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

# The Entropy of Ethyl Chloride. Heat Capacity from 13 to 287°K. Vapor Pressure. Heats of Fusion and Vaporization

BY JOSEPH GORDON AND W. F. GIAUQUE

This paper presents the results of a low temperature calorimetric investigation on ethyl chloride. Linnett[1] has calculated the entropy of the gas for several assumed atomic distances and the cases of completely free and completely restricted internal angular motion about the carbon–carbon bond. In the absence of more complete molecular data these calculations leave an uncertainty of the order of one or two cal. deg.$^{-1}$ mole$^{-1}$ in the entropy.

**Ethyl Chloride.**—Ethyl chloride, $C_2H_5Cl$, was obtained from the Eastman Company in five 100 g. ampoules. The material was purified by the following procedure: Two fractional crystallizations were carried out in a bulb equipped with a side arm. The resulting material was pumped to remove air and then dried by condensing it in a bulb of phosphorus pentoxide. Following this the material was alternately solidified and melted several times and a vacuum of $10^{-6}$ mm. was pumped on the solid after each such crystallization to insure the removal of air or any other volatile material. The ethyl chloride was then distilled in two lots in a silvered, vacuum-jacketed column about 1.3 cm. i.d., which was packed for a length of 50 cm. with small glass helices. A reflux ratio of the order of 30:1 was used. The rate of removal was controlled by means of a system of capillaries which led to a receiving vessel where the product was obtained as a solid by condensation in liquid air. As usual the glass receiving vessel was protected from the liquid air by means of a metal sheath in case of breakage. The condenser of the fractionating column was cooled by ice. The two middle fractions were combined to give about 100 cc. of the final product.

The small amount of heat due to premelting observed in connection with heat capacity measurements just below the melting point was used to estimate the liquid-soluble solid-insoluble impurity as of the order of 0.02 mole per cent.

**Method and Apparatus.**—The measurements were made in a calorimeter which has been described previously[2,3,4] and given the laboratory designation Gold Calorimeter II. The most detailed description of this type of calorimeter has been given by Giauque and Egan.[5] An accident to the apparatus necessitated winding a new gold resistance thermometer-heater which was practically the same as had been used previously. A small platinum well was fused to the bottom of the gold calorimeter and filled with Rose's metal to facilitate contact with the junction of the standard thermocouple.

The standard thermocouple which has the laboratory designation W was, as usual, compared with the triple and boiling points of hydrogen and the vapor pressure of liquid oxygen by liquefying these substances in the calorimeter. The comparison served to emphasize the importance of considering a standard thermocouple and the potentiometer used to measure its e. m. f. as a unit to be calibrated together. The potentiometer had been returned to the manufacturer for reconditioning prior to its use in this research. In terms of temperature the comparison using the reconditioned potentiometer indicated that the thermocouple read high by 0.70° at the triple point of hydrogen, 13.95°K., and 0.45° high at the boiling point of hydrogen 20.37°K. Since two other standard thermocouples compared under similar conditions showed almost identical deviations it was clearly evident that the absolute reading of the potentiometer had been altered. At 72°K. the apparent change was 0.04° high and at 78°K., 0.05° high. As nearly as the change could be allocated between thermocouple and potentiometer it appeared that the actual change of the thermocouple was in the direction to read about 0.1° low at liquid hydrogen temperatures if the potentiometer had not been altered. It was of course not necessary to allocate the change in using the thermocouple to determine temperature.

**Vapor Pressure of Ethyl Chloride.**—The vapor pressure was measured by means of a mercury manometer with an inside diameter of 1.6 cm., and a standard meter bar suspended between the manometer tubes. A Société Génévoise cathetometer with a precision of 0.002 cm. was used as a comparison instrument.

The manometer line was connected to the calorimeter which provided almost ideal temperature control. The data of Cawood and Patterson[6] were used to correct for capillary depression. The data were corrected to international cm. by means of the thermal expansion of mercury as given in the "I.C.T."[7] and the acceleration of gravity[8] which was taken as 979.973 cm. sec.$^{-2}$ for this location. The standard acceleration used was 980.665 cm. sec.$^{-2}$.

The vapor pressure data covering the range 217 to 286°K. are represented by the equation

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[1] Linnett, *Trans. Faraday Soc.*, **36**, 527 (1940).

[2] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

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

[4] Blue and Giauque, *ibid.*, **57**, 991 (1935).

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

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

[7] "International Critical Tables," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1926.

[8] Landolt, Bornstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

$$\log_{10} P \text{ (int. cm. Hg)} = (-1777.378/T) - 0.0115789T + 1.06734 \times 10^{-5}T^2 + 10.54417$$

The observations are compared with the above equation in Table I. The temperatures are given to thousandths of a degree to permit the calculation of accurate derivatives from the precise remometer data although the absolute temperatures may be in error by as much as 0.05°.

The equation gives the value of the boiling point as 285.37°K.

TABLE I

VAPOR PRESSURES OF ETHYL CHLORIDE

(0°C. = 273.10°K.)

| T, °K. | P obsd. (int. cm. Hg) | P obsd. −P calcd. | T obsd. −T calcd. |
|---|---|---|---|
| 217.223 | 2.245 | +0.005 | −0.031 |
| 229.456 | 5.045 | − .004 | + .013 |
| 237.659 | 8.245 | − .006 | + .012 |
| 245.015 | 12.413 | + .003 | − .005 |
| 253.106 | 18.841 | + .006 | − .007 |
| 259.621 | 25.786 | − .002 | + .002 |
| 265.464 | 33.661 | − .006 | + .004 |
| 271.222 | 43.219 | + .002 | − .001 |
| 276.548 | 53.899 | + .031 | − .014 |
| 279.591 | 60.830 | + .002 | − .001 |
| 283.590 | 71.037 | + .001 | .000 |
| 285.611 | 76.683 | − .002 | + .001 |

$dP/dT$ = 2.8591 cm./degree at 1 atm.

TABLE II

MELTING POINT OF ETHYL CHLORIDE

0°C. = 273.10°K.

| Per cent. melted | T, °K. thermocouple | T, °K. resistance thermometer |
|---|---|---|
| 10 | 134.69 | 134.702 |
| 30 | 134.84 | 134.803 |
| 60 | 134.80 | 134.804 |
| 80 | 134.81 | 134.808 |
| Accepted value | 134.80 ± 0.05°K. | |

TABLE III

COMPARISON OF MELTING AND BOILING POINT DATA OF ETHYL CHLORIDE

0°C. = 273.10°K.

| Melting point, °K. | Boiling point, °K. | Observer |
|---|---|---|
| .... | 285.28 | Linnemann[9] (1871) |
| .... | 285.43 | Schacherl[10] (1880) |
| .... | 285.6 | Jenkin and Shorthose[11] (1923) |
| 133.7 | 285.30 | Kanolt[12] (1926) |
| .... | 285.50 | Fuchs[13] (1930) |
| 134.4 | .... | Timmermans and Hennaut-Roland[14] (1937) |
| 134.80 | 285.37 | This research |

**Melting Point of Ethyl Chloride.**—As usual the melting temperature was observed with various fractions of the material, in the calorim-

TABLE IV

MOLAL HEAT CAPACITY OF ETHYL CHLORIDE

0°C. = 273.10°K. Molecular weight, 64.517. 1.3946 moles in calorimeter

| T, °K. | Approx. ΔT | $C_P$ Cal. deg.$^{-1}$ mole$^{-1}$ | Series |
|---|---|---|---|
| 14.55 | 2.4 | 1.20 | |
| 17.08 | 2.4 | 1.93 | |
| 19.99 | 3.3 | 2.73 | |
| 23.62 | 3.6 | 3.61 | |
| 27.43 | 3.9 | 4.51 | |
| 31.40 | 4.0 | 5.37 | |
| 35.33 | 3.9 | 6.18 | |
| 39.03 | 3.5 | 6.97 | |
| 42.71 | 3.8 | 7.58 | |
| 46.61 | 4.0 | 8.21 | |
| 50.87 | 4.5 | 8.79 | |
| 55.55 | 4.7 | 9.54 | I |
| 60.34 | 4.9 | 10.20 | |
| 65.15 | 4.4 | 10.78 | |
| 69.78 | 4.9 | 11.34 | |
| 74.70 | 5.0 | 11.92 | |
| 79.96 | 5.5 | 12.58 | |
| 85.67 | 5.3 | 12.95 | |
| 91.50 | 6.1 | 13.32 | |
| 97.49 | 5.8 | 13.95 | |
| 103.74 | 6.5 | 14.78 | |
| 110.19 | 5.903 | 15.68 | |
| 115.90 | 5.351 | 16.68 | |
| 121.08 | 4.868 | 17.83[a] | |
| 126.82 | 6.427 | 19.70[a] | |
| 134.80 | | Melting point | |
| 139.82 | 6.0 | 23.16 | I |
| 145.83 | 5.8 | 23.07 | |
| 151.09 | 5.4 | 23.00 | |
| 156.55 | 5.2 | 22.99 | |
| 162.39 | 5.9 | 22.91 | |
| 168.30 | 5.7 | 22.84 | |
| 174.10 | 5.5 | 22.84 | |
| 179.75 | 5.3 | 22.90 | |
| 185.14 | 5.2 | 22.87 | |
| 190.62 | 5.7 | 22.90 | |
| 199.72 | 5.4 | 22.83 | II |
| 205.44 | 5.3 | 22.89 | |
| 210.87 | 5.1 | 22.92 | |
| 216.72 | 5.7 | 23.06 | |
| 222.68 | 5.5 | 23.08 | |
| 228.54 | 5.3 | 23.22 | |
| 234.25 | 5.2 | 23.26 | |
| 239.77 | 5.0 | 23.35 | |
| 244.51 | 4.9 | 23.46 | III |
| 250.29 | 5.3 | 23.62 | |
| 255.97 | 5.2 | 23.78 | |
| 261.68 | 5.1 | 23.86 | |
| 267.74 | 5.0 | 24.03 | |
| 273.67 | 4.8 | 24.24 | |
| 279.47 | 4.7 | 24.41 | |
| 284.47 | 4.1 | 24.49 | |

[a] Premelting.

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(9) Linnemann, *Ann.*, **160**, 214 (1871).

(10) Schacherl, *ibid.*, **206**, 68 (1880).

(11) Jenkin and Shorthose, *Dept. of Sci. and Ind. Res.*, No. 14, (1923).

(12) Kanolt, *Bur. of Standards Sci. Paper* **520**, 619 (1926).

(13) Fuchs, *Z. Physik*, **63**, 838 (1930).

(14) Timmermans and Hennaut-Roland, *J. chim. phys.*, **34**, (1937).

eter, melted. The data are given in Table II. Each of the temperatures given was obtained by waiting a long period for equilibrium after each addition of heat to alter the fraction melted. The observations extended over a period of 35 hours.

The melting and boiling point observations of other observers are given in Table III for comparison with those found in the present research.

**Heat Capacity of Ethyl Chloride.**—The heat capacity from 13°K. to the boiling point was measured in the same manner as has been used in many similar researches[3] in this Laboratory.

The value 4.1833 international joules was taken equal to one calorie. The amount of ethyl chloride in the calorimeter was 89.978 g., equivalent to 1.3946 moles, using 64.517 as the molecular weight. Correction was applied for the small amount of heat used in vaporization into the gas space above the liquid in the calorimeter.

Values of the heat capacity read at even values of the temperature from a smooth curve through the observations are given in Table V. It is estimated that the smooth curve represents the heat capacity to within 0.2% above 35°K., within 1% at 20°K. and within 3% at 15°K. due to the low temperature coefficient of the resistance thermometer.

TABLE V

HEAT CAPACITY OF ETHYL CHLORIDE

Smooth curve through observations

(0°C. = 273.10°K.; molecular weight, 64.517)

| $T$, °K. | $C_P$ cal. deg.$^{-1}$ mole$^{-1}$ | $T$, °K. | $C_P$ cal. deg.$^{-1}$ mole$^{-1}$ |
|---|---|---|---|
| 15 | 1.35 | 140 | 23.15 |
| 20 | 2.73 | 150 | 23.04 |
| 25 | 3.95 | 160 | 22.95 |
| 30 | 5.07 | 170 | 22.90 |
| 35 | 6.10 | 180 | 22.86 |
| 40 | 7.08 | 190 | 22.86 |
| 45 | 7.96 | 200 | 22.89 |
| 50 | 8.73 | 210 | 22.94 |
| 60 | 10.15 | 220 | 23.04 |
| 70 | 11.36 | 230 | 23.19 |
| 80 | 12.58 | 240 | 23.37 |
| 90 | 13.20 | 250 | 23.60 |
| 100 | 14.26 | 260 | 23.85 |
| 110 | 15.65 | 270 | 24.12 |
| 120 | 17.58 | 280 | 24.40 |
| 130 | 20.22 | 290 | 24.69 |
| 134.80 | 21.71 (solid) | | |
| Melting point<br>134.80 | 23.23 (liquid) | | |

**Heat of Fusion of Ethyl Chloride.**—Three determinations of the heat of fusion of ethyl chloride were made in the usual way. Heat input started somewhat below the melting point and ended at a temperature somewhat above. A correction was made for the small amount of premelting which had occurred below the starting temperature. The results are summarized in Table VI.

TABLE VI

HEAT OF FUSION OF ETHYL CHLORIDE

Melting point 134.80°K.; molecular weight 64.517

| Temperature interval, °K. | Total heat added cal. mole$^{-1}$ | Pre-melting cal. mole$^{-1}$ | $\int C_p\,dT$ cal. mole$^{-1}$ | $\Delta H$ fusion cal. mole$^{-1}$ |
|---|---|---|---|---|
| 130.109–135.698 | 1181.6 | 1.5 | 119.0 | 1064.1 |
| 131.837–138.162 | 1203.1 | 2.4 | 141.0 | 1064.5 |
| 132.242–136.095 | 1145.1 | 2.7 | 84.6 | 1063.2 |

Average 1064 ± 1

**Heat of Vaporization of Ethyl Chloride.**—The heat of vaporization was measured by vaporizing the material from the calorimeter into a bulb where it was condensed by means of liquid air. The pressure was maintained constant during vaporization at approximately 1 atmosphere by means of a system of capillary tubes, which could be used in various combinations, between the calorimeter line and the condensation bulb. Only the heater on the lower half of the calorimeter was used in these measurements and only liquid in the upper half of the calorimeter was evaporated. This avoided possible superheating of the gas following vaporization.

The temperature of vaporization was obtained by observing the vapor pressure during the heat input. The rate of vaporization used in such measurements in this Laboratory is kept low enough so that vaporization occurs quietly at the surface with no bubble formation Since some superheat occurs toward the bottom of the liquid the final temperature after heating and condensation is ended will be somewhat different than the initial temperature or the vaporization temperature. Accordingly correction was applied for the heat capacity, heat leak and vaporization into the known gas volume, including the volume previously occupied by the liquid. A small correction was applied to correct the values of the heat of vaporization to the exact temperature 285.37°K., the normal boiling point of ethyl chloride.

The experimental observations are given in Table VII. The value calculated from the vapor pressure equation and the assumption that the gas volume may be calculated by assuming a Berthelot gas is in excellent agreement but is given no weight in comparison with the direct observations.

TABLE VII

HEAT OF VAPORIZATION OF ETHYL CHLORIDE

Boiling point, 285.37°K.

| Run | Moles evaporated | Time of energy input, minutes | $\Delta H$ vaporization cal. mole$^{-1}$ |
|---|---|---|---|
| 1 | 0.15210 | 40 | 5894 |
| 2 | .14240 | 40 | 5898 |
| 3 | .13736 | 40 | 5897 |
| 4 | .13379 | 40 | 5891 |
| 5 | .17709 | 45 | 5886 |
| 6 | .17732 | 45 | 5885 |

Average 5892 ± 6

Value calculated from vapor pressure equation 5875 cal. mole$^{-1}$.

**The Entropy of Ethyl Chloride.**—The calculation of the entropy of ethyl chloride from the calorimetric data is summarized in Table VIII.

TABLE VIII

CALCULATION OF THE ENTROPY OF ETHYL CHLORIDE

| | Cal. deg.$^{-1}$, mole$^{-1}$ |
|---|---|
| 0–15°K., Debye extrapolation | 0.50 |
| 15–134.80°K., graphical | 18.725 |
| Fusion, 1064/134.80 | 7.893 |
| 134.80–285.37°K., graphical | 17.401 |
| Vaporization, 5892/285.37 | 20.647 |
| Entropy of actual gas at boiling point | 65.17 ± 0.10 |
| Correction for gas imperfection | 0.14 |
| Entropy of ideal gas at boiling point | 65.31 |

The correction for gas imperfection given in Table VIII was calculated by assuming that Berthelot's equation of state represented the gas imperfection. For this case the equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ gives

$$S_{\text{ideal}} - S_{\text{actual}} = (27RT_c^3P)/(32T^3P_c) = 0.14 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The values $T_c = 460.3$°K. and $P_c = 52$ atm. were taken from the "International Critical Tables."

**Entropy Calculations Based on Molecular Data.**—Since the potential barrier for internal rotation of ethyl chloride has not been observed spectroscopically the entropy could not be completely calculated from molecular data. However, the data are otherwise sufficiently complete so that the entropy due to internal rotation may be evaluated by difference. "I.C.T." values of natural constants were used in the calculations.

The following distances were adopted as a basis for the calculation C–C, 1.54 Å.; C–H, 1.09 Å.; C–Cl, 1.75 Å. Tetrahedral angles were assumed in the absence of definite information since the error due to this assumption should not have much effect on the entropy calculation. The vibrational assignment given by Linnett[1] was adopted except that we accepted a suggestion of Professor K. S. Pitzer to delete the values 1000 and 1120 cm.$^{-1}$, and add 1319 and 1385 cm.$^{-1}$ although the change has little effect on the vibrational entropy at the boiling point since this is principally due to the lower frequencies. The assignment used is 337, 655, 790, 970, 1050, 1070, 1290, 1319, 1385, 1400, 1450(2), 3000(5).

The principal moments of inertia were calculated to be $I_1 = 30.20 \times 10^{-40}$, $I_2 = 159.7 \times 10^{-40}$ and $I_3 = 178.5 \times 10^{-40}$ g. cm$^2$., where $I_3$ is perpendicular to the plane of symmetry. The angle between the C–C direction and the principal axis of $I_1$ was found to be $45°48' = \theta$. The reduced moment of inertia was calculated from the formula

$$I_{\text{red.}} = I_{\text{CH}_3}\left[1 - I_{\text{CH}_3}\left(\frac{\cos^2\theta}{I_1} + \frac{\sin^2\theta}{I_2}\right)\right]$$

given as Formula (1a) by Pitzer and Gwinn.[15] $I_{\text{red.}}$ was found to be $4.73 \times 10^{-40}$ g. sq. cm.$^{-2}$.

The entropy calculation for the gas at the boiling point is summarized in Table IX.

TABLE IX

CALCULATION OF THE ENTROPY OF ETHYL CHLORIDE GAS FROM MOLECULAR DATA AT ITS BOILING POINT, 285.37°K.

| | Calories degree$^{-1}$ mole$^{-1}$ |
|---|---|
| Translation | 38.20 |
| Rotation (rigid molecule) | 23.58 |
| Vibration | 1.98 |
| | 63.76 |
| Total entropy, measured | 65.31 |
| Entropy due to internal rotation | 1.55 |

The potential barrier may be evaluated from the tables prepared by Pitzer and Gwinn.[15] If the internal rotation were completely free the entropy corresponding to the reduced moment of inertia given above would be 3.46 cal. deg.$^{-1}$ mole$^{-1}$ at 285.37°K. $S_{\text{free}} - S_{\text{restricted}} = 3.46 - 1.55 = 1.91$ cal. deg.$^{-1}$ mole$^{-1}$. In the present case there are three potential minima per revolution and the potential barrier corresponding to the suppression of internal rotation by 1.91 cal. deg.$^{-1}$ mole$^{-1}$ is found to be 4700 cal. mole$^{-1}$.

A summary of the entropy calculation for 298.1°K. is given in Table X.

TABLE X

ENTROPY OF ETHYL CHLORIDE GAS AT 298.1°K.

| | Calories degree$^{-1}$ mole$^{-1}$ |
|---|---|
| Translation | 38.42 |
| Rotation (rigid molecule) | 23.70 |
| Vibration | 2.19 |
| Internal rotation | 1.60 |
| | 65.91 |

The entropy value 65.91 cal. deg.$^{-1}$ mole$^{-1}$ does not include the effects of isotopes and nuclear spin since these effects should be ignored in ordinary thermodynamic calculations.

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

## Summary

The heat capacity of ethyl chloride has been measured from 13 to 287°K.

The melting and boiling points were found to be 134.80 and 285.37°K., respectively.

The heat of fusion was determined to be 1064 cal. mole$^{-1}$ and the heat of vaporization 5892 cal. mole$^{-1}$.

The vapor pressure was measured and represented by the equation $\log_{10} P(\text{inter. cm. Hg}) = (-1777.378/T - 0.0115789T + 1.06734 \times 10^{-5}T^2 + 10.54417$ which applies over the range 217 to 286°K.

The entropy of the gas at the boiling point was found to be 65.31 cal. deg.$^{-1}$ mole$^{-1}$ of which 1.55

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[15] Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

cal. deg.$^{-1}$ mole$^{-1}$ was shown to be due to internal rotation, corresponding to a potential barrier of 4700 cal. mole$^{-1}$.

The entropy at 298.1° K. and 1 atmosphere was found to be 65.91 cal. deg.$^{-1}$ mole$^{-1}$.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

# The Chlorophyll-sensitized Photoöxidation of Phenylhydrazine by Methyl Red. II. Reactivity of the Several Forms of Methyl Red[1]

BY ROBERT LIVINGSTON AND RUDOLPH PARISER

In a previous study[2] of this reaction a mechanism was suggested which led to the prediction that the quantum yield should increase with increasing concentration of phenylhydrazine. Direct measurements, in the range from 0.01 to 0.20 $M$ phenylhydrazine, showed a definite although small decrease in the yield with increasing concentrations. Since it was noticed that the color of methyl red was also affected by this change in concentration, a series of measurements using varying mixtures of phenylhydrazine and phenylhydrazine hydrochloride were made. Both the concentration of a "red" form of the methyl red and the yield of the reaction increased with increasing acidity of the solution, the yield approaching a limiting value of about 0.5. Since methyl red has three colored forms,[3] it was necessary to determine the absorption spectra of each of these forms, before it was possible to analyze the solutions spectrophotometrically. Using this method of analysis, it was found that only the intermediate form of methyl red reacted in the solutions used. Making allowance for the variation of quantum yield with dye concentration, it can be shown that the yield is also a (symbatic) function of the phenylhydrazine concentration. The yield appears to be independent of intensity. A relatively simple reaction mechanism is consistent with these observations.

## Part I. Spectrophotometric Analysis of Methyl Red

### Experimental Methods and Materials

**Materials.**—The methanol was purified by treating synthetic methanol with an amount of sodium estimated to be three times as much as was required to react with the water present, refluxing with an excess of methyl phthalate,[4] and then distilling through an efficient packed column. The purification of the methyl red has been described.[2] Alcoholic hydrochloric acid was prepared by bubbling dry hydrogen chloride into methanol. Sodium methylate solutions were prepared by allowing weighed quantities of clean sodium to react completely with methanol. The concentrations of the acid and base solutions were checked by titration with aqueous standard solutions. The several solutions were made from stock solutions of methyl red and of either sodium methylate or alcoholic hydrochloric acid. All measurements were made with $2 \times 10^{-5}$ $M$ methyl red. As only ordinary precautions were taken to keep the solutions out of contact with laboratory air, it is probable that the sodium methylate solutions contained some carbonate and hydroxide.

**Methods.**—The photometric measurements were made with a Beckmann spectrophotometer at room temperature (24 to 27°). Measurements were made at 100 Å. intervals in the range from $\gamma$ 3600 to 6000 Å. Duplicate preparations and measurements were made for each solution studied.

### Experimental Results

The solutions studied were made up to contain, in addition to $2 \times 10^{-5}$ $M$ methyl red, the following added substances: (1) 0.40 $M$ HCl, (2) $10^{-3}$ $M$ HCl, (3) $10^{-4}$ $M$ HCl, (4) $10^{-5}$ $M$ HCl, (5) $10^{-6}$ $M$ $NaOCH_3$, (6) $10^{-5}$ $M$ $NaOCH_3$, (7) $2 \times 10^{-5}$ $M$ $NaOCH_3$, (8) $5 \times 10^{-5}$ $M$ $NaOCH_3$, and (9) $10^{-3}$ $M$ $NaOCH_3$.

Further increase of the hydrochloric acid concentration above 0.40 $M$ did not affect the extinction curve. At the other end of the range, use of concentrated sodium methylate results in a fading of the yellow color. This fading is reversible. It is not complete even in very basic solutions. The extinction coefficients at wave lengths near the maximum decrease about 30% as the concentration of methylate is increased from $10^{-3}$ to 1 $M$. The absorption spectrum of the dye is practically unchanged in the range from $2 \times 10^{-4}$ to $5 \times 10^{-3}$ $M$ $NaOCH_3$.

The extinction curves for solutions 1, 3, 6, 7, and 9 are plotted in Fig. 1. The curves corresponding to solutions 4, 5 and 8 have been omitted from the plot to simplify it. They belong to the same family of curves as those plotted. It should be noted that the curves intersect at one of two points, corresponding to either $\lambda$ 4360 or 4800 Å. One curve, number II, passes through both points of intersection.

It is apparent that the dye can exist in three different colored forms. From the variation of the absorption curves with the acidity of the solutions, it may be safely assumed that curves 9 and 7 correspond, respectively, to the pure forms I and III.[5] It is impossible to calculate exactly the extinc-

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[1] This work was supported jointly by the Graduate School of the University of Minnesota and by the Office of Naval Research (Contract N6ori-212, T. O. I) to whom the authors are indebted.

[2] R. Livingston, D. Sickle and A. Uchiyama, *J. Phys. Colloid Chem.*, **51**, 775 (1947).

[3] A. Thiel, A. Dassler and F. Wülfkin, *Fortsch. Chem. Physik. physik. Chem.*, **18**, no. 3 (1924).

[4] We are indebted to Dr. R. Arnold of the Organic Division of this department for suggesting this method.

[5] It is possible that solution 9 contains a trace of the colorless form. However, the practical independence of the curve from the methylate concentrations over a wide range is evidence that the percentage of the dye present in the colorless form is small.