

F. Summary.

1. The interaction equilibrium between mixed chloride solutions of potassium and strontium and dilute liquid amalgams has been studied, at various amalgam concentrations, in the following cases:

(a) Solutions of equivalent salt ratio, ranging in total concentration from 0.05 *N* to 3.0 *N*, at 25°, and with a total concentration ranging from 0.05 *N* to 0.8 *N*, at 40°.

(b) Solutions of varying salt ratio, at total concentrations ranging from 0.2 *N* to 0.8 *N*, at 25°.

2. The value of the "equilibrium expression" C_c increases directly with the concentration of the amalgam in all cases for amalgams containing up to about 0.3 milli-equivalent of metal per 10 g. of mercury.

3. With the assumption as a starting point that in solutions mixed in equivalent proportions, at a total concentration of 0.05 *N*, the simple K^+ -ion and Sr^{++} -ion fractions are 0.6666 and 0.3333, ion-fraction calculations are offered for solutions containing the salts in equivalent proportions and also in varying proportions. The ion fractions are not directly proportional to the mol fractions of the salts.

4. The effect of temperature on the interaction equilibrium between 0.05 *N*, 0.1 *N*, 0.2 *N*, 0.4 *N*, and 0.8 *N* solutions and amalgams of varying concentration has been studied between 15° and 40°, and the heats of the different interactions have been calculated by means of the van't Hoff equation. This interaction heat increases gradually with decreasing total salt concentration.

5. The mass-action expression $[Me]/[MeHg_x] = K_{Me}$ has been shown to hold for potassium and strontium hydrargyrides in the presence of one another at total concentrations up to about 2 milli-equivalents per 100 g. of mercury.

6. The results of the investigation, in so far as the salt mixtures are concerned, have been shown to be in harmony with A. Werner's conceptions concerning the formation and dissociation of higher-order compounds.

URBANA, ILL.

AN ACCURATE METHOD FOR MEASURING THE DENSITY OF GASES.

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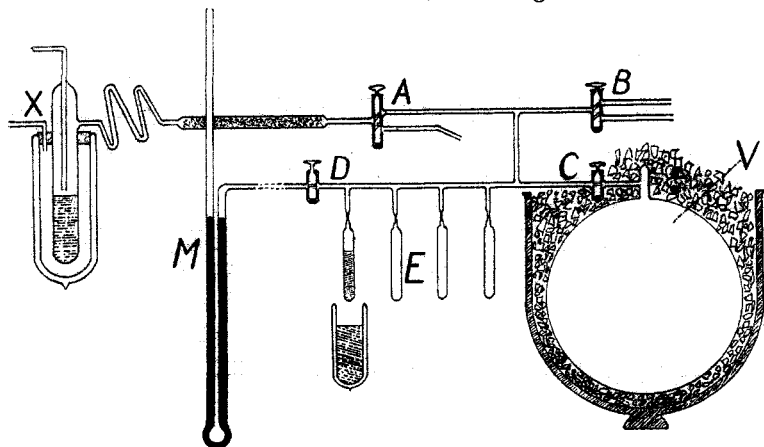
In the course of another research the densities of certain gases, which had not been established with adequate accuracy, were required; consequently they were redetermined by a method which we consider sufficiently useful and interesting to justify its publication.

The method is applicable to gases which can be condensed by liquid air or some other freezing agent. A known volume of the gas at known

pressure and temperature is liquified in a small bulb attached to the containing vessel; the bulb is sealed off and the liquified gas weighed at room temperature. This procedure is advantageous in enabling one to weigh a large quantity of gas on a small sensitive balance, and to weigh it in a vessel whose weight is of the same order as that of the gas itself. Once the apparatus employed has been calibrated, density measurements can be made rapidly.

Reference should be made at this point to a somewhat similar method by Jacquered and Pintza,¹ which has been brought to the authors' attention. There the gases, sulfur dioxide and oxygen were obtained from vessels containing these, respectively, as the liquid and as a constituent of potassium permanganate. The quantity of substance was determined by first weighing the containers and the gas was then evolved into the known volume. It may be pointed out that this procedure would not be feasible with many gases; for instance, liquid acetylene at ordinary temperatures can only be weighed in a sealed vessel, as no tap would withstand the high pressure without leaking.

The details of manipulation are best brought out in conjunction with the accompanying diagram, which is drawn to scale with the exception of the manometer. V designates a large flask, the volume of which was carefully determined as follows: the flask was dried by keeping it for some time under a vacuum of 0.001 mm., first weighed full of air, and then



when filled with distilled water. Correcting for the weight of the air and the density of the water at the temperature of measurement, the volume of the flask at 0° was calculated to be 2240.9 cc. The manometer M was made by a method described by McIntosh and Maass² using specially purified mercury. The manometer scale, which was etched on a mirror,

¹ *Compt. rend.*, **139**, 129 (1904).

² *Trans. Roy. Soc. Can.*, **8**, 65 (1914).

was calibrated by means of a comparometer and could be read to 0.1 mm.; by means of plumb lines it was ascertained that the manometer was perfectly upright. At the end of the determinations the volume of the tubing between the taps A, B, C and D was determined accurately by weighing with and without water; it was 22.4 cc. The manometer also was taken apart and the capacity of its tubing determined so that the volume above the mercury at any pressure could be calculated. At E were 4 tubes, about 6 cm. in length, of such a size that the condensed liquid would just about fill them, and capable of withstanding a pressure of 100 atmospheres. All joints were of glass and all taps mercury sealed. The substance whose vapor density was to be determined was distilled into X and the delivery tube sealed off. The air in the tubing from it to the tap was eliminated by opening the two-way tap A to the atmosphere and boiling the liquid in X for some time. The large flask V, with all tubing and bulbs at E, was evacuated to 0.0001 mm. pressure by means of an automatic mercury pump connected to two-way tap B; the pump was of an especially efficient type and would accomplish this in a very short time. The tap B was then shut off and the tap at A opened, connecting the flask to the tube X, in which the liquid was boiled till the flask V was filled with gas to about atmospheric pressure, when the tap A was closed. The system was now allowed to stand for some time till the gas in the flask V, previously surrounded by cracked ice, had become of uniform temperature; the manometer was read every 5 minutes until there was no change in pressure over a period of 15 minutes. The tap at C was then closed and the tubing and bulbs thoroughly exhausted. There was then in V a known volume of gas under known pressure and temperature. When the tubing was completely evacuated, the tap at C was opened and the gas condensed in one of the bulbs at E by means of liquid air or solid carbon dioxide. This bulb was then sealed off and the pressure of the gas remaining in the system read after equilibrium was again established. The bulb with its contents was allowed to warm up to room temperature and weighed very carefully; then immersed in liquid air, the tip cut off, the contents allowed to evaporate and the dried bulb together with its tip re-weighed, correction being made for the weight of the air. Thus the weight of the gas condensed was determined accurately. The temperature of the room at the time of experiment was taken in order to correct for mercury expansion in the manometer and for the temperature of the gas remaining in the tubing. The following formula gives D , the weight of one liter of the gas:

$$D = \frac{76 \cdot W \cdot 1000}{(P - p)V - 273 pv/273 + t}$$

W = the weight of the condensed gas.

P = the initial pressure of the gas in the large flask, the height of the mercury column being corrected to 0° .

p = the pressure remaining in the system after condensation of the gas.

V = the volume of the large flask (2240.9 cc.).

v = the volume of the system from the taps at B and C to the tap at A and the level of the mercury in the manometer (24.1 cc.).

t = the temperature of tubing etc. outside of the ice bath.

A short discussion of the above formula will bring out the accuracy attainable by this method. When experimental values are substituted $(P - p)V$ is 10,000 times as large as $pv273/273 + t$. Therefore as large an error as 10% in the latter will cause an error of only one part in 100,000 in D , and on this fact depends the ease of manipulation; for the volume v , of tubing and bulbs, need be known only approximately, and the changes in this volume, due to the sealing on of fresh bulbs for further determinations, may be neglected. Furthermore, the temperature of the apparatus outside of V and M need not be kept constant; in other words no appreciable error is caused by the so-called dead space. In the particular measurements described here, W and V were measured to better than one part in 10,000 but a probable error of 0.3 mm. was made in the measurement of $P - p$ and hence the results quoted below are only correct to one part in 2000. If a cathetometer were used for measuring the height of the mercury column in the manometer, the probable error of the method would be cut down to less than one part in 10,000.

As the original object of this research was the rapid determination of the densities of certain gases which were being used, none of the extraordinary precautions were taken in their preparation which are usual in atomic weight work. Acetylene was prepared by dropping water on calcium carbide covered with alcohol. It was passed through two wash-bottles containing chromic acid and potassium hydroxide respectively, through a tube of phosphorus pentoxide and condensed in a large test-tube by means of carbon dioxide-ether mixture under vacuum. The chromic acid removed the phosphine, which is invariably present, the potassium hydroxide removed the carbon dioxide, and the phosphorus pentoxide, the water. The condensation by solid carbon dioxide under vacuum eliminated the nitrogen and carbon monoxide, which are sometimes present in samples made by this method. The substance thus collected was redistilled twice through wash-bottles containing fresh reagents, through a phosphorus pentoxide tube and into the tube X, only the middle portions being taken.

Methyl ether was prepared by dropping methyl alcohol on conc. sulfuric acid, passing the gas thus evolved through water into conc. sulfuric acid where it was absorbed. The gas was regenerated from this by drop-

ing water on the acid solution, and the product thus prepared condensed by means of carbon dioxide-ether mixture, redistilled twice through phosphorus pentoxide, taking only the middle portions.

Hydrobromic acid was prepared by dropping bromine on phosphorus in water and passing the gas thus evolved through wash-bottles containing phosphorus and water, and through phosphorus pentoxide tubes. It was condensed by means of carbon dioxide-ether mixture, and was redistilled twice, using only the middle portions.

In the density measurement of the hydrobromic acid, in order to avoid contamination of the mercury in the manometer and the consequent introduction of inaccuracy into the pressure readings the following procedure was adopted: The system was evacuated as usual, when the tap D was turned off, the tap at A opened to the bromide until the pressure in V became somewhat greater than atmospheric, by the warming of the liquid bromide in X. The tap at B was then opened slowly to the atmosphere; when the acid had issued for a short time from B, A was closed and the pressure of gas allowed to reach equilibrium. The gas in the system was now at atmospheric pressure which was read from a barometer whose length had been previously calibrated with respect to the manometer described above. B and C were then closed and the tubing between the four taps evacuated by opening the two-way tap at B, this time to the pump. The gas was then condensed as above in one of the small bulbs at E and the bulb sealed off. Then only was the tap D opened to the manometer and the pressure quickly read, and as soon as possible the tubing evacuated. Thus there was but a small pressure of the bromide in contact with the mercury for a very short time.

That the error due to actual measurements is of the order calculated is brought out by the following values of the weight of a liter of gas each determined on a separate occasion: for acetylene, 1.1698 and 1.1692; for methyl ether, 2.1104 and 2.1101; for hydrobromic acid, 3.6381, 3.6392 and 3.6410.

The following table gives the average values of the densities of acetylene, methyl ether and hydrobromic acid, when prepared and purified in the manner described above. The second column gives the values as determined by others.

Acetylene.....	1.1695	
Methyl ether.....	2.1103	2.1096 ¹
Hydrobromic acid.....	3.6397	3.6438 ²

Considerable importance is attached of late to the accurate determination of the density of gases, and the advantages of the method described above as compared to the ordinary globe method have been pointed out.

¹ G. Baume, *J. chim. phys.*, 6, 1 (1908).

² Murray, *Compt. rend.*, 164, 182 (1917).

The probable error in the density determinations is less than 0.05%; with the aid of a cathetometer it can be reduced to 0.01%.

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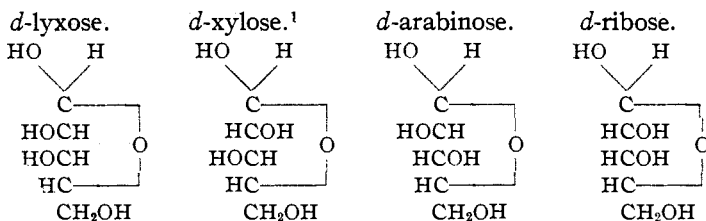
[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF THREE ALDOPENTOSEs.

By EDGAR T. WHERRY.

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The aldopentoses, of which the general formula is $C_5H_{10}O_5$, have each a *d*- and an *l*-form, and each of these in turn exists in an α - and a β -modification, as brought out by the following formulas:



The arrangement used is the conventional method of representing the *d*-forms; the *l*-forms would have the positions of all the groups along either side of the carbon chain reversed. The lactone structure is adopted because it is the only one which makes it possible to bring out the difference between the α - and β -modifications. These differ in the relative positions of the uppermost H and OH groups, although it has not yet been ascertained which position corresponds to each.

The crystallographic and optical properties of *d*- and *l*-forms are necessarily the same, except that the positions of (*hkl*) faces would be toward the right and toward the left of the crystal in the two cases. It would seem probable that the α - and β -isomerism has a more fundamental effect on the crystallization, and the following studies were undertaken to ascertain the extent of this effect, as well as to compare the properties of as many of the members of the group as possible. Three were obtainable in crystals of sufficient size for measurement of their angles, and one additional isomer in a form suitable for optical examination under the microscope.

The identities of the isomers measured were established by the following specific rotations $[\alpha]_D^{20}$:

¹ In the case of xylose, Fischer regarded the formula given as belonging to the *l*-form, but Rosanoff (*THIS JOURNAL*, 28, 114 (1906)) pointed out that this conclusion was based on erroneous assumptions, and Hudson (*Ibid.*, 31, 70 (1909)) has fully confirmed this view.