solid solution at 258°. Mazzotto's explanation[17] of a similar hysteresis in the lead-tin eutectic is that the eutectic supercools with relation to the separation of tin. A similar supercooling with relation to antimony does not seem to be the explanation of our results, since the freezing point is not raised by seeding.

My thanks are due to Mr. G. S. Rutherford in charge of the Chemical Division for his interest and coöperation in this work.

Summary

Investigation by means of differential heating curves and microscopic examination has shown that antimony is soluble in solid lead up to between 2% and 3% of antimony at the eutectic temperature.

The alloys containing up to 13% show a higher eutectic temperature on heating than on cooling. A suggestion for the interpretation of this is made and a tentative equilibrium diagram drawn.

This investigation is being carried further to determine the solubility curve for antimony in lead at temperatures below the eutectic and to obtain further data on the possible existence of a compound in the system.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY, AND THE FIXED NITROGEN RESEARCH LABORATORY]

ANALYSIS OF HYDROGEN FOR TRACES OF NITROGEN[1]

BY R. L. DODGE

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The usual method for the determination of hydrogen in a mixture of gases by combustion over copper oxide has been modified and applied to the determination of traces of nitrogen in hydrogen. The details of the modified procedure are described in this paper. This procedure was employed in the analysis of hydrogen used for some special tests on ammonia catalysts. It is also useful for the analysis of hydrogen which is to be liquefied, since traces of nitrogen interfere materially with the liquefaction.[2]

Briefly, the method consists in burning large amounts (12–20 liters) of hydrogen over heated copper oxide in an evacuated system, circulating the residual gases over copper oxide to insure complete removal of the hydrogen, collecting the residual unburned gases (designated as nitrogen), and measuring them by the usual gas volumetric method. The volume

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[17] Mazzotto, *Intern. Z. Metallog.*, **2**, 269 (1911).

[1] The expenses of this investigation were in large part defrayed by the United States Fixed Nitrogen Research Laboratory.

[2] Dr. C. W. Kanolt of the Bureau of Standards, Washington, D. C., in connection with his study of the liquefaction of hydrogen, developed, subsequent to this work and independently of it, a similar procedure.

of hydrogen burned is calculated from the volume of water formed by the combustion.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1.

The combustion tube A is of Pyrex glass, approximately 34 cm. long and 25 mm. in internal diameter, and contains about 350 g. of copper oxide.[3] The heating is accomplished by means of the external resistance heater B. A Pyrex glass buret C, immersed in ice water, serves to collect the water formed by the combustion. Connection to the rest of the apparatus, which is of soft glass, is made through the ground glass joint (x, y). The bulb D (about 300 cc.) and stopcocks (d, e) make possible the circulation of the residual gases through the copper oxide to insure complete combustion of the hydrogen. The stopcock (c) controls the rate of admission of the hydrogen to the combustion system. The Töpler pump F serves to evacuate the combustion system. The McLeod gage J indicates the degree of evacuation. The gases removed by the Töpler pump are collected and measured in the water-jacketed buret G. H is a phosphorus pentoxide tube for the absorption of the traces of water uncondensed in the buret C.

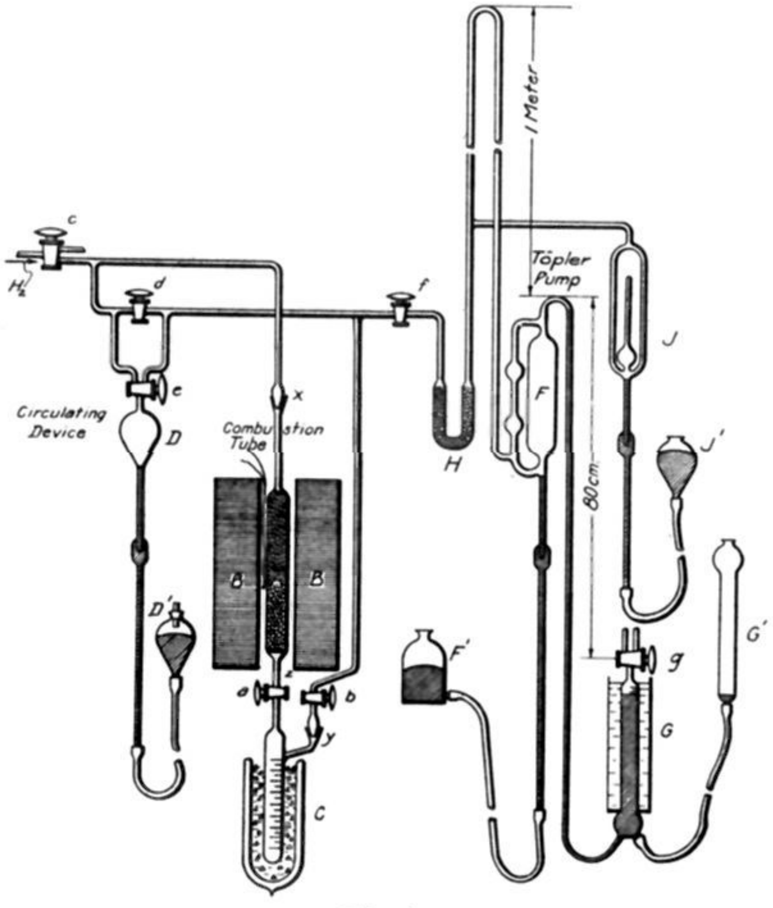

Fig. 1

Procedure.—The hydrogen to be analyzed is dried and admitted through the Cock c to the combustion system, which has previously been evacuated to a pressure of 0.01 mm. of mercury.[4] During the combustion,

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[3] A great excess of copper oxide is necessary, since reoxidation after an analysis is slow. The reoxidation is accomplished by heating the material to about 400° in a current of oxygen.

[4] When both the initial and final evacuations are carried to the same point, errors due to incomplete evacuation are negligible.

Cocks d and f are closed. The rate of admission of the hydrogen is limited by the temperature of the combustion in the copper oxide tube, which should not exceed 400°, as above this temperature metallic copper forms a slag with Pyrex glass. Care must be taken to maintain a pressure in the hydrogen supply line greater than atmospheric to avoid inadvertent contamination of the hydrogen with air.

After a sufficient amount of hydrogen has been burned, as indicated by the water collected in the buret C, Cock c is closed and the gases remaining unburned in the combustion system are circulated through the copper oxide tube and buret by manipulation of the leveling bulb D′ and the 3-way cock (e). Warming the combustion tube at z during the circulation insures transfer of all condensed water to the buret.

When continued circulation causes no further diminution in volume of the residual gas (indicated by using the bulb D as a rough McLeod gage) Cocks a and b are shut and d and f opened. The residual gas is then pumped into the water-jacketed buret G, where its volume is measured.

An error of 0.05 cc. in the volume of nitrogen causes an error of about 0.0005% in the percentage of nitrogen. An error of 0.01 cc. in the water formed causes an error of about one part in 200 in the actual percentage of nitrogen or, with a nitrogen content of 0.5%, an error of 0.002%.

The nitrogen lost by solution in the water formed during the combustion is, for an apparatus of this size, less than 0.04% of the total nitrogen.

The nitrogen left in the free space of the water buret is less than 1% of the nitrogen collected. This is within the limit of accuracy of the method for hydrogen containing less than 0.5% nitrogen. In using the method for hydrogen containing more than this amount of nitrogen, it is advisable to open the water buret to the combustion system for an instant after the first removal of the nitrogen and to collect this additional nitrogen by a second evacuation.

Results.—The method was standardized by analysis of "pure" hydrogen. This gas was generated in a modified form of Edwards' hydrogen generator[5] from C. P. air-free sulfuric acid and C. P. mossy zinc. The generator was equipped with mercury-sealed stoppers and was evacuated before the acid was admitted. A 50% excess of zinc was used. The results of the analysis are given in Table I.

The analyses of "pure" hydrogen indicate that any errors due to liberation of incombustible gas by reduction of copper oxide or by solution of the zinc and the acid of the generator are less than[6] 0.005%.

[5] Edwards, *J. Ind. Eng. Chem.*, **11**, 961 (1919).

[6] Auxiliary experiments show that the gas liberated by the copper oxide on solution in acid is less than 0.5 cc. for every 90 g. of CuO, this being the limit of accuracy of the determination. It is probable that the actual value is considerably below this. See Richards, *Proc. Am. Acad.*, **26**, 276 (1890).

Table I

Results

Gas analyzed		Observed volume H_2O Cc.	Vol. of H_2 0°, 760 mm. burned Liters	Obs. vol. "N_2"[a] 0°, 760 mm. Cc.	% "N_2"	Av.
"Pure"	1.......	10.0	12.4	0.52	0.004	
	2.......	9.2	11.4	0.42	0.004	
						0.004
"Special"	1.......	11.4	14.2	6.51	(0.046)[b]	
	2.......	11.4	14.2	5.78	.041	
	3.......	10.9	13.6	5.75	.042	
						.043
Ordinary	1.......	11.0	13.7	64.28	.470	
	2.......	9.5	11.8	55.40	.470	
						.470

[a] That is incombustible gas, unadsorbed by cuprous ammonium chloride or potassium hydroxide; it may contain argon and other inert gases.

[b] The hydrogen supply line was under less than atmospheric pressure for a short time allowing possible contamination of the hydrogen with air.

"Special" hydrogen was taken from a commercial tank which had been filled as nearly as possible directly from electrolytic cells, special precautions being taken to remove all air from compressors, lines and tank before filling. It is probable that 0.04% represents the minimum percentage of inert constituents in commercial electrolytic hydrogen.

"Ordinary" hydrogen was taken from a commercial tank chosen at random.

In conclusion the author wishes to express his appreciation for the valuable assistance of Professor Arthur B. Lamb, under whose supervision this work was conducted.

Summary

A modification of the usual method for the determination of hydrogen by combustion over copper oxide has been devised and applied to the analysis of hydrogen for traces of nitrogen.

Large quantities of hydrogen (12–20 liters) were burned by circulation over heated copper oxide in a previously evacuated system and the hydrogen determined by measuring the water formed. The residual nitrogen was pumped off and measured.

The method is accurate to 0.005%.

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and Washington, D. C.