9. The net heats of adsorption per cc. of liquid are very nearly identical for all the liquids studied.

10. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force—and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 cc. of liquid is adsorbed on 10 g. of charcoal.

11. The molar adsorbability, that is the number of cc. of gas adsorbed at a fixed gaseous pressure (20 mm.), is inversely proportional to the molecular volume of the liquid.

12. The molar adsorbability is inversely proportional to the net molar heat of adsorption. This, at first sight, surprising behavior is shown to follow necessarily from the previously mentioned regularities.

13. It is shown that all the above evidence indicates that the liquid films we have studied are all at least one and usually very many molecules thick, and this is confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal.

WASHINGTON, D. C.

NEW DETERMINATION OF THE ABSOLUTE VALUE OF THE RADIUM : URANIUM RATIO.[1]

By S. C. Lind and L. D. Roberts.

Received March 27, 1920.

1. Historical.

The value of the radium : uranium ratio, first determined by Rutherford and Boltwood[2] in uraninite from North Carolina, was originally reported as 7.4×10^{-7}. The following year it was found[3] that a serious error had been made in the value of the radium standard solution, caused by partial precipitation of the radium. Accordingly, the value of the ratio was changed to 3.8×10^{-7}. A little later, Boltwood[4] redetermined the uranium content of the standard uraninite, which lowered the value still further to 3.4×10^{-7}. This remained the accepted value for several years.

After the International radium standard was adopted in 1910, Rutherford[5] made a comparison with his previously used radium standard,

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[1] Published with the permission of the Director of the U. S. Bureau of Mines under the coöperative agreement with the Colorado School of Mines.

[2] Rutherford and Boltwood, *Am. J. Sci.*, [4] **20**, 55–6 (1905).

[3] Rutherford and Boltwood, *ibid.*, **22**, 1 (1906).

[4] Boltwood, *ibid.*, [4] **25**, 296 (1908).

[5] Rutherford, *Phil. Mag.*, [6] **28**, 320–7 (1914).

which indicated a change from 3.4 to 3.23×10^{-7} for the radium : uranium ratio.

In 1913 Heimann and Marckwald[1] examined 8 specimens of pitchblende from the principal uranium deposits of the world and found the ratio to be constant within 0.4% and reported the absolute value as 3.328×10^{-7}. Their radium solution was made from 4.85 mg. of radium chloride of 30% purity, obtained from the Institut f. Radiumforschung in Vienna.

In 1915 Becker and Jannasch[2] determined the ratio in selected Austrian pitchblende which was analyzed with great care, not only for uranium, but for all the other elements present. Their standard radium solutions were prepared from 2 portions of radium chloride containing 2.144 and 2.249 mg. of radium element, respectively, which were also obtained from the Radium Institute in Vienna. The solutions were prepared with due regard for the protection of radium in solution by the addition of barium and of hydrochloric acid. The values reported by Becker and Jannasch were "$3.383 \times 10^{-7} \pm 1.0\%$ for the solution method, and $3.415 \times 10^{-7} \pm 0.7\%$ for the fusion method" of treating the pitchblende.

Between the corrected Rutherford value (3.23×10^{-7}) and that of Becker and Jannasch, there is a discrepancy of about 5.5%, and about 2% between the value of Heimann and Marckwald and that of Becker and Jannasch. It, therefore, appeared very desirable to redetermine this important constant which has not only great theoretical but also much practical interest, since pitchblende is very commonly used in standardizing emanation electroscopes for the determination of radium by the emanation method.

For example, if the radium determinations for plant control in the production of radium were being carried on by means of electroscopes standardized with analyzed pitchblende, the value of the radium: uranium ratio would have a direct influence on the accuracy of the results. If all the measurements were based on this ratio, they might all be relatively correct among themselves, but absolutely in error by the amount of error in the ratio. Usually, however, radium is withdrawn from the crystallizing system and measured by the γ-ray method, which is independent of the radium: uranium ratio since it depends solely on the International standard. It will, therefore, be seen that if the radium were being measured into such a system by means of the ratio amd taken out by the γ-ray measurement, an accumulative discrepancy would be produced between the real and the apparent radium content of the crystallizing system, which in time would become a very large one.

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[1] Heimann and Marckwald, *Jahrb. Radioakt. Elektronik.*, **10**, 299–323 (1913).

[2] Becker and Jannasch, *ibid.*, **12**, 1–34 (1915).

2. Sources of Error.

Briefly, the sources of error may be summarized as follows.

1. As regards the radium standard solution, accurate results could not be obtained until the careful atomic weight work of Hoenigschmid and Mme. Curie had opened the way to the establishment of a correct radium standard. Even then, the small quantities of radium that had usually been available for determining the ratio have rendered an exact knowledge of the radium content of the standard solutions fairly doubtful. A γ-ray measurement of rather small quantities of radium sometimes had to be followed by the weighing out of still smaller quantities of radium salt, which is rather hygroscopic.

2. As regards the radium solution prepared from the standard salt, there arises the difficulty of maintaining all the radium in solution. This was extremely difficult before the protective action of an excess of barium and acid was thoroughly understood. If partial precipitation occurs, the solution does not yield its full quantity of emanation. It has now been demonstrated[1] that radium is retained in a properly protected solution. With respect to pitchblende, the difficulty of keeping radium in solution is enhanced by the sulfur impurities in the ore. This disadvantage is encountered only when the pitchblende is dissolved and stored for the accumulation of emanation.

3. The difficulty of the correct analytical determination of uranium is not inconsiderable, as has been clearly shown by Becker and Jannasch.[2]

4. The difficulties of the electroscopic determination of radium emanation have also to be contended with. Owing to the nature of the instrument, a rather large number of repetitions of each determination is necessary to insure any degree of precision.

3. Experimental Procedure.

A. Preparation of a Radium Standard Solution.—One of the portions of radium salt prepared from Colorado carnotite by the U. S. Bureau of Mines[3] consisted of a tube of anhydrous radium chloride of a total salt content of 0.2067 g. Comparison by the γ-ray method with the International standard of the U. S. Bureau of Standards showed a content of radium element of 157.3 mg. Since the salt was believed to be 100% $RaCl_2$, the radium content could also be calculated directly from its known weight, using Hoenigschmid's value (226.0)[4] for the atomic weight of radium. This calculation also gives 157.3 mg. of radium, thus affording an independent check of the radium content, and giving great reliability to the value.

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[1] J. Moran, *Trans. Roy. Soc. (Canada)*, 10$^{\text{III}}$, 77–84 (1916).

[2] *Loc. cit.*

[3] Bur. Mines, *Bull.* **104**.

[4] O. Hoenigschmid, *Sitzb. Akad. Wiss., Wien*, **120**, Abt. II*a*, 1617–52 (1911).

The tube was opened, and the salt content dissolved in 5% redistilled, sulfate-free hydrochloric acid solution. The salt went completely into solution without any trace of cloudiness.[1] The tube was carefully washed several times with more of the 5% acid and the solution was finally diluted to one liter of acid of the same strength and thoroughly mixed.

From this solution 10 cc. containing 1.573 mg. of radium element was immediately pipetted into 5% HCl and made up to one liter, to which was added about 23 mg. of $BaCl_2.2H_2O$. From this solution, after thorough mixing, 10 cc. containing 1.573×10^{-5} g. of radium was immediately pipetted into a solution which was made up to one liter with 5% HCl and to which 2 g. of $BaCl_2.2H_2O$ were added. From this solution, after thorough mixing, 100 cc. containing 1.573×10^{-6} g. of radium was at once pipetted into a solution which was made up to one liter of 5% HCl and 2 g. of $BaCl_2.2H_2O$. This solution, when thoroughly mixed, constituted the final standard solution, in which the radium was protected by one million fold of barium and 5% HCl.

From this standard solution, 12 portions of 10 cc. each, containing 1.573×10^{-8} g. of radium, were at once pipetted into 1 : 1 nitric acid solution, half filling twelve 125 cc. Pyrex flasks. Four different pipets and 4 different measuring flasks were calibrated for use in the dilutions just described, no vessel was used for more than one concentration of solution. By having all preparations previously made, only 1.5 hours were consumed from the time the radium tube was opened until the 12 solutions were sealed up in 1 : 1 nitric acid for the accumulation of radium emanation, thus avoiding the possibility of precipitating radium sulfate by slowly dissolving sulfate from the glass vessels.

Before the accumulation of emanation, the solutions were boiled 15 minutes in Pyrex flasks to reduce the emanation to zero, and were then sealed by drawing out the neck of the Pyrex flask in an oxygen-gas flame so that a connection could be later made with rubber tubing, enabling the breaking of the glass tips under the rubber connection. This practice precluded the possibility of loss of emanation by leakage. By this procedure, it is believed that all errors, mentioned under Sections 1 and 2 above, were practically eliminated. The emanation was allowed to accumulate for various periods from 5 to 10 days before boiling off for the electroscopic determination.

B. Analysis of Pitchblende.—The standard pitchblende used was selected Colorado pitchblende, as homogenous and free from sulfur as possible. The sulfur content was not determined, since the method employed of directly dissolving the pitchblende, instead of storing the solution, renders the presence of sulfur far less objectionable than when the pitchblende is allowed to stand in solution for the accumulation of radium emanation. The pitchblende was ground to pass 200 mesh. Its

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[1] Since this portion of radium chloride had been prepared about 2 years previous to its opening, it was interesting to note that 100% $RaCl_2$ is not rendered insoluble in acid by its own radiations.

emanating power was determined by the Boltwood method[1] of storing for one month in a closed tube and then drawing air slowly over it into the electroscope chamber. The emanating power, or per cent., of emanation spontaneously diffusing from the ground sample, was found to be 5.65% of the total possible.

The uranium content was determined by the Ledoux method, which has been in use for several years at the U. S. Bureau of Mines, and has been described as applied to carnotites by Lind and Whittemore.[2] Such parts of the procedure as referred to the separation of vanadium were omitted in the case of pitchblende. The gravimetric determination of the U_3O_8 from 1 g. of pitchblende gave a value of 0.7796 g., which, using the Hoenigschmid value[3] for the atomic weight of uranium (238.2), is equivalent to 0.6612 g. of uranium per gram of pitchblende.

C. Treatment of Pitchblende for the Radium Determination.—40 to 50 milligrams was carefully weighed on an assay balance and removed from the pan into a small (7 cm.) quantitative filter paper. The pan was cleansed with a small piece of the same paper which was included in the determination. The determination was then carried out as described by Lind.[4] Twenty determinations of the emanation content were carried out in 3 different emanation chambers with 2 different electroscope heads (see Section E), in order to obtain a precise average result.

D. Treatment of the Radium Standard Solutions.—After the 12 solutions had accumulated emanation for periods of 5 to 10 days, they were connected to the emanation collecting apparatus just as in the case of pitchblende. After breaking the tips under rubber connection, the solutions were boiled off in the same manner. The gas was then transferred into the electroscope emanation chamber, where it was allowed to stand until equilibrium was attained with induced activity.

E. The Electroscopic Measurements.—The "interchangeable head" type of electroscope employed by the Bureau of Mines was used.[5] Three chambers and two interchangeable heads were used; each combination being standardized by at least 3 determinations, both with pitchblende and with a radium standard solution. The latest types of the instruments were employed.[6]

The only further precaution concerns the pressure and temperature of the air in the electroscope chamber at the time of measurement. After introducing the emanation into the chamber, a slight vacuum was left during the 3-hour period of accumulating induced activity. This served

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[1] B. B. Boltwood, *Phil. Mag.*, **9**, 599 (1905).

[2] THIS JOURNAL, **36**, 2076 (1914).

[3] O. Hoenigschmid, *Z. Elektrochem.*, **20**, 452 (1914).

[4] S. C. Lind, *J. Ind. Eng. Chem.*, **7**, 1024 (1915).

[5] S. C. Lind, *Ibid.*, **7**, 406 (1915); modified form, *ibid.*, **12**, 469 (1920).

[6] *Loc. cit.*

the double purpose of avoiding the possibility of any outward leak, and also of permitting some regulation of the external room temperature at the time of final equalization of pressure to the prevailing barometric pressure. At this elevation the average of pressure is about 620 mm. Therefore, 620 mm. and 20° were chosen as normal conditions. Any departure of the barometric pressure from 620 was compensated as far as possible by a corresponding regulation of room temperature so as to avoid correction. The nature of the correction for electroscopes of one-half liter gas capacity can hardly be linear, but, apparently from comparison of results of O. C. Lester[1] for larger chambers and lower pressures, would not be far from direct proportionality; so that such small corrections as have been applied (average 0.6%; maximum 1.5%) were made linearly, doubtless improving the results even though some slight over-compensation may have resulted.

The natural leaks which were subtracted from the electrical discharge were the results of actual blanks carried out with all the reagents, except radium, just as in the determination. They exceeded the usual natural leaks of the instruments themselves by about two-fold; but even then constituted corrections on the rate of discharge of only 0.4 to 1.0%, which remained quite constant.

4. Experimental Results.

The 3 electroscope chambers used were designated I, II and III; the 2 interchangeable heads, A and B. By reading each chamber with each head, 6 combinations were obtained: A_{I}, B_{I}, A_{II}, B_{II}, A_{III} and B_{III}. Standardization of each combination in terms of grams of radium $\times 10^{-8}$ for a discharge of $\frac{1 \text{ div.}}{1 \text{ sec.}}$ was established by 3 or 4 determinations each with standard pitchblende and with the radium standard solution. The provisional ratio used for pitchblende was the Heimann and Marckwald value, 3.328×10^{-7}, correction for the emanating power of the pitchblende was, of course, applied. The results are shown in Table I.

The results indicate that the Heimann and Marckwald value (3.328×10^{-7}) is low by 2.1%. Multiplying it by the value, 1.021, gives as the final radium : uranium ratio of these determinations $3.40 \times 10^{-7} \pm 0.03$. This value is in spendid agreement with those of Becker and Jannasch ("3.383 ± 1% and 3.415 ± 0.7%;" average 3.399×10^{-7}), and indicates that the old Rutherford and Boltwood value, 3.4×10^{-7} is correct to within less than 1%.

It is assumed that the relative constancy of the radium : uranium ratio for different pitchblendes has already been thoroughly established by Heimann and Marckwald.[2] Lind and Whittemore[2] have also shown that

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[1] O. C. Lester, *Am. J. Sci.*, 44, 225 (1917).

[2] *Loc. cit.*

the same ratio holds for carnotite when the sample represents sufficiently large quantities of the ore to compensate local concentration.

TABLE I.

Values Refer to Radium in g. × 10^{-8} for a Discharge of $\frac{1 \text{ div.}}{1 \text{ sec.}}$

Electroscope.	Ra solution.	Average.	Pitchblende.	Average.	Relative ratio.
	8.175		7.989	7.994	
AI....................	8.042	8.099	7.980		101.3
	8.081		8.013		
	7.536		7.300		
BI....................	7.649	7.600	7.357	7.329	103.7
	7.614		7.330		
	8.065		8.021		
AII..................	8.104	8.112	8.030	8.053	100.7
	8.168		8.065		
			8.097		
	7.698		7.391		
BII..................	7.501	7.609	7.326	7.336	103.7
	7.628		7.348		
			7.278		
	8.137		8.106		
AIII.................	8.254	8.228	8.179	8.125	101.3
	8.299		8.091		
	7.544		7.485		
BIII.................	7.637	7.591	7.432	7.442	102.0
	7.593		7.409		Final average 102.1 ± 1%

NOTE.—The question has recently been raised whether duplicate emanation chambers could be practically constructed so as to have identical calibration constants in order to avoid the necessity of calibrating more than one chamber. Some interesting light is thrown on this subject by comparing the results of Table I. The chambers were used as furnished by the makers; no especial efforts having been made to have them exactly identical. It will be seen that Chambers I and II have identical constants within the limits of experimental error, as indicated by the results for both heads A and B. Chamber III shows a small apparently real deviation. These results indicate that with a small amount of care on the part of the maker, chambers can be duplicated which will have identical constants for all ordinary purposes.

5. Summary.

1. A standard radium solution was prepared by dissolving in one liter of 5% redistilled hydrochloric acid, 0.2067 g. of 100% radium chloride containing 157.3 mg. of radium element, as shown both by calculation from the chemical formula and by the γ-ray comparison of the U. S. Bureau of Standards with the International radium standard. The clear solution was diluted with 5% hydrochloric acid until one liter contained 1.573×10^{-6} g. of radium, protected by one-million fold of barium chloride.

2. The standard radium solution was used to standardize by the Bureau

of Mines method 3 electroscope chambers, each of which was measured with 2 interchangeable leaf chambers.

3. The same chambers and heads were standardized against U. S. Bureau of Mines standard pitchblende from Colorado.

4. The results give as final average of 18 determinations $3.40 \times 10^{-7} \pm 0.03$ for the ratio radium : uranium. The result agrees with the average of Becker and Jannasch, 3.399×10^{-7} obtained at the Radiological Institute at Heidelberg, using standard radium salt from the Institute of Radium Research in Vienna, and with the old uncorrected value 3.4×10^{-7} of Rutherford and Boltwood.

The writers express with pleasure their indebtedness to Messrs. J. P. Bonardi and J. E. Conley for their kindness in recrystallizing the 100% radium bromide from which the pure radium chloride was prepared, and also to Dr. N. E. Dorsey, of the U. S. Bureau of Standards, for making the γ-ray comparison with the International standard.

GOLDEN, COLORADO.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

A WEIGHT BURET FOR GAS ANALYSIS.[1]

BY E. R. WEAVER AND P. G. LEDIG.

Received April 3, 1920.

The use of a weighing method for making gas measurements was suggested by the great advantages of a weight buret for liquids over the older volumetric burets. The apparatus here described was designed primarily for use in a forthcoming study of gas-analysis methods; but it appears to have sufficient application, for any gas volumetric measurements requiring greater precision than is easily obtainable with an ordinary gas buret, to warrant publication at this time. A description of the apparatus and its method of use will first be given; then the reasons for various details of construction will be considered; the principal sources of error will be pointed out; and finally some typical experimental results which show the precision obtainable will be given.

Description and Method of Use.

For the sake of clearness, the apparatus is represented in Fig. 1, as though constructed in a single plane. Actually, the tubes and bulbs may be arranged in any convenient manner, if the relative levels of the different parts are kept approximately as shown. In the apparatus constructed all the parts which had to be water-jacketed, fitted neatly into a round battery jar of about twice the diameter of Bulb A.

By means of connections to vacuum and air pressure, which are sup-

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[1] Published by permission of the Director of the Bureau of Standards.