

atmosphere the fraction of carbon monoxide in an equilibrium mixture would be 41.6 and 66.0%. These values are on the upper limits which Fraenkel² assigned from his study of this reaction: 25 – 40% at 1500° and 50 – 65% at 1600°.

Summary

Apparatus has been devised and methods have been extended for the study of chemical equilibria at incandescent temperatures at pressures of 0.01 mm. Determinations were made for the reaction $4\text{AlN} + 3\text{C} = \text{Al}_4\text{C}_3 + 2\text{N}_2$. The increases in free energy and heat content that would attend this reaction between 1775°K. and 1910°K. at one atmosphere pressure were found to be those given by the equations $\Delta F^\circ = 253,630 - 90.58T$, and $\Delta H = 253,630$ cal. At 1875°K. the equilibrium pressure is 0.0100 mm. and the free-energy change is 83,800 calories.

Calculations have been made for the reaction $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$. The corresponding equations are $\Delta F^\circ = 127,065 - 67.5T$ and $\Delta H = 127,065$ cal. These values are in agreement with the observations of Fraenkel on this reaction.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 183]

APPARATUS FOR MICRO GAS ANALYSIS

By C. H. PRESCOTT, JR.¹

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In connection with measurements on the equilibrium between aluminum carbide and nitrogen² it was necessary to analyze quite small quantities of gas to determine the partial pressure of nitrogen. Langmuir³ has briefly described methods by which quantities of gas as small as one cubic millimeter at atmospheric pressure may be subjected to quantitative analysis. The author has seen this apparatus through the courtesy of Dr. Langmuir and recalls that the methods consisted in treating very small volumes of gas with aqueous reagents at atmospheric pressure.

In the present technique the gases are handled at low pressure over mercury using solid reagents. The volumes are of reasonable size and no gases need be introduced but those actually undergoing analysis. The methods would seem capable of a sensitivity at least as great as that indicated by Langmuir, though this has not been necessary for our present work. The apparatus was developed during one phase of the work on

¹ National Research Fellow in Chemistry.

² Prescott and Hincke, *THIS JOURNAL*, 50, 3228 (1928).

³ Langmuir, *ibid.*, 40, 1378 (1918); *Ind. Eng. Chem.*, 20, 333 (1928).

zirconium oxide and carbon,⁴ but was not used till recently for quantitative measurements.

The apparatus was designed to operate on samples whose volumes would be a third of a cubic centimeter or less at one atmosphere, and to determine carbon dioxide, carbon monoxide, hydrogen and nitrogen. The pressure in the absorption tubes usually started at less than two millimeters. The carbon dioxide was absorbed in soda lime; the carbon monoxide and hydrogen were oxidized by copper oxide at 250° and the water absorbed in phosphorus pentoxide; the carbon monoxide, now dioxide,

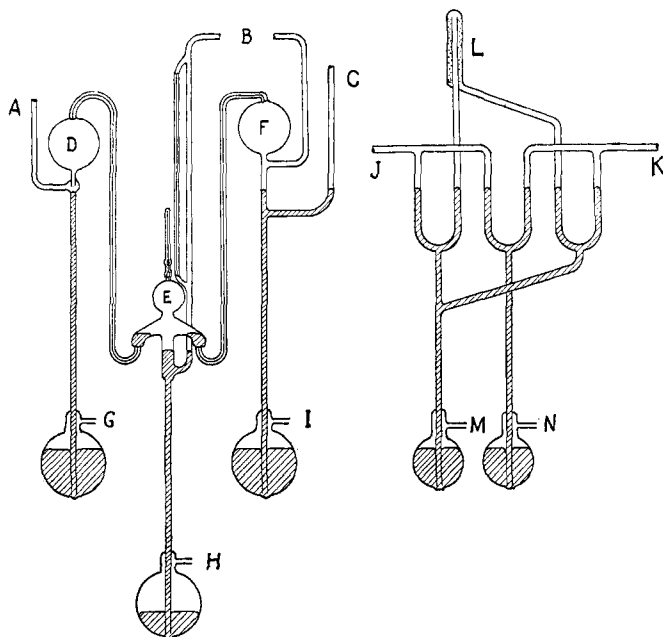


Fig. 1.—Gas analysis apparatus.

was absorbed in soda lime, leaving the nitrogen. After each absorption the gas was collected and compressed to one of a series of graduations in a capillary pipet and the pressure measured on a comparison tube as in a pressure reading on a McLeod gage. The time necessary for each absorption and collection for measurement was about an hour. As only nitrogen was significant for our purposes and the soda lime absorbed both carbon dioxide and water, only one absorption was necessary in a routine analysis.

The arrangement of apparatus is shown in Fig. 1. The tube A is connected to the apparatus containing at low pressure the gas to be analyzed. A mercury diffusion pump is connected to C. The absorption train is inserted at B, one element of which is shown at the side. Suction is applied

⁴ Prescott, *THIS JOURNAL*, **48**, 2534 (1926).

to H, I, M, N, etc., withdrawing the mercury from all the cut-offs, and the pipet and absorption train are evacuated to 10^{-4} mm. through the tube C. The suction is then released and by applying compressed air at G the Toepler pump D drives a sample of gas into the pipet E. The sample is compressed into the capillary by applying pressure at H, and its pressure-volume product measured. Suction is next applied at H, allowing the gas to flow up the comparison tube and through the absorption train to the pump F. The pump is operated by applying pressure at I and the gas circulated by pumping back into E. The contraction and expansion of volume resulting helps to clear the dead space in E. The suction at H is then released and the gas pumped back into the pipet and measured. The absorption tubes are each located as at L, and connected in series by the tubes J and K, etc. To pass the gas through a tube, suction is applied at M, withdrawing the mercury below the two cut-offs. To by-pass the gas around a tube suction is applied at N, releasing the suction at M. To clear the apparatus all the cut-offs are lowered as before and the gas escapes through C.

One absorption tube (L) contained $\frac{1}{3}$ g. of copper oxide, which was calculated to be sufficient for several thousand analyses. The next contained 1.2 g. of soda lime and the last about 0.6 g. of phosphorus pentoxide mixed with powdered pumice stone. These were baked *in vacuo* to the softening point of the Pyrex glass to drive off adsorbed gases. No gas could then be pumped off the copper oxide or soda-lime when they were cold. A little could be obtained from the phosphorus pentoxide and pumice stone. By circulating until there was no further absorption, it was determined that twenty cycles of the pump was sufficient. Fifteen cycles sufficed to recover the unabsorbed gas.

On several samples of pure nitrogen initial and final readings checked to the same scale division (0.3%). Absorption of hydrogen and carbon monoxide were practically complete. Analyses were made on two known mixtures of carbon monoxide and nitrogen. The composition was initially determined from pressures measured in the rest of the apparatus with a McLeod gage. A small correction was made for 0.23% nitrogen in the carbon monoxide. The results of the analyses are shown in Table I. The

TABLE I
RESULTS OF GAS ANALYSES

PV, cc. mm.		Composition by analysis		Composition by synthesis	
Initial	Final	N ₂ , %	CO, %	N ₂ , %	CO, %
91.5	27.05	29.6	70.4	29.7	70.3
21.98	6.56	29.8	70.2	29.7	70.3
7.59	2.41	31.7	68.3	29.7	70.3
130.0	11.99	9.23	90.77	9.16	90.84
383.0	35.1	9.18	90.82	9.16	90.84
10.63	0.986	9.27	90.73	9.16	90.84

quantities are expressed in cubic centimeters at a pressure of one millimeter of mercury.

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PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF WYOMING]

THE DECOMPOSITION OF FORMIC ACID BY SULFURIC ACID. II¹

BY ERNEST R. SCHIERZ AND HENRY T. WARD

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Introduction

In a previous paper by one of the authors² it was found that the velocity of decomposition of formic acid in sulfuric acid showed some irregularities when the concentration of sulfuric acid was 91.8%. Knietsch³ found that specific conductance, melting point and viscosity do not increase continuously on progressive dilution of sulfuric acid. Abnormal values for these properties occur in the range of concentration 92–93.5%.

The present investigation was undertaken to determine the velocity constants for the rate of decomposition of formic acid for various concentrations of sulfuric acid from 85–97% at temperatures of 15, 25, 35 and 45° and to observe whether the irregularity referred to above existed at other concentrations.

Experimental Part

Preparation and Purification of Materials.—The formic acid and the sulfuric acid were prepared by the same methods as those previously used. The formic acid distilled at 25.0–25.5° at 37–38 mm.; $d_{20}^{20} = 1.220$; refractive index (Abbé) $n_D^{20} = 1.3708$ and melted at 8°.

Apparatus.—The apparatus used was modified to a slight extent only. The measuring burets were of 100-cc. capacity so that it would not be necessary to use a smaller amount of formic acid. The volume of carbon monoxide evolved from 0.07 cc. of formic acid was about 63 cc. at 45° and the prevailing average pressure 585 mm.

The Effect of Water on the Decomposition of Formic Acid by Sulfuric Acid.—The effect of water on the velocity of the reaction was determined by proceeding in the same manner as in the previous investigation, using like amounts of reagents. The results are summarized in Table I. In

¹ The work included in this paper is from the thesis presented by Henry T. Ward in partial fulfillment of the requirements for the degree of Master of Science at the University of Wyoming.

² Schierz, *THIS JOURNAL*, 45, 447 (1923).

³ Knietsch, *Ber.*, 34, 4089 (1901).