

results from the dissociation of the complex ion. The extent of the dissociation of these complex ions is not accurately known although Latimer¹³ estimates a dissociation constant of around 10^{-10} for the ferric oxalate complex. Considering this and also the fact that silver and calcium ions will form slight oxalate precipitates with both of the complex ions, it is probable that the oxalate ion concentration in a solution of 0.01 *M* complex ion is of the order of magnitude of 10^{-4} *M*. Consequently an interchange reaction that is rapid under the conditions of the present investigation and a stability of the optically active complex of the extent reported by Thomas and Wahl are not entirely incompatible.

The present work, of course, sets only a lower limit to the speed of interchange. The speed could be very much faster and still be in accord with the interchange results. In this case the possibility of comparatively stable optical isomers could probably be ruled out. Attempts have been made to study the interchange reaction under conditions more nearly comparable to the conditions under which the optical activity has been studied. This involves concentrating the radio-carbon in much smaller amounts of potassium oxalate and then studying the interchange

(13) "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 212.

with only a minute amount of added oxalate. So far these attempts have not been successful. Thus the present work, although it makes the possibility of a stable optically active complex quite unlikely, does not suffice to eliminate the possibility of an optically active ion with a short life in aqueous solution.

Summary

The interchange of oxalates between uncombined oxalate ions and complex oxalate ions of aluminum, ferric and cobaltic have been studied using radio-carbon. Under the given experimental conditions the ferric and aluminum trioxalate complexes show a rapid interchange. The cobaltic complex, like the previously studied chromic complex, shows no interchange. These results are in accord with the assumption that the bonds in the chromic and cobaltic complexes are probably primarily covalent whereas those in the ferric and aluminum complexes are ionic.

The possibility of the resolution of the ferric and aluminum trioxalate salts into their optically active isomers has been discussed in the light of the present work and it is concluded that a stable optically active ion is unlikely. However, the present work does not exclude the possibility of a short-lived optically active ion.

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[CONTRIBUTION FROM THE BAILEY CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

A Precision Method for the Determination of Molecular Weights

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We have developed a method and apparatus¹ for the very rapid and yet precise determination of the molecular weights of gases and vapors. By means of this instrument the molecular weights may be read directly without any calculations, and on pure substances results reproducible to 0.01 of a unit of molecular weight may be obtained.

The only measurement involved is the determination of the flotation effect of the gas or vapor on a sealed body of known volume, at a temperature automatically adjusted to the momentarily existing atmospheric pressure in such a manner that a constant gaseous density is maintained.

(1) U. S. Letters Patent No. 2,023,164.

Apparatus

We have found a special chainomatic balance of the Westphal type very satisfactory for measuring the flotation. The balance is easily sensitive to 0.02 mg. and is graduated in units equivalent to 2 mg. A working temperature of around 200° was chosen simply because this temperature is above the boiling point of most liquids. The volume of the float is made such that an ideal gas having a molecular weight of 1.00 would exert, at a pressure of around 740 mm. and a temperature of about 200°, a flotation of 2.00 mg. on the sealed bulb. Calculations indicate that the bulb should have a volume of about 80 cc. It is evident that 80 cc. of an ideal gas having a molecular weight

of 1.00 will have a mass of 2.00 mg. under a given pressure only at one certain temperature.

The heart of the apparatus is a device which automatically adjusts the temperature of the gas or vapor under observation to that single temperature at which, under the existing atmospheric pressure, the ideal gas with a molecular weight of 1.00 would exert a flotation of exactly 2.00 mg., and hence would give a reading of one unit of molecular weight on the balance. This means that the apparatus will maintain a given gaseous substance flowing through it at a constant density by matching each change in pressure with a compensating change in temperature. At this constant density the flotation of gaseous substances as read by the balance gives the molecular weight of the substance to 0.01 of a unit directly, without any other observation or calculation.

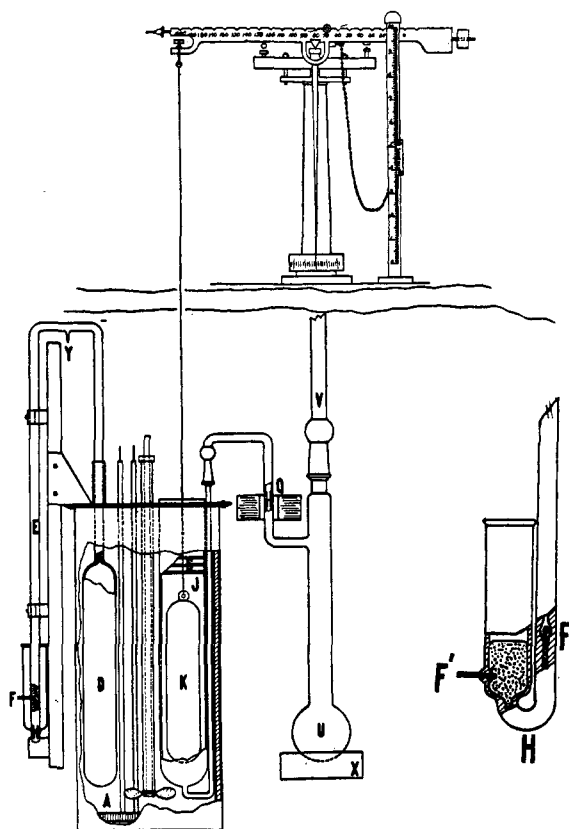


Fig. 1.

The proper adjustment of the temperature to the existing atmospheric pressure is secured and maintained by the action of a constant volume gas "thermometer" whose bulb (shown at D, Fig. 1) is immersed in the oil of the electrically heated oil-bath A, surrounding the vapor chamber

J which contains the float K. The bulb of the gas "thermometer" is large, and the gas in it is trapped there by mercury in a U-shaped bend H (Fig. 1 and inset) at the bottom of a fine capillary E; this bend is located on the outside of the oil-bath where it will be nearly at room temperature. A fine tungsten contact point F is sealed through the capillary tube E on the "thermometer" side of the mercury trap. The other side of the bend, open to the atmosphere, is made of much larger tubing and contains a sealed-in contact F', so that electrical connection may be established between these points through the mercury in the trap. The constant volume gas thermometer D contains an amount of gas such that at any given atmospheric pressure, the temperature of the oil-bath A will be controlled to the proper value previously determined by the T/P ratio required by the given float volume.

Calculations show that, in order to make possible the measurement of the molecular weight of a substance having a molecular weight of 100 to 0.01 of a unit, the regulator would have to be set at a pressure known to 0.03 mm., and a corresponding temperature known and controlled to 0.02° . Ordinary barometers do not give sufficiently accurate data as to the atmospheric pressure. In addition, even carefully certified mercury thermometers cannot be relied upon to give temperature measurements of sufficient accuracy at 200° .

Practical experience soon showed that accurate barometry was so slow and entailed such involved calculations that even on days when, for most purposes, the barometer would be considered steady, the atmospheric pressure changed so rapidly that before it could be measured and the bath A brought to the corresponding temperature, the pressure would have altered enough to demand a new set of measurements.

In order to overcome these difficulties, we have developed special apparatus by means of which we can maintain indefinitely and measure very accurately a constant air pressure in what we call an "artificial atmosphere."² Knowing this pressure we can calculate the corresponding temperature required in the oil-bath, and then adjust the quantity of gas in the regulator until the bath is operating at an average temperature within $\pm 0.01^\circ$ of this value; the variation in temperature during the regulating cycle is about

(2) This apparatus will be described in a later paper.

0.04°. The regulator is then sealed off at the point Y, and its operation thoroughly checked over a range of pressures. The temperature measurements are made by means of certified platinum resistance thermometers and a calibrated and thermostated Mueller precision thermometer bridge.

The purpose of this careful adjustment of the regulator D is to control through relays the electric current which heats the bath A, so that the temperature of the latter may be kept at that at which the ideal gas of unit molecular weight may exert a buoyancy of exactly 2 mg. on the float K. It will be observed that after the regulator is set and sealed a very slight rise in temperature of the bath A will cause the mercury in the trap H to break contact with F. This break in contact opens a relay through a vacuum tube circuit, cuts out part of the heating current and allows the bath to cool slowly until contact between F and the mercury is reestablished. Continuous repetition of this cycle will keep the bath at constant temperature so long as the pressure on the outer mercury remains unchanged. If this pressure is increased, mercury will be pressed up against F until the temperature of the bath is raised to that at which the gas in D has a pressure equal to the enhanced atmospheric pressure.

The mass of the regulating gas is of course constant, and its volume, save for the slight expansion of D with rising temperature, is the same as that when the regulator was set, and hence the density of the regulating gas will be that which it had on setting. The ideal gas or any other gaseous fluid in the vapor chamber J will be exposed to the same conditions of temperature and pressure as the gas in the regulator D, and will have the same density as it would have had at the temperature and pressure at which the regulator was originally set. The slight expansion of the bulb of regulator D will cause it to maintain the bath at a slightly higher temperature than if the volume had been absolutely constant. This tends to decrease the density of the gas in J, hence its buoyancy on float K would be too small were it not for the fact that the float also expands with rising temperature. The float K and the bulb D are each made of the same Pyrex glass and so have the same coefficient of expansion; therefore, fortunately, the effects of their expansion or contraction with temperature changes cancel each other.

The diffusion of air into the vapor chamber would seriously interfere with the accurate determination of molecular weights. This is avoided by the use of a series of mica baffle plates, S, in the top of the vapor chamber. There are six of these discs supported about one centimeter apart on a glass framework. Each disc extends horizontally across the vapor chamber and fits the side walls of the latter fairly closely. At the center of each disc there is a small hole (2 mm. diam.) through which the platinum wire supporting the float K from the balance arm moves freely without contact.

The vapors of the substance under investigation pass through J and escape through these central openings around the wire and also through the small spaces between the edge of each disc and the adjacent chamber walls. These openings are sufficient to allow the pressure of the vapor to fall almost instantly to that of the atmosphere upon closure of the magnetic valve. Air does diffuse back slowly through these small openings, but since each baffle area contains successively smaller ratios of air to vapor, the space around the float is kept air free long enough to allow accurate determination of molecular weight.

Experimental Procedure

For a series of determinations of the molecular weight of a substance, pure, dry air, free from carbon dioxide, is passed through the vapor chamber J, and the balance is adjusted so that, when it is set for the apparent molecular weight of air at atmospheric pressure and 200° (28.95), the balance will be in equilibrium. If the substance under investigation is a liquid, some of it is placed in the distilling flask U. It is then boiled by means of the electric heater X, and the heating regulated so that the top of the hot vapor column stands 30 to 40 cm. above the side arm on the air-cooled reflux condenser V. The vapor will then flow by gravity through the vapor chamber J. Backward diffusion of air into the vapor chamber is retarded by the series of circular mica baffle plates.

When the air is displaced, the flow of the vapor is momentarily stopped by closing the magnetic valve Q, the balance is brought back into equilibrium by means of the rider and chain, and the molecular weight read. The valve Q is then opened, and a fresh lot of vapor from U flows in, after which another reading may be made. This will be a new determination of the molecular weight of a fresh sample of the substance. Each of these determinations takes only a few seconds; so a long series of readings can be made in a short time. If the substance in U is really pure, or if it consists of a constant boiling mixture, these determinations will check time after time and day after day very closely indeed, generally to 0.01 unit. If, on the other hand, the material in U is not a pure substance the molecular weights observed may cover a wide

range of values, depending upon the nature of the impurities present.

These facts may be illustrated by our experience with normal butyl alcohol. We have a group of six series of determinations made over a period of weeks on as many different specimens of the alcohol, purified at different times, and each of the separate seventy-one determinations gave 75.24 for the molecular weight. The original starting material was considered to be quite pure, but a series of thirty molecular weight determinations, made as described above, gave results beginning at 62.22, rising slowly to 74.98, then falling to 74.33 and rising again to 75.24. Here the molecular weight remained constant for six determinations before gradually dropping again to 74.90. These results indicate the presence of several impurities of lower boiling point and lower molecular weight than *n*-butyl alcohol, as well as one of higher boiling point and lower molecular weight.

If the substance under investigation is a gas it is passed in a slow stream through the vapor chamber, with appropriate provision for by-passing the gas while the magnetic valve Q is closed.

A series of ten determinations of the molecular weight of carbon dioxide gave four values of 44.00 and six of 44.01. These data were obtained from carbon dioxide snow made from the liquid. "Dry-Ice" tends to give slightly low results although usually close to 44.00. We think this is due to gases held in solid solution in the dry-ice.

A determination of the molecular weight of oxygen prepared by the electrolysis of water and purified by liquefaction, followed by partial evaporation, gave fifteen values all of 32.00.

Discussion

The molecular weights given by the apparatus are referred to an ideal perfect gas as a standard; hence, any discrepancy between the observed results and that calculated from the known composition of the substance and the well established atomic weights of its elements, will be due not to errors in the method but to the deviation of the gaseous substance from the gas laws under the working conditions of about 200° and one atmosphere pressure. Besides such obvious causes for deviation as association and dissociation, the gas may show a molecular weight higher than that calculated because of intermolecular attraction, or a lower one due to the effect of the volume of the molecules. Usually both effects are operating; so occasionally the molecular weight may check the calculated value very closely, as for example in the case of carbon dioxide or oxygen.

n-Butyl alcohol gave very reproducible molecular weights of 75.24; that calculated from the

atomic weights is 74.12. This is 1.12 units lower than the observed. We interpret this as a measure of the deviation of *n*-butyl alcohol vapor from an ideal gas, and think that it shows a relatively high degree of intermolecular attraction.³

We have not as yet worked with any substances showing a molecular weight distinctly lower than calculated, but hydrogen is a familiar example, its apparent molecular weight at 0° and 760 mm. being 2.013 as against 2.016 calculated.⁴

We are accumulating a large amount of data on the molecular weights of pure substances, some of which appear to be of considerable interest as tending to establish a relationship between the boiling points of isomers and the deviation of their vapors from the gas laws. Also, there are indications that the difference between the measured and the calculated molecular weights of the normal alcohols is related definitely to the number of carbon atoms per molecule of the alcohol.

The device also shows promising possibilities in the study of maximum and minimum boiling mixtures.

The results of investigations along these and other lines will be presented in additional papers to be submitted in the near future.

Summary

1. A new device for the precise, accurate, and rapid determination of the apparent molecular weights of gaseous substances at atmospheric pressure and 200° has been described. Values are reproducible to 0.01 unit. The accuracy is within ± 0.01 unit.
2. The method has been found to be a reliable guide in the purification of substances.
3. The differences between the calculated and observed molecular weights are considered as a measure of the deviations from the ideal gas laws.

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(3) The discrepancy is not due to the presence of an impurity in the samples. Boiling points were determined directly at pressures very close to 760 mm., using our artificial atmosphere, and the normal boiling point found to be 117.73°. Wojciechowski, *J. Research Natl. Bur. Standards*, **17**, 721-726 (1936), R. P. 940, found 117.726°.

(4) Calculated from data found on page 3, Volume 3, of the "International Critical Tables." Our present apparatus is not well adapted to the determination of molecular weights much lower than that of air, although the necessary modifications may be readily made.