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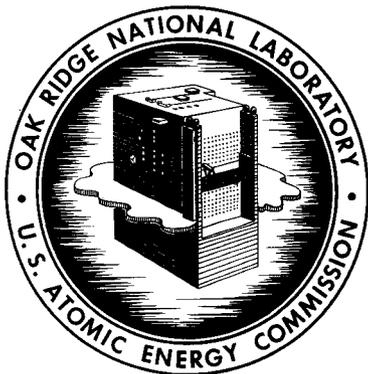
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REVIEW OF ORNL THERMAL DIFFUSION PROGRAM

JANUARY - DECEMBER 1963

T. A. Butler
W. R. Rathkamp
H. B. Greene



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ISOTOPE DEVELOPMENT CENTER REPORT

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MAY 1964

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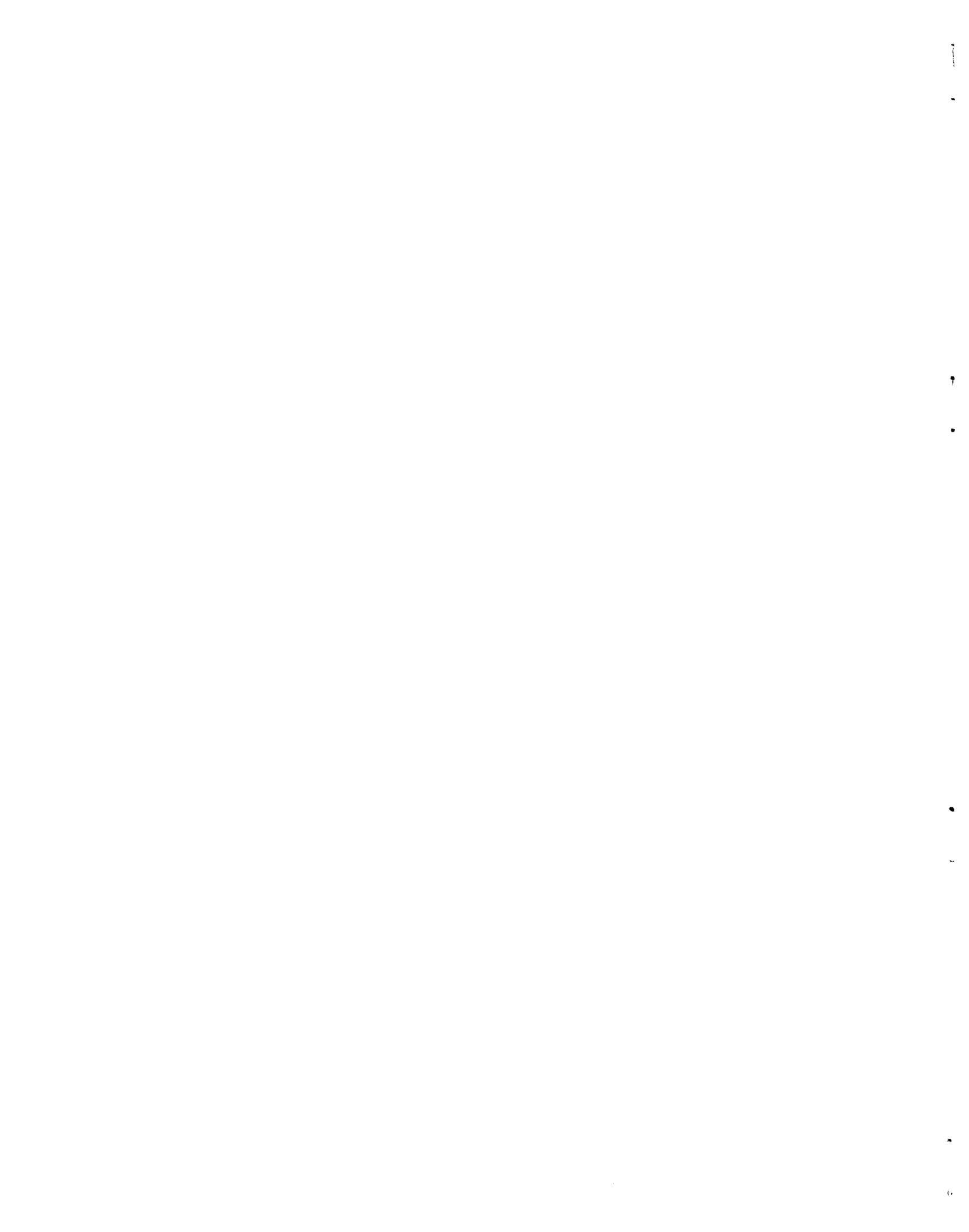


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REVIEW OF ORNL THERMAL DIFFUSION PROGRAMJANUARY - DECEMBER 1963

T. A. Butler, W. R. Rathkamp, H. B. Greene

ABSTRACT

This report reviews activities of the ORNL Thermal Diffusion Program for 1963 and covers equipment used, theoretical studies, and production data.

I. INTRODUCTION

The ORNL Thermal Diffusion Program makes available enriched isotopes which either cannot be provided by other separation methods or are more costly when prepared by alternate means with emphasis on concentrating isotopes of the inert gases. The heaviest and lightest isotopes in such mixtures (e.g. Ne²⁰, Ne²², or Ar³⁶) can easily be enriched to any desired concentration if a diffusion system is constructed of sufficient length. A cascade to enrich an isotope of other than the greatest or least mass in a mixture of three or more components becomes more complicated in arrangement and offers design problems relative to length, width, and flow rates.

Construction of thermal diffusion columns presents engineering problems associated with supporting heated central elements. At the present time ORNL columns are designed to use standard, commercial tubular heaters which are 0.440 in. in diameter with an effective length of 7 ft. In some cases the column length is doubled by inserting a second heater through the bottom. Columns have an annular gas space 1/8 in. wide, and heaters are held along the axis of the tube by small dimples impressed into the cold walls. These tubular units replace the 0.022-in.-diameter Nichrome wire previously used as the heating element.

Approximately 200 columns are installed in the thermal diffusion laboratory. To conserve space, 36 columns are enclosed in a common water jacket 8 in. in diameter (Fig. I-1). Four of these "bundles" are in use. Since all columns are sealed individually when the "flat head" alternate arrangement is used, individual columns can be interconnected externally to give any desired shape of cascade. Within the same bundle, some tubes can be used for enriching one isotope, while at the same time other columns are being used to enrich a different isotope or a different element.

II. THERMAL DIFFUSION DEVELOPMENT PROGRAM

Separation Factors

If an efficient tapered cascade is to be designed to enrich an isotope from some small concentration (e.g. Ar³⁶ at 0.34% natural abundance) to some higher concentration (e.g. 99.9%), the thermal diffusion characteristics of a given column system must be determined. These characteristics can be computed theoretically.¹ To test the validity of this theory, a series of experiments was performed to determine the agreement between observed values of thermal diffusion separation factors and the theoretical values calculated according to Jones and Furry.

The data taken during these experiments are shown in Fig. II-1. The theoretical and observed separation factors for Ne, Kr, and Xe as functions of gas pressure are plotted to the same scale in Fig. II-2 and show that the maximum equilibrium separation factor occurs at a lower pressure for the higher mass gases and that the value of this maximum separation factor is much smaller for krypton and xenon than for neon.

The separation factor per mass unit is

$$q^* = \frac{H^*L}{K_c + K_d},$$

where

- H* = coefficient of thermal diffusion transport per unit mass,
- K_c = coefficient of convective remixing,
- K_d = coefficient of diffusive remixing,
- L = length of the column.

The H*, K_c, and K_d factors can be written as functions of pressure and take the form

$$H^* = AP^2,$$

$$K_c = BP^4,$$

$$K_d = C,$$

where A, B, and C are constants determined by column geometry and temperature and by properties of the gas. The ratios B/A and C/A can be determined from equilibrium data, but a different kind of experiment must be performed to estimate A and allow calculation of B and C. These ratios may be computed from the equations

¹R. C. Jones and W. H. Furry, Revs. Modern Phys. 18(2): 151-224 (1946).

$$B/A = \frac{L}{2P^2 \log q^*}, \text{ and}$$

$$C/A = \frac{LP^2}{2 \log q^*},$$

where

P = gas pressure at which the maximum separation factor occurs,
 q^* = separation factor per unit mass at the maximum in the curve.

The observed and theoretical ratios for Ne, Kr, and Xe are given in Table II-1.

Table II-1. Theoretical and observed ratios for neon, krypton, and xenon

Element	Theoretical			Observed		
	B/A	C/A	C/B	B/A	C/A	C/B
Neon	0.89	980	1100	1.05	1280	1220
Krypton	79.2	166	2.10	118	389	3.30
Xenon	450	137	0.305	668	315	0.472

A second experiment was performed with neon to measure H^* and A. Neon gas was allowed to flow through the top of the experimental column to maintain constant concentration at this feed point, and enriched Ne^{22} was withdrawn from the bottom at various rates. From the withdrawal rate and corresponding concentration data, H^* was calculated to be $7.65 \times 10^{-7} \times P^2$. A comparison of observed and theoretical values for neon follows.

	<u>Theoretical</u>	<u>Observed</u>
H^*	$9.80 \times 10^{-7} \times P^2$	$7.65 \times 10^{-7} \times P^2$
K_c	$8.70 \times 10^{-7} \times P^4$	$8.05 \times 10^{-7} \times P^4$
K_d	9.60×10^{-4}	9.81×10^{-4}

Experiments show that observed values for K_c and K_d are in good agreement with theoretical values, but theory over-estimates the value for H^* .

In addition to the terms K_c and K_d , the coefficient of remixing (K) may contain a parasitic remixing term K_p which arises due to unknown inaccuracies within the column (e.g. nonuniform surface temperature distribution and poor centering of the heater in the cold tube). This K_p factor theoretically behaves in very much the same manner as K_c and if present will appear as an apparent increase in K_c . Since the observed

value of K_c is actually a bit lower than expected, any parasitic remixing must be small.

Complete analyses of H^* , K_c , K_d , and K_p for krypton and xenon will be made when experiments to measure H^* are finished.

Gas Viscosity Measurements

One of the best ways to calculate thermal diffusion characteristics of a gas is from data on viscosity; however, reliable viscosity data are meager and in the case of several gases (notably krypton) are quite inadequate. Figure II-3 shows the apparatus recently assembled to measure viscosity of gases at elevated temperatures. Trial runs using He, Ne, Ar, and N_2 (gases for which good viscosity data have been published) showed agreement within 2-3% between ORNL measured values and published data from other sources.

Observed values for krypton viscosity are plotted in Fig. II-4 as a function of temperature, and these measurements are compared with a few published values established for lower temperatures. Observed and published values for argon are included for comparison.

III. PRODUCT ENRICHMENTS

Neon

In the neon thermal diffusion cascade, concentration of Ne^{21} is being emphasized with high purity Ne^{20} and Ne^{22} being collected as by-products. The progress of the system for January - May 1963 is shown in Table III-1. An assay taken at the position listed (indicating the number of columns from the bottom of the system) gave the enrichment of Ne^{21} at that point in the cascade at the end of the month. The values listed for March show that the peak of the Ne^{21} distribution was about halfway between these points with an enrichment >12%. By May the Ne^{21} peak had worked its way up to the center of the system.

Table III-1. Enrichment of Ne^{21} achieved
January - May 1963

Month	Position	Percentage of Ne^{21}
January	1	> 1.5
February	2	>12.0
March	1	12.0
March	2	11.0

Table III-1. - continued

Month	Position	Percentage of Ne ²¹
April	2	16.9
April	3*	13.7
May	3*	20.3

* center of the system

In June the columns were rearranged so that all ten units (each 15 ft in length) were in series. Since this rearrangement increased the length of the system, it could now sustain higher gradients. Progress after the modification is shown in Table III-2.

Table III-2. Enrichment of Ne²¹ achieved
June - December 1963

Month	Position	Percentage of Ne ²¹
June	4	29.6
July	4	27.8
August	4	23.0
September	4	31.8
October	2	29.7
November	1	22.5
December	2	31.5

(Since the total height of the system is now 10 columns, 5 columns from the bottom represents the center of the system.)

After reaching 29.6% enrichment in June, operational difficulties slowed progress of the system. In September the highest enrichment reached thus far in the cascade (31.8%) was attained. Since that time, additional operating difficulties have prevented exceeding this value.

Neon-20 was discarded from the top of the system during January. In February a special interest in Ne²⁰ arose, and 25 liters (STP) of neon was collected with an enrichment of Ne²⁰ >99.98% and a chemical purity >99%. From March to October, Ne²⁰ was again discarded from the system.

A renewed interest in highly enriched Ne²⁰ with high chemical purity (<1% H₂ contamination) arose in October, and during the remainder of the year ~39 liters of neon were collected at an enrichment of ~99.99% Ne²⁰ with a chemical purity >99%. A total of 9.4 liters with <0.3%

H₂ contamination was transferred directly to inventory. The effort to collect highly enriched Ne²⁰ slows accumulation of Ne²¹ in the system. Ordinarily Ne²⁰ is withdrawn when it reaches a concentration of 99% which allows additional normal material to enter the cascade. Several extra days are required for the Ne²⁰ in the 5-liter end-volume to enrich to >99.98% so it can be removed.

Table III-3 shows neon production during the year. In addition to the material placed in inventory, 14 liters of Ne²² at an enrichment >99.9% was removed from the system and is being held as in-process material.

Table III-3. Enriched neon isotopes released to inventory
January - December 1963

Isotope	Enrichment, %	Weight of contained element, mg
Ne ²¹	8.5	324
Ne ²¹	12.6	18
Ne ²¹	10.8	90
Ne ²¹	20.6	18
Ne ²¹	30.8	18
Ne ²⁰	>99.98	22,500
Ne ²⁰	99.99	2,142
Ne ²⁰	99.99	6,300

Argon

The thermal diffusion system for concentrating argon isotopes was first used to enrich Ar³⁶. Later interest was centered on enriching Ar³⁸, and the cascade was modified to collect Ar³⁸ on the first pass.

When it became evident that enrichments of Ar³⁸ as great as 20% would be difficult to achieve, the columns of the system were rearranged and connected in series to give one long system (effective length ~112 ft) a single column in width. This rearrangement will permit a larger Ar³⁸ inventory to be accumulated in the center of the system without the tails of the peak concentration spilling over to the ends of the system and being lost. A 1-liter volume is provided at the extreme top of the system for the collection of the light-end impurities and a 1-liter volume is provided one column down for the accumulation of Ar³⁶. A 100-ml volume is located at a position 7 columns below the Ar³⁶ volume (about the vertical center of the system) for accumulation of Ar³⁸.

Table III-4 shows progress of the system for the year. The enrichment listed for each month represents either the maximum Ar³⁸ concentration noted each month or the enrichment of a sample taken near the end of

that month. The position of the sample tap represents the number of columns below the provided Ar³⁶ volume.

Table III-4. Enrichment of Ar³⁸ achieved
January - December 1963

Month	Position	Percentage of Ar ³⁸
January	top	3.9
February	top	5.8
March	2	5.8
April	2	14.1
May	5	13.8
June	6	19.2
July	7	20.4
August	9	21.8
September	8	22.2
October	7	23.1
November	7	22.1
December	7	18.9

The highest Ar³⁸ enrichment achieved with this system (23.1%) was reached on October 21, and it became evident during November that this enrichment was about as high as could be sustained with the present system. A decision was made early in December to withdraw Ar³⁸ at values >20% for production inventory and to establish a production rate for Ar³⁸ $\geq 20\%$ with the existing equipment. Argon production is given in Table III-5.

Table III-5. Enriched Ar³⁸ released to inventory
January - December 1963

Month	Enrichment, %	Weight of contained element, mg
February	4.7	18
March	8.3	18
April	11.0	18
November	22.1	21
December	>20.0	199

Carbon

One of the most persistent problems encountered in the C¹³ thermal diffusion cascade is decomposition of the process gas (methane) into free hydrogen and carbon. Since this decomposition could be catalyzed by

the surface of the central heater, a series of experiments was conducted to evaluate methane decomposition on various metal surfaces. These tests revealed that in the temperature range 400 to 600°C, decomposition of methane on stainless steel surfaces was much greater than on aluminum surfaces.

To permit further testing of this observation, a thermal diffusion column was constructed using a heater made by swaging a soft aluminum sheath over a standard stainless steel calrod. The column was fitted with sampling valves at top and bottom, a pressure gage connected to the gas annulus, a thermocouple attached to the heater sheath, and a Pyrex window at the bottom to allow observation for free carbon particles. Methane decomposition was detected by: (1) mass spectrometric analysis of samples from the top of the column to determine hydrogen content; (2) increase in gas pressure with time as CH₄ decomposed to form 2H₂; and (3) decrease in heater temperature with time as hydrogen, having greater thermal conductivity than CH₄, accumulated in the upper part of the column.

No perceptible decomposition of methane was observed at 400°C heater temperature; some decomposition was noted at 500°C after two weeks of operation; severe decomposition was observed at temperatures above 500°C. Past experience with stainless steel calrod heaters showed severe decomposition of methane at 400°C.

These observations indicate that aluminum heaters should give no decomposition of methane at 400°C, the operating temperature for which the C¹³ cascade was designed. Further investigations are to be made concerning the practicability of raising the operating temperature above 400°C to improve the diffusion efficiency of the columns, operating with a controlled rate of decomposition, and establishing a regular schedule of maintenance shutdowns to remove accumulated carbon.

Krypton

A system for enriching both the heavy (Kr⁸⁶) and the light (Kr⁷⁸) isotopes of krypton has been in operation for six months. Sixteen columns are connected in series to form a cascade one column in width and 240 ft long. A 6-liter volume has been connected into the center of the system between the eighth and ninth columns for use as a feed reservoir, and a double-ended bellows pump has been connected across the extreme ends of the system to provide for inter-column mixing of gas.

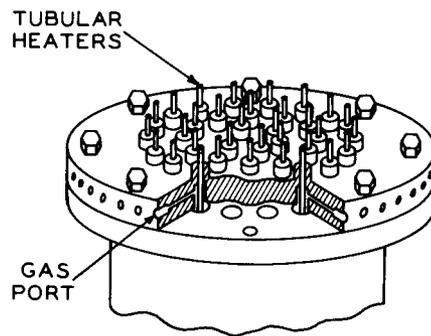
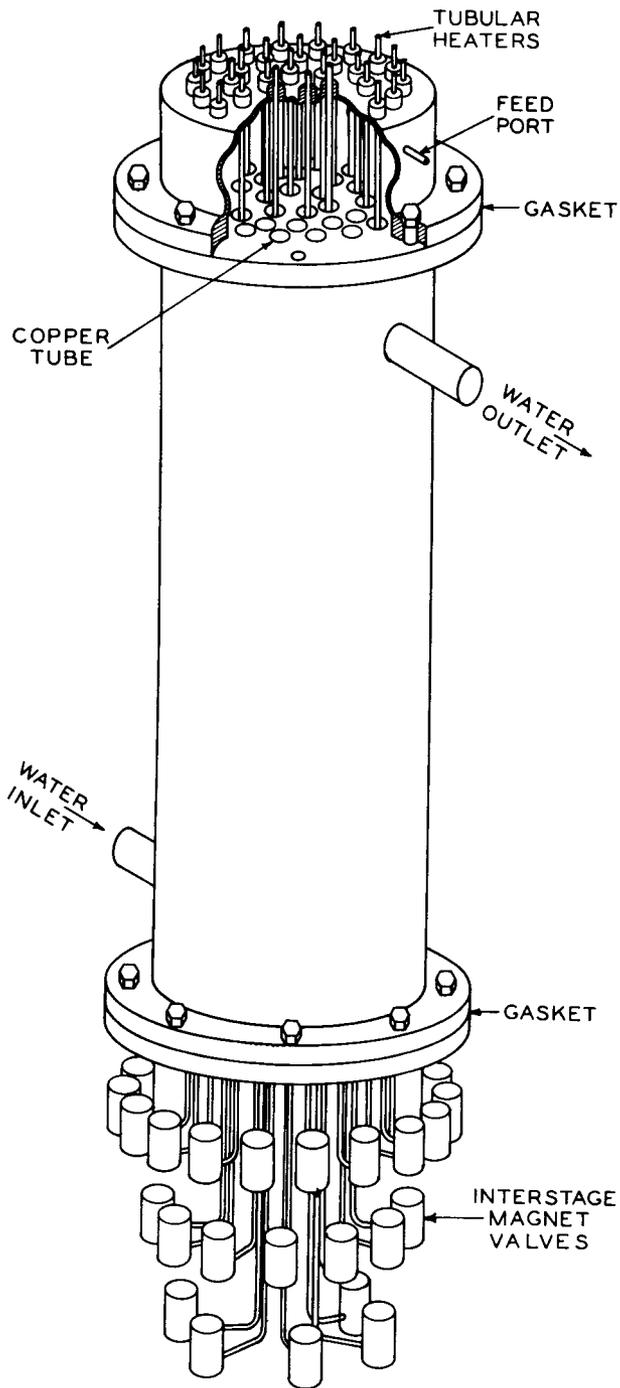
In October the operation was stopped, and krypton in the system was removed and stored so that column shells and heaters could be cleaned. Krypton was returned to the system on October 11, and by the end of the month Kr⁸⁶ enrichment was 74.3%.

Operational difficulties and equipment failures have limited progress in this cascade; but Kr⁸⁶ at the bottom of the system, representing ~400 ml (STP), had increased to 81.2% at the end of December.

Xenon

A 36-column cascade to enrich Xe^{124} from its natural abundance of 0.094% to 10% achieved a concentration of 4.4%. Operation of the cascade has been restricted by leaks in the system, but all components are now operating normally. Additional increases in Xe^{124} concentration are anticipated.

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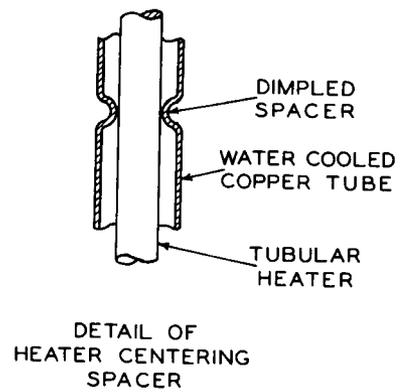


Fig. I-1. Thermal Diffusion Column Bundle.

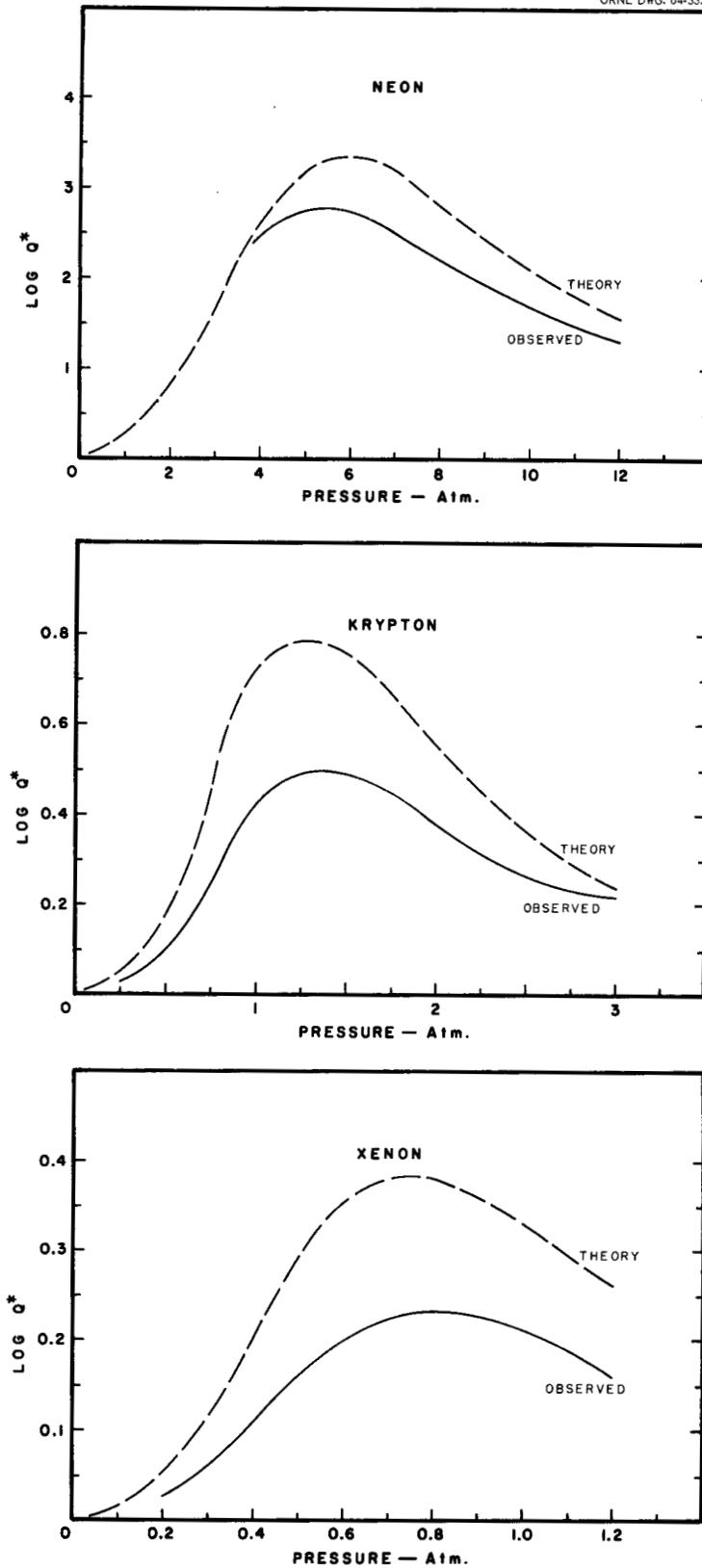
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Fig. II-1. Separation Factor vs Gas Pressure for Neon, Krypton, and Xenon.

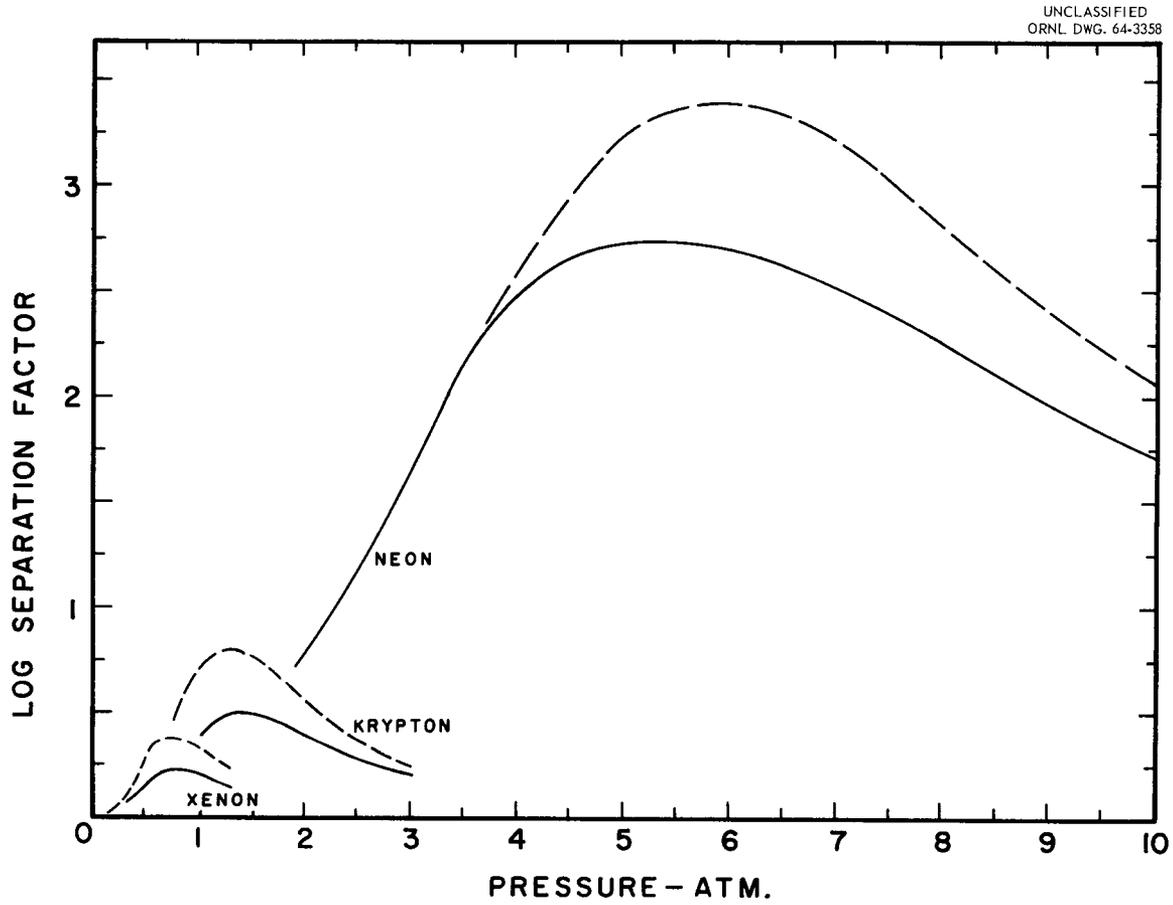
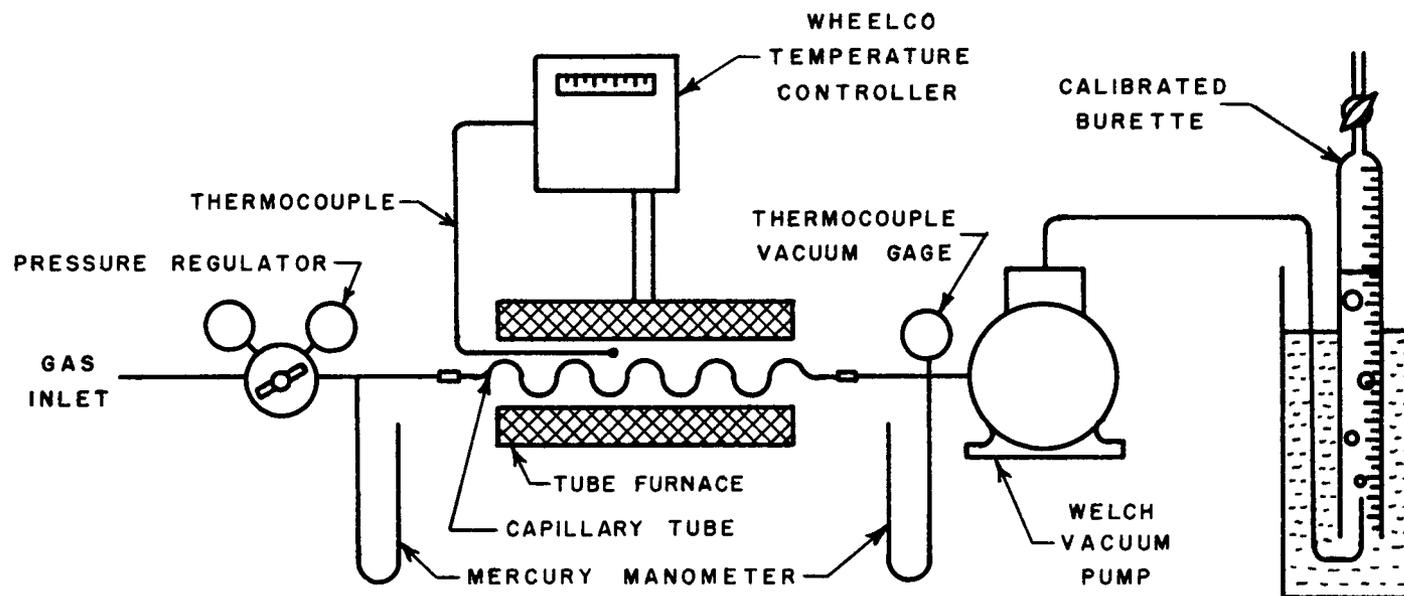


Fig. II-2. Comparison of Separation Factors vs Gas Pressure for Neon, Krypton, and Xenon.

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Fig. III-3. Equipment Used to Measure Viscosity of Gases.

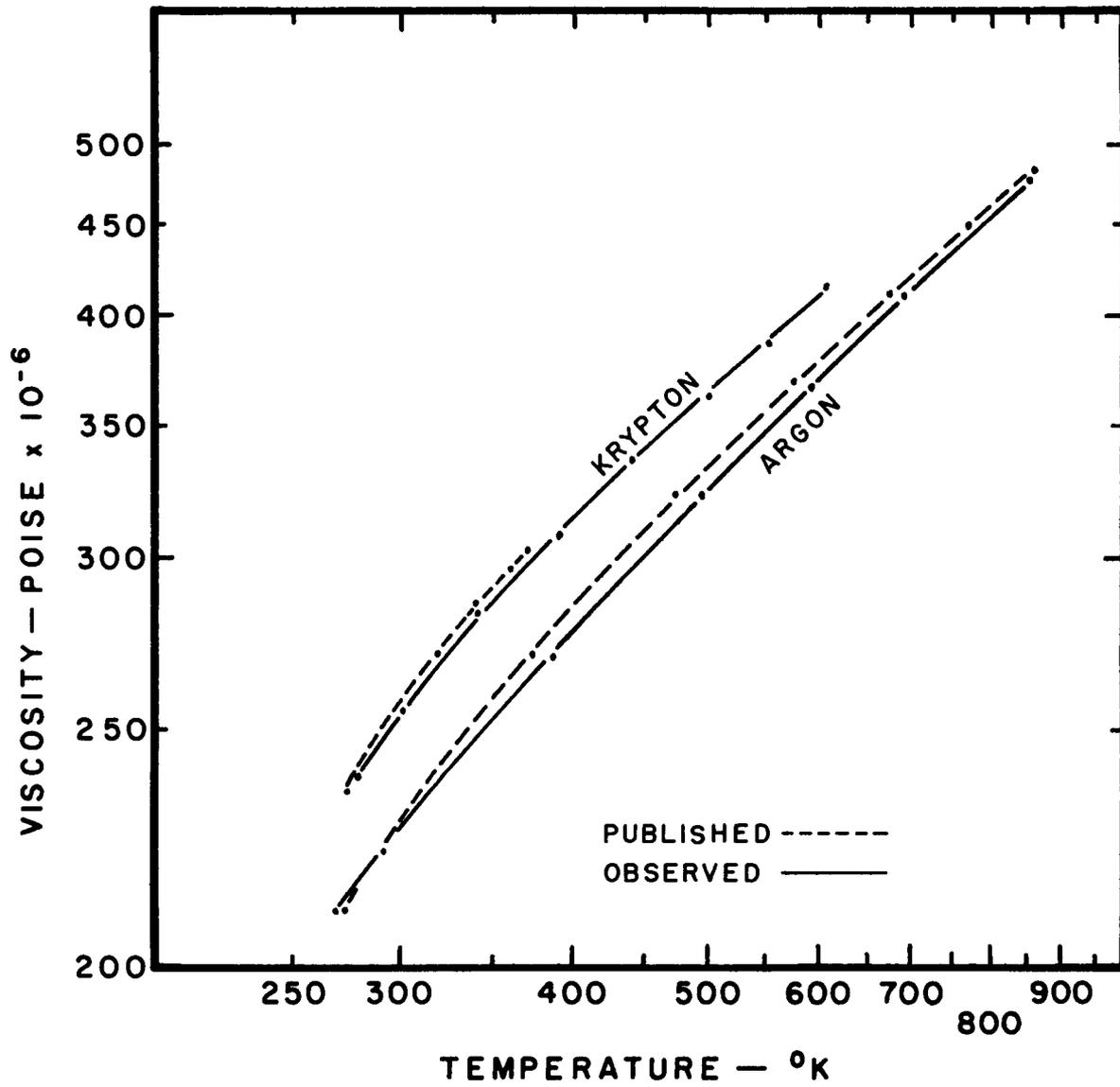
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Fig. II-4. Viscosity of Krypton at Elevated Temperatures.

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