The exact correspondence of the absorption spectra of gossyfulvin and dianilinogossypol, and their dissimilarity with that of gossypol have been assumed as evidence that gossyfulvin and dianilinogossypol possess identical basic structures and that both are different from the preponderant tautomeric form of gossypol.

The isomerism of the three oximes formed from gossypol, dianilinogossypol, and gossyfulvin has been presented as evidence for the lability of the carbonyl groups of gossypol.

Evidence has been presented indicating that the acetyl derivative formed in preponderant amounts upon acetylation of gossypol is tetraacetoxygossypol, and that formed from gossyfulvin is a hexaacetyl derivative.

NEW ORLEANS, LOUISIANA

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# Vapor Pressures and Saturated Liquid and Vapor Densities of Cyclopentane, Methylcyclopentane, Ethylcyclopentane and Methylcyclohexane

BY WEBSTER B. KAY[1]

Studies on the physical properties of petroleum hydrocarbons in the gasoline boiling range[1a] have been continued with the determination of the vapor pressure and saturated liquid and vapor densities of cyclopentane, methylcyclopentane, ethylcyclopentane and methylcyclohexane. The measurements here presented cover the temperature range from the standard boiling point to the critical point and were made with particular care on samples of exceptional purity.

## Description of Materials

The hydrocarbons were samples of API–NBS hydrocarbons which were made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44. The samples were purified at the National Bureau of Standards by the API Research Project 6 on the "Analysis, purification and properties of hydrocarbons" under the supervision of Frederick D. Rossini from material supplied by the following laboratories: cyclopentane and ethylcyclopentane, by the API Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under the supervision of Cecil E. Boord; methylcyclopentane, by the Houdry Process Corporation of Pennsylvania, Marcus Hook, Pennsylvania, through the courtesy of E. A. Smith, and methylcyclohexane by the API Project 45 and the Barrett Division of the Allied Chemical and Dye Corporation.

The impurities in the samples were stated to be as follows: cyclopentane 0.02 ± 0.01 mole per cent.; ethylcyclopentane 0.22 ± 0.10 mole per cent.; methylcylclopentane 0.16 ± 0.06 mole per cent. and methylcyclohexane 0.10 ± 0.08 mole per cent.

The samples were received from the National Bureau of Standards in sealed glass ampules and were used without further purification.

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(1a) W. B. Kay, THIS JOURNAL, 68, 1336 (1946).

## Apparatus and Procedure

The static method of measurement was employed. The apparatus was basically the same as described in an earlier paper.[2] However, for the purpose of increasing the accuracy of the measurements a number of changes were made which included the reconstruction of the high temperature bath and thermocouple, replacement of the electromagnet by a permanent magnet in the stirring device, use of precision bore tubing for the experimental tubes and the replacement of the spring dial gage by a dead weight piston gage for the pressure measurements.

**High Temperature Bath.**—The experimental tube (H) (Fig. 1) containing the sample under investigation was surrounded by a jacket (G) and held at a constant temperature by the condensing vapors of a series of pure organic liquids which were heated in a side arm boiler (E) by means of an electric heater (B). To prevent excessive heat loss the jacket was constructed with a double wall with the inner walls silvered and the inner space evacuated. Two narrow unsilvered strips, diametrically opposite each other, were left to serve as a window for observing the tube. The upper part of the jacket was connected through a side arm to a manometer and a simple pressure regulating assembly (DD), manually operated, for regulating the pressure on the boiling liquid in E. By the use of highly purified compounds and by close regulation of the pressure any temperature within a range of 30 to 40°, constant to within 0.01°, was obtained with a single compound. The compounds used and their working temperature range were as follows: carbon tetrachloride, 55–75°; chlorobenzene 75–131°; bromobenzene, 131–155°; aniline, 155–183°; naphthalene, 183–218°; diphenyl ether, 218–256°; α-bromonaphthalene, 256–280°; benzophenone, 280–305°.

**The Thermocouple.**—The temperature to which the experimental tube was heated was
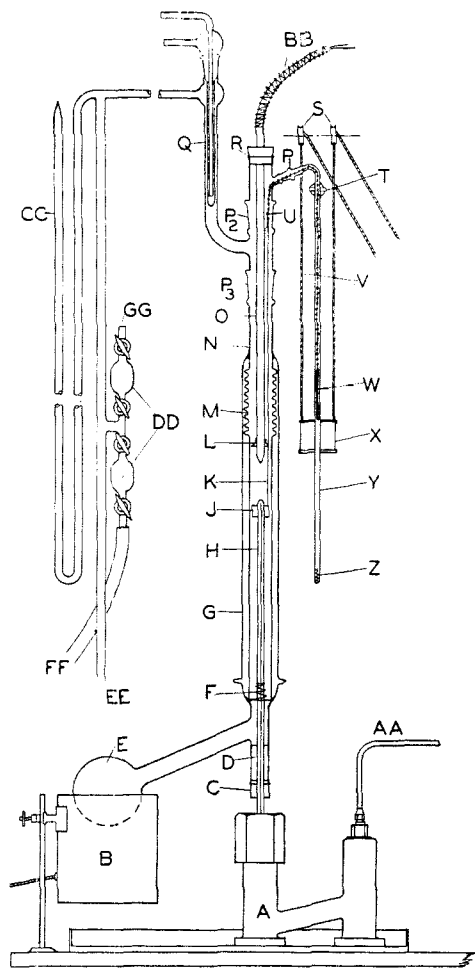
(2) W. B. Kay, Ind. Eng. Chem., 28, 1014 (1936).

Fig. 1.—Vapor pressure apparatus: A, compressor block; B, electric heater; C, rubber stopper; D, mercury layer; E, boiler; F, chromel wire coil safety stop for magnet; G, high temperature jacket; H, experimental tube; J, cylindrical "Alnico" permanent magnet; K, chromel wire attached to magnet; L, conical metal shield for thermocouple; M, glass expansion section; N, air-cooled condenser; O, thermocouple; $P_1, P_2, P_3$, ground glass joints; Q, water-cooled condenser; R, rubber stopper; S, pulleys; T, spherical joint; U, bead chain attached to K; V, cord for supporting magnet; W, soft iron rod attached to U; X, electromagnet; Y, side tube; Z, chromel wire safety stop for W; AA, to dead weight gage and compressed gas cylinder; BB, steel spring around thermocouple to prevent bending of couple wire; CC, closed-end mercury manometer; DD, bulbs and stopcocks for making minute adjustments in pressure in E; EE, to 3 five-gallon bottles for absorbing small fluctuations in pressure; FF, to vacuum pump; GG, to atmosphere.

measured with a 2-junction copper–constantan thermocouple using a Leeds and Northrup Type "K" potentiometer measuring to one microvolt for the e. m. f. measurements. The couple was calibrated using the standard temperatures of the ice point,[3] transition point of sodium

(3) G. K. Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

sulfate decahydrate,[3] steam point,[3] boiling point of naphthalene[3,4] and boiling point of benzophenone,[3,4] with the cold junction in a bath of melting ice. The calibration at the boiling points was carried out with the couple in place in the constant temperature jacket (G) as shown in Fig. 1. A conical metal shield (L) was placed about 3 cm. above the hot junction to prevent liquid from running back over the junction. In the calibration as well as in the use of the couple the line of condensation was held at the top of the double-walled section so that the depth of immersion of the couple in the constant temperature zone was constant and equal to 21 cm. In this way possible errors due to non-homogeneity of the thermocouple wires were eliminated.

**Magnetic Stirrer.**—In order to bring about equilibrium quickly between the sample and mercury vapor in the narrow bore experimental tube and to initiate vaporization when the pressure on the sample was reduced to the vapor pressure, a steel ball bearing, about 1.6 mm. dia., was moved through the sample by means of a small cylindrical "Alnico" permanent magnet (J) which surrounded the tube in the high temperature jacket. The magnet was connected by a piece of "chromel" wire (K) and a bead chain (U) through a side arm to an iron rod counterweight (W) in a side tube (Y) and was moved by an electromagnet (X) operating on the iron rod.

**The Experimental Tubes.**—Because of the great range in the vapor pressure as well as in the volumes of the saturated liquid and vapor, two experimental tubes of different size were required, one of small volume for high pressure measurements, the other of large volume, principally for measurements of the volume of the saturated vapor at low pressure. The working sections of these tubes were constructed from precision bore Pyrex capillary. The tubes were approximately of the same dimensions as those described earlier[5] and were carefully calibrated by weighing the mercury required to fill them to various points. The volume of each tube was expressed in terms of the distance from the sealed end. This distance was measured by a cathetometer reading to 0.05 mm.

**Pressure Measurements.**—Pressures up to 3 atmospheres were measured to within 1 mm. of mercury with an open-end mercury column; higher pressures were measured by means of a gage of the dead weight piston type with mechanical oscillation. A mercury-in-steel U-tube separated the oil system of the gage from the compressed gas which was used to counterbalance the vapor pressure exerted by the hydrocarbon in the experimental tube. Insulated steel needles of equal length in the legs of the U-tube served to indicate, by electrical means, the relative position of the mercury levels and to detect equilibrium

(4) J. L. Fink and R. M. Wilhelm, THIS JOURNAL, **47**, 1577 (1925).
(5) W. B. Kay, *Ind. Eng. Chem.*, **30**, 459 (1938).

between the loaded piston and the pressure to be measured. The sensitivity of the gage was about 0.005 atm. (4 mm. mercury). The area of the piston calculated from the diameter which was measured at the National Bureau of Standards was such that one kilogram on the piston was equivalent to a pressure of 5.415 atm. The calibration of the gage was checked by a determination of the vapor pressure of carbon dioxide near $0°$. The results were as follows: $34.533 \pm 0.005$ atm. at $0.15°$. Values at this temperature interpolated from the data of Bridgeman[6] and Meyers and Van Dusen[7] are 34.537 and 34.534 atmospheres, respectively.

**Procedure.**—The experimental tube with the steel ball inside was loaded with a sample of pure gas-free liquid in the manner previously described[1] and fastened in the compressor block (A). The constant temperature jacket (G) was then put in place. Next, the pressure on the sample was raised to a value higher than the estimated vapor pressure and the current to the electric heater (B) turned on. As soon as temperature equilibrium was established the pressure was reduced slowly and the sample stirred intermittently until the sample occupied the complete working section of the tube. The stirring was then continued at constant pressure for about twenty minutes. At the end of this period the pressure was again raised by small increments until the dew point was reached. This procedure was adopted in order to ensure that the mercury exerted its equilibrium partial pressure during the vapor pressure determination. The dew point was detected by noting the relatively large decrease in volume when the pressure was increased by an extremely small amount above the condensation pressure. Finally, the pressure was increased until the boiling point was reached. Readings of the temperature, pressure and position of the mercury meniscus with reference to the end of the tube were taken at both the boiling point and dew point. In the case where the sample could not be completely vaporized within the working section of the tube, vapor pressure determinations were made at as large a $V/L$ ratio (ratio of vapor volume to liquid volume at equilibrium conditions) as possible. Corrections were applied: (a) to the pressure readings for the vapor pressure of mercury, for the difference in mercury levels (corrected to $0°$) in the experimental tube and compressor block and for capillarity of the mercury; (b) to the volume readings for the steel ball, for the mercury meniscus and for the thermal expansion of the tube.

In addition to the vapor pressure and density measurements above atmospheric pressure the liquid density at room temperature and the standard boiling point were determined. For the liquid density a pycnometer of about 23-ml. ca-

pacity was used while a Swietoslawski ebulliometer[8] was used in the boiling point determinations.

A test of the over-all accuracy of the temperature and pressure measurements was made by the determination of the vapor pressure of pure water and the comparison of the results with the high precision data on water obtained at the Bureau of Standards.[9] The measurements were made at several temperatures covering the same temperature and pressure range as covered in the measurements on the hydrocarbons. The apparatus and procedure were the same as used with the hydrocarbons except that the experimental tube was constructed from quartz tubing and the steel ball for stirring was omitted. Table I gives the results and also the temperature changes equivalent to the difference in vapor pressure computed from the temperature coefficients at the respective temperatures.

TABLE I

VAPOR PRESSURE OF WATER TESTS TO DETERMINE OVER-
ALL ACCURACY OF THE APPARATUS

| Temp., °C. | Pressure, atm. Found | Pressure, atm. Lit.[9] | Difference Lit. found, atm. | Difference Lit. found, °C. |
|---|---|---|---|---|
| 131.80 | 2.803 | 2.805 | 0.00 | .. |
| 155.91 | 5.491 | 5.491 | .00 | .. |
| 183.43 | 10.71$_0$ | 10.702 | .01 | 0.03 |
| 217.37 | 21.78$_8$ | 21.767 | .02 | .05 |
| 257.23 | 44.29$_8$ | 44.279 | .02 | .03 |

These data were obtained before beginning the measurements on the hydrocarbons. At the conclusion of the measurements a redetermination of the vapor pressure of the same sample at $217.37°$ gave 21.77$_3$ atm. as compared with the previous value of 21.78$_8$ atm. The accuracy indicated by the results, therefore, would appear to be better than $0.05°$ in temperature and better than 0.02 atm. in the pressure.

### Experimental Results

The liquid densities at $20°$, the standard boiling points and the critical points of the four hydrocarbons are given in Table II. The values of the density were calculated by means of the empirical equations which will be described later. The boiling points and densities are compared with the latest determinations made at the Bureau of Standards. The critical points were determined by the disappearance of the meniscus method. With the aid of the magnetic stirrer the critical temperature could be located to within $0.01°$ with the variation in pressure in separate determinations on the same sample amounting to about 0.01 atm. The critical density was obtained by extrapolating the mean density line to the critical temperature.

The vapor pressure data for each of the hydrocarbons have been represented by the standard

(6) O. C. Bridgeman, This Journal, 49, 1174 (1927).

(7) C. H. Meyers and M. S. Van Dusen, Bur. Standards J. Research, 10, 381 (1933).

(8) W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945.

(9) W. S. Osborne, H. F. Stimson, E. F. Fiock and D. C. Ginnings, Bur. Standards J. Research, 10, 155 (1933).

TABLE II

STANDARD BOILING POINTS, LIQUID DENSITIES AT 20° AND CRITICAL CONSTANTS OF CYCLOPENTANE, METHYLCYCLO-
PENTANE, ETHYLCYCLOPENTANE AND METHYLCYCLOHEXANE

| | B. p., °C. | | Liq. density at 20°C. | | Critical point | | |
| | Expt. | Lit.[10] | Calcd., g./cc. | Lit.[11] | Atm. | °C. | G./cc. |
|---|---|---|---|---|---|---|---|
| Cyclopentane | 49.26 | 49.262 | 0.7454 | 0.74538 | 44.550 | 238.60 | 0.270 |
| Methylcyclopentane | 71.82 | 71.812 | .7486 | .74860 | 37.364 | 259.61 | .264 |
| Ethylcyclopentane | 103.45 | ..... | .7666 | ..... | 33.526 | 296.30 | .262 |
| Methylcyclohexane | 100.94 | 100.934 | .7694 | .76936 | 34.322 | 299.13 | .285 |

TABLE III

CONSTANTS IN VAPOR PRESSURE AND DENSITY EQUATIONS FOR CYCLOPENTANE, METHYLCYCLOPENTANE, ETHYLCYCLO-
PENTANE AND METHYLCYCLOHEXANE

| | $A$ | $B$ | $\log k$ | $m$ | $n$ | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|---|---|---|
| Cyclopentane | 4.45663 | −1436.91 | 0.19976 | 0.38405 | 1.3326 | 0.7652 | $-9.43 \times 10^{-4}$ | 0 |
| Methylcyclopentane | 4.46125 | −1539.05 | .20063 | .37896 | 1.3927 | .7671 | $-9.0 \times 10^{-4}$ | $-8.33 \times 10^{-8}$ |
| Ethylcyclopentane | 4.50388 | −1696.18 | .21535 | .38401 | 1.3698 | .7849 | $-9.01 \times 10^{-4}$ | $-8.29 \times 10^{-8}$ |
| Methylcyclohexane | 4.43411 | −1658.80 | .20984 | .38401 | 1.3453 | .7863 | $-8.36 \times 10^{-4}$ | $-3.38 \times 10^{-8}$ |

vapor pressure equation $\log p = A + (B/T)$ supplemented with a deviation curve. The constants in the equation, given in Table III, were evaluated using the temperature in °K. and pressure in atmospheres at the standard boiling point and the critical point. The deviation curves are shown in Fig. 2. The size of the circles and crosses represent approximately the precision of the experimental data.
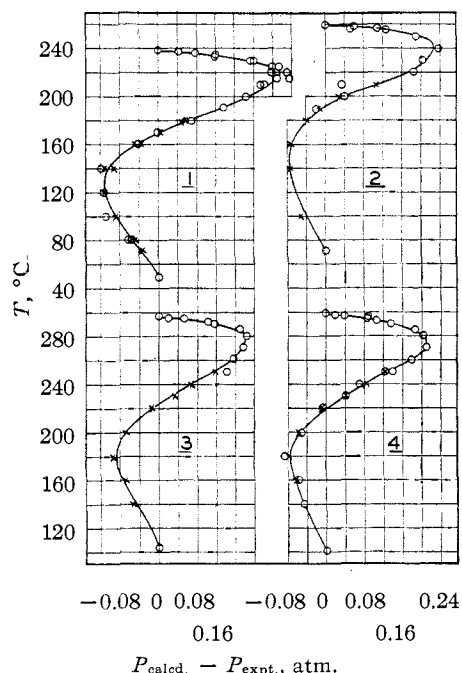


Fig. 2.—Deviations of the observed vapor pressures from the standard vapor pressure equation: X and ⊙ refer to data obtained on different samples of the same hydrocarbon: 1, cyclopentane; 2, methylcyclopentane; 3, ethylcyclopentane; 4, methylcyclohexane.

The densities of the saturated liquid and vapor, computed from the measured volumes of the sample, have been expressed analytically, as was done for the isomeric hexanes,[1] by a combination of the equation of Fales and Shapiro[12] log log $\rho_L/\rho_V = \log k + m \log (1 - T_R^2) - n \log T_R$
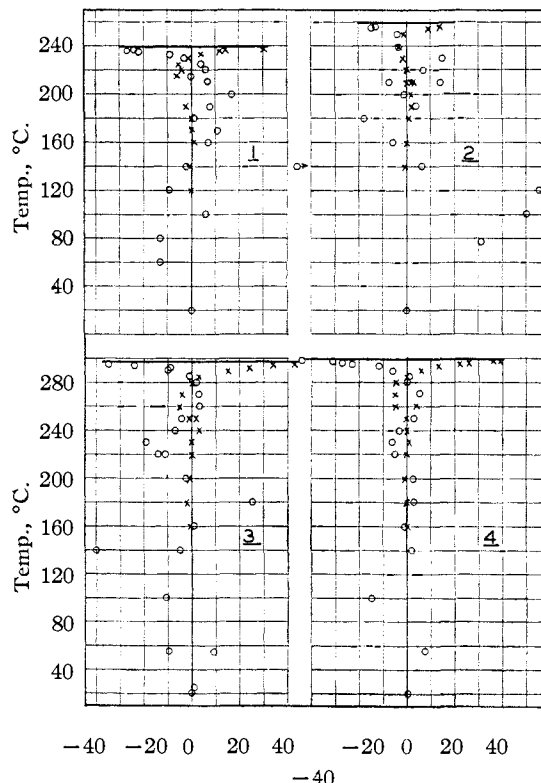


Fig. 3.—Deviations of the observed densities from the density equations: ⊙ and X refer to the liquid and vapor states, respectively: 1, cyclopentane; 2, methylcyclopentane; 3, ethylcyclopentane; 4, methylcyclohexane.

(10) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, Bur. Standards J. Research, 35, 219 (1945).

(11) A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham and F. D. Rossini, ibid., 36, 129 (1946).

(12) H. A. Fales and C. S. Shapiro, THIS JOURNAL, 58, 2418 (1936).

(where $T_R$ is the reduced temperature) and the equation for the sum of the saturated liquid and vapor densities

$$\rho_l + \rho_v = \alpha + \beta t + \gamma t^2$$

The values of the constants in the equations, derived from the experimental data, are given in Table III when the density is expressed in g./cc. and temperature in °C. The extent to which the equation represents the data is shown by the curves in Fig. 3 where the difference between the calculated and experimental values of both liquid and vapor densities have been plotted against the temperature. The precision of the measurements is of the order of 0.0015 g./cc. for the liquid and 0.0002 g./cc. for the vapor at near room temperature and increases for the liquid and decreases for the vapor with an increase in temperature becoming the same somewhere between these values at the critical temperature. As will be noted the points fall within these limits except for methylcyclopentane whose liquid density data below 140° show relative large deviations. It is believed that the data in this temperature region are subject to large accidental errors of observation and that the equations, the constants of which were derived from the data above 140°, represents more nearly the true densities. Near the critical point the deviations become large for all compounds. This results from the form of the equation since the quantity $(1 - T_R{}^2)$ becomes so small as to

be greatly influenced by errors in the measurement of the critical temperature. Hence, in this narrow region the equation cannot be expected to hold with the same accuracy as at lower temperatures.

**Acknowledgment.**—Grateful acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of the samples measured in this investigation.

### Summary

1.   The standard boiling points and the critical constants for cyclopentane, methylcyclopentane, ethylcyclopentane and methylcyclohexane were carefully determined.

2.   The vapor pressures and saturated liquid and vapor densities of these compounds were determined from near their standard boiling points to their critical points. The data have been represented by empirical equations: (a) the vapor pressure data by equations of the type $\log \rho = A + B/T$ supplemented by deviation curves; (b) the density data by means of the equation of Fales and Shapiro, $\log \log \rho_L/\rho_v = \log k + m \log (1 - T_R{}^2) - n \log T_R$ together with the equation for the sum of the liquid and vapor densities, $\rho_L + \rho_v = \alpha + \beta t + \gamma t^2$. Values of the constants in the equations are given for each hydrocarbon.
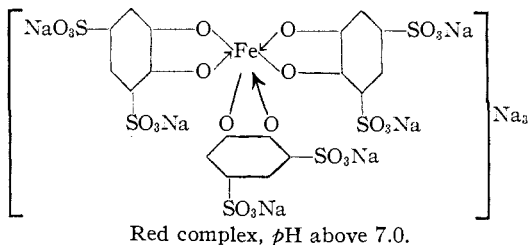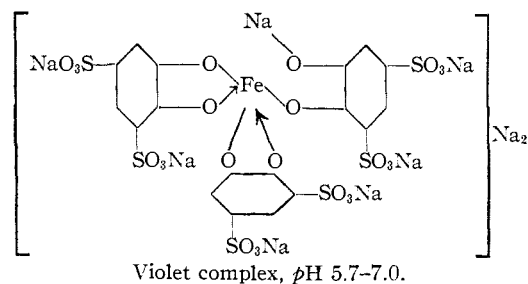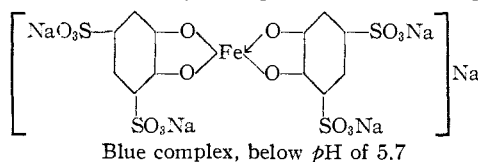
WHITING, INDIANA    RECEIVED DECEMBER 7, 1946

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

# A Magnetic Study of the Type of Bonding Existing in Some Complexes of Ferric Iron with Sulfonated Pyrocatechol

BY A. L. JONES[1] AND L. B. YEATTS

According to investigations conducted by Yoe and Jones,[1a] disodium 1,2-dihydroxybenzene-3,5-disulfonate was found to produce an intensely colored, stable complex with ferric iron which exhibited various color changes upon altering the $p$H of solutions of the complex. Below a $p$H of 5.7 the color of the complex with iron is blue; from 5.7–7 it is violet; and above a $p$H of 7, red.

As a result of their spectrophotometric studies and by analogy with the iron–pyrocatechol complexes,[2,3] Yoe and Jones postulate the complexes



Blue complex, below $p$H of 5.7

(1) Present address: Standard Oil Company (Ohio), 2127 Cornell Road, Cleveland 6, Ohio.

(1a) Yoe and Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

(2) Karrer, "Organic Chemistry," by A. J. Meek, Nordeman Publishing Co., N. Y., 1938, p. 397.

(3) Reihlen, *Z. anorg. Chem.*, **43**, 173 (1922).

Violet complex, $p$H 5.7–7.0.



Red complex, $p$H above 7.0.

shown for the three iron–pyrocatechol disulfonate complexes formed.