

siderably different from the values obtained by Barratt and Stein,<sup>8</sup> but they agree well with the values obtained for the dissociation in vapor phase.

A true absorption curve for the bromine chloride molecule can now be drawn by subtracting the known amounts of bromine and chlorine absorption from the absorption curve of the equimolar mixture of the two halogens. This absorption curve is given in Fig. 2. The position of the maximum is now at 370 m $\mu$  instead of 380 and the value of the molar absorptancy index is 135 instead of 102.

Measurements were also made at temperatures of 15 and 10°. The results were essentially the same as those obtained at 25°, variation being only slightly higher than the experimental error. This agrees well with the small heat of formation of bromine chloride.

Blair and Yost<sup>5</sup> have determined experimentally the heat of formation of bromine chloride in carbon tetrachloride solution. However, since they have

taken the dissociation of bromine chloride to be 52.4% the value of  $\Delta H_{298}^{\circ}$  they obtained was too high. Recalculation of heat of formation on the basis of 43.2% dissociation gives  $\Delta H_{298}^{\circ} = -317$  cal. Likewise,  $\Delta F_{298}^{\circ}$  and  $\Delta S_{298}^{\circ}$  can be recalculated as shown by Table II.

TABLE II  
THERMODYNAMIC CONSTANTS FOR THE REACTION

	Blair and Yost	This paper
$\Delta H_{298}^{\circ}$ , cal.	-378	-312
$\Delta F_{298}^{\circ}$ , cal.	-357	-572
$\Delta S_{298}^{\circ}$ , cal./deg.	- 0.0705	+ 0.872

**Acknowledgment.**—It is a pleasure to gratefully acknowledge the discussion of this article with Professor Don M. Yost of the California Institute of Technology.

IOWA CITY, IOWA

RECEIVED JULY 20, 1951

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## A Spectrophotometric Study of Chromate-Phosphate Complexes in Solution

BY FRANK HOLLOWAY<sup>1</sup>

The spectrum of chromic acid is reported. Spectrophotometric investigation of chromic acid-phosphoric acid solutions indicate that two chromate-phosphate complex ions are formed. The equilibrium constants for the formation of the two complexes were determined at 25° and ionic strength equal to 0.25.

In the course of the study of the chromic acid oxidation of isopropyl alcohol<sup>2</sup> in buffered systems, it became necessary to consider the possibility of the interaction of chromic acid and buffer components, giving rise to complex molecules or ions. A preliminary spectrophotometric study of the systems employed indicated that the chromic acid-phosphoric acid system exhibited the largest spectral changes from the spectrum of chromic acid alone. Subsequent studies of this system, reported here, led to the determination of the number of complexes formed and the equilibrium constants for their formation at 25° and an ionic strength of 0.25.

These data led to an internally consistent analysis of the rate data for the dihydrogenphosphate-phosphoric acid buffer catalyzed chromic acid oxidation of isopropyl alcohol. However, the resulting kinetic equations, because of alternative mathematical formulations, did not permit a unique interpretation of the observed catalysis.

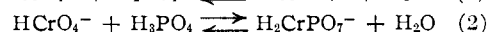
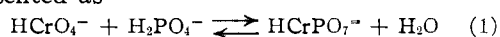
Viterbi and Krausz<sup>3</sup> have reported the spectrum of chromic acid. Their work is in qualitative agreement with the work here reported, in the wave length range of 230 to 390 m $\mu$ , and in quantitative agreement in the wave length range of 400 to 480 m $\mu$ . The observations of Brownell<sup>4</sup> and of Lingane and Collat<sup>5</sup> substantiate the positions of the near

ultraviolet maxima here reported for the chromic acid or chromic acid-phosphoric acid systems. The spectra for these systems were determined from 220 to 480 m $\mu$ .

Figure 1 describes the essential differences in the absorption spectra of chromic acid and chromic acid-phosphoric acid systems. In all cases the concentration of the buffer was in excess of the concentration of chromic acid. The absorption due to the buffers was small and was compensated by employing a solvent blank containing the same buffer.

Increasing concentrations of the buffer lowered and shifted the peak in the 250 m $\mu$  region, lowered the peak at 350 m $\mu$ , and decreased the apparent specific extinction coefficient between 300 and 450 m $\mu$ . Studies were made which indicated that these observed changes were not due to any appreciable degree to pH, ionic strength or asymmetrical ion effects. The 250 m $\mu$  region was selected for detailed analysis because of the presence there of two separate absorption bands.

**Determination of the Number of Complexes.**—The very close correspondence between the experimental data and a mathematical model (see appendix) which assumes two complexes, confirms the existence of two complexes. The reactions which give rise to the complexes may be represented as



**Determination of Formation Equilibrium Constants and Specific Extinction Coefficients for the Complexes.**—It is shown in the appendix that the

(1) University of Illinois, Division of Physical Sciences, Chicago 11, Illinois.

(2) F. Holloway, M. Cohen and F. H. Westheimer, *THIS JOURNAL*, **73**, 65 (1951).

(3) E. Viterbi and G. Krausz, *Gazz. chim. ital.*, **57**, 690 (1927).

(4) R. M. Brownell, Doctorate Dissertation, University of Chicago, 1947.

(5) J. J. Lingane and J. W. Collat, *Anal. Chem.*, **22**, 166 (1950).

apparent specific extinction coefficient for this system is given by Equation (3).

$$\epsilon_0 = \frac{\epsilon_1 K_1 (\text{H}_2\text{PO}_4^-) + \epsilon_2 K_2 (\text{H}_3\text{PO}_4) + \epsilon_3}{1 + K_1 (\text{H}_2\text{PO}_4^-) + K_2 (\text{H}_3\text{PO}_4)} \quad (3)$$

where

$\epsilon_0$  is the observed apparent specific extinction, obtained by dividing the observed corrected optical density by the total concentration of chromium, for a one centimeter absorption cell.

$\epsilon_3$  is the specific extinction coefficient for  $\text{HCrO}_4^-$ , directly measured.

$\epsilon_1$  is the specific extinction coefficient for  $\text{HCrPO}_7^-$ .

$K_1$  is the equilibrium constant for the formation of  $\text{HCrPO}_7^-$ .

$\epsilon_2$  is the specific extinction coefficient for  $\text{H}_2\text{CrPO}_7^-$ .

$K_2$  is the equilibrium constant for the formation of  $\text{H}_2\text{CrPO}_7^-$ .

$(\text{H}_2\text{PO}_4^-)$  is the molar concentration of dihydrogenphosphate.  $(\text{H}_3\text{PO}_4)$  is the molar concentration of phosphoric acid.

Equation (4) is a rearranged form of Equation (3).

$$\epsilon_0 - \epsilon_3 = (\epsilon_1 - \epsilon_0) K_1 (\text{H}_2\text{PO}_4^-) + (\epsilon_2 - \epsilon_0) K_2 (\text{H}_3\text{PO}_4) \quad (4)$$

It is to be noted that  $\epsilon_1$ ,  $K_1$ ,  $\epsilon_2$  and  $K_2$ , constitute the unknowns of Equation (4). However, the following method of successive approximations was developed, in which the number of algebraic unknowns is effectively reduced to two.

At low  $p\text{H}$ , very little of the observed absorption is due to the complex formed from dihydrogenphosphate and acid chromate. Under such conditions, the dihydrogenphosphate term can be neglected, and Equation (4) reduces to Equation (5).

$$\epsilon_0 - \epsilon_3 = (\epsilon_2 - \epsilon_0) K_2 (\text{H}_3\text{PO}_4) \quad (5)$$

This equation leads to the simultaneous solution of a pair of widely separated curves, corresponding to a low  $p\text{H}$  but different  $\text{H}_3\text{PO}_4$  concentrations, for an approximate value for  $\epsilon_2$ . The value for  $\epsilon_2$  so obtained is substituted in Equation (5) and an approximate value for  $K_2$  is obtained.

The values for  $\epsilon_2$  and  $K_2$ , obtained by using Equation (5), are substituted in Equation (4). This equation may be applied to a pair of widely separated curves, corresponding to a relatively high  $p\text{H}$ , resulting in obtaining first approximation values for  $\epsilon_1$  and  $K_1$ .

A repetition of the process of approximation, using Equation (4), leads to consistent values for  $\epsilon_1$ ,  $\epsilon_2$ ,  $K_1$  and  $K_2$ . Values for these parameters were obtained at various wave lengths between 230 and 280  $m\mu$ . The values for  $\epsilon_1$  and  $\epsilon_2$  varied with wave length, of course, but the values for  $K_1$  and  $K_2$ , which should be constants, were always close to the values  $3(\text{M./l.})^{-1}$  and  $9(\text{M./l.})^{-1}$ , respectively. Typical data for the variations of  $K_1$  and  $K_2$  with wave length are listed in Table I. The values for  $\epsilon_1$  so obtained, scattered about the smooth curve drawn for a plot of  $\epsilon_1$  versus wave length, with maximum deviations of about 4% from the probable value for  $\epsilon_1$  in the middle of the region considered. The values for  $\epsilon_2$  plotted versus wave length gave a smooth curve.

TABLE I

VARIANCE OF  $K_1$  AND  $K_2$  WITH WAVE LENGTH

$\lambda, m\mu$	235	245	250	255	260	265	275	Average
$K_1(\text{m./l.})^{-1}$	2.7	3.4	2.2	3.7	3.4	2.1	2.6	2.9
$K_2(\text{m./l.})^{-1}$	6.5	10.7	7.6	9.2	10.1	13.6	7.9	9.4

The variations in the values for  $K_1$  and  $K_2$  and the scattering of the calculated values for  $\epsilon_1$

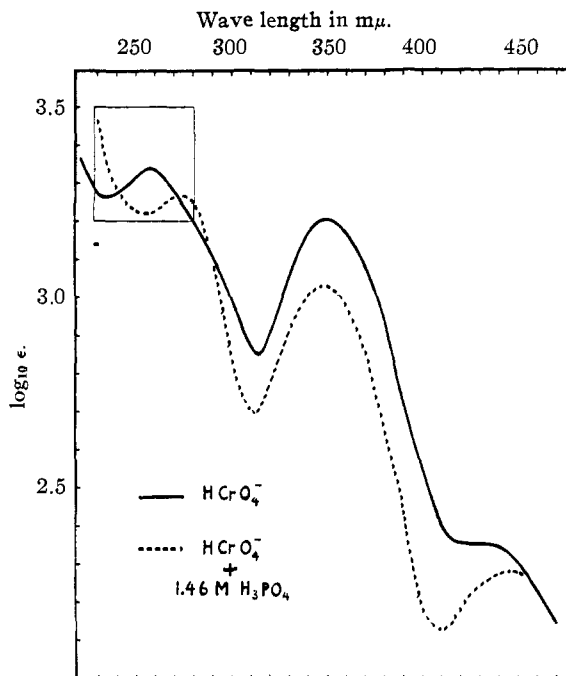


Fig. 1.—Absorption spectra of chromic acid and a chromic acid solution 1.46  $M$  in phosphoric acid.

are attributed largely to errors inherent in the calculations, involving small differences between two relatively large numerical values.

However, by assuming  $K_1 = 3(\text{M./l.})^{-1}$  and  $K_2 = 9(\text{M./l.})^{-1}$ , the values for  $\epsilon_1$  then obtained led to a smooth plot of  $\epsilon_1$  versus wave length which is practically identical with the smooth curve drawn through the previously described scattered points. These assumed values for  $K_1$  and  $K_2$  permit the calculation of values for  $\epsilon_2$  which are practically identical with those obtained for  $\epsilon_2$  by the method of successive approximation.

Table II lists the values for  $\epsilon_1$ ,  $\epsilon_2$  and  $\epsilon_3$  at 5- $m\mu$  intervals between 235 and 280  $m\mu$ , where the values for  $\epsilon_1$  and  $\epsilon_2$  depend on the assumed constancy of  $K_1$  and  $K_2$ .

TABLE II

TABULATION OF CALCULATED VALUES FOR  $\epsilon_1$  AND  $\epsilon_2$  EMPLOYING  $K_1 = 3(\text{M./l.})^{-1}$  AND  $K_2 = 9(\text{M./l.})^{-1}$  AND OBSERVED VALUES FOR  $\epsilon_3$  APPLICABLE TO CHROMATE-PHOSPHATE SYSTEMS AT 25° AND  $\mu = 0.25$

$\lambda, m\mu$	$\epsilon_1$	$\epsilon_2$	$\epsilon_3$
235	2780	2006	1820
240	2595	1842	1958
245	2495	1707	1948
250	2478	1571	2050
255	2473	1531	2130
260	2460	1591	2120
265	2416	1680	2040
268	2370	1750	1955
275	2120	1839	1732
280	1882	1717	1600

Table III lists the compositions of the chromate-phosphate solutions studied. The spectral curves for six of the solutions are reproduced in Fig. 2. In this figure, all circles represent experimental values, whereas all lines (except for Solutions IV)

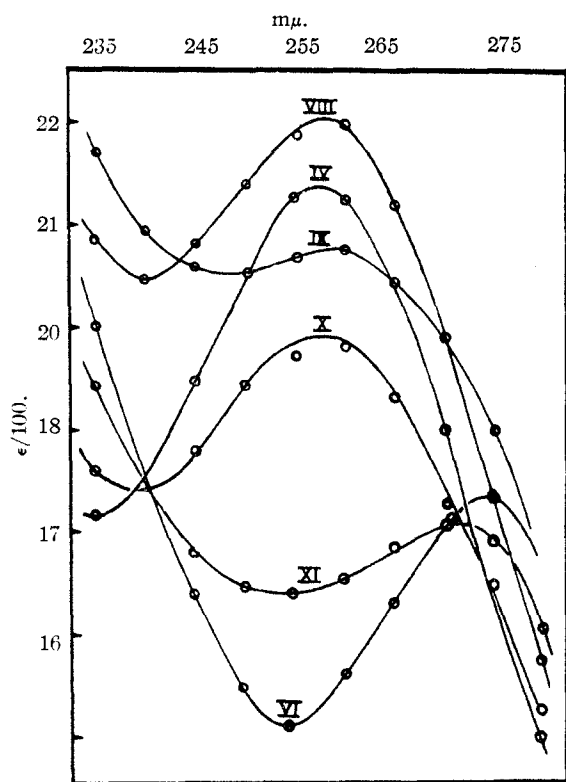


Fig. 2.—Absorption spectra for chromic acid (IV) and some chromate-phosphate solutions between 235 and 280 m $\mu$ . See Table III for solution compositions.

represent smooth curves drawn through calculated values. All calculated values were obtained by applying Equation (4) with the values for extinction coefficients and equilibrium constant as listed in Table II. The concentrations of dihydrogenphosphate and phosphoric acid are those listed in Table III.

TABLE III  
COMPOSITION OF THE CHROMATE-PHOSPHATE SOLUTIONS STUDIED

Solution number	(CrO <sub>3</sub> ) <sup>a</sup>	(H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> )	(H <sub>3</sub> PO <sub>4</sub> )	(H <sup>+</sup> )
II <sup>b</sup>	0.000505	0.82	0.045	0.0008
III	.000598	.2488	.0142	.0008
IV <sup>c</sup>	.000598	.0000	.0000	.2500
V	.000604	.2529	.2393	.0125
VI	.000599	.0486	.9000	.2500
VIII	.000599	.1238	.0072	.0008
IX	.000599	.2502	.0743	.0040
X	.000599	.0019	.0352	.2500
XI	.000599	.0075	.1390	.2500
XII	.000598	.0109	.0091	.0109
XIII <sup>d</sup>	.000599	.0604	.0644	.0140
XIV	.000604	.1372	.2556	.0250

<sup>a</sup> (CrO<sub>3</sub>) is the total hexavalent chromium. <sup>b</sup>  $\mu = 0.82$ .  
<sup>c</sup> HClO<sub>4</sub> added to make  $\mu = 0.25$ . <sup>d</sup>  $\mu = 0.22$ .

All ionic strengths equal to 0.25, by addition of NaClO<sub>4</sub> where required, unless otherwise noted.

### Experimental

**Materials.**—The chromic acid was Mallinckrodt reagent grade, purified by two crystallizations from water.<sup>6</sup>

(6) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 279.

J. T. Baker analyzed 85% phosphoric acid was diluted with distilled water and refluxed overnight to ensure absence of pyrophosphates. G. F. Smith sodium perchlorate was recrystallized several times from distilled water and dried at 110°. The final crystallization was conducted above 50° and the material dried at 150°. J. T. Baker analyzed grade perchloric acid was used.

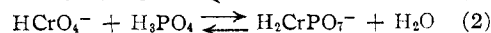
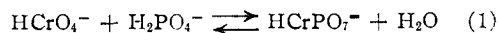
**Preparation of Standard Solutions.**—Stock solutions of chromic acid were standardized iodometrically against thiosulfate. Stock solutions of phosphoric acid and sodium dihydrogenphosphate were standardized against carbonate free sodium hydroxide according to the method outlined by Kolthoff.<sup>8</sup> Sodium perchlorate solutions were made by dissolving weighed quantities of the well-dried salt in volumetric flasks. Stock solutions of perchloric acid were standardized against carbonate-free sodium hydroxide.

**Apparent Ionization Constant for Phosphoric Acid.**—The apparent ionization constant for phosphoric acid at 25° and  $\mu = 0.25$  was calculated to be 0.0135 by Kielland's method,<sup>9</sup> employing Nims'<sup>10</sup> value for the true ionization constant.

**Spectrophotometric Technique.**—A Beckman quartz spectrophotometer, model DU8 with accessory hydrogen arc discharge lamp was used for these studies. Check values within five parts per thousand were required to establish a transmission value. The temperature was maintained at  $25 \pm 1^\circ$  by air cooling of the cell compartment.

### Appendix

The equations used in the spectrophotometric analysis of chromate-phosphate systems were developed as follows: assume the reactions



Indicate the equilibrium concentrations of the three absorbing species as

$$C_1 = (\text{HCrPO}_7^{2-}) = K_1 C_3 (\text{H}_2\text{PO}_4^-) \quad (6)$$

$$C_2 = (\text{H}_2\text{CrPO}_7^-) = K_2 C_3 (\text{H}_3\text{PO}_4) \quad (7)$$

$$C_3 = (\text{HCrO}_4^-) \quad (8)$$

Assume that the sum of the concentrations of these three species is equal to the total concentration of Cr<sup>VI</sup> when the concentration of Cr<sup>VI</sup> is so dilute that the concentration of dichromate is negligible. (The concentration of dichromate may be neglected when the total concentration of Cr<sup>VI</sup> = 0.0006 molar. The equilibrium constant for the reaction  $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$  is approximately 0.02.<sup>11</sup> Also, in most of the systems studied, a large fraction of the total chromic acid was in the form of complexes, thus further reducing the concentration of dichromate.)

Assume that the observed optical density is a strictly additive function of the optical densities of the absorbing species.

$$D_0 = \epsilon_1 C_1 + \epsilon_2 C_2 + \epsilon_3 C_3 = \epsilon_0 C \quad (9)$$

$$C_1 + C_2 + C_3 = C = (\text{Cr}^{\text{VI}})_t \quad (10)$$

Then, a combination of equations 6, 7 and 10 gives 11

$$C = K_1 C_3 (\text{H}_2\text{PO}_4^-) + K_2 C_3 (\text{H}_3\text{PO}_4) + C_3 \quad (11)$$

or

$$C_3 = \frac{C}{1 + K_1 (\text{H}_2\text{PO}_4^-) + K_2 (\text{H}_3\text{PO}_4)} \quad (12)$$

(7) J. W. Mellor, "Textbook of Inorganic Chemistry," Vol. II Longmans, Green and Co., New York, N. Y., 1922, p. 395.

(8) I. M. Kolthoff and E. B. Sandell, "Quantitative Analysis," The Macmillan Co., New York, N. Y., 1943, p. 563.

(9) J. Kielland, THIS JOURNAL, **59**, 1675 (1937).

(10) I. F. Nims, *ibid.*, **56**, 1110 (1934).

(11) J. D. Neuss and W. Rieman, *ibid.*, **56**, 2238 (1934).

Similarly

$$C_1 = \frac{CK_1(\text{H}_2\text{PO}_4^-)}{1 + K_1(\text{H}_2\text{PO}_4^-) + K_2(\text{H}_3\text{PO}_4)} \quad (13)$$

and

$$C_2 = \frac{CK_2(\text{H}_3\text{PO}_4)}{1 + K_1(\text{H}_2\text{PO}_4^-) + K_2(\text{H}_3\text{PO}_4)} \quad (14)$$

Combination of equations 9, 12, 6 and 14 gives

$$\epsilon_0 = \frac{\epsilon_1 K_1(\text{H}_2\text{PO}_4^-) + \epsilon_2 K_2(\text{H}_3\text{PO}_4) + \epsilon_3}{1 + K_1(\text{H}_2\text{PO}_4^-) + K_2(\text{H}_3\text{PO}_4)} \quad (3)$$

**Acknowledgment.**—The author is indebted to Dr. F. H. Westheimer for his critical interest in the course of the investigation reported and his assistance in interpreting the results of the work.

CHICAGO 37, ILLINOIS

RECEIVED JULY 27, 1951

[CONTRIBUTION FROM MOUND LABORATORY, A. E. C. INSTALLATION<sup>1a</sup>]

## The Vapor Pressures of Tellurium and Selenium

BY L. S. BROOKS<sup>1b</sup>

The vapor pressures of tellurium and selenium have been measured with quartz Bourdon gages, with the following results:

	A	B	T <sub>b</sub>	L <sub>v</sub>
Tellurium	7.5999 ± 0.0136	5960.2 ± 14.5	989.8 ± 3.8	27.26 ± 0.07
Selenium	8.0886 ± 0.0048	4989.5 ± 4.5	684.9 ± 1.0	22.82 ± 0.02

in which *A* and *B* are constants in the equation  $\log p = A - B/T$ , *p* is the pressure in mm., *T* the absolute temperature, *T<sub>b</sub>* the boiling point in degrees centigrade and *L<sub>v</sub>* the latent heat of vaporization in kcal./mole, the probable errors being stated in each case.

### Introduction

The vapor pressures of tellurium and selenium have been measured with quartz Bourdon gages, at pressures up to about one-third atmosphere for tellurium, and just over one atmosphere for selenium. Earlier work with tellurium was done by Doolan and Partington<sup>2</sup> with a transport method that yielded values at 0.46, 3.34 and 14.1 mm., and by Schneider and Schupp<sup>3</sup> with the same method with improvements, in the range 8.15 to 67.2 mm. The vapor pressure above the solid was observed by Niwa and Sibata<sup>4</sup> between 0.887 and  $45 \times 10^{-3}$  mm. Selenium was studied by Le Chatelier<sup>5</sup> who obtained a boiling point of 688°, followed by Berthelot,<sup>6</sup> Preuner and Brockmüller,<sup>7</sup> Dodd,<sup>8</sup> Neumann and Lichtenberg,<sup>9</sup> Niwa and Sibata<sup>10</sup> and Selincourt.<sup>11</sup> Of these, only Preuner and Brockmüller worked over an extended range (3 to 970 mm.), and their results differ from those of Selincourt in the vicinity of the boiling point. The results of the present work, which covers the range from about 0.4 to 786 mm., are in agreement with those of Selincourt.

### Experimental

Tellurium was measured with a quartz spiral gage<sup>12</sup> and a sickle gage, identified as P and Q, respectively, and selen-

ium with three different sickle gages, M, N and O. The general design of the sickle gage apparatus is shown in Fig. 1 with the gage assembly directly above the temperature control apparatus in which it is placed for a run. The gage is used as a deflection instrument at low pressures and as a null device at higher pressures as described below.

**Temperature Control.**—The sample bulb with its thermocouple well at G, Fig. 1, is placed in a copper cylinder 20 cm. long and 7.5 cm. in diameter, in which the temperature is maintained stable and uniform in a region centered about point W. A smaller cylinder, 10 cm. long and 5 cm. in diameter, was used for the first tellurium experiment with the spiral gage, and a check performed after completing the measurements showed that temperature gradients of several tenths of a degree per cm. existed along the axis of the block, enough to allow temperature uncertainties of a degree or two to exist. The large cylinder was used thereafter, and tests under simulated operating conditions showed that a temperature uniform within 0.1° could be maintained over a region of 8 cm. along the axis, centered on point W, the location of the sample thermocouple junction. Auxiliary windings on the ends of furnace B were used to control the temperature distribution.

During operation the temperature of the cylinder as indicated by a thermocouple at K and that of the sample at W were brought into equilibrium within 0.1°. The absence of a temperature gradient between points U and V in the cylinder was checked during each measurement with a movable thermocouple. Additional thermocouples at L and J were used to ascertain that the temperatures of the connecting tubing and the gage bulb were above that of the sample bulb. Furnace A was used to keep the gage bulb at a constant high temperature, generally 750°. The connecting furnace C prevented the occurrence of a cold spot between furnaces A and B.

The platinum-10% rhodium thermocouples used to measure the temperature at W were calibrated by the procedure of Roeser and Wensel<sup>13</sup> with standard melting point samples of metals from the National Bureau of Standards.

**Pressure Measurements.**—The deflection of the sickle gage pointer was observed through a quartz window at Y by means of a viewing telescope with a micrometer eyepiece. The sensitivity of each gage was about 0.02 mm. per scale division as calibrated by introducing air into the jacket surrounding the gage bulb with the sample bulb cold. Deflections of the gage were used to measure pressures up to about 3 mm. Above that value, the pressure was balanced by admitting air or nitrogen, the balancing pressure being measured with a closed tube mercury manometer that had a precision of 0.05 mm. The manometer readings were reduced to equivalent mercury columns at 0° and corrected

(1) (a) Operated by Monsanto Chemical Company, Miamisburg, Ohio, under Contract AT-33-1-GEN-53; (b) Physics Department, University of Michigan, Ann Arbor, Michigan.

(2) J. J. Doolan and J. R. Partington, *Trans. Faraday Soc.*, **20**, 342 (1924).

(3) A. Schneider and K. Schupp, *Z. Elektrochem.*, **50**, No. 6/7, 163 (1944).

(4) K. Niwa and Z. Sibata, *J. Faculty Sci., Hokkaido Imp. Univ.*, **3**, Ser. III, 75 (1940).

(5) H. Le Chatelier, *Compt. rend.*, **121**, 323 (1895).

(6) D. Berthelot, *Ann. chim. phys.*, **26**, 105, 142 (1902); *Compt. rend.*, **1**, 705 (1902).

(7) G. Preuner and I. Brockmüller, *Z. physik. Chem.*, **81**, 129 (1912).

(8) L. E. Dodd, *This Journal*, **42**, 1579 (1920).

(9) K. Neumann and E. Lichtenberg, *Z. physik. Chem.*, **A184**, 89 (1939).

(10) K. Niwa and Z. Sibata, *J. Faculty Sci., Hokkaido Imp. Univ.*, **3**, Ser. III, 53 (1940).

(11) M. De Selincourt, *Proc. Phys. Soc. (London)*, **52**, 348 (1940).

(12) G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

(13) W. F. Roeser and H. T. Wensel, *Bur. Standards J. Research*, **14**, 247 (1935) (RP768).