

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PURDUE UNIVERSITY]

## EXTRACTION OF KRYPTON AND XENON FROM LIQUID AIR RESIDUES<sup>1,2,3</sup>

BY F. J. ALLEN AND R. B. MOORE

RECEIVED APRIL 15, 1931

PUBLISHED JULY 8, 1931

### Introduction

On account of the difficulty and expense of obtaining any considerable quantities of krypton and xenon, there has been little experimental work done with these elements except such as required only small amounts of the gases. Much credit is due to the pioneers in this field, who, in many instances, made up for scarcity of material with what might well be called a microtechnique.

Early in the study of the extraction of krypton and xenon from air it became evident that the evaporation of liquid air brought about an increased concentration of krypton and xenon in the residual liquid and this suggested that liquid air residues might well be the best source of these gases. Experience has confirmed this idea; hence the opportunity to obtain liquid air residues from a plant which carried on fractionation of liquid air on a large scale was welcomed in the hope that sufficient quantities of krypton and xenon might be obtained to permit of a more careful determination of some of their properties.

**Source of Raw Material.**—The Air Reduction Sales Company of New York kindly supplied cylinders of compressed gas. The bulk of gas in each cylinder was oxygen, but nitrogen, carbon dioxide, argon, krypton and xenon were also present, the latter two in proportions much greater than in ordinary air.

In the fractionation of liquid air the higher vapor pressure of nitrogen allows the liquid air in the still to become mainly oxygen, but with continuous operation there collect in this liquid oxygen the less volatile krypton and xenon.

It has been the custom at certain plants to discard periodically this liquid from the still. Arrangements, however, were made with the company referred to above to transfer liquid so withdrawn to large vacuum-walled vessels and to permit it to reduce its volume by evaporation and thus increase its proportion of krypton and xenon. When the volume had

<sup>1</sup> A preliminary note in regard to this work has already been published, *THIS JOURNAL*, 52, 4173 (1930).

<sup>2</sup> This paper represents part of a thesis submitted by F. J. Allen to the Graduate School of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

<sup>3</sup> Since the completion of this research, Dean R. B. Moore has died. This paper has not, therefore, had the benefit of his criticism. The thesis of which this is a part was, however, carefully gone over by Dr. Moore.

diminished sufficiently, the remaining liquid was poured into a metal cylinder of the type used for marketing compressed oxygen. The cylinder had been previously cooled with liquid oxygen. The valve was screwed in and the pressure checked after the cylinder and contents had come to room temperature. This cylinder was then sent to our laboratory.

Unfortunately, only the briefest sort of record was kept at the plant in regard to this procedure. Knowledge as to the quantity of liquid oxygen from the still, the fraction of this allowed to evaporate and kindred information would have been of much interest.

F. J. Metzger of the Air Reduction Company states that, "Each cylinder of gas represents the rare gases which we have been able to collect from about fifteen million cubic feet of air." It will be seen later that only a small proportion of the krypton and xenon actually in that volume of air got into the cylinders. Rabinowitsch<sup>4</sup> has concluded from a study of all the available data that the most reliable values that can be assigned for the percentages of krypton and xenon in the air are, respectively, 0.0001 and 0.00001. Six cylinders in all were received and the inert gases were extracted in a manner later to be described.

### Experimental

**Separation of Inert Gases from Liquid Air Residues.**—The following workers have reported on the extraction and purification of krypton and xenon: Ramsay and Travers,<sup>5</sup> Ladenburg and Krügel,<sup>6</sup> Moore,<sup>7</sup> Dewar,<sup>8</sup> Valentiner and Schmidt,<sup>9</sup> Aston,<sup>10</sup> Claude<sup>11</sup> and Le Pape.<sup>12</sup>

A number of patents<sup>13</sup> dealing with the extraction of krypton and xenon have been granted.

The extraction of krypton and xenon for the present work had been completed before the papers of Claude and Le Pape were noted, the methods used following in general the principles established by earlier investigators.

The gas from the cylinder was freed from carbon dioxide by bubbling through a concentrated solution of potassium hydroxide and was next dried by calcium chloride and

<sup>4</sup> Rabinowitsch, *Z. angew. Chem.*, **39**, 737 (1926).

<sup>5</sup> Ramsay and Travers, *Trans. Roy. Soc. London*, **A197**, 47 (1901).

<sup>6</sup> Ladenburg and Krügel, *Sitzb. preuss. Akad. Wiss.*, 727 (1900).

<sup>7</sup> Moore, *Proc. Roy. Soc. (London)*, **A81**, 195 (1908).

<sup>8</sup> Dewar, *ibid.*, **68**, 362 (1901).

<sup>9</sup> Valentiner and Schmidt, *Sitzb. preuss. Akad. Wiss.*, **38**, 806 (1905)

<sup>10</sup> Aston, *Proc. Roy. Soc. (London)*, **A103**, 462 (1923).

<sup>11</sup> Claude, *Compt. rend.*, **187**, 581 (1928).

<sup>12</sup> Le Pape, *ibid.*, **187**, 231 (1928).

<sup>13</sup> British Patent 226,783, Dec. 26, 1923, and British Patent 218,266, June 29, 1923, both assigned to Soc. anon. d'éclairage et d'applications électriques; British Patent 227,800, Jan. 19, 1924, and British Patent 236,217, June 25, 1924, both assigned to Soc. l'air liquide, and Soc. anon. pour l'étude et l'exploitation des procédés G. Claude.

passed through charcoal at the temperature of liquid air. At first the gas was metered out through a small gas meter, but experience soon showed that the rate could be adjusted suitably by the bubbling in the solution of potassium hydroxide and the total quantity of gas taken out in a given run could be calculated with sufficient accuracy from the initial and final pressures of the gage and the size of the cylinder.

The apparatus was in process of evolution throughout the entire investigation, but a few trials brought it to a fairly satisfactory stage. Figure 1 shows the plan of operation. It represents the set-up as used in the later runs. The various units were joined by means of heavy pressure tubing, but these connections are not shown in the figure.

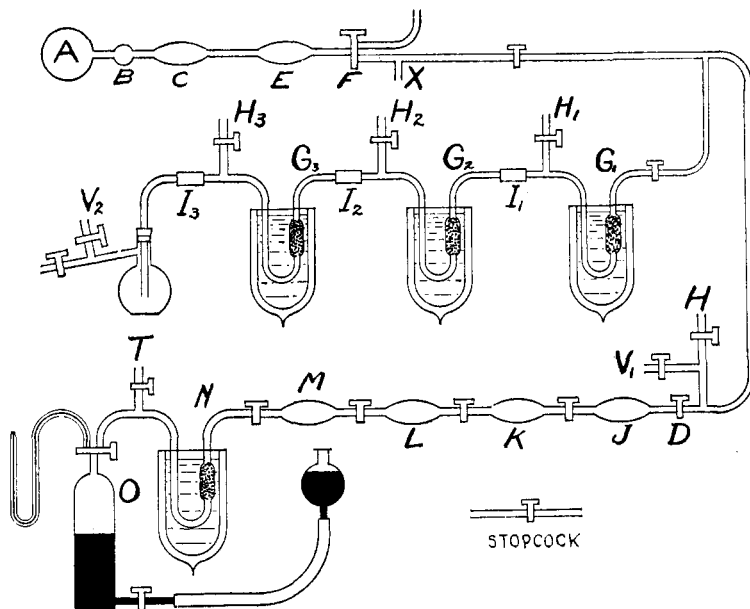


Fig. 1.—Diagram illustrating apparatus used to extract krypton and xenon from liquid air residues.

Gas from the cylinder A was passed through the gage B, the carbon dioxide adsorbers C, the drying agent E and through the two-way stopcock F. The two-way stopcock was put in as a safety unit to permit release of pressure in the event of the line becoming plugged. From F the gas flowed past a connection to a manometer X and on to the charcoal tubes  $G_1$ ,  $G_2$ ,  $G_3$ , which were cooled in liquid air.

It was not found practicable to prevent the formation of liquid oxygen in the charcoal tubes though reduced pressure was tried in the hope of doing so. The assumption was that krypton and xenon would be taken out by the cooled charcoal while the bulk of the oxygen passed on through. The results partly confirm this idea.

An average run consisted of passing about 300 liters of gas from the cylinder through the liquid-air cooled charcoal. The average rate of flow varied from one-half liter to one liter per minute.

When the gas from the cylinder was shut off, the charcoal tubes were clamped off and kept cooled by liquid air.  $G_1$  was then permitted to deliver its gas through what is called, for want of a better name, the "inerting" line. By a suitable adjustment of stopcocks and of the clamps between the charcoal tubes, the gas could be sent from  $G_1$ ,

$G_2$  or  $G_3$  through D and through the soda lime J, the copper K, the drying agent L, the calcium M and could be taken into the charcoal tube N. This process of delivering from  $G_1$  a large volume of gas, which, in the inerting line, is reduced to a small volume of inert gas capable of being collected over mercury in the reservoir O, is believed to be a new procedure. It obviates the use of large reservoirs for the collection and storage of the gases from  $G_1$ . Some care was required in the manipulation, such as a slow rate of addition of the oxygen-rich gas from  $G_1$  to prevent over-heating in the copper filled tube.

Previous to use all charcoal tubes were baked out for about two hours under a vacuum of about 0.001 mm. and at a temperature of about  $400^\circ$ . The charcoal used was "Adsorbite," supplied by the Barnebey-Cheney Engineering Company of Columbus, Ohio.

Calcium was obtained in finely divided form by various methods, all of which were tedious. It would be a great advantage if this element were marketed in larger and more coherent lumps. With fair sized pieces good shavings were obtained on the lathe or shaper. Some shavings were drilled out but this is wasteful unless the honeycomb pieces remaining can be utilized. By far the most efficient results were obtained with a milling machine using a slow speed, spiral-grooved, cylindrical cutting tool. With larger lumps of calcium this method would be almost ideal.

The copper was prepared by reducing four mesh copper oxide with hydrogen. Care was taken to bring about the reduction at the lowest possible temperature and thus to obtain the copper in a condition of maximum porosity. The reduction can be carried out in an iron pipe but in the line the copper was contained in a large tube of Pyrex glass. This permits observation but is otherwise subject to criticism. Temperatures higher than the glass can safely stand are easily obtained by the action of the oxygen on the copper.

The "inerting" line, with the exception of the tube N which was baked out separately, was pumped out and the pumping maintained for about four hours while the calcium and copper tubes were strongly heated with bunsen burners. It was usually possible to attend to this part of the work while the run was going on; then as soon as the gas from the cylinder was shut off the gas from a G tube could be admitted through D and the soda lime to the copper by suitable clamp adjustment at  $I_1$ ,  $I_2$ , etc.

The rate of flow of gas from  $G_1$  could be controlled by regulation of the outlet stop-cock and the depth of immersion in the liquid air. The line was kept open to the manometer and in all the work a reduced pressure was maintained whenever possible. This meant that in the event of a leak, gas would not be lost but only contaminated by having some air leak into it.

The copper had to be hot to start its action with the oxygen, but once started the burner could be removed, the action being so strongly exothermal as to cause a red glow to travel down inside the tube marking the zone of reaction. It was easy to overheat to the extent of having the glass soft enough to be pressed in against the tube contents. If this occurred only slightly it was usually possible to complete the run, especially if the defective place was kept hot, for on cooling such places often cracked.

As gas collected in the copper tube it was gradually let on through the drying agent to the calcium, which was kept as hot as the Pyrex tube in which it was contained would permit, and thence to the charcoal tube N.

When no more gas came from  $G_1$  by removal of its liquid air bath, its temperature was gradually increased to about  $450^\circ$  with the line open all the way to N, which was cooled in liquid air. The manometer would soon show a fair vacuum. Tube N could then be closed to the line and allowed to deliver its gas to the mercury-filled reservoir O. On heating N to  $450^\circ$  practically all the remaining gas could be pumped off through the T connection to the Töpler pump and added to the gas in O.

H could be put in connection with  $H_2$ , or  $H_3$  when the gas was to be sent from  $G_2$  or  $G_3$ , respectively, to the inerting line.  $V_1$  and  $V_2$  are for connection to the vacuum pump. T could be put in connection with the vacuum pump or the Töpler pump.

At any time during operation the gas from the line could be drawn back into  $G_1$  or N. This was very convenient for example when a copper or a calcium tube needed to be replaced.

The gas from O was subsequently "re-inerted," that is, subjected to the action of fresh calcium. As a rule this "re-inerting" was carried out by passing the gas from O through an appropriate line to another reservoir and thence back to O, this process being repeated until no further diminution in volume was observed. The line contained copper, copper oxide, soda-lime and a drying agent in addition to calcium. This was considered necessary because of the possibility of some moisture getting to the calcium or to the calcium nitride and forming hydrogen or ammonia. Soddy<sup>14</sup> and more recently, Leatherman and Bartlett<sup>15</sup> have shown that under the proper conditions calcium is very efficient in removing all but the inert gases, but in this work a tube was sometimes used overlong with consequent loss of efficiency, hence the "re-inerting."

In the early trials only one 25-g. charcoal tube was used but later a second and third were added. In the last runs three tubes were used, each containing about 50 g. of charcoal. Inert gas was obtained from each one. Whether this gas was carried from one tube to the next by the action of liquid oxygen or whether too large a volume of gas was taken from the cylinder for the total capacity of the charcoal used or whether some other factor was operating remains to be investigated.

The average time for a run was twelve to fifteen hours, and several times as long was usually required between runs in getting the line in shape for use again. Unusual good fortune favored the work in that the accidents which occurred were not at critical times.

About 1100 ml. of inert gas was obtained from the six cylinders. A test run was made on a portion of the gas from the last cylinder received. A volume of 16 liters of gas from this cylinder was freed from all but the inert gases by passing it directly into the inerting line. The 16 liters reduced to 30 ml. of inert gas. This corresponds to about 0.2% inert gas in the gas from the cylinder. Since the cylinder contained 260 liters of gas from which 173 ml. of inert gas was obtained by the charcoal separation it appears that in this case the efficiency of extraction was about 35%.

The inert gas was made up largely of argon, not more than one-third of its volume being krypton and xenon.

### Separation of Krypton and Xenon from Mixtures of Inert Gases and Preparation of Samples of Krypton and of Xenon of High Purity

The mixtures dealt with were made up of argon, krypton and xenon. The separation of these was checked by density determinations, the apparatus and method being that of Ramsay and Travers.<sup>5</sup>

The general scheme of purification starting with a sample of the inert gas mixture as it came from the "re-inerting" line will be first considered. The gas was condensed to a liquid or solid by making connection between the reservoir and an evacuated bulb dipping into liquid air. The bulb contents were next allowed to evaporate by reducing the pressure and several fractions thus obtained. The fraction coming off most readily would be mostly argon and that least readily, mostly xenon. The inter-

<sup>14</sup> Soddy, *Proc. Roy. Soc. (London)*, **A78**, 429 (1906).

<sup>15</sup> Leatherman and Bartlett, *Ind. Eng. Chem., Anal. Ed.*, **1**, 223 (1929).

mediate fractions ranged in composition from krypton in argon to krypton in xenon. This general method is that used by Moore<sup>7</sup> in his work. In any given series the fractions in numerical order are in order of increasing density.

In the preliminary work no attempt was made to check up on the density of the various fractions. When, however, several series of fractions had been obtained in the same way, combinations were made of the corresponding fractions in the several series and density determinations made for these composite samples.

The a, b and d series were thus grouped into the e series for which some data are given in Table I.

TABLE I  
DATA FOR SERIES E FRACTIONATIONS

Sample number	Vol. of sample, ml.	Density of sample, g./l.
1	85	2.85
2	52	2.90
3	68	3.04
4	40	3.51
5	50	3.76
6	20	4.13
7	22	5.07
8	22	5.44

Since krypton and xenon have rather slight vapor pressures at the temperature of liquid air, some attempts to separate them were carried out at about  $-150^{\circ}$ .

To obtain and hold this temperature a method was employed which will be referred to again later and which will be called "cold-air-stream cooling." The stream of cold air was obtained by forcing air through a copper coil immersed in liquid air. By careful regulation of the rate of flow of air through the coil and the depth of immersion of the coil in the liquid air a fair regulation of temperature could be obtained in an unsilvered "Dewar" tube into which the cold air was passed. By this method various temperatures from  $-170$  to  $-100^{\circ}$  were obtained. With extreme painstaking a temperature could be maintained within  $1^{\circ}$  for as long as fifteen to twenty minutes but for the fractionation work it was not felt necessary to maintain such careful control.

The fractionation of the samples richer in krypton and xenon was carried out in a manner somewhat different from that used with the first inert gas samples. Figure 2 will help make this clear.

Sample 1 is divided according to the best judgment of the worker into a more volatile fraction 7 and a less volatile fraction 8. Sample 8 is added to sample 2 which is the next less volatile than 1 in the starting series used here (numbers 1-6) and fractions 9 and 10 obtained. The less volatile 10 with 3 gives 11 and 12, etc.

Samples 7, 9, 11, 13, 15, 17, 18 thus obtained are used as the starting series for repeating the process and obtaining eight new samples. A large number of fractionations of this sort were carried out and most of the argon was separated from the krypton and xenon.

Reference has been made to studies which showed differences in the adsorptive power of charcoal for argon, krypton and xenon at certain temperatures. These deal in the main with the idea of allowing a mixture of the gases to be adsorbed by charcoal and then obtaining a degree of

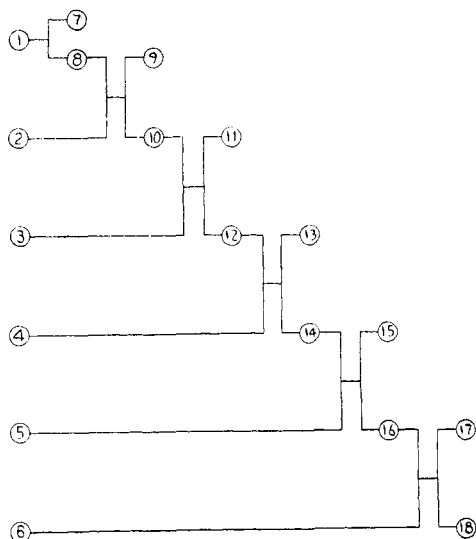


Fig. 2.—Diagram to explain fractionation of inert gas mixture.

separation by either slowly raising the temperature of the charcoal and collecting the gas first set free as mainly argon, the next as mainly krypton and that held most firmly and hence last to be given off as mainly xenon; or by a temperature difference between the gas containing charcoal and a fresh tube of charcoal free from any gas. In the latter case, for example, connection might be made between a charcoal tube containing the three gases at say  $-140^{\circ}$  and a gas-free charcoal tube at the temperature of liquid air. With this temperature difference maintained for a period of one, two, or more hours the gas held

least firmly would to a large degree migrate to the cooler tube.

A number of experiments were performed making use of the above method but it was soon apparent that a line was required which could be maintained "vacuum-tight" for hours at a time. The use of even the best obtainable vacuum tubing permitted some air to leak in. About fifteen trials were made, however, and the general indications were very favorable. A typical trial is described in the following paragraph.

A sample of gas of density 3.0 g./l. was taken into a five-gram charcoal tube (A) at the temperature of liquid air. Tube A was then allowed to warm up to  $-120^{\circ}$  and was then placed in connection with a similar tube (B) which was at the temperature of liquid air. After three hours the connection between the tubes was closed and B was freed from gas by the usual process of baking and pumping out. The gas from B had a density of 1.7 g./l. Tube A was now brought to  $-80^{\circ}$  and left for one hour in connection with B at liquid-air temperature. This time the gas obtained

from B had a density of 3.2 g./l. The operation was repeated with A at 20° and B in liquid air again. This time fifteen minutes were allowed for gas to go from A to B and the gas from B had a density of 3.8 g./l. On baking out A a gas of density 4.7 g./l. was obtained. As stated before this method is not new but a density check on the separation as given above has not been previously reported.

The same general results were obtained in the other trials and as a result of these experiments considerable progress was made toward getting pure samples of krypton and xenon.

An inventory of inert gas samples on hand at this time gave results as shown in Table II.

TABLE II

DATA ON FRACTIONS OBTAINED IN PRELIMINARY PURIFICATION

Sample number	Density, g./l.	Approx. vol., ml.
I	1.8 ± 0.1	404
II	2.0 ± 0.1	114
III	2.3 ± 0.1	142
IV	2.7 ± 0.1	95
V	3.4 ± 0.1	63
VI	3.6 ± 0.1	154
VII	4.7 ± 0.1	53
VIII	5.4 ± 0.1	29

The accepted densities for argon, krypton and xenon in grams per liter are, respectively, 1.78, 3.708 and 5.851.

Samples V–VIII show by their densities that they consist mainly of krypton and xenon. Accordingly steps were taken toward final purification. The method now employed was that which Ramsay<sup>5</sup> used in his final purifications, namely, the sparking of gas over moist potassium hydroxide after pure oxygen had been added to the inert gas. When further sparking gave no reduction in volume, the excess oxygen was removed by phosphorus, the usual precautions being taken to produce vigorous combustion.

Sample VI so treated increased its density from 3.6 to 3.9 g./l. It should be kept in mind that in all this work the gases were handled over mercury and every precaution was taken to avoid contamination of the samples, but even so traces of air got in, especially when samples had been transferred many times from tube to tube and from tube to reservoir or to pump and thence to other tubes as was necessary in carrying out the various steps in the purification. As higher grade samples were obtained, greater care was used to avoid contamination; in fact, "seasoned" tubes were used; that is to say, a krypton sample if transferred to the pump or fractionating bulb was returned to the tube which had contained it rather than to a tube in which the air had just been displaced by mercury.

Samples V, VII and VIII were also treated in the manner that has just been described for sample VI.



The next step in purification was fractionation and in the case of krypton this was a tedious process, since this gas, having a vapor pressure intermediate between argon and xenon, is hard to separate from them. Enough krypton must be allowed to distil away to carry out all the argon so that the process is far from economical. Better efficiency obtains in getting krypton from xenon but even in such a case some samples must be set aside which, though very largely krypton, contain traces of xenon. Repeated reworking of these "border line" samples permitted getting more and more of the krypton from them. The general scheme involved in fractionation has been explained already.

Sample VI after its purification by sparking yielded on fractionation a sample judged to be mostly krypton, since its density was 3.81 g./l. This fraction, about 90 ml. in volume, was refractionated to give five samples. Of these the first was set aside as possibly containing argon, although in these higher density samples the chance for argon to be present was rather slight. The second and third samples totaling about 60 ml. were fairly pure krypton, but the fourth and fifth were set aside as possibly containing xenon.

The 60 ml. of krypton referred to in the preceding paragraph was divided into three fractions and the middle one of about 30 ml. volume was used. Its density was found to be 3.733 g./l. The temperature of its triple point agreed closely with that of the sample of which it was the middle fraction and with that of another sample of high purity krypton the preparation of which will next be reported.

All second best samples of krypton which had been accumulated in the process of getting out the most nearly pure sample just referred to above were mixed together and repeatedly passed over strongly heated copper, copper oxide and then over calcium and were then dried by standing over phosphoric anhydride. This process was assumed to remove any gases not inert that might have got in as impurities. The treatment with oxygen followed by sparking in contact with potassium hydroxide was omitted. An all-glass apparatus was used which gave no evidence of leakage over a period of twenty-four hours.

The inert gas thus obtained was fractionated from a bulb which was connected to a manometer. There was small evidence of impurities more volatile than krypton; nevertheless, the first 10 or 12 ml. was pumped off and set aside. The next fraction, about 30 ml. in volume, was high grade krypton and its density was found to be 3.728 g./l. It is significant that the vapor pressure remained constant during the entire time that this second fraction was being pumped out. In fact no change was observed in the vapor pressure while the third and most of the fourth fractions were being pumped out. The pumping was stopped from time to time to check up on this by allowing time for equilibrium to be established. Toward the

last the vapor pressure diminished, which was taken to indicate the presence of a small trace of xenon.

After the two samples of krypton of respective densities 3.733 and 3.728 g./l. had been used in vapor pressure studies, they were combined into one sample, and this was fractionated into five samples of which the first and last were very small (2-3 ml. each). The density of fraction 2 was found to be 3.737 g./l. and that of fraction 4 was 3.725 g./l., the difference being not greater than the probable experimental error and in the wrong direction to indicate the presence of xenon. The density bulb used held 21.92 ml. and the weight of krypton contained usually varied from 0.0500 to 0.0700 g. depending on the pressure at which the gas was supplied when the bulb was filled. An Ainsworth analytical balance was used and the weighings were not in error by more than  $\pm 0.0001$  g.

The average of all density determinations on the high grade krypton gave a value of 3.733 g./l. and this gives a value for the atomic weight of krypton about 1% higher than that which is now accepted. Aston<sup>16</sup> states that his recent mass spectrograph studies indicate that the present atomic weight assigned to krypton is too low. He also states that there is good reason to believe that much of the information in the literature concerning krypton and xenon is subject to revision.

The atomic weight of krypton calculated from the 3.733 g./l. value and using Watson's<sup>17</sup> value for the compressibility of krypton comes out 83.6.

The xenon was purified by taking the highest density gas into a bulb at the temperature of liquid air and pumping out several fractions through the Töpler pump. A middle fraction of about 50 ml. was fairly pure xenon. From this 50 cc. a middle fraction was taken later which was xenon of high purity. Its vapor pressure checked closely with a sample of xenon which Dr. R. B. Moore kindly loaned and which was known to be of high purity since it had been very carefully purified in order to determine the density of xenon. The present atomic weight of xenon was established from this sample of xenon. Also Aston had tested this sample and found it to show no evidence of krypton.

The density of xenon was found to be  $5.887 \pm 0.007$  g./l. From this value the atomic weight of xenon would be 131.4 using Watson's<sup>17</sup> value for the compressibility of xenon.

### Summary

A new method of handling liquid air residues from compressed gas cylinders has been used. This method permits obtaining the bulk of the inert gases present in the liquid air residues without the use of large gasometers and otherwise affords many advantages in manipulation.

<sup>16</sup> Aston, *Proc. Roy. Soc. (London)*, **A126**, 511 (1929).

<sup>17</sup> Watson, *J. Chem. Soc.*, **97**, 833 (1910).

Krypton and xenon of high purity have been extracted from liquid air residues.

Preliminary density determinations on the most carefully purified krypton and xenon indicate that the atomic weights assigned to these elements are too low.

New quantitative data on the partial separation of argon, krypton and xenon by means of suitably cooled charcoal have been reported.

Fractionations were carried out with a manometer in connection, thus permitting a check on the degree of separation by the change in vapor pressure.

LAFAYETTE, INDIANA

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PURDUE UNIVERSITY]

## DETERMINATION OF CERTAIN PHYSICAL CONSTANTS OF KRYPTON AND XENON<sup>1</sup>

BY F. J. ALLEN AND R. B. MOORE

RECEIVED APRIL 15, 1931

PUBLISHED JULY 8, 1931

The preparation of samples of krypton and xenon has been reported by the authors in a previous paper.<sup>2</sup> On account of the small amount of experimental work that has been done with these elements it seemed desirable to recheck some of the physical constants. Accordingly plans were made to redetermine the triple point temperatures and pressures as well as the vapor pressures of the krypton and xenon in the range from the temperature of liquid air up to the boiling points of these gases.

The apparatus for the vapor pressure studies was of simple design and in part was patterned after that of Ramsay and Travers.<sup>3</sup> It consists, as shown in Fig. 1, of a siphon pipet (A) through which the gas may be introduced, a trap (B) to stop mercury, the bulb (C) which in operation dipped into an unsilvered Dewar tube into which also extended the copper tube supplying cold air and the platinum resistance thermometer and the open arm manometer (F) which was clamped to a glass scale ruled on a mirror. It should be noted that bulb C is offset, thus permitting more easy adjustment of the cooling assembly. Hair felt was packed snugly about the tubes leading into the Dewar so as to plug the neck and also

<sup>1</sup> This paper represents part of a thesis submitted by F. J. Allen to the Graduate School of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

Since the completion of this research, Peters and Weil have reported work on purification and properties of krypton and xenon: *Z. physik. Chem.*, [A] **148**, 1-35 (1930); *Z. angew. Chem.*, **43**, 608 (1930). The results reported in this paper in general agree very well with those reported by Peters and Weil.

<sup>2</sup> Allen and Moore, *THIS JOURNAL*, **53**, 2512 (1931).

<sup>3</sup> Ramsay and Travers, *Trans. Roy. Soc. London*, **A197**, 47 (1901).