

IV

pounds most of their interest. The covalency of cuprous copper seldom exceeds 3, hence the compounds should be cupric and possess an anion other than the covalent phenyl group. This is supported by their color and their reaction with potassium ferricyanide (yellow-green precipitate). However, uncoordinated arylcopper compounds react with water,¹⁰ organic halides,⁴ hydrochloric acid and chloroacetyl chloride³ to yield inorganic cuprous compounds. In support of the cuprous condition is the analogy with copper iodide, which is only stable in the cuprous state. When considering the coordinated arylcopper compounds it should be noted that cupric iodide forms a complex with ethylenediamine which shows no tendency to revert to the cuprous condition.¹¹

From theoretical considerations a 5-covalent copper should be cupric, since its effective atomic number (E. A. N.) would be 37, with krypton at 36 and pentavalent cuprous copper at 38. By Sidgwick's maximum-covalency rule¹² a covalency of 6 is possible for copper. Werner long ago recorded cuprous halogen complexes with 3, and cupric halogen complexes with 6 molecules of pyridine.¹³

Another possibility is complete ionization of the copper-carbon bond. It may be that the influence of electrons donated by nitrogen decreases

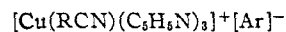
(10) Reich, *Compt. rend.*, **177**, 322 (1923).

(11) Sneed and Maynard, "General Inorganic Chemistry," D. Van Nostrand, New York, N. Y., 1942, p. 823.

(12) Sidgwick, "The Electronic Theory of Valency," Oxford, London, 1927, p. 169.

(13) Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 1923, pp. 182, 189.

the apparent electronegativity of the metal and the arylpyridinium-copper-nitrile complexes could conform to the known cuprous type (V) (E. A. N. = 36).



Conclusions

The facts lead the authors to suggest a hypothesis for arylcopper compounds and their complexes: All organocopper compounds themselves and their nitrile complexes contain copper in the colorless cuprous state. The addition of pyridine to either causes a rapid transformation to colored-pyridinium complexes with copper in the cupric state. The oxidizing agent and the new anion joining the copper are unknown. However, the oxidizing agent in such cases may be very weak, as shown by the rapid oxidation of cuprous-ammines in air. This idea lends a much greater significance to the study of organocopper compounds, and it suggests new lines of work on electrode-potentials of such systems, on X-ray diffraction of the compounds, and on possible oxygen-carrying power of the compounds in biological systems.

Summary

1. Several new organocopper compounds have been synthesized from the corresponding diazonium borofluorides, and the reaction conditions have been studied.

2. Complexes of arylcopper compounds with nitriles have been prepared and also complexes containing both pyridine and a nitrile.

3. The latter complexes appear to be pentavalent cuprous compounds, but the hypothesis is proposed that organocopper compounds and their nitrile complexes are cuprous, while the pyridinium complexes are all cupric.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 1027]

An Instrument for Determining the Partial Pressure of Oxygen in a Gas¹

BY LINUS PAULING, REUBEN E. WOOD, AND J. H. STURDIVANT

On October 3, 1940, at a meeting in Washington called by Division B of the National Defense Research Committee, mention was made of the need for an instrument which could measure and indicate the partial pressure of oxygen in a gas. During the next few days we devised and constructed a simple and effective instrument for this purpose. This instrument measures the volume

(1) This work was done in whole under the Contracts Nos. ND-Crc-38, NDCrc-200, OEMsr-326, and OEMsr-584 between the California Institute of Technology and the Office of Scientific Research and Development, which assumes no responsibility for the accuracy of the statements contained herein. A brief description of this instrument has been published in *Science*, **103**, 2672 (1946).

magnetic susceptibility of the gas; its use as an oxygen meter is based on the fact that the magnetic susceptibility of molecular oxygen is very much greater than that of any other common gas. The volume magnetic susceptibility of oxygen at 20° and one atmosphere pressure (standard conditions) is $+142 \times 10^{-9}$ c. g. s. m. u.; all other common gases are diamagnetic, with susceptibilities very much smaller in magnitude: nitrogen -0.40×10^{-9} ; hydrogen -0.165×10^{-9} ; carbon dioxide -0.83×10^{-9} ; helium -0.078×10^{-9} ; etc. The magnetic susceptibility of a mixture of common gases is hence de-

pendent mainly on the partial pressure of oxygen in the gas; a change of a few hundred millimeters of mercury in the partial pressure of the diamagnetic gases would affect the magnetic susceptibility only as much as a change of one millimeter of mercury in the partial pressure of oxygen.²

The forces due to the action of achievable magnetic fields on a gas, even such a strongly magnetic gas as oxygen, are very small, and their measurement is not easy. The instrument as originally proposed was to embody the following features. A strong inhomogeneous magnetic field would be created between suitably shaped pole pieces of a permanent magnet, made from a highly retentive alloy such as Alnico. Suspended in this field on a taut silica fiber would be a glass test body and attached mirror so arranged that the test body and mirror could rotate through regions of varying magnetic field strength by twisting and untwisting the fiber. The magnetic force acting on a small test body in an inhomogeneous magnetic field is proportional to the product of the field strength, the gradient of the field strength, and the difference in volume magnetic susceptibility of the test body and the gas surrounding it. The equilibrium orientation of the test body, as determined by the magnetic force and the torsional force of the fiber, would accordingly be dependent on and would provide a measure of the magnetic susceptibility of the gas. The orientation could be indicated by a light beam reflected from the mirror onto a scale; the scale could be calibrated to read directly the partial pressure of oxygen in the gas.

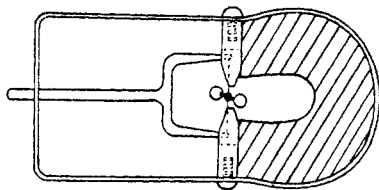


Fig. 1.—The first experimental magnetic oxygen meter.

This design was closely followed in the experimental model and in the later instruments. The experimental model (October, 1940) had as test body a dumbbell of two thin-walled glass spheres 4 mm. in diameter sealed to a glass rod 6 mm. long. A silica fiber 8 μ in diameter was stretched between the prongs of a silica fork,³ and the glass dumbbell was cemented with shellac to the middle of the fiber, perpendicular to it. A plane glass mirror 2 mm. square was also cemented near the middle of the fiber. The suspension was balanced

(2) The gases nitric oxide, nitrogen dioxide, and chlorine dioxide, each of which consists of molecules containing an odd number of electrons, are strongly paramagnetic, and hence their presence in appreciable amounts in a gas would interfere with the use of the magnetic instrument as an oxygen meter. Each of these gases has about one-half the volume magnetic susceptibility of oxygen.

(3) We are grateful to Professor H. Victor Neher of the Norman Bridge Laboratory of Physics for advice and instruction in silica-fiber technique.

approximately by use of shellac, and was coated with aluminum by evaporation.

A four-ounce Alnico permanent magnet was mounted in a brass yoke. Two wedge-shaped pole pieces of soft iron, each with a slot sawed part way through it, were also attached, and the dumbbell assembly was inserted with the ends of the silica fiber in the slots and the spheres of the dumbbell between the pole pieces, one sphere being a little in front and the other a little behind the plane of the pole pieces, as shown in Figure 1.

This instrument was laid in a vacuum desiccator with the fiber vertical. A flashlight bulb was set up outside the desiccator, and the position of the spot of light reflected by the meter mirror was observed on a piece of tissue paper pasted to the desiccator wall. The experimental results given in Table I were obtained.

TABLE I

RESULTS OBTAINED WITH THE FIRST EXPERIMENTAL MAGNETIC OXYGEN METER

Gas in desiccator	Angular displacement of light beam (radians)
Air, 1 atm.	(0)
Air, 0.02 atm.	+0.18
Nitrogen, 1 atm.	+0.18
Oxygen, 1 atm.	-0.52
Oxygen, 0.20 atm.	0.00

The readings are seen to be determined by the partial pressure of oxygen in the gas.

Some changes in design have been incorporated in later models of the instrument. The improved dumbbell assembly is shown in Fig. 2. The dumbbell consists of two thin-walled glass spheres, matched for volume (diameter about 3 mm.) and weight, fused to the ends of a glass rod about 4 mm. long. This rod is bent at its midpoint through a small angle, in order that the silica fiber to which it is cemented by silver chlo-

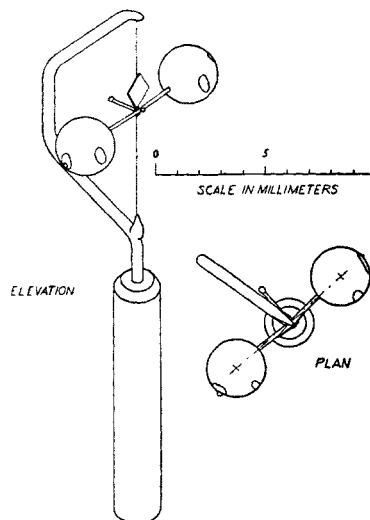


Fig. 2.—The assembly of dumbbell, mirror, and balancing rod mounted on a taut silica fiber.

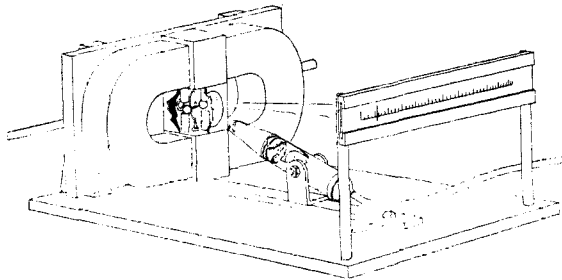


Fig. 3.—Diagram of instrument, showing dumbbell assembly mounted between pole pieces of two small permanent magnets, source of light, and scale.

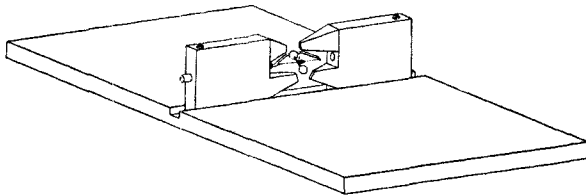


Fig. 4.—Dumbbell assembly and pole pieces (of different design), with magnets removed from back plate.

ride may pass through the center of volume of the dumbbell. Another small glass rod, used in balancing the assembly, is fused to the dumbbell during its construction, and the small mirror is cemented to the dumbbell. The moving part of the instrument (dumbbell and mirror) now weighs about 3 mg. The Y-shaped fork has been replaced by a silica yoke such that the cylindrical brass sleeve into which its end is cemented is coaxial with the fiber. The dumbbell is balanced roughly by attaching minute droplets of a low-melting lead borate glass and then precisely by evaporating silver halides onto it from an electrically heated wire.

The permanent magnets are now made of Alnico V, which has a higher retentivity than Alnico II, which was first used. It has been customary to use a pair of magnets weighing five ounces each, arranged as shown in Fig. 3. Pole pieces of various designs have been found to be satisfactory; examples are illustrated in Figs. 3, 4, and 5. A sensitive instrument containing a single large magnet, weighing about six pounds, has also been designed and built (Fig. 5).

Three methods of taking care of effects of change of temperature have been used. The simplest method is to calibrate the instrument at

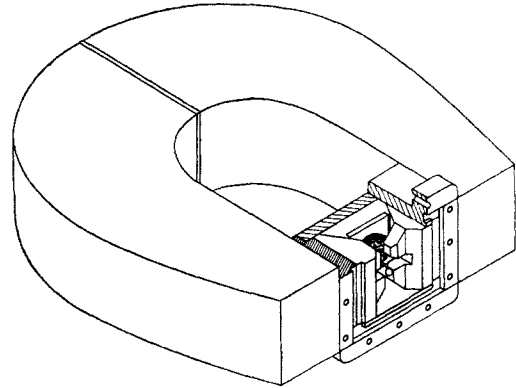


Fig. 5.—Large magnet with test chamber enclosing pole pieces and dumbbell assembly; windowed cover and gasket have been removed from test chamber.

various temperatures and to provide correction tables or graphs. Another method is to adjust the temperature coefficient of the magnetic susceptibility of the dumbbell suitably (its paramagnetic component at mid-point of temperature range numerically twice the diamagnetic component) and to cause the magnetic field strength to vary with temperature in such a way (direct proportionality to absolute temperature) as to compensate the other effects of temperature on the reading of the instrument; this compensation can be effected by placing across the permanent magnet a shunt made from an iron-nickel alloy with a very high negative temperature coefficient of magnetic permeability. The third method is to provide a heater and thermostatic regulator

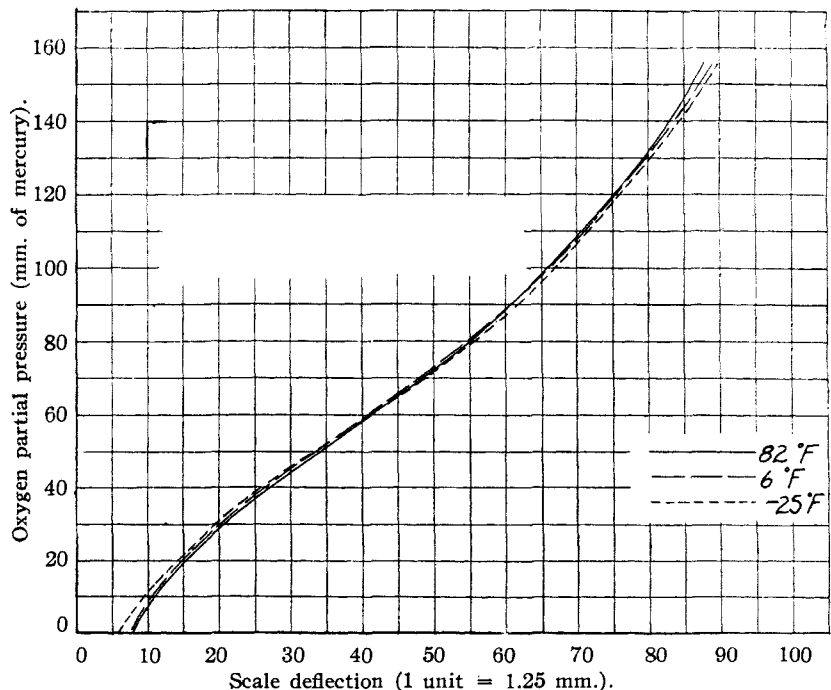


Fig. 6.—Calibration curves for a meter at three temperatures.

for the meter, and thus to maintain it and the sample of gas at the calibration temperature.

The gas to be tested may be drawn or forced at the rate of a few cubic centimeters per minute through the test chamber, which in present models has a volume of about 4 ml., or it may be introduced after evacuating the test chamber. The instrument indicates correctly the magnetic susceptibility of the gas in the test chamber within a few seconds; the main delay in reading the instrument is caused by the time required to introduce the gas.

Meters have been constructed to cover various ranges of partial pressure of oxygen, including 0 to 20 mm. of mercury, 0 to 80, 0 to 160, 110 to 190, and 0 to 800. Dr. A. O. Beckman has also devised a meter which can be switched from one partial-pressure region to another.

Calibration curves for a typical "Model P" meter at three different temperatures are shown in Figure 6. This meter has been compensated for temperature changes in the manner described above. The accuracy of a meter is usually about 1% of the range covered.

The instrument may also be used for determining the magnetic susceptibility of paramagnetic and diamagnetic gases or for any analysis dependent on magnetic susceptibility, such as the determination of nitric oxide or nitrogen dioxide in a gas not containing oxygen.

Several dozen meters were constructed at the California Institute of Technology before the summer of 1942. Dr. Arnold O. Beckman, 11 West State Street, Pasadena 2, California, who then took over the production of the meter, has manufactured several hundred. Descriptions of the various models will be published elsewhere. Some recording models of the instrument are available.

We are glad to acknowledge the assistance of David P. Shoemaker, James B. Edson, Harold Herd, Dr. Herbert Sargent, Dr. Charles D. Wagner, and Beckie Bradford in the development of this instrument at the California Institute of Technology.

Summary

A simple instrument for determining the partial pressure of oxygen in a gas is described. This instrument, the use of which as an oxygen meter depends on the fact that the magnetic susceptibility of oxygen is very much greater than that of other common gases, consists of a small glass dumbbell with attached mirror suspended on a stretched fused-silica fiber in an inhomogeneous magnetic field produced by a small permanent magnet. In the simpler models of the instrument the partial pressure of oxygen is indicated on a scale by a beam of light reflected from the mirror.

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{CONTRIBUTION FROM THE RESEARCH LABORATORY, U. S. STEEL CORPORATION}

The System Iron-Oxygen. II. Equilibrium and Thermodynamics of Liquid Oxide and Other Phases

BY L. S. DARKEN AND R. W. GURRY

This paper, an extension of a previous paper¹ on the equilibrium between iron, oxygen and wüstite throughout its field of stable existence, deals with the results of similar measurements at the higher temperatures at which a liquid phase appears. The data, in conjunction with those in paper I, suffice not only for the construction of phase diagrams showing the relation between temperature, gas composition (oxygen pressure) and composition of the oxide phases, liquid or solid; but also for evaluation of the following thermodynamic quantities: activity and partial molal heat of iron and of oxygen throughout the several homogeneous fields, heat of formation and of fusion of iron oxide of any composition realizable at oxygen pressures up to one atmosphere.

The general method was, as before, to pass a gas mixture of constant known composition over the condensed phase, maintained at one of a series of constant temperatures, until equilibrium was

attained, then to quench the iron oxide phase and determine its composition. The temperature ranged up to 1640°; the equivalent partial pressure of oxygen in the gas phase from 10⁻¹⁰ up to 1 atm.; the atom ratio of oxygen to iron in the liquid oxide from about 1.03, that in equilibrium with iron, to about 1.38, somewhat beyond Fe₃O₄. In the region studied there are several distinct, though related, equilibria, each of which must be considered separately; the system as a whole is therefore somewhat complex. For this reason, and so that the reader may more readily apprehend the precise inter-relations, it was deemed best to begin by presenting as a summary diagram, in Fig. 1, our final temperature-composition diagram for the iron-oxygen system, solid as well as liquid, at an oxygen pressure ranging up to one atmosphere and a total pressure of one atmosphere throughout. The other phase diagrams have been lettered to correspond as far as possible thereto. It is to be remarked that change in composition of the condensed phase, at least at its surface, follows quite rapidly any

(1) L. S. Darken and R. W. Gurry, *THIS JOURNAL*, **67**, 1398 (1945); hereafter referred to as paper I.