Metal System for Chemical Reactions and for Studying Properties of Gases and Liquids

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An all-metal system, made of copper, is herein described. It is suitable for working with those chemicals which do not attack copper. In particular it has been found very useful in the purification of BF_3 and $B(CH_3)_3$. Some important features of such a system are (1) a complete absence of contaminants; (2) reactions may be carried out up to 500°C; (3) pressures up to several hundred pounds per square inch may be used; (4) flow of gases from very low to very high pressures may be easily controlled; (5) the system is very rugged. This latter point is particularly desirable where noxious or inflammable gases (such as $B(CH_3)_3$) are used. A method is also described whereby gases from sealed-off containers under either high or low pressures may be easily retrieved without introducing impurities. Other important advantages of such a system are mentioned in the text.

I. INTRODUCTION

THE system to be described was developed primarily for investigating the properties of the two boron gases—boron trifluoride, BF_3, and boron trimethyl, $B(CH_3)_3$—as possible filling gases for ionization chambers for the detection of thermal neutrons. It is very desirable to produce these gases in as high a state of purity as possible to reduce to a minimum any recombination of the ions. The results of these experiments will be published elsewhere. The all-metal system developed for this purpose is the subject treated here.

The difficulties encountered in a glass system when working with such gases as BF_3 are well known.[1] This gas attacks organic compounds such as stopcock grease. The impurities resulting therefrom are difficult to remove. Furthermore, the glass system cannot readily be baked out, and one is usually limited to pressures no greater than one atmosphere.

II. ASSEMBLY OF THE SYSTEM

To illustrate the various techniques involved, part of the all-copper system employed will be used for illustration. In Fig. 1 the two containers *A* and *B* may be heated with a surrounding oven or cooled by immersion in liquid air or other coolant. Chamber *C* had a volume approximately 100 times that of *A* or *B*. It served for storage of the gas, while *D* was the test chamber. The second chamber was enclosed in an oven which allowed a temperature of 400°C to be reached.

The system was assembled from copper tubing. Tubes *a* and *b* were of $\frac{3}{8}$-in. diameter while the other connecting tubing was of $\frac{1}{4}$-in. diameter.[2] The $\frac{3}{4}$-in. diameter vacuum line was sealed to a glass liquid-air trap by means of a copper-glass seal. The outer glass wall of the liquid-air trap was removable, by means of a ground joint as shown in Fig. 1 to allow easy disposal of condensed gases. A mercury diffusion pump, vacuum gauge, and fore pump completed the vacuum system.

The system was assembled, using Phos-copper[3] as a brazing material, a continuous flow of hydrogen passing through. After assembly, those parts of the system that

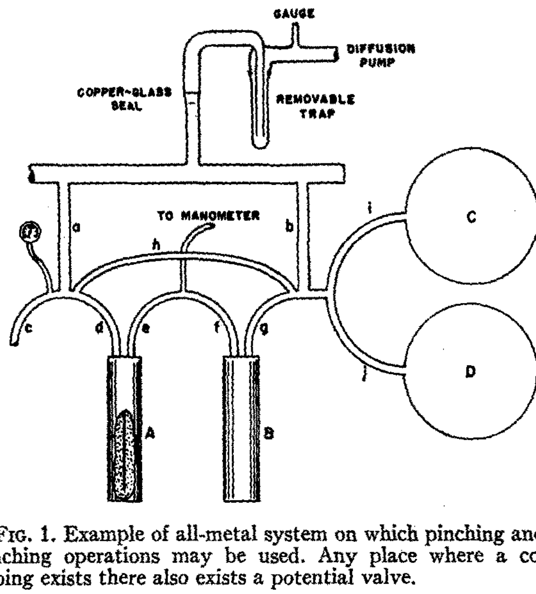

FIG. 1. Example of all-metal system on which pinching and depinching operations may be used. Any place where a copper tubing exists there also exists a potential valve.

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[1] Tongiorgi, Hayakawa, and Widgoff, Rev. Sci. Instr. 22, 899 (1951).

[2] Copper tubing of various sizes with $\frac{1}{32}$-in. wall is used for refrigeration equipment. Also available commercially are various kinds of fittings such as T's, elbows, reducers, etc.

[3] "Phos-copper" is an alloy of copper and phosphorus (melting point 750°C), and is extremely useful on copper. The phosphorus reduces the oxides. It is obtainable from Westinghouse Electric and Manufacturing Company. The eutectic alloy of silver and copper may also be used. In this case the silver solder is placed at the appropriate location inside *A* or *B*, for example, and heat applied from the outside. Hydrogen flowing through acts as a flux to reduce the oxides.

Metals and solders containing components with high vapor pressures, such as cadmium, zinc, and lead should not be used. The powder, coming from the vaporized metal, interferes with the free flow of the molten metal.

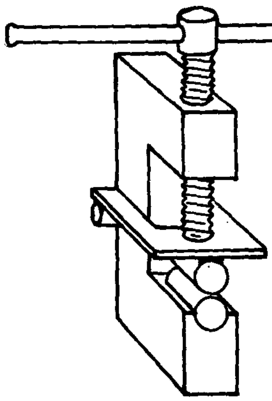

FIG. 2. Steel clamp used in sealing the pinch. The jaws are slightly smaller in diameter than the jaws of the pinching tool. [See Rev. Sci. Instr. 25, 517 (1954).]

were not already heated sufficiently were heated to a dull red temperature to reduce the oxides and to drive various impurities from the walls. On cutting apart any piece after such treatment, the metal will be found to have a bright copper luster. To test for leaks, as much of the system as possible was temporarily sealed off with several atmospheres pressure of hydrogen inside and immersed under water.

III. PINCHING AND DE-PINCHING TECHNIQUES

A tool has previously been described[4] for use with copper tubing that will form a cold, diffusion weld that will be vacuum or pressure tight. The same tool may be used to pinch the copper tubing just sufficiently to bring the opposite inside walls of the tubing together. A clamp like that shown in Fig. 2 may then be applied at the pinch, in which case the pinch may be made pressure or vacuum tight. The de-pinching or opening process consists in using a pair of adjustable pliers,[5] with the jaws reshaped as shown in Fig. 3. After the proper adjustment of the pliers, the jaws are applied at right angles to the original pinch. The tubing opens to nearly its original inside diameter. This process is easily applied to copper tubing up to $\frac{3}{8}$-in. diameter with a $\frac{1}{32}$-in. wall. The same place should not be so treated more than once because of danger of causing a leak. However, the process may be repeated a diameter of the tube on either side.

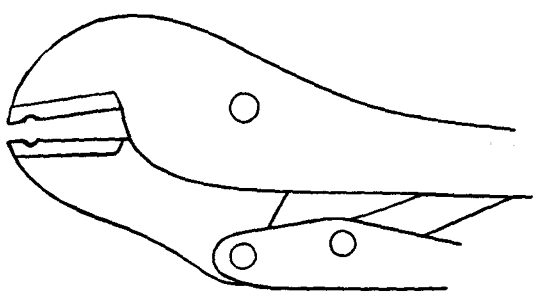

FIG. 3. Adjustable tool used in de-pinching the tubing. The de-pinched tube opens up nearly to its original inside diameter.

The uses of such a technique are very interesting. In essence, wherever there exists a section of tubing, there also is a possible valve. Where a high pressure difference exists, the clamp may be sufficient to control the flow of the gas or liquid. If the pressure difference is small, the pinch, as formed by the pinch-off tool, may completely close the tube. In this case the flow of gas or liquid is adjusted by de-pinching a controllable amount by means of the adjustable pliers.

The pinching and de-pinching operations are best performed on tubing that has been heated to a dull red heat with hydrogen inside. Such annealed copper is highly ductile and the clean inner surfaces at the pinch will readily make a tight seal when the clamp is applied.

Referring to Fig. 1 again, suppose tube c leads to a source of gas. In the purification of BF_3 this might be the complex $CaF_2 \cdot BF_3$ which may be degassed up to 200°C. To remove HF, an intermediate cylinder containing NaF, which can be baked out or cooled to solid CO_2 temperatures, may be inserted.[1] The whole system is baked either with flames or in ovens until a vacuum of say 10^{-5} mm of mercury is reached. The tube to the mercury manometer consists of a coiled length of 10 or 20 ft of $\frac{1}{16}$-in. inner diameter copper tubing which had previously been heated with hydrogen flowing inside. A copper-glass seal connects this tubing to the manometer. The clean copper absorbs the mercury vapor, thus eliminating contamination from this source. Metal pressure gauges may also be inserted at appropriate places.

When a sufficiently good vacuum is obtained, tubes a and b are sealed by means of the technique described above. A given amount of gas, e.g., BF_3, may then be admitted to the system by heating the complex to 300°C and noting the pressure of gas in the given volumes. Tube c may then be sealed, and the gas experimented with at will.

Distillation may be carried out by condensing the gas in container A, which contains copper turnings on each side of a sealed partition. This is done by closing tubes f and g and then placing liquid air around A, in the case of BF_3. If the BF_3 contains considerable quantities of impurities not condensable in liquid air, A may fill up with these gases before all the BF_3 is removed from C and D. In this case tube h may be sealed temporarily, tube a opened and such gases removed.

By silver soldering thermocouples to the walls of the copper cylinders A and B, their temperatures may be easily determined and distillation carried out at the temperature of baths with which they are surrounded. Cylinder B, for example, may be kept at liquid air temperature and A gradually warmed. Tubes d and g would be closed for this process while e and f would be

[4] H. V. Neher and Alan R. Johnson, Rev. Sci. Instr. 25, 517 (1954).

[5] These may be obtained from Peterson Manufacturing Company, Dewitt, Nebraska. The 10-in. length model is best suited for this purpose.

open. Because of the properties of BF_3, it would then sublime from A and appear as frost on the walls and copper turnings inside B. The manometer would indicate the pressure drop of the gas flowing in tube f. When the BF_3 has all collected in B, tube f is sealed and the whole system pumped to a good vacuum. At this stage all parts except B may be again heated to 400°C to degas.

IV. ADVANTAGES AND TECHNIQUES POSSIBLE WITH AN ALL-METAL SYSTEM AND THE PINCHING—DE-PINCHING PROCESS

In the following, the foregoing as well as some of the other more obvious techniques and procedures of the above-described process are collected:

A. Assembly of the metal system is carried out with hydrogen flowing inside, thus eliminating contamination due to fluxes.

B. The whole system may be heated with hydrogen inside to reduce oxides and drive off volatile substances.

C. It may be baked to 500°C, with a vacuum inside, to degas.

D. High gas pressures, up to several hundred pounds in.$^{-2}$ may be used and the system immersed in water to locate leaks.

E. Due to the complete absence of contaminants, the chemicals may be left in the system for an indefinite period of time without fear of the appearance of impurities. (The time element is of importance where a glass system with stopcocks is used as in the usual purification of BF_3.[1])

F. The system is not fragile. Connecting tubes may be bent with either pressure or vacuum inside.

G. A container may be agitated while on the system because of the flexibility of the tubing.

H. Reactions and processes may be carried out at temperatures up to 500°C and pressures up to several hundred lb in.$^{-2}$. It becomes as simple to operate with such pressures with such a metal system as it is with pressures below 1 atmos with a glass system.

I. By forming the inlet and outlet tubes, to a given container, in a double helix (Fig. 4), the contents of the container may be weighed.

J. The pinching and de-pinching process permits a copper tube to be closed and opened on the usual refrigeration copper tubing up to $\frac{3}{8}$-in. diameter. With a thicker wall, larger sizes of tubing may be so treated. The tube may be pinched and de-pinched at intervals of one tube diameter. The pinched tube may be made tight, even against high pressures, by applying a suitable clamp.

K. By adjustment of the clamp, in the case of high pressures, or by de-pinching an adjustable amount by means of a modified pair of commercial pliers, the flow of gas through the tube may be controlled as readily as with a needle valve.

L. Metal pressure gauges may be inserted at any point in the system. These may have varying ranges.

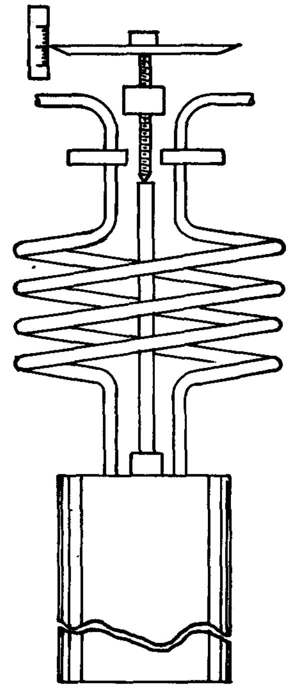

FIG. 4. Working within the elastic limit of the helical tubing, the weight of condensed chemicals may be accurately determined by the above system. Deflection is determined by electrical contact at the point of the screw.

When the end of the scale of any one is reached, it may be sealed off from the system by means of pinching and the application of the clamp.

M. A mercury manometer may be used and mercury vapor effectively eliminated from the system by adsorption of the vapor on the walls of a long copper tubing that has been previously heated with hydrogen inside.

N. By means of the pinching tool,[4] the copper tubing may be very simply pinched in two and a container detached, in which case the tubing will be sealed by a diffusion weld. The copper tubing should be clean inside for such a seal always to be tight. Tubing of $\frac{1}{4}$-in. diameter may be so sealed while gas pressures of several hundred lb in.$^{-2}$ are inside. Such seal-offs are useful for a variety of metal apparatus such as Geiger counters, neutron counters, ionization chambers, etc.

O. Where a gas is to be recovered, such as enriched BF_3 from a neutron counter, this may be done without contaminating the gas by the following procedure: (1) The copper tubulation on the counter is pinched and clamped just back of the seal, thus closing the tube. (2) The tube is then cut off and fastened to a metal system by means of, say, Phos-copper. Hydrogen may be used inside the tubing to prevent oxidation. (3) A vacuum is pumped in the system, where suitable arrangements have been made to store the BF_3. (4) The tube is de-pinched according to the procedure described in the text. The BF_3 may then be removed by condensing it in a container by means of liquid air.

A few precautions should be added about the use of hydrogen as a flux in the fabrication of metal systems. (1) The pieces to be brazed should fit tightly together so that a flow of hydrogen may be maintained throughout the whole system. (2) The air in the system must be thoroughly displaced by the hydrogen before any attempt is made to braze, or to ignite the gas. The use of some sort of flow indicator, either in the form of a water manometer or a flowmeter is desirable. A volume of hydrogen several times that of the system should be run through to thoroughly flush the containers and lines. After this is done, the hydrogen may be ignited at the outlet. The flow of hydrogen at all times should be sufficient to maintain a positive pressure inside to exclude any air.

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Compensation of the Earth's Magnetic Field

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A system is described for producing a highly homogeneous, variable, and directable magnetic field. This system, which was used in gyromagnetic ratio experiments, was directed against the earth's magnetic field to obtain very nearly a field free space. Horizontal fields in this working space were held to less than 0.01% of the earth's horizontal component.

INTRODUCTION

DURING the past several years, direct gyromagnetic determinations have been made by the General Motors Research Staff, for a number of metals and alloys.[1] Successful determination of these ratios requires the accurate measurement of extremely small mechanical inertia forces. These forces were measured by suspending the ferromagnetic material being studied, in a sensitive torsional system, magnetizing it and observing the resulting rotation. Normally torques which are vastly greater than those being measured would act on the suspended system due to coupling with the earth's magnetic field. It was, therefore, of extreme importance in this work to obtain a space in which all magnetic fields were very nearly eliminated. The system to be described was capable of reducing magnetic fields in the working space to about 0.01% of the value of the earth's horizontal component, and to hold it at this reduced value for an extended period of time.

The earth's magnetic field can be represented as a vector inclined to the vertical which is continually undergoing small changes both in magnitude and in direction. At a location which is remote from any concentration of ferromagnetic material this field is highly homogeneous. The problem of compensation hence becomes one of designing a coil system capable of producing magnetic fields of high homogeneity, and also of designing a system whereby the naturally occurring variations in the earth's magnetic field can be followed.

The system to be described was located in a special laboratory building so as to obtain the initial field homogeneity required. The coil array is shown in Fig. 1. It consists of three coil systems, producing magnetic fields in the vertical, north-south, and east-west directions. These magnetic fields were directed against the earth's field to produce compensation. Variometers were used to follow the changes occurring in the north-south and east-west components. The vertical variations were not followed since very small vertical fields could be tolerated in these experiments. The use of a three component system also made it possible to produce highly homogeneous horizontal fields of several oersteds. This was very useful in measuring magnetic moments.

The coil system, variometers, and field detection equipment will be described in order.

THE COMPENSATING SYSTEM

Compensation of the earth's magnetic field was accomplished by an array of five different Helmholtz coils. The Helmholtz coil, which consists of two identical circular coaxial conductors having centers separated by the conductor radius, produces a highly uniform magnetic field throughout a considerable volume. Equations expressing the field homogeneity of a Helmholtz coil have been developed by Ruark and Peters.[2]

Since the magnetic fields required in this work were of

[1] G. G. Scott, Phys. Rev. **82**, 542 (1951); **83**, 656 (1951); **87**, 697 (1952); **89**, 618 (1953); **99**, 1241 (1955); **99**, 1824 (1955); **103**, 561 (1956); **104**, 1497 (1956).

[2] Ruark and Peters, J. Opt. Soc. Am. **13**, 205 (1926).