compared with thermocouple W-22, the present laboratory standard, which was calibrated against the laboratory helium gas thermometer. As the calorimeter could be used as a vapor pressure thermometer, comparisons of W-21 were made against oxygen and hydrogen vapor pressures. The calibration was found to agree within 0.05 degree. Below 20°K. the resistance thermometer was calibrated directly in terms of the vapor pressure of hydrogen. In conformity with other investigations carried out in this Laboratory, 0°C. was taken as 273.10°K.

Vapor Pressure.—As the calorimeter is well suited to maintaining a constant temperature for long periods of time, it was convenient to measure the vapor pressure of the carbonyl sulfide using a large diameter manometer which was connected to the calorimeter for that purpose. A Société Génoise cathetometer with a precision of 0.002 cm. was used to compare the mercury levels with a standard meter hanging beside the manometer. The pressures were corrected to International centimeters of mercury, using data from the "I. C. T." for all the corrections with the exception of the meniscus height corrections which were taken from the work of Cawood and Patterson.⁵ The standard acceleration of gravity was taken as 980.665 cm./sec.² Sternwarte⁶ has given 979.973 cm. sec.² as the acceleration of gravity for this location.

The observations on the vapor pressure of liquid carbonyl sulfide have been represented by the following equation for the temperature region between 161.8 and 223.8°K.:

$$\log_{10} P(\text{int. cm. Hg}) = -(1318.260/T) + 10.15309 - 0.0147784T + 0.000018838T^2 \quad (1)$$

The results are summarized in Table I.

The calculated pressure differences given in column three were obtained by assuming the temperature observations to be correct. In column four, the calculated temperature differences were obtained by assuming the observed pressures to be correct. Although the absolute values of the tem-

(5) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).
 (6) Sternwarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

TABLE I
 VAPOR PRESSURE OF CARBONYL SULFIDE
 Boiling point, 222.87°K.; 0°C. = 273.10°K.

T, °K.	$P_{\text{obs.}}$		$T_{\text{obs.}} - T_{\text{calcd.}}$
	Int. cm. Hg	$P_{\text{obs.}} - P_{\text{calcd.}}$	
161.797	1.282	+0.001	-0.009
161.809	1.283	+ .001	- .005
166.097	1.913	+ .001	- .006
170.560	2.826	- .002	+ .009
175.404	4.219	+ .003	- .009
180.073	6.055	+ .001	- .002
185.100	8.733	.000	.000
190.205	12.388	+ .001	- .002
195.714	17.652	+ .004	- .004
201.401	24.851	- .001	+ .001
211.832	44.134	+ .005	- .002
216.628	56.266	- .010	+ .005
220.522	67.969	.000	.000
223.791	79.189	- .002	.000

peratures may be in error by several hundredths of a degree, the observed temperatures are given to 0.001° because of the high relative accuracy.

Melting Point.—The melting point was observed as a function of the percentage melted. Table II gives the results of these observations.

TABLE II
 MELTING POINT OF CARBONYL SULFIDE
 0°C. = 273.10°K.

Date and time	% Melted	T , °K. resistance thermometer	T , °K. thermocouple
12/2/35 11:10 A.M.		Heated into melting point	
1:05 P.M.	10	134.283	134.29
4:25 P.M.	10	134.275	134.27
5:05 P.M.		Supplied heat	
12/3/35 10:30 A.M.	25	134.298	134.29
1:30 P.M.	25	134.295	134.30
2:00 P.M.		Supplied heat	
5:35 P.M.	50	134.304	134.31
12/4/35 11:00 A.M.	50	134.303	134.30
Accepted value 134.31 ± 0.05			

In obtaining the accepted value, it was recognized that the small amount of impurity present caused an appreciable melting point lowering.

Table III contains a comparison of the melting and boiling points obtained in this research with those obtained by other observers.

TABLE III
 MELTING AND BOILING POINT TEMPERATURES OF
 CARBONYL SULFIDE
 0°C. = 273.10°K.

Melting point, °K.	Boiling point, °K.	Observer
.....	225.6	Hempel ⁷ (1901)
134.9	222.9	A. Stock and Kuss ⁸ (1917)
134.31 ± 0.05	222.87 ± 0.05	This research

(7) Hempel, *Z. angew. Chem.*, **14**, 865 (1901).
 (8) A. Stock and Kuss, *Ber.*, **50**, 159 (1917).

Measurement of the Amount of Carbonyl Sulfide.—The method of measuring the amount of carbonyl sulfide depended upon the fact that carbonyl sulfide is soluble in ethyl alcohol. By using liquid air, it was possible to condense the carbonyl sulfide in an ordinary glass bulb containing enough alcohol to lower the pressure of the carbonyl sulfide to about 2.5 atmospheres when it was warmed to room temperature. A bulb containing about 140 cc. of alcohol sufficed for weighing about 13.5 g. of carbonyl sulfide. Each bulb was fitted with a stopcock and one end of an interchangeable ground glass joint. A constriction was made in the stem of each bulb so that it could be sealed by fusing the glass, as it was considered unwise to subject the stopcocks to the pressure which was developed when the carbonyl sulfide was warmed to room temperature.

In order to measure heats of vaporization at a constant pressure, the gas was allowed to vaporize into a carefully calibrated five-liter bulb which was connected to a manometer and a constant pressure regulating device which has been described by Giauque and Johnston.⁹ The five-liter bulb was thermostated at 25.00°C. The pressures were measured with the Société Générale cathetometer used as a comparison instrument in connection with a standard meter. The line volume outside of the thermostat was carefully determined and only amounted to 165 cc.

The procedure in determining the amount of carbonyl sulfide was as follows. After filling the large measuring bulb, the carbonyl sulfide was condensed in a weighed, evacuated bulb immersed in liquid air. The bulb was then taken off the line and its stem fused at the constriction. Although it was not necessary to use the measuring bulb after completing measurements of the heat of vaporization, its use was continued as a precaution against any accident which might have occurred to any of the weighing bulbs. Twelve weighing bulbs were required to complete the measurement of the amount of carbonyl sulfide.

The above procedure led incidentally to a value, 2.4849 ± 0.0005 g./l., of the density of carbonyl sulfide gas at 25°C. and one atmosphere. This value was derived from an average of eleven determinations at about one atmosphere.

The Heat Capacity of Carbonyl Sulfide.—The heat capacity measurements were made using the method fully described in previous papers from this Laboratory.^{3,9} Calibrations of the resistance thermometer against thermocouple W-21 were taken simultaneously with the heat capacity measurements. From these data, a smooth table of resistance against temperature was constructed for use as a temperature scale for the heat capacity measurements. This procedure was followed because of the high precision of the resistance thermometer in measuring small temperature increments.

TABLE IV

HEAT CAPACITY OF CARBONYL SULFIDE
Molecular weight, 60.065; 2.534 moles in calorimeter.
0°C. = 273.10°K.

T, °K.	ΔT	C _p cal./deg./mole	Series
15.53	2.284	1.507	II
15.62	2.776	1.535	III
18.16	2.942	2.162	II

(9) Giauque and Johnston, THIS JOURNAL, 51, 2300 (1929).

18.65	3.292	2.259	III
20.89	2.617	2.846	II
21.88	3.126	3.106	III
23.56	2.762	3.488	II
25.13	3.254	3.811	III
26.49	3.011	4.093	II
28.79	4.027	4.560	III
29.97	3.825	4.835	II
33.07	4.530	5.457	III
34.14	4.448	5.714	II
37.81	4.965	6.322	III
38.87	5.002	6.472	II
43.02	5.445	6.983	III
44.13	5.549	7.114	II
48.32	5.145	7.534	III
49.53	5.271	7.636	II
53.77	5.715	8.032	III
55.11	5.890	8.155	II
59.54	5.792	8.459	III
61.08	6.049	8.654	II
66.01	7.232	8.837	III
66.72	5.177	8.941	II
71.96	5.157	9.195	II
75.16	11.004	9.342	III
77.47	5.713	9.487	II
83.50	6.308	9.782	II
86.80	12.063	9.951	III
90.13	6.850	10.12	II
97.07	6.920	10.38	II
100.37	13.622	10.49	III
103.87	6.463	10.70	II
110.48	6.513	10.97	II
113.38	13.697	11.06	III
117.14	6.644	11.26	II
123.47	5.805	11.55	II
127.07	13.318	12.03 ^a	III
128.04	3.250	11.81	II
131.07	2.647	12.38 ^a	II
134.31	Melting point		
137.33	2.587	17.49	I
141.61	5.762	17.44	I
147.96	6.788	17.29	I
154.74	6.559	17.18	I
162.35	6.392	17.09	I
167.97	6.231	17.02	I
174.26	6.077	17.00	I
180.67	6.421	16.93	I
187.21	6.239	16.93	I
193.75	6.527	16.95	I
200.53	6.370	16.94	I
207.43	6.949	16.97	I
214.49	6.746	17.00	I
220.87	5.430	17.04	I
222.87	Boiling point		

^a These points do not give the true heat capacity, but include some premelting.

The following constants were used in calculating the energy: 1.0004 absolute joules = 1 international joule, 4.185 absolute joules = 1 calorie. Table IV gives the observed heat capacities. Table V gives values of the heat capacities taken from the smooth curve. The data are shown graphically in Fig. 1.

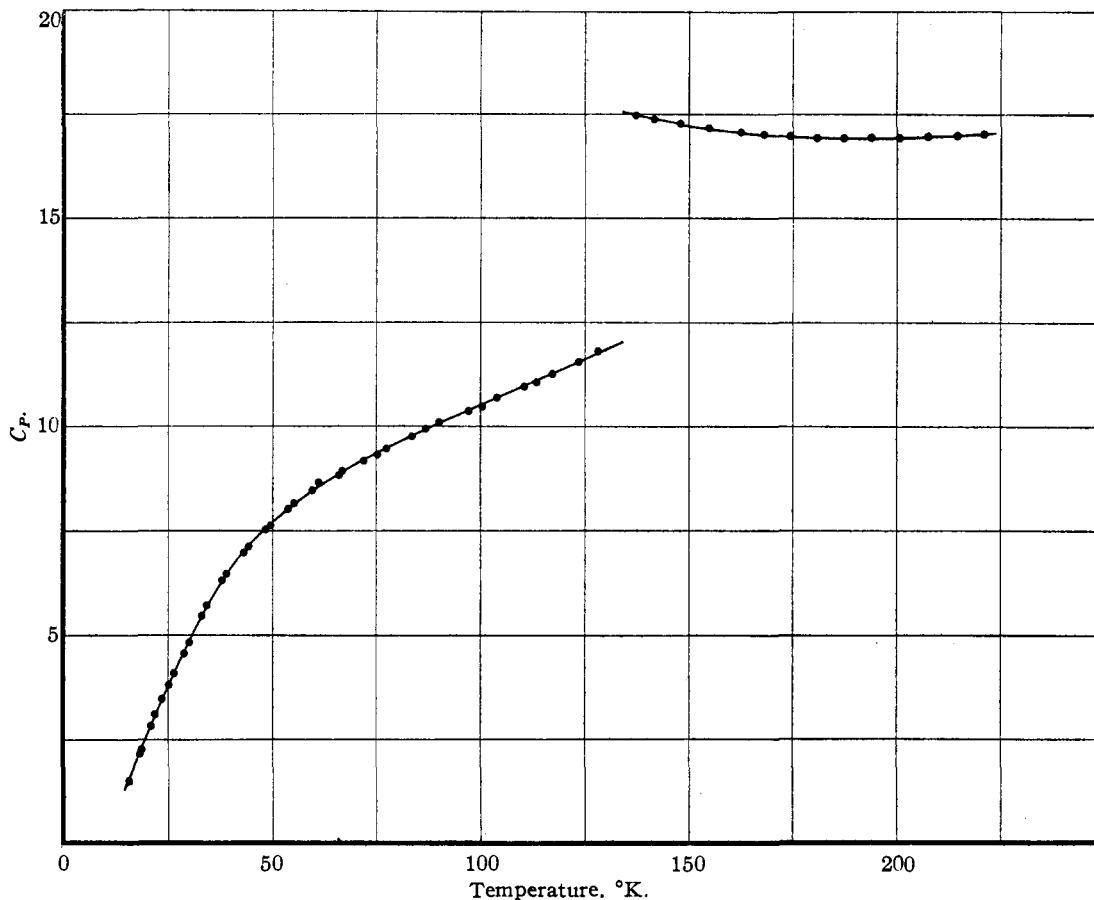


Fig. 1.—Molal heat capacity of carbonyl sulfide in calories per degree.

TABLE V
HEAT CAPACITY OF CARBONYL SULFIDE

Molecular weight, 60.065

Values taken from smooth curve through observations

T , °K.	C_p , cal./deg./mole.	T , °K.	C_p , cal./deg./mole.
20	2.63	130	11.85
30	4.84	140	17.46
40	6.62	150	17.26
50	7.70	160	17.11
60	8.48	170	17.00
70	9.08	180	16.96
80	9.62	190	16.93
90	10.09	200	16.95
100	10.53	210	16.98
110	10.95	220	17.03
120	11.40		

Two series of heat capacity measurements were taken on solid carbonyl sulfide. For Series II, the carbonyl sulfide was cooled very slowly, forty-eight hours being required to complete solidification and another forty-eight hours to cool it to 60°K. In Series III, the carbonyl sulfide was cooled rapidly. It required about twelve

minutes to complete solidification and about forty minutes more to cool it to 60°K. Further cooling to 15°K. required about two hours.

In both series, when 60°K. was approached in warming from 15°K., it became difficult to obtain thermal equilibrium due to some disturbance in the solid after the period of energy input. Normally, thermal equilibrium is obtained in the calorimeter in about five minutes after the period of energy input, but for the measurements from 60°K. to the melting point, 134.31°K., it required about an hour before thermal equilibrium was obtained.

The point of Series II at $T = 61.08^\circ\text{K}$. is high by about 1% due probably to this lack of thermal equilibrium. The points of Series III are slightly lower than the points of Series II in the region of poor equilibrium. We believe that the slow attainment of thermal equilibrium was due to the difficult process of molecular rearrangement to give the equilibrium number of random end for end orientations.

Heat of Fusion.—Table VI gives a summary of the measurements on the heat of fusion. Each measurement started a short interval below the melting point and ended somewhat above the melting point. Correction was made for the $\int C_p dT$ and the premelting effect.

TABLE VI
HEAT OF FUSION OF CARBONYL SULFIDE
Molecular weight, 60.065

Temperature interval	Corrected heat input/mole	$\int C_p dT$ + pre-melting heat effect	ΔH cal./mole
132.477–138.090	1246.5	117.0	1129.5
133.730–138.186	1223.9	94.5	1129.4
132.054–137.807	1248.2	117.8	1130.4
Mean			1129.8 \approx 1.0 cal.

Heat of Vaporization.—The heat of vaporization was measured using the constant pressure regulator mentioned in the paragraph under the measurement of amount of carbonyl sulfide. Table VII contains a summary of the heat of vaporization measurements.

TABLE VII
HEAT OF VAPORIZATION OF CARBONYL SULFIDE
Boiling point, 222.87°K.: molecular weight, 60.065

Moles vaporized	Time of energy input, minutes	ΔH at 760 mm, cal./mole
0.21247	40	4424
.20469	40	4422
.20050	40	4423
.20396	40	4421
Mean		4423 \approx 4 cal.
From vapor pressure Equation 1, assuming a Berthelot gas		4415

The heat of vaporization may be calculated using the vapor pressure data and Berthelot's equation of state of the gas in connection with the equation $\Delta H = (dP/dT)(T\Delta V)$. The expression for ΔH finally takes the form

$$\Delta H = \frac{dP}{dT} \frac{RT^2}{P} \left[1 + \frac{9PT_c}{128P_c T} \left(1 - 6 \frac{T_c^2}{T^2} \right) - \frac{PV}{RT} \text{ liq.} \right]$$

$T_c = 378.1^\circ\text{K.}$, $P_c = 61$ atmospheres.¹⁰

The resulting value for ΔH is 4415 cal./mole.

The heat of vaporization, assuming an ideal gas, is 141 cal./mole greater than that calculated on the basis of Berthelot's equation.

The Entropy from Calorimetric Data.—A summary of the calculation of the entropy of carbonyl sulfide at its boiling point, 222.87°K., is given in Table VIII.

The close agreement between the calculated value and the calorimetric value of the heat of vaporization lends plausibility to the use of

(10) "Int. Crit. Tables," 3, 231 (1928).

Berthelot's equation in making a small entropy correction for the change from the actual to the ideal gas state. Berthelot's equation with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ gives the following expression for the correction:

$$\Delta S = 27RT_c^3 P / 32T^3 P_c$$

$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 0.13$ E. U. at the boiling point.

TABLE VIII

CALCULATION OF ENTROPY OF CARBONYL SULFIDE	
0–15°K.. Debye function $h\nu/k = 95$	0.55
15–134.31°K.. graphical	14.96
Fusion, 1129.8/134.31	8.41
134.31–222.87°K.. graphical	8.66
Vaporization 4423/222.87	19.85

Entropy of actual gas at boiling point 52.43 \approx 0.10 E. U.
Correction for gas imperfection 0.13

Entropy of ideal gas at boiling point 52.56 E. U.

Entropy from Molecular Data.—The entropy of carbonyl sulfide has been calculated from band spectra data and electron diffraction measurements, using the following well-known equations

$$S_{\text{Trans.}} = 3/2R \ln M + 5/2R \ln T - R \ln P - 2.300$$

$$S_{\text{Rot.}} = R \ln IT + 177.676$$

$$S = R \sum_{\nu_1, \nu_2, \nu_3} \left[\frac{x}{1 - e^{-x}} - \ln(e^x - 1) \right]$$

where $x = h\nu/kT$ and ν_2 has a weight of two in the summation.

The moment of inertia of carbonyl sulfide, 137×10^{-40} g. cm.², has been obtained from the electron diffraction experiments of Brockway and Cross,¹¹ who give as the C=O and C=S distances 1.16 ± 0.02 Å. and 1.56 ± 0.03 Å., respectively. The uncertainty in this value leads to an uncertainty of ≈ 0.1 E. U. in the calculated entropy. Bartunek and Barker¹² have given the following equation summarizing the vibrational energy levels.

$$E_{\text{vib.}} = 863.4V_1 + 518.95V_2 + 2050.5V_3 - 4.2V_1^2 - 0.10V_2^2 - 2.35V_1V_2 + 9.3V_1V_3 + 3V_2V_3 + 2.65^2 \text{cm.}^{-1}$$

In making the calculation, the anharmonic terms were ignored as they do not contribute appreciably to the entropy at room temperature or lower. With this approximation, the equation gives the following vibrational frequencies: $\nu_1 = 859.2$, $\nu_2 = 521.50$, $\nu_3 = 2050.5$ (in cm.⁻¹).

A summary of the calculation with a comparison of the experimental and spectroscopic entropies is given in Table IX.

(11) Brockway and Cross, *J. Chem. Phys.*, 3, 821 (1935).

(12) Bartunek and Barker, *Phys. Rev.*, 48, 516 (1935).

TABLE IX

	ENTROPY OF CARBONYL SULFIDE FROM MOLECULAR DATA	
	222.87°K.	298.1°K.
Translation	36.761	38.206
Rotation	15.19	15.77
Vibration	0.711	1.389
Calculated entropy	52.66 E. U.	55.37 E. U.
Experimental entropy	{ Actual gas 52.43 E. U. { Ideal gas 52.56 E. U. 55.27 E. U.	

Cross¹³ has also calculated the entropy at 298.1° K. His value is 0.03 E. U. higher than the calculated value given above. The difference is due to his use of slightly different vibrational constants.

The good agreement between the entropy value obtained from the third law of thermodynamics and that calculated from molecular data and quantum statistics proves that no random molecular orientation exists in carbonyl sulfide at low temperatures.

Summary

The heat capacity of liquid and solid carbonyl sulfide has been determined from 15°K. to the boiling point.

The melting point is 134.31°K., the boiling

(13) Cross, *J. Chem. Phys.*, **3**, 825 (1935).

point, 222.87°K. (0°C. = 273.1°K.). The heat of fusion is 1129.8 cal. per mole and the heat of vaporization at the boiling point, 4423 cal. per mole.

The vapor pressure of liquid carbonyl sulfide has been measured and the data are represented very closely by the equation: liquid carbonyl sulfide 161.8 to 223.8°K.

$$\log_{10}P(\text{int. cm. Hg}) = -(1318.260/T) + 10.15309 - 0.0147784T + 0.000018838T^2$$

The density of carbonyl sulfide gas at 25°C. and 1 atm. is 2.4849 ± 0.0005 g./l.

From the experimental data the entropy of the ideal gas at the boiling point was found to be 52.56 cal./deg. per mole. This may be compared with the value 52.66 cal./deg. per mole, calculated from electron diffraction measurements and spectroscopic data.

The good agreement between the experimental and calculated values of the entropy indicates that the difference in size between the oxygen and sulfur ends of the carbonyl sulfide molecule suffices to prevent random orientation of the type found in carbon monoxide and nitrous and nitric oxides at low temperatures.

BERKELEY, CALIF.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Osmotic and Activity Coefficient Data of Some Aqueous Salt Solutions from Vapor Pressure Measurements

BY ROBERT A. ROBINSON

The isopiestic vapor pressure method has been¹ applied to the determination of the activity coefficients of some alkali halides, nitrates, acetates and *p*-toluenesulfonates and of some bivalent metal sulfates. The object of this communication is to describe: (1) the determination of the activity coefficients of some thallos salts; (2) the completion of the data for the nitrates and acetates by the inclusion of figures for the rubidium and cesium salts; (3) a redetermination on some rubidium and cesium halides and (4) the extension of measurements to polyvalent electrolytes, namely, barium chloride, lanthanum chloride, aluminum sulfate and potassium ferrocyanide.

(1) (a) Robinson and Sinclair, *THIS JOURNAL*, **56**, 1830 (1934); (b) Robinson, *ibid.*, **57**, 1161, 1165 (1935); (c) Robinson and Jones, *ibid.*, **58**, 959 (1936).

All data in this paper refer to 25°.

I. Thallos Salts.—Thallos nitrate, perchlorate and acetate were prepared by interaction between the carbonate and the corresponding acid, the first salt being recrystallized five times and the other two salts four times. They were balanced against isopiestic solutions of potassium chloride and thence the osmotic and activity coefficients calculated in the manner described previously.^{1c} The densities of aqueous solutions of the perchlorate and acetate, not hitherto recorded, have also been measured. Table I gives the data relevant to these salts, $\gamma(D. H.)$ being the activity coefficient calculated on the limiting Debye-Hückel equation. Eleven determinations were made on the nitrate and twelve on the perchlorate. Twenty-nine measure-