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.

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DETERMINATION OF CERTAIN PHYSICAL CONSTANTS OF KRYPTON AND XENON[1]

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

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The preparation of samples of krypton and xenon has been reported by the authors in a previous paper.[2] 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.[3] 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

[1] This paper represents part of a thesis submitted by F. J. Allen to the Graduate School of Purdue University in partial fulfilment 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.

[2] Allen and Moore, THIS JOURNAL, **53**, 2512 (1931).

[3] Ramsay and Travers, *Trans. Roy. Soc. London*, **A197**, 47 (1901).

extend some 5 cm. above the vessel itself. The copper tube supplying the cold air was insulated by a hair felt wrapping throughout the major part of the length from its liquid air bath to the neck of the Dewar tube.

After the work on vapor pressure was once in progress, no gas was admitted to the line except the samples of krypton and xenon and since the less pure samples were used in the first trials it would seem reasonable to think that these served to "wash out" the apparatus. On several occasions the apparatus was left standing under vacuum for more than a week with no perceptible inleak of gas.

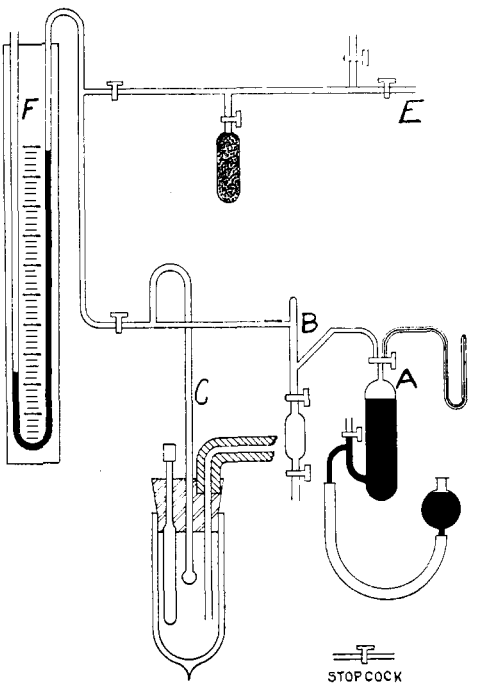

Fig. 1.—Apparatus for finding melting points, boiling points and vapor pressures of krypton and xenon.

The apparatus once exhausted was supplied with the krypton or xenon through A, and C was cooled to the desired temperature. The temperature was then allowed to rise very slowly, thus causing a gradual increase of the vapor pressure. At intervals readings were taken on the manometer, barometer and resistance box. These readings were not quite simultaneous since for the most part they were all made by one observer, but it was possible to adjust the resistance box to the proper reading to get the temperature from the platinum resistance thermometer and then very quickly to read the manometer. The barometer reading could then be obtained with some leisure since its change was not likely to be rapid enough to matter even if the reading were taken several minutes later.

Experience showed that on cooling, the vapor pressure was slow to diminish to a minimum value for a given temperature, hence the idea of taking the readings while the temperature was slowly increasing. If, for example, the equilibrium pressure at $-150°$ was desired, the gas would be cooled several degrees below that temperature and allowed to increase slowly to $-150°$. The temperature change was at the rate of about $0.05°$ per minute.

Table I shows the vapor pressures found for krypton. Sample A is the one of density 3.728 g./l. and sample B is the one of density 3.733 g./l.

The error in the temperature reading was probably of the order of 0.1° and of the vapor pressure ±20 mm., except for the equilibrium pressure at the triple point of krypton, which is not in error by more than ±3 mm. The results indicate that Ramsay and Travers'[3] value on the melting point is far from correct. They give −169.1° for krypton as compared with the −156.6° found in this investigation.

TABLE I

VAPOR PRESSURES OF KRYPTON

Sample A		Sample B	
Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
−158.3	524	−159.0	476
−158.0	530	−158.0	503
−157.4	539	−157.1	528
−157.1	549	−156.6[a]	556
−156.7[a]	558	−156.3	599
−156.6[a]	558	−154.8	653
−156.3	609	−154.7	679
−155.5	634	−154.4	681
−155.2	649	−154.1	705
−154.4	707	−154.0	716
−154.3	705	−153.6	726
−153.6	750	−153.4	739
−152.9	787	−153.1	749
−152.7	790	−152.9	764
−152.3	816	−152.7	775
−152.0	824	−152.2	803

[a] Values for the triple point.

The results also show that the accepted value of −151.8° for the boiling point of krypton is too high, a better value being −153.1°, although the results here reported are not so satisfactory for the boiling point as for the triple point.

The triple point was best observed by getting the solid krypton or xenon in the bulb in as fluffy and snow-like a form as possible and watching for it to melt as the temperature rose. The snow-like form could be produced by cooling the element in the liquid form to the temperature where it was about to solidify and then quickly reducing the pressure for an instant, *e. g.*, by opening momentarily to a low pressure space in A. This usually resulted in a sort of "explosion" of the liquid into solid. The temperature was next kept slightly below the temperature of the triple point found on previous trials until time had been allowed for attainment of equilibrium and then was permitted to rise slowly. With krypton the vapor pressure rose as the temperature rose, up to the triple point, where the pressure held constant until most of the solid had melted. The earlier trials served to develop a technique which permitted more careful work in later ones.

Dr. R. B. Moore and Mr. G. C. Finger assisted in checking the triple

point for the krypton from which the sample of density 3.733 grams per liter was later taken as a middle fraction. The average of five trials gave $-156.5°$, the lowest temperature being $-156.8°$ and the highest $-156.3°$.

Xenon was less satisfactory to deal with than krypton. The change from solid to liquid was not nearly so sharply defined nor was the corresponding pressure. The quantity of xenon which had been most carefully purified was insufficient to fill the apparatus at the pressure of the triple point and was accordingly supplemented by the high purity xenon loaned by Dr. Moore. Results are shown in Table II.

TABLE II

VAPOR PRESSURES OF XENON

Sample of density 5.887 g./l.

Trial 1		Trial 2	
Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
−117.2	465	−119.1	454
−116.2	491	−116.2	482
−115.3	501	−114.4	525
−114.4	525	−113.5	544
−113.4	560	−112.2	571
−113.2	583	−112.0	581
−113.0	586	−111.7	581
−112.9	588	−111.6	585
−112.7	590	−110.7	602
−112.6	594	−107.6	750
−112.2	600	−107.2	755
−112.0	604	−107.0	760
−111.7	618		
−109.2	723		
−109.0	717		
−108.0	756		
−107.1	760		
−106.9	771		
−104.3	846		

The erratic behavior of xenon in the vicinity of its triple point suggests the possibility of a transition point of the solid xenon to a different solid form just below the triple point. The results show the triple point of xenon to be between $-111.0°$ and $-112.0°$ and the boiling point to be between $-106.9°$ and $-107.4°$. The only other value that has been reported for the triple point is that of Ramsay and Travers, namely, approximately $-140°$. The above investigators gave $-109.1°$ for the boiling point of xenon. Patterson, Cripps and Whytlaw-Gray, using some of the xenon purified by Moore,[4] reported a boiling point of $-106.9°$, but since this was based on extrapolated values they considered it of doubtful accuracy.

In this connection it may be pointed out that the literature shows rather a small range of temperature between the melting and boiling points

[4] Moore, *Proc. Roy. Soc.* (London), **A81**, 195 (1908).

of the other rare gases. This work indicates the range for krypton and xenon to be more in keeping with other members of the family.

A summary of the values which this work indicated to be most reliable is found in Table III.

TABLE III

SUMMARY OF RESULTS

	Krypton	Xenon
Density in grams per liter.....	3.733 ± 0.007	5.887 ± 0.009
Atomic weight.....	83.6 ± 0.2	131.4 ± 0.3
Boiling point, °C.....	−152.9 ± 0.3	−107.1 ± 0.3
Triple point temperature, °C.....	−156.6 ± 0.1	−111.5 ± 0.5
Triple point pressure, mm.....	557 ± 3	600 ± 20

The temperatures were determined by the use of a platinum resistance thermometer, a Wheatstone box bridge set-up being used to measure the resistances.

The galvanometer was of the cylindrical type manufactured by the Leeds and Northrup Company of Philadelphia. It was mounted on a wall shelf and fitted with a telescope and scale. It far exceeded the need as to sensitivity since a difference in resistance corresponding to 0.01° could be detected easily and temperatures are given in this report to 0.1°.

The accuracy of the box bridge was checked by connecting a resistance box calibrated by the Bureau of Standards, in place of the platinum resistance thermometer. The bridge was not in error over the range used with krypton and xenon by an amount sufficient to affect the temperature values given as stated above to 0.1°.

The platinum resistance thermometer was also a Leeds and Northrup instrument of the type designed especially for low temperature work. Constants for the Van Dusen[5] equation were supplied by a calibration made by the Bureau of Standards and this equation was used to calculate a set of data relating temperature and resistance. From the data so obtained a curve was plotted so that if a value were known for the resistance of the platinum, the corresponding temperature could be read from the curve. The scale used made one mm. equal 0.2° and one mm. equal 0.02 ohm.

Grateful acknowledgment is made to colleagues in the Chemistry Department of Purdue University for helpful suggestions as well as occasional assistance with the experimental work.

Mr. W. E. Fish, department mechanician, often worked after regular hours and on holidays preparing the liquid air which was needed for the work, sometimes in amounts up to fifteen or twenty liters per day. His helpful coöperation has been greatly appreciated.

[5] Van Dusen, THIS JOURNAL, **47**, 326 (1925).

Summary

New values are reported for temperatures and pressures for the triple points of krypton and xenon.

Studies of the vapor pressures of krypton and xenon have been made, principally in the range of temperature just including the triple points and boiling points. The results indicate the accepted values for the boiling points to be in error and new values are reported.

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THE PHOTO-POLYMERIZATION OF STYRENE AND VINYL ACETATE

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In a number of oxidation processes sensitive to light the chain reaction theory has been shown to account satisfactorily for the phenomenon of inhibition of oxidation in such systems. An examination of the quantum yield of these photo-reactions shows that a large number of molecules react per light quantum absorbed, that the light absorbed, therefore, starts a chain of secondary oxidation processes. It has been known now for some time that many polymerization processes are light sensitive and also show the phenomenon of inhibition by added agents. Thus far, however, quantitative studies similar to those with oxidation reactions have been lacking. An additional interest attaches to such studies with processes of polymerization. It has been shown by Alyea and Bäckström,[1] in certain reactions, that the inhibitor in oxidation processes is oxidized in the process of breaking the reaction chains. Such a fate for the inhibitor molecule is impossible in polymerization processes carried out in the absence of oxygen. The question suggests itself, therefore, as to the nature of the inhibitory act in a polymerization reaction. It was to gain some insight into the quantitative aspects of the photo-polymerization that the following studies were made.

Only recently has any attention been given to the quantitative side of the question although references to qualitative experiments and reaction products are frequent. The theoretical side of the polymerization has drawn attention more recently as is indicated by the work of Carothers,[2] Staudinger[3] and Moureu and Dufraisse.[4]

[1] Alyea and Bäckström, THIS JOURNAL, **51**, 90–109 (1929).

[2] Carothers, *ibid.*, **51**, 2548 (1929).

[3] Staudinger, *Ber.*, **62**, 2893 (1929); **62**, 2933 (1929).

[4] Moureu and Dufraisse, *Bull. soc. chim. France*, [4] **35**, 1564 (1924). Since the completion of this work an article has appeared by Starkweather and G. B. Taylor [THIS JOURNAL, **52**, 4708 (1930)] describing experiments made to determine the kinetics of the thermal polymerization of vinyl acetate.