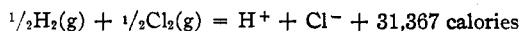
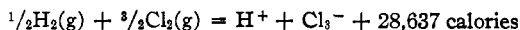


According to Lewis and Randall at 25°



By addition of these two free-energy equations there results



That is, $\Delta F_{298} = -28,637$ calories for Cl_3^- (or for one formula weight of aqueous HCl_3).

Summary

The solubility of chlorine was determined at 25° and 1 atmosphere in solutions of sulfuric acid, of hydrogen chloride, of sodium chloride, of potassium chloride and of barium chloride, and compared with the corresponding solubilities of oxygen. By means of such a comparison the salting-out effect of these electrolytes on the dissolved chlorine was estimated. This made it possible to compute from the total solubility of chlorine the extent of trichloride formation in the chloride solutions, and the corresponding value for the equilibrium constant of the reaction $\text{Cl}_2(\text{g}) + \text{Cl}^- = \text{Cl}_3^-$. The value for this constant was found to be 0.01, the corresponding free energy of formation of trichloride ion, in the system of Lewis and Randall being $-28,637$ calories.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE COMPARISON OF CERTAIN COMMERCIAL GETTERS

BY MARY R. ANDREWS AND JOHN S. BACON

RECEIVED JANUARY 26, 1931

PUBLISHED MAY 6, 1931

For many years certain materials have been used in lamps and vacuum tubes for the removal of traces of gases so as to improve the vacuum. These materials may be divided into two classes: (1) those acting as adsorbents by virtue of their finely divided condition or activation, that is, those having tremendous surfaces upon which gases can be strongly held by adsorption, and (2) those which possess high chemical activity. To the first class belong active charcoal, copper oxide powder, powdered thoria, etc. The second class includes the alkali metals, alkaline earth metals, and probably phosphorus—the material so much used in incandescent lamps. All of these materials are called "getters" in the technical slang of the day.

The work reported here is confined to a comparison of the efficacy of the common getters of class two. We have tested calcium, barium, magnesium, sodium and phosphorus for the degree of vacuum produced under given conditions and the speed with which this vacuum is reached. These getters are all used as thin coatings on the walls of bulbs or tubes. They

are produced by evaporation and deposition of the element at much reduced pressures. This gives a film of large surface and presumably of material which has been freed of gas.

Kaye, in his book on high vacua (page 31), says that a pressure of 10^{-8} mm., or approximately 10^{-6} baryes, is probably the lowest *measured* pressure reached as yet. Working with Dr. Dushman, Mr. Bacon, in the Research Laboratory, recently attained a pressure of less than 5×10^{-9} mm. in a gage connected to a large tube of well degassed charcoal immersed in liquid air. This, then, is a degree of vacuum which it would be desirable to reach in production of vacua with getters. The best pressure we have attained in the experiments reported below is about 10^{-7} mm., but it is hoped that further work will so improve getter technique that this pressure may be materially reduced.

Method.—A 40-watt lamp-bulb containing the getter (see Fig. 1) was connected to an ionization gage of the type developed by Dushman and Found.¹ There was a short side arm at C by which the set was sealed to the exhaust system. The anode and leads of the gage were of molybdenum and the filaments of tungsten so that the whole could be thoroughly degassed by current, electron bombardment and high frequency induction heating. The bulb and gage were usually of soft glass.

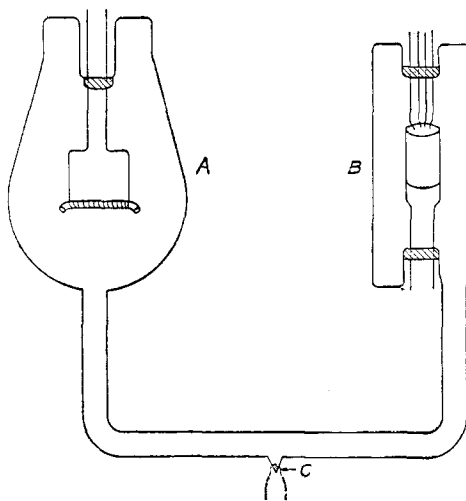


Fig. 1.—A, Bulb containing getter; B, ionization gage; C, point of exhaust and seal-off.

After exhaust and "bake-out" for an hour at 360° , the gage was thoroughly degassed and then enough getter vaporized and condensed on the walls of the lamp bulb to form a mirror over most of the inside surface. During the vaporization of the getter a considerable amount of gas which had been contained in it was evolved. This was reabsorbed in large part by the getter during its deposition, but an appreciable amount remained free. Therefore liquid air was applied to a trap below the set to catch any mercury vapor diffusing from the McLeod gage and traps and, after a short interval of pumping to remove gases that had not been absorbed by the getter during deposition, the set was sealed off. Pressures were usually read immediately after seal-off and at suitable intervals thereafter.

¹ Dushman and Found, *Phys. Rev.*, 17, 7 (1921); 23, 734 (1924).

The ideal method of laying down a getter of this type would be to vaporize and deposit it in a perfect vacuum so that immediately after deposition it is completely gas free. Gases appearing later in the bulb would then find a clean reagent in the best condition for reacting with or absorbing them. In practice there are several different methods of obtaining deposited getters. First is the chemical pellet, that is, a mixture of dry reagents which when heated to a high temperature will react to produce the desired metal, which is volatile at the temperature of the reaction. Thus sodium is produced from a mixture of $\text{NaCl} + \text{Ca}$. While this method has been much used, it has the objection that it is difficult, always,

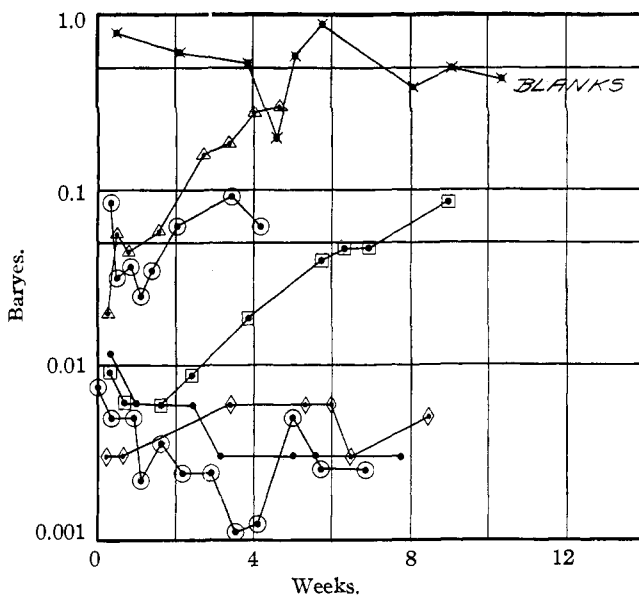


Fig. 2.—Magnesium: effect of increasingly thorough degassing.

to remove the gas completely from any finely powdered material. It is bound to act like a getter of the first class mentioned at the beginning of the paper, retaining in considerable quantities adsorbed gas which will be freed when the mixture is heated. Moreover, if the reaction is exothermic, the temperature of the powdered mix rises suddenly once the reaction is started, and the metal is thrown out almost explosively. It would appear inevitable that in such a case a considerable quantity of dust from the mixture should be carried out with the metal vapor and be deposited on the walls of the bulb, where it might easily adsorb gas and later free it. The gas thrown out at the moment of reaction often gives a pressure of 25–50 baryes or more. It follows that the metal would deposit in the bulb in the presence of gas and possibly be contaminated with a considerable amount

of powdery solids. The reason for the widespread use of such pellets is, of course, the convenience of handling the mixtures as compared with that of introducing the inflammable, low-melting metal as such.

A second method, used in depositing such metals as calcium and magnesium which can be produced in the form of large diameter wire, or rods, is to mount a short piece inside a spiral filament. When a current is passed through the filament, the metal inside is vaporized. The objection to this method is that the wire as manufactured at present always contains a large amount of gas and it appears to be impossible to preheat it evenly with the spiral so as to degas completely before vaporizing.

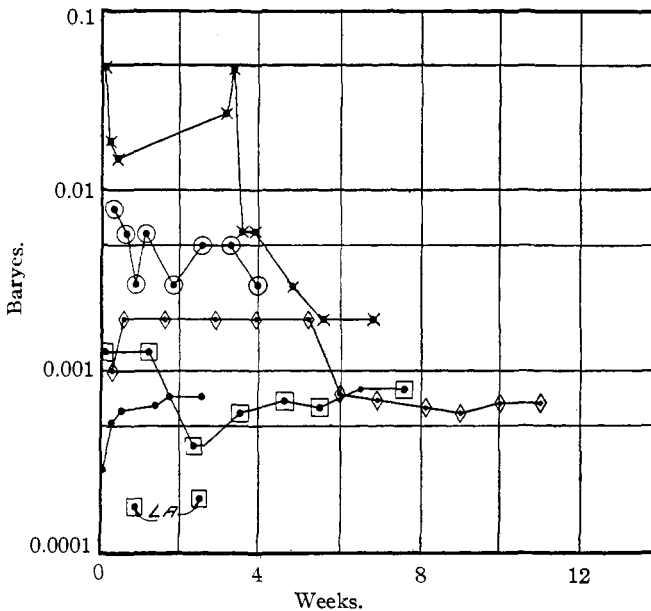


Fig. 3.—Calcium: effect of degassing.

A third method is to enclose the getter either pure or as an alloy in an envelope of a highly refractory metal such as molybdenum which will not give off any appreciable amount of gas and which can be heated by high frequency induction to a low temperature at first for degassing and later to a higher temperature for vaporizing the getter. This gives better results than the other two methods, as is shown in the curves.

Figure 2 shows the very marked effect of degassing magnesium in a spiral and in an envelope. The upper curve gives the average of two tubes run without getter, the two next lower curves are of magnesium flashed from spirals without a previous degassing, the next is of magnesium degassed by running the spiral at a bright red temperature for about fifteen minutes before the temperature was raised to vaporize the metal. The

fifth and sixth curves are of magnesium degassed in molybdenum envelopes at a dull red for about fifteen minutes. The seventh curve is of magnesium in a molybdenum envelope, very well degassed and slowly vaporized in a system which pumped off the gas very rapidly.

Figure 3 shows the action of calcium. The two upper curves are of metal degassed for fifteen minutes in spirals, the three lower of metal much more carefully degassed. Two of these were calcium heated in

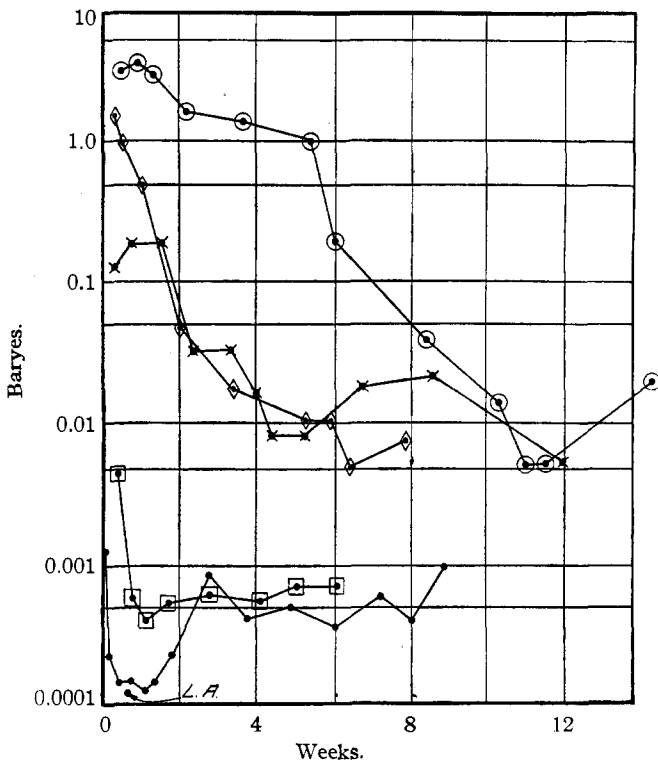


Fig. 4.—Sodium: effect of degassing. Note slow rate of clean-up by gassy material.

spirals just to the evaporation point so that deposits were formed in two hours. The third was calcium which had been distilled twice in vacuum in a side tube before being distilled into the bulb. Barium gave very similar curves. It was used in the form of the barium-aluminum alloy (50-50) from which the barium metal was vaporized by high frequency induction heating.

Sodium (Fig. 4) shows some interesting characteristics. For the three upper curves, chemical pellets were used. The clean-up was very slow and not very complete, though the pellets were always preheated to degas

them as well as possible. But when sodium was deposited in the bulb by submerging the latter in a bath of molten sodium nitrate and passing sodium into the bulb by electrolysis, clean-up occurred quickly and very much more completely, as is shown in the two lower curves.

Phosphorus (Fig. 5) was deposited by coating tungsten filaments with a suspension of red phosphorus and flashing them to a high temperature. This vaporizes the phosphorus very quickly, which seems to be essential to its effectiveness as a getter. There has been considerable work² done on the action of phosphorus as a getter, but our curves show this material to be only fair. Possibly larger amounts would yield better results. Our bulbs were tinged yellow by the deposit but were completely transparent.

We are unable to account with certainty for the irregularity of the curves shown. During our earlier tests we had some difficulty with readings obtained with the ionization gages when the pressures were low, in that they occasionally became negative. We found that when this occurred, the gage was generating oscillations of audible frequency so that a telephone inserted in the plate circuit emitted noises. We eliminated this by lowering the potential of the plate, but it appears possible that there might be

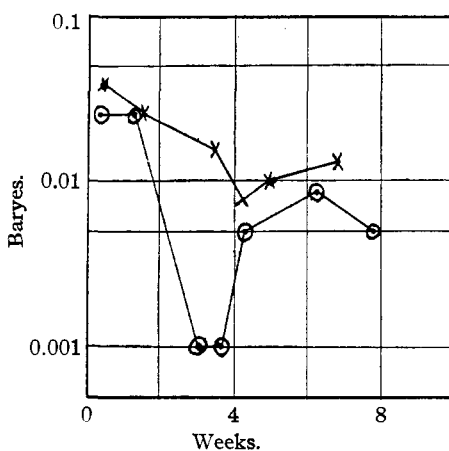


Fig. 5.—Phosphorus.

higher frequency oscillations present at times, which would affect, somewhat, the pressure readings. We have not verified this. We thought temperature might have some influence, but tests on all the getters made after they had cleaned up most of the gas in the tube showed that the pressure was not affected by change of temperature from 0 to 90°. We are now testing other forms of ionization gages designed to operate without oscillating.

The above results point so conclusively to the fact that getters are good getters only when they are deposited quite gas-free that we are making experiments on vacuum fusion of them before they are used in vacuum tubes. The results will be reported later. That it is impossible to degas getters properly in a spiral and probably impossible without fusion, but that an effective getter can absorb considerable quantities of gas and eventually produce a fair vacuum, is shown by Fig. 6. This is the record of calcium held in a tungsten spiral which had been degassed for three

² N. R. Campbell, *Phil. Mag.*, 41, 685 (1921); 43, 914 (1922).

hours by running the spiral at red heat. Before the getter was deposited, the tube was sealed off. The bulb containing the getter was then immersed in liquid air (point L.A. Fig. 6) and the getter deposited by heating the spiral. It had been thought that by this procedure the depositing metal might carry down and hold all gases evolved from the hot calcium rod, but the gas pressure rose to some tenths of a barye during deposition (see point B). After complete deposition, the bulb was removed from the liquid air.

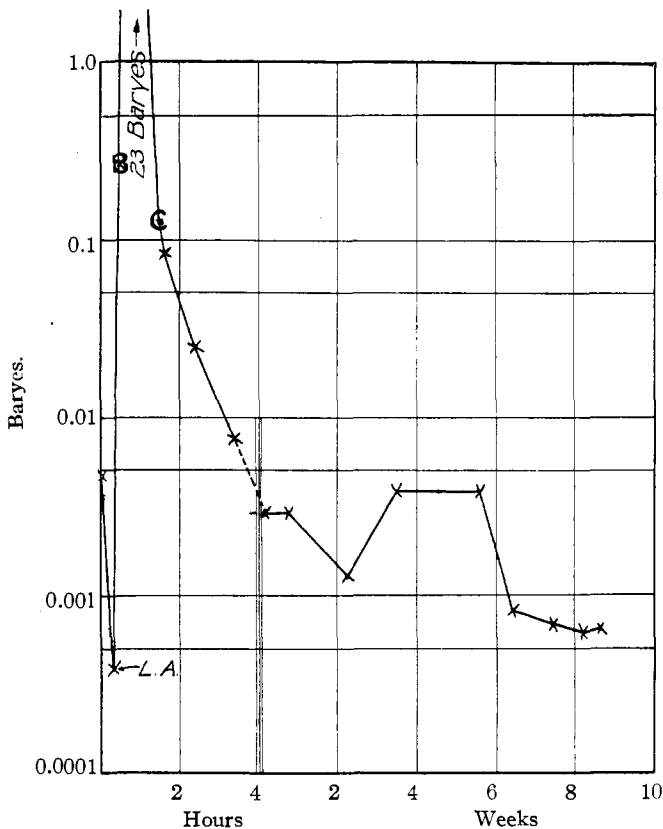


Fig. 6.—Calcium vaporized and deposited after seal-off.

The pressure promptly rose to twenty-three baryes. But the getter was active and absorbed this gas rapidly so that in half an hour the pressure had fallen to a small fraction of a barye (point C) and in the course of some weeks had gone below a thousandth of a bar, *i. e.*, less than 10^{-6} mm.

It seems probable that some of these getters may have specific reactions with certain gases. The above experiments were all made with residual gas, that is, chiefly gas freed from the getter itself plus the possible traces escaping from the walls and metals of the getter bulb and gage. We have

under way, however, a series of experiments in which getters are dosed with pure gases such as hydrogen, water vapor, etc. These will be reported later also.

The curves obtained from getters in vacuum suggest that the final clean-up of traces of gas in vacuum tubes is due to voltage discharge, *i. e.*, voltage clean-up. We are undertaking some experiments of this effect both without getters and in their presence.

Summary

Measurements made on a series of chemically active getters show that differences in the previous treatment of the getters to remove gas are of far greater importance than differences between the getters themselves in production of high vacuum. Poorly degassed getters absorb residual gas slowly and reach equilibrium at higher pressures than those attained by more gas-free material. These pressures do not depend on temperatures between 0 and 90°.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF UNION COLLEGE]

THE THERMAL DISSOCIATION OF CALCIUM HYDRIDE

BY CHARLES B. HURD AND KENNETH E. WALKER

RECEIVED JANUARY 29, 1931

PUBLISHED MAY 6, 1931

Introduction

The thermal dissociation of the hydrides of the alkali metals and of the alkaline earth metals has been the subject of considerable study. Various methods have been used, the general procedure being to heat the solid hydride to a definite temperature and measure the equilibrium pressure of the gaseous hydrogen.

In the earlier studies little or no attempt was made to shield the glass or quartz system from possible chemical action with the metal hydrides or their dissociation products. This action is serious at the high temperature at which calcium hydride undergoes appreciable dissociation. Recent investigators have attempted to shield the quartz tubing from chemical action. In the present paper, the writers describe an apparatus which is the result of experiments over a period of about four years. The apparatus is the only one which has been found to work satisfactorily with calcium hydride. It will, we believe, give satisfactory results in any of the higher temperature hydride investigations. Results are given here for the dissociation of calcium hydride. The dissociation of barium hydride is being studied and it is hoped that work on strontium hydride may be started soon.