9. In no case do the observed changes coincide with those reported by Harris and Hopkins during the concentration of illinium.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THREE LABORATORY DEVICES: A VACUUM STIRRER, A PRESSURE ALTERNATOR AND A GAGE FOR MEASURING LOW PRESSURES OF PERMANENT GASES IN CONDENSABLE VAPORS[1]

BY ROGER K. TAYLOR

RECEIVED JULY 30, 1928 PUBLISHED NOVEMBER 6, 1928

An apparatus devised by the author for the stirring of liquids *in vacuo* has been of service in several researches at this University, and may be useful elsewhere. The purpose for which it has been used is the freeing of liquids from dissolved gases; periodic removal of the vapor above the liquid is ineffective, unless the liquid is stirred.

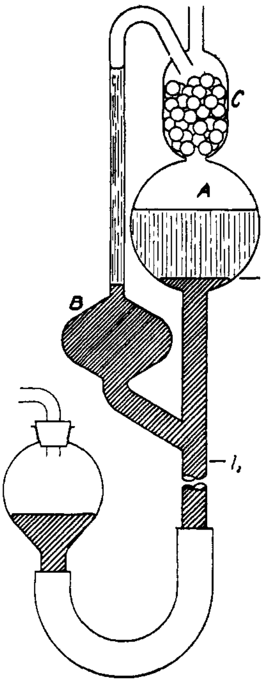

Fig. 1.

One form of the device is shown in Fig. 1. The liquid, resting above mercury, is contained in bulb A; above it is C, a tower of beads. By a method to be described, the level of the mercury is alternated between l_1 and l_2. The cycle of operation is this: when the mercury falls to l_2, it drains from the small bulb B, which fills with the liquid from A. Then, as the mercury rises again to l_1, it refills B, and the liquid contained is forced into C, where it spreads over and trickles through the beads and returns to A. In this way the establishment of equilibrium of dissolved gas between the liquid and vapor phases, which ordinarily is a very slow process, is rapidly effected. This results both from the large surface offered by the beads and the fact that the liquid is constantly being withdrawn from the bottom and returned to the top of A. Periodic removal of the vapor in A and C soon leaves the liquid practically free of dissolved gases.

In one case, where air was to be removed from an alcoholic soap solution, it was feared that the beads would occasion troublesome foaming. The difficulty was avoided by replacing C with a helix of tubing wide enough to permit the solution to flow along its bottom instead of filling it completely.

---

[1] In memory of Ira Remsen.

A pressure alternator, designed to operate the stirrer just described, is shown in Fig. 2. By its use atmospheric pressure, and a pressure less than atmospheric by any desired amount, may be alternately applied, the operation being automatic.

A water pump or other vacuum pump is attached to C; the apparatus in which the pressure is to change is connected to B, and A is open to the air. As the pump operates, the pressure in C and B decreases, and the mercury in A rises until it reaches the position a. Thus the pressure in B, originally atmospheric, falls by an amount represented by the vertical distance from a to the mercury level in A. Further pressure decrease causes the mercury to siphon rapidly into B, shutting off communication between B and the pump and leaving B open, through A, to the atmosphere. The distance h_2 is made greater than h_1, so that further decrease in pressure in C must take place before the mercury rises to b; that is, time is allowed for the pressure in the apparatus connected to B to rise fully to atmospheric. When the mercury finally carries over from B into C, it returns quickly through the bottom of C to A, stopping the admission of air, and the cycle starts afresh.

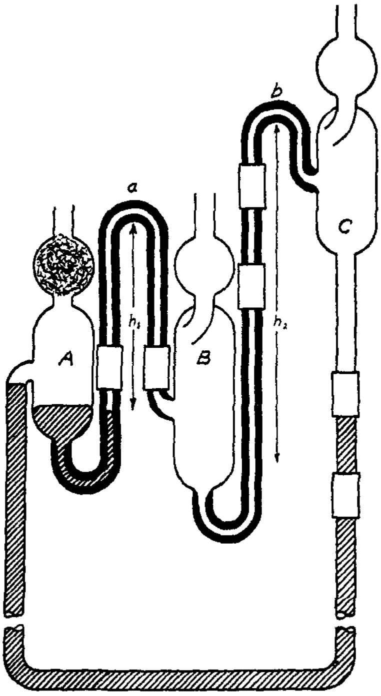

Fig. 2.

The amount by which the pressure changes is, of course, determined by the distance h_1. The time required for the pressure to decrease by this amount depends on the volume of the apparatus attached to B, and on the rate at which the pump is operating. The time that B remains open to the atmosphere depends on the rate of operation of the pump and on the difference between h_1 and h_2. All of these factors may be readily adjusted.

An apparatus of this sort may be used for various purposes. As an actuating mechanism for the stirrer previously described, B is simply attached to the leveling bulb, which is so placed that atmospheric pressure within it holds the mercury at l_1, and h_1 is made equal to the difference between l_1 and l_2.

This pressure alternator was designed without a search of the literature for similar devices; the fundamental principle, however, is not new. Maass[2]

---

[2] Maass, THIS JOURNAL, **41**, 53 (1919).

describes something of the sort and mentions a number of possible applications; and recently Weaver and Shepherd[3] depict a modification as the actuating mechanism for an automatic high-vacuum pump. The present device, however, contains one feature absent from Maass' apparatus, namely, the arrangement to cut off communication with the pump while the pressure in B is rising to atmospheric; and as compared with the corresponding part of Weaver and Shepherd's ingenious apparatus, this is of somewhat simpler construction.

A McLeod gage, slightly modified, may be employed to detect the presence and determine the partial pressure of small amounts of permanent gases in a condensable vapor, for instance, traces of air in water vapor.

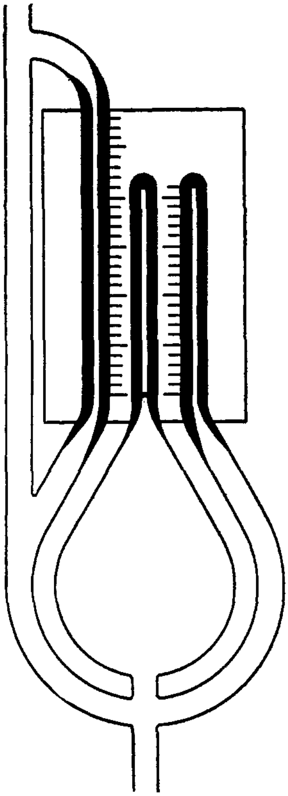

Fig. 3.

The arrangement is shown in Fig. 3. If the volume of the bulb and capillary is A, and the volume of the capillary above the mark is a, then when a permanent gas is present alone at low pressure and the mercury is brought to the mark on the central capillary, the pressure is given by the reading on the scale of the open capillary multiplied by a/A. It may also be determined by reading the position of the mercury on the scale of the closed capillary: if r is the latter reading, b the volume of the right-hand capillary above the mercury when the reading is taken, and B that of the entire side tube, then $P = ar/[A - (Ba/b)]$. As B is small in relation to A, the ratio a/b does not need to be known accurately; since the capillaries are all supposedly of the same bore, a comparison of the corresponding lengths on the scale is close enough. When r is small, the simpler expression $P = ar/(A - B)$ is approximately true.

If now in addition to the permanent gas there is present a condensable vapor, in such amount that condensation takes place in the closed capillaries when the mercury is brought to the mark, *it contributes the same pressure*, namely, the vapor pressure of the liquid in question at the temperature of the gage, *in both capillaries;* accordingly, the partial pressure of the permanent gas is determined by

---

[3] Weaver and Shepherd, THIS JOURNAL, 50, 1829 (1928).

taking the same readings on the right-hand capillary and making the same calculations as when the condensable vapor is absent.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC CARBONATES[1]

BY FREDERICK K. BELL[2]

RECEIVED AUGUST 1, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

There are few instances in which an acid, the metallic salts of which are available in large crystals, also yields a series of well-defined organic salts or esters. These conditions are fulfilled, at least partially, by carbonic acid. A number of inorganic carbonates are found in nature in crystals of sufficient size to permit cutting, polishing, etc., for optical examination. Similarly a considerable number of esters of carbonic acid have been prepared and are described in the literature.

In a rather recent paper Schaefer and his co-workers[3] have measured the infra-red absorption spectra between 1.0 and 17.0μ of six inorganic carbonates: $MgCO_3$, $CaCO_3$, $CaMg(CO_3)_2$, $FeCO_3$, $BaCO_3$ and $PbCO_3$. In view of this work it seemed to the present author that a similar examination of a series of organic carbonates would yield results of particular significance and interest. The absorption spectra of such a series of compounds might be expected to offer also further information concerning the $C{=}O$ bond, which is surely among the most common linkages of organic compounds. The organic carbonates also represent one of the numerous series of compounds of organic chemistry which are especially suited for spectroscopic study of a systematic nature, one part of the molecule remaining unchanged as different hydrocarbon residues are introduced.

It is with these ideas in mind that the infra-red absorption spectra of seven organic carbonates have been examined between 1.0 and 12.0μ. The results of these examinations are presented and discussed in this paper.

Experimental

A detailed description of the experimental method employed in the present work has been given elsewhere.[4] The preparation of the absorption cells, however, has been altered. All cells were prepared from polished plates of rock salt.

---

[1] In memory of Ira Remsen.

[2] Grafflin Scholar.

[3] Schaefer, Bormuth and Matossi, *Z. Physik*, **39**, 648 (1926).

[4] F. K. Bell, THIS JOURNAL, **47**, 2194 (1925).