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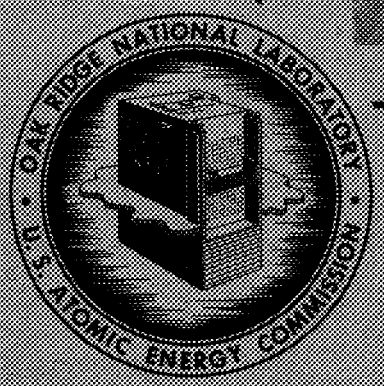
MULTIKILOCURIE PRODUCTION OF KRYPTON-85

R. E. McHenry



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ABSTRACT

An adsorption process has been developed and placed in operation for the recovery of multiliter quantities of radioactive krypton from fission gases resulting from spent-uranium fuel dissolution. The method is also useful for the separation of large quantities of purified xenon and may be useful for concentrating long-lived fission gases for storage.

The raw fission gases were passed through charcoal at 900°C to convert the oxides of nitrogen to nitrogen and carbon monoxide. The gas was then adsorbed on activated charcoal at temperatures from −30 to −125°C. Elution of the adsorbed gas with helium (through another activated charcoal column) permitted the collection of separate fractions of krypton, xenon, and the other gases (mostly nitrogen). Collection was made in cold traps operating at liquid-nitrogen temperature.

The chemical purity of the krypton product was > 99% and the radiochemical purity of the Kr^{85} was essentially 100%. The xenon product purity was > 98%.

The method is not advantageous for use in removing krypton and xenon from gases where their concentration is less than about 1%. It is most effective for final processing of rare gases that have been enriched by other processes.

INTRODUCTION

A process has been developed and a plant has been constructed and placed in operation for the separation and purification of multiliter quantities of fission rare gases from uranium fuel dissolver off-gas concentrates. The process which is described in this report is based on a combined procedure of selective adsorption of the desired gases on activated coconut charcoal followed by elution with a carrier gas.

This work was initiated to obtain long-lived Kr^{85} for the isotope program of the Oak Ridge National Laboratory. A later objective was to separate large quantities of purified xenon containing only traces of Kr^{85} activity. A further objective was to demonstrate a feasible method for concentrating the long-lived fission gases so that they could be more

easily stored if it became necessary to prevent their release to the atmosphere. The data for the production runs which are given in this paper were taken from a number of runs starting in late 1957 and extended over a period of approximately 2 1/2 yr. However, the process which is described was developed in 1953 and was used for routine small-scale production from early 1954.

Following the discovery[1] of the rare-gas elements by Sir William Ramsay and his associates, several investigators, Valentiner and Schmidt,[2] Dewar,[3] Aston,[4] Moureu and Lepape,[5] and others, succeeded in separating small quantities of relatively pure krypton and xenon from the atmosphere. Through the use of various combinations of distillation, adsorption, and chemical purification procedures, they were able to isolate and purify enough of the rare gases to determine their physical properties. These procedures recovered only a small fraction of the rare gases in the air that was processed and resulted in large errors in the reported values for the atmospheric abundance of krypton and xenon. Much later, Damköhler[6] using a similar procedure made a quantitative recovery of krypton and xenon from air and established their concentration in the atmosphere.

Peters and Weil[7,8] determined the adsorption isotherms for argon, krypton, and xenon and proposed a method for separating these gases. With their method the gases to be separated were adsorbed on activated charcoal, then desorbed by pumping at a low temperature. They claimed that, with sufficient adsorbent and at a temperature sufficiently low, the separation factor between the least adsorbed component and the next lower adsorbed component was great enough to effect complete separation in a single stage. They also claimed that under these conditions the rate of removal was sufficient for an appreciable production of these gases.

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[1] M. W. Travers, The Discovery of the Rare Gases, Arnold, London, 1928.

[2] S. Valentiner and R. Schmidt, Sitzber. kgl. preuss. Akad. Wiss. No. 27/7, 816 (1905).

[3] J. Dewar, Proc. Roy. Inst. Gt. Brit. 18, 433, 747 (1906).

[4] F. W. Aston, Proc. Roy. Soc. (London) 103A, 462 (1923).

[5] C. Moureu and A. Lepape, Compt. rend. 183, 171 (1926).

[6] G. Damköhler, Z. Elektrochem. 41, 74 (1935).

[7] K. Peters and K. Weil, Z. angew. Chem. 43, 608 (1930).

[8] K. Peters and K. Weil, Z. physik. Chem. A148, 1 (1930).

The separation of a combined krypton-xenon mixture from an oxygen plant distillation residue has been described by Fastovskii.[9] The basic method of concentrating krypton and xenon in a distillate residue had been previously patented by Claude.[10] Fastovskii removed the oxygen (99.4% in residue) by combustion with hydrogen, then removed the argon by distillation. The krypton and xenon were not separated.

In a later paper Fastovskii[11] proposed the separation of krypton from oxygen-krypton mixtures by a procedure similar to that proposed by Peters and Weil. Still later, Fastovskii[12] demonstrated a distillation procedure for the industrial-scale production of krypton-xenon-oxygen concentrates containing 40% mixed krypton-xenon. The final removal of oxygen was accomplished chemically. From the above it seems that Fastovskii abandoned his efforts to make use of a method based on fractional desorption from activated charcoal.

Arrol, Chackett, and Epstein[13] succeeded in applying the method of Peters and Weil to a multiple-stage batch process. With a nine-unit apparatus they were able to separate cubic millimeter quantities of relatively pure fission rare gases.

The first application of a chromatographic technique to the separation of gases was made by Zeldes and Brosi.[14] They used a flow of helium gas to elute the adsorbed gases through a column of activated coconut charcoal. The various components of the gases to be separated were eluted along the charcoal column at a rate inversely proportional to their degree of adsorption. Thus, with a sufficiently long column any desired separation could be obtained. This in effect provided a continuous method of repeating the procedure of Peters and Weil.[7,8] The effectiveness of the gas chromatographic technique is demonstrated by the 560 theoretical plates

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[9]V. G. Fastovskii, J. Chem. Ind. (U. S. S. R.) 14, 1416 (1937).

[10]G. Claude, Brit. Pat. 432, 644 (1933–35).

[11]V. G. Fastovskii, J. Gen. Chem. (U. S. S. R.) 9, 1666 (1939).

[12]V. G. Fastovskii, Kislorod 4, 5 (1947).

[13]W. J. Arrol, K. F. Chackett, and S. Epstein, Rare Gas Separation, CRC-297 (no date).

[14]H. Zeldes and A. R. Brosi, Chem. Div. Quart. Progr. Rept. Mar. 31, 1950, Part I: Chem. Research, ORNL-685, pp 53–61.

obtained by Zeldes and Brosi with a 50-cm-long column of activated charcoal at −98°C.

The principles of elution chromatography, as well as frontal analysis and displacement chromatography, were earlier set forth by Claesson in his work with liquid-solid chromatography.[15] Although he used the frontal analysis and displacement techniques with a gas-solid column, he did not use the elution procedure with the gas-solid column.

The technology of concentrating the krypton-xenon components from air is well established on an industrial scale.[12,16,17] These industrial units produce 1–2% krypton-xenon by variations of the method of Claude.[10]

In the past, gas chromatography has not been used to prepare large quantities of pure gases. Previous workers, for the most part, have been concerned with the development of gas chromatography as an analytical tool, or at most as a means of preparing quantities of various gases sufficient for research purposes.

A chromatographic method has several attractive qualities, especially when radioactive materials are being processed. High separation is obtainable in a trouble-free, easily controlled, inexpensive piece of equipment that is reasonably small. The greatest disadvantage is the loss of product capacity when the feed material is dilute. Also, since low temperatures are required for efficient operation, the use of coolant is excessive when large volumes of gases are processed. The equipment described in this report routinely separates and purifies in excess of 1000-liter batches of fission rare gases from concentrates containing 5–60% total rare gas.

THEORY

Separation Effects During Loading

If a pure gas is allowed to equilibrate with a quantity of activated charcoal, a portion of the gas will be adsorbed by the charcoal. The amount

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[15] S. Claesson, Arkiv Kemi, Mineral. Geol. A23(1), 1 (1946).

[16] R. E. Kirk and D. F. Othmer (eds.), Encyclopedia of Chemical Technology, vol 7, p 417, Interscience, New York, 1951.

[17] M. Ruhemann, The Separation of Gases, Clarendon, Oxford, 1940.

adsorbed will be determined by the temperature, the pressure of the gas, and the adsorption capacity of the charcoal.

The adsorption capacity of activated charcoal depends on its surface area. Different batches of charcoal may have different surface areas; an average value is 775 m^2/g. However, in the following discussion, the surface area will be assumed to be constant.

The adsorption of a pure gas as a function of the pressure at constant temperature can be expressed by the equation of Freundlich,[18]

$$V = K(P)^{1/n} \quad , \tag{1}$$

where

V = volume of gas at STP adsorbed per gram of adsorbent,

K and n are constants (dependent on temperature, the adsorbent, and the adsorbate),

P = pressure.

Hamfray[19] proposed the following empirical equation to express the adsorption of various gases on activated charcoal at constant pressure:

$$\frac{d \ln (x/m)}{dt} = -K \quad , \tag{2}$$

where K = constant, x = cc of gas adsorbed, and m = grams of charcoal.

If a mixture of gases is equilibrated with activated charcoal the quantity of each gas adsorbed will be lower than would be obtained if a pure gas were equilibrated at the same partial pressure. The amount of each gas adsorbed depends on the partial pressure and adsorption characteristics of the other components.

Two techniques are available for separation of gases on activated charcoal by use of their different adsorption characteristics. The older of the techniques has been referred to as "frontal analysis." This method was originally used as an analytical technique but is now seldom used because more powerful techniques are available. The other method is the elution separation. This method uses a flow of pure lightly adsorbed gas

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[18]H. Freundlich, Colloid and Capillary Chemistry, p 110, Methuen, London, 1926.

[19]I. F. Hamfray, Z. physik Chem. 74, 129 (1910).

to elute the adsorbed gases in inverse order of their adsorption strength. Both techniques are combined in the present process and will be described.

If a quantity of gas of nonvarying composition containing krypton and nitrogen is passed into one end of a tube containing activated charcoal in a helium atmosphere, the particles of charcoal at the entrance of the tube will rapidly become equilibrated with the gas stream. The composition of the gas which is adsorbed depends on the relative degree that the krypton and nitrogen are adsorbed, the composition of the gas phase, and the temperature. The ratio of the mole fraction of krypton in the adsorbed phase to the mole fraction in the gas phase is the concentration factor for one equilibrated stage. The lower the temperature, the higher will be the concentration factor. Since krypton is more readily adsorbed than nitrogen, the adsorbed phase is enriched in krypton.

Downstream of the equilibrated particles of activated charcoal, the flowing stream is depleted of krypton. This depletion continues farther downstream until the gas phase contains no krypton.

The gas which emerges first from the exit end of the activated-charcoal-filled tube will be the least adsorbed gas in 100% concentration. If the flow of gas is continued into the tube, eventually krypton will be detected in the gas at the exit end of the tube. A schematic representation of the tube is shown in Fig. 1.

With the above procedure only nitrogen can be obtained in a pure fraction; however, the krypton can be concentrated without loss. In Fig. 1b, if the flow of gas is stopped at the moment krypton is first detected in the exit stream and the adsorbed gases are removed from the activated carbon, the desorbed gases will contain a greater fraction of krypton than did the original gas. If the tube is long, the degree of concentration will approach the concentration factor obtainable at equilibrium under the same conditions. This is one stage.

Figure 2 is a representation of a three-component gas: nitrogen, krypton, and xenon. The xenon, which is very strongly adsorbed, reduces the quantity of krypton and nitrogen that is adsorbed. The krypton in turn reduces the quantity of nitrogen that is adsorbed in its presence.

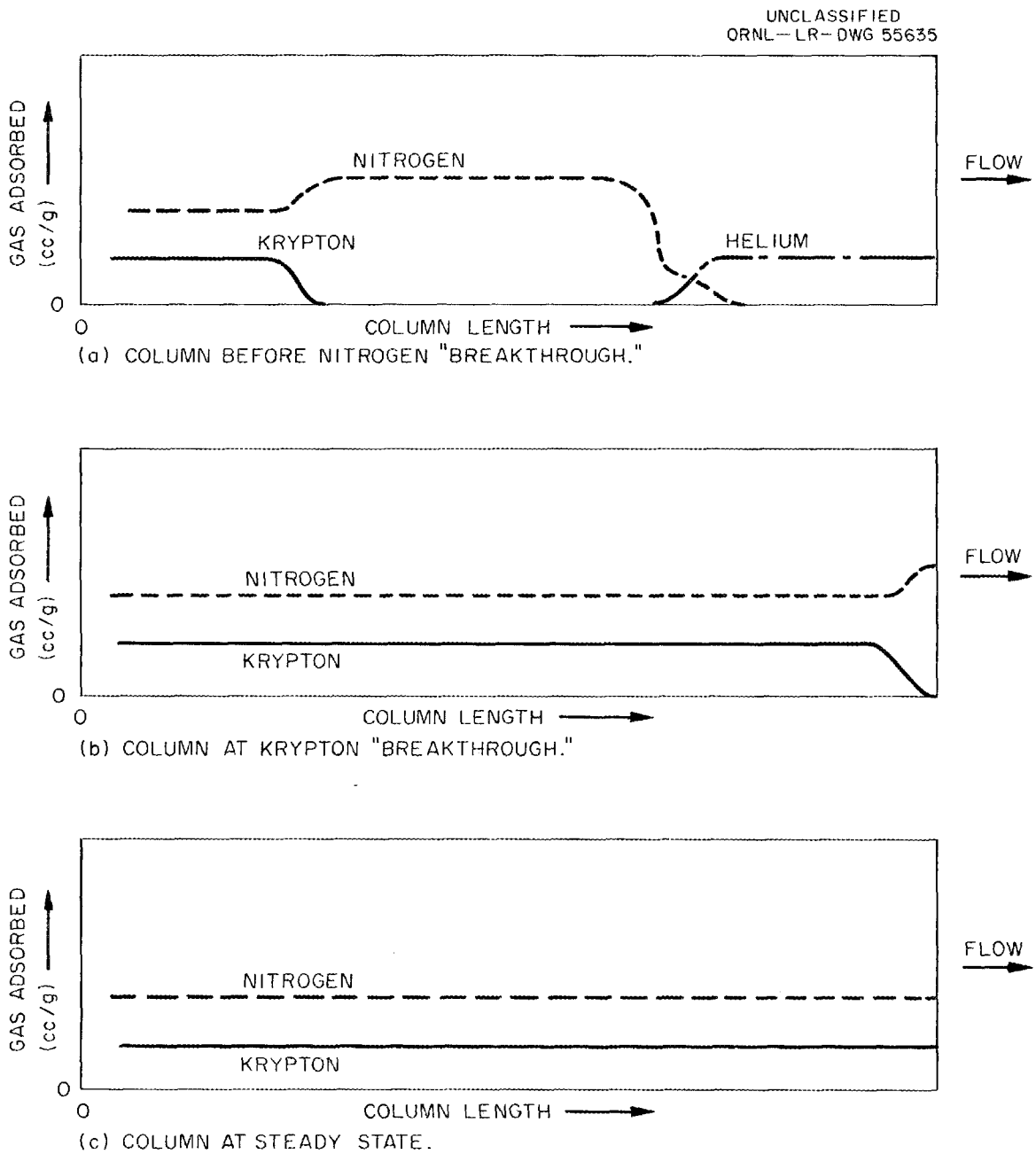

Fig. 1. Distribution of Two Components on Gas Chromatographic Column.

As more of the three-component gas is flowed through the activated charcoal the xenon will displace, to a larger extent, the krypton band. This results in a "pileup" of krypton in front of the xenon.

At the time of the nitrogen "breakthrough" a partial separation has occurred between the xenon, krypton, and nitrogen. Also, the bulk of the nitrogen has been removed from the xenon and krypton.

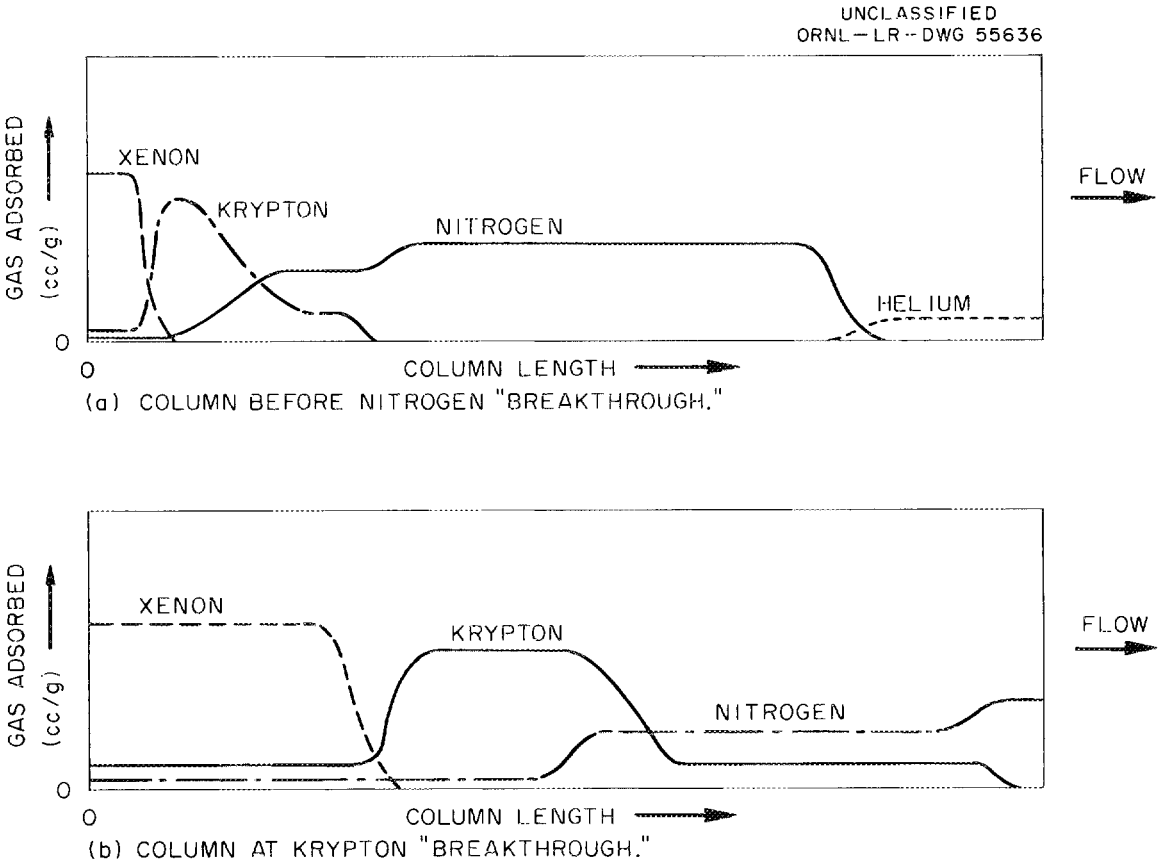

Fig. 2. Distribution of Three Components on Gas Chromatographic Column.

The preceding paragraphs have described in idealized form the effects which occur during loading of the separation column. In practice, the gases contain many components: H_2, N_2, O_2, Ar, CO, N_2O, Kr, CO_2, Xe, and NO_2. These gases may be divided into three groups: (1) the nitrogen group, which includes all the gas less strongly adsorbed than krypton, (2) krypton, and (3) the xenon group, which includes all the gases that are more strongly adsorbed than krypton.

Elution

Elution chromatography makes use of a flow of lightly adsorbed gas to preferentially elute the adsorbed gases from the activated charcoal. The less the eluting gas is adsorbed, the greater will be the separation effect obtained. If the eluting gas is adsorbed to an appreciable extent, it will tend to displace the gases which are being eluted and reduce the separation effect of the activated charcoal. In separation procedures

where the fractions are to be recovered, it is important that the eluting gas be easily separable from the fractionated gases. If the eluting gas is adsorbed only to a small extent, this can be easily accomplished.

The influence of the eluting gas on the gases to be separated occurs only (assuming the eluting gas is not adsorbed) on the molecules which are in the gas phase. The gas which is least adsorbed will be eluted first. Also, a gas with less tendency to remain in the adsorbed state will make longer "jumps" while it is in the gas phase.

Linearity

If a gas does not obey Henry's law, the adsorption isotherm is nonlinear and there is competition between molecules of the same gas for adsorption space. Because of this competition, at higher concentrations the molecules will make longer "jumps." Such nonlinearity is exhibited by krypton and xenon. Typical elution curves for krypton show the steep front and drawn out tail of nonlinearly adsorbed gases. The nonlinearity of the adsorption and the resulting drawn out tail of the elution curve tend to make separation of the krypton from xenon incomplete. No difficulty has been encountered in routinely preparing krypton with no xenon detectable by mass spectrographic analysis. However, a small amount of krypton is always present in the xenon.

To reduce Kr^{85} activity in the xenon product, the separation column could be made sufficiently long or the column could be operated with less loading, and the required separation could be attained with a single elution. However, since it is necessary to recycle the xenon to remove CO_2, it is more efficient to run two elutions to remove the krypton. It probably would be more efficient to rerun the xenon elution cycle even if it was not necessary to remove CO_2.

Effect of Composition

If a gas mixture containing krypton and a totally unadsorbed (hypothetical) gas is equilibrated with activated charcoal and the quantity of krypton adsorbed by the charcoal is plotted versus the partial pressure of krypton in the gas phase, the curve obtained should be identical with

the adsorption isotherm. When krypton is diluted with a real gas and equilibrated with activated charcoal, the quantity of krypton adsorbed will be less than the value predicted by the adsorption isotherm. In effect the adsorption curve exhibits a negative deviation from the isotherm and intercepts the isotherm at 0% and 100% krypton. The extent of the negative deviation depends on the adsorptivity of the diluting gas.

In the two-component system nitrogen and krypton, if the effect of nitrogen is proportional to its concentration, the adsorptive capacity of activated charcoal for krypton is

$$f = (1 - k_1 C_{N_2}) K (P_{Kr})^{1/n} \quad , \tag{3}$$

where

f = cc of krypton adsorbed per gram of charcoal,

n, K, and k_1 = constants,

C_{N_2} = fraction of nitrogen,

P_{Kr} = partial pressure of krypton.

The term $K(P)^{1/n}$ is the familiar Freundlich expression for the adsorption isotherm.

When the total pressure above the charcoal is maintained at atmospheric pressure, $P_{Kr} = 760\ C_{Kr}$, where C_{Kr} is the fraction of krypton in the gas. Equation (3) then becomes

$$f = (1 - k_1 C_{N_2}) K (760\ C_{Kr})^{1/n} \quad . \tag{4}$$

If the effect of a third component is proportional to its concentration, then for the three-component system nitrogen, krypton, and xenon,

$$f = (1 - k_1 C_{N_2} - k_2 C_{Xe}) K (760\ C_{Kr})^{1/n} \quad . \tag{5}$$

For a long column containing M grams of charcoal, where the amount of krypton adsorbed approaches the equilibrium value, the capacity of the column for krypton is

$$C = M(1 - k_1 C_{N_2} - k_2 C_{Xe}) K (760\ C_{Kr})^{1/n} \quad . \tag{6}$$

Where the capacity, C, is in cc the equation $C = MK(760\ C_{Kr})^{1/n}$ gives the capacity of the column for a krypton pressure equal to $760\ C_{Kr}$ with no other gases present.

The term $(1 - k_1 C_{N_2} - k_2 C_{Xe})$ is the fraction of the pure krypton capacity obtainable with nitrogen and xenon present.

EQUIPMENT

The basic components of the krypton-xenon separation system were the activated-charcoal-filled separation columns, charcoal-bed reactor, activated-charcoal-filled cold traps, condensation cold traps, flow controllers, analytical instruments, and a shielded enclosure to contain the equipment. Also included in the system were the necessary valves, piping, and storage tanks to facilitate operation. This is shown in Fig. 3.

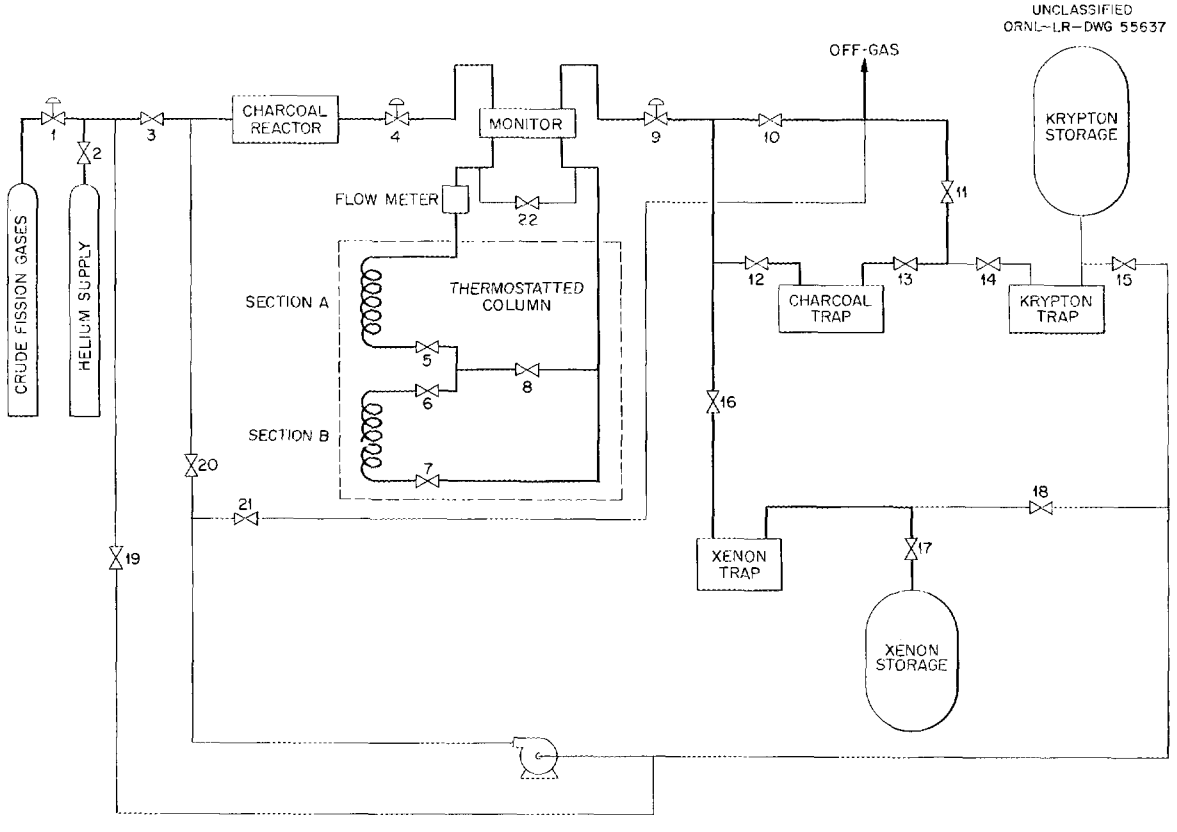

Fig. 3. Krypton-Xenon Process Flowsheet.

Separation Column

The column used to separate krypton and xenon was constructed in two sections, A and B. The A section was 36 ft long and was constructed of 2-in.-diam by 0.065-in.-wall stainless steel tubing. The B section was 20 ft long and was constructed of 1-1/2-in.-diam by 0.065-in.-wall stainless steel tubing.

The two sections were coiled in series to form a single helix 20 in. in diameter and 26 in. high. The column was contained in an insulated enclosure which could be cooled to the required temperature by use of liquid nitrogen. Thermostatically controlled heaters were also provided so that the column could be heated to 300°C. The two column sections were connected by 3/8-in.-OD tubing to a manifold outside the container. The manifold was arranged so that the A section could be used separately or in series with the B section, or the entire column could be bypassed.

Each section of the column was filled with 6–14-mesh Fischer activated coconut charcoal. The A section contained 9400 g and the B section 3300 g of charcoal. The column was shielded with 2 in. of lead. Manifold valves were operated remotely by use of extension handles.

The separation column used in the earlier runs (described later in this report) was made in four parts 12 ft in length with a 1-1/2-in. OD and a 0.065-in. wall. Each of these parts was filled with 1850 g of 6–14-mesh activated charcoal.

Cold Traps

There were three cold traps in the krypton-xenon system, one of which was filled with activated charcoal and two which were condensation traps. All traps were operated at −195°C by cooling with liquid nitrogen.

The charcoal-filled cold trap was 5 in. in diameter and 20 in. high and was filled with 2000 g of 6–14-mesh coconut charcoal. A finned, coiled Calrod heating element was placed inside the trap in contact with the charcoal so that the trap could be heated to 300°C during desorption. The temperatures of the heater and the charcoal were indicated by thermocouples.

The condensation cold traps were 5 in. in diameter and 12 in. high. These traps could be heated, when required, by heating units which were brazed to the exterior of the traps. During operation, the gas stream entered the cold traps at the top, passed through a distributor baffle near the bottom of the traps, and exited through a tube which extended through the top.

The cold traps were cooled by liquid nitrogen contained in stainless steel Dewar flasks which could be raised and lowered remotely by pneumatic

motors. Liquid nitrogen was added to the flasks as required through insulated tubing. The liquid nitrogen level in a Dewar flask was indicated by the vapor pressure of argon in two argon-filled dip tubes positioned at the desired high and low levels in the flask. When the liquid nitrogen level was raised above a dip tube, the argon condensation was indicated by a pressure drop on a gage.

Charcoal-Bed Reactor

The charcoal-bed reactor, which was used to remove the oxides of nitrogen from the gas stream, was 8 in. in diameter by 30 in. long and contained 12 lb of 6–14-mesh activated charcoal. The reactor was heated to the operating temperature of 900°C by an 8-in. tube furnace.

Krypton Storage

As a safety precaution, the Kr^{85} product was stored at pressures less than atmospheric. To reduce the volume required, it was stored in equilibrium with activated charcoal. At room temperature and atmospheric pressure, 13 liters of krypton could be contained in a 1-liter volume which was filled with 6–14-mesh activated charcoal. In the storage vessel, the charcoal was contained in thirty-one 2-in.-diam by 8-1/2-ft-long stainless steel tubes. These tubes were bundled in parallel inside a water-cooled jacket. The krypton capacity of the storage vessel was 2000 liters.

Instruments and Controls

Three pressure-control units regulated the flow of gas through the krypton-xenon system. A complete control unit consisted of a pressure transmitter, a controller, and a pneumatic valve. One pressure control unit reduced the inlet gas pressure from 500 to 5–10 psi. The other two controlled the flow through the separation column by regulating the inlet and outlet pressure. The controlled pressure was transmitted to a pressure gage outside the shielded equipment enclosure.

The on-off valves which were used in the system were equipped with pneumatic motors for remote operation. The valves were made of stainless steel and had bellows-sealed stems and Teflon seats.

Three radiation monitors were used in the system, one each at the inlet and outlet of the column and another at the cell exhaust. The monitors were gas-flow beta ion chambers (ORNL-Q-1873) used with an ac electrometer (ORNL-Q-826). With 0.01% krypton (mixed fission) in a gas stream at atmospheric pressure, the monitor would yield full-scale deflection (equivalent to 10^{-11} amp). Background was usually less than 10^{-12} amp. With 100% krypton (mixed fission), the current obtained was approximately 2.75×10^{-7} amp.

A Gow-Mac Instrument Company model 9454 thermal conductivity cell and meter were used with a Brown Electronik recorder to plot the thermal conductivity of the column exit stream. The column sweep gas (pure helium) was used as a reference. Because of the pressure sensitivity of the instrument, it was necessary to rezero the instrument for any change in flow conditions through the column.

PROCEDURE

Prior to the start of each run, the separation column was stripped of adsorbed gases by purging with helium for 30 min with the column at 300°C. The cleanup of the column was indicated by the activity monitor and thermal conductivity analyzer. The column was then cooled to the required temperature and filled with helium at atmospheric pressure. When the charcoal-bed reactor was charged with fresh charcoal, it was necessary to remove condensables by purging with helium at 600°C for approximately 1 hr. This procedure removed any adsorbed gases which might be released during a run and form a plug in the separation column. The traps and lines were either evacuated or purged free of impurities and filled with helium.

The fission gases which were processed contained 1–18% krypton and up to 65% xenon. These gases were contained in standard 1-1/2-ft^3 gas cylinders at pressures up to 500 psi. The cylinders were attached to the system as shown in Fig. 3.

Loading Cycle

The fission gas concentrates from the cylinders were reduced in pressure to 15 psi by a pressure control unit (valve 1, Fig. 3) and passed

through the charcoal-bed reactor at a rate of 0.1 to 1 cfm. In the reactor, the charcoal at 900°C reacted with the oxides of nitrogen to produce nitrogen and carbon monoxide.

The gas flow to the column was controlled by two pressure control units (valves 4 and 9, Fig. 3). Controller 9 was set to open at 1 psi. Controller 4 was adjusted to maintain sufficient pressure, usually less than 5 psi, to give the required flow through the column.

While the A section of the column was being loaded, the B section of the column was bypassed through valves 5 and 8. The effluent gas (nitrogen, oxygen, and carbon monoxide) from the column was exhausted through valve 10 to the off-gas line. The flow of gas to the column was continued until the concentration of krypton in the effluent gas reached approximately 1% of the concentration of the feed gas. The feed gas flow was then stopped and the A and B sections of the column were valved in series (valve 8 closed, valves 6 and 7 open).

Krypton Elution Cycle

Helium was then passed through both sections of the column in series at approximately 1 cfm. The flow was regulated by pressure controllers 4 and 9. The helium and the fraction of gas which eluted prior to krypton were exhausted through valve 10.

When krypton began to elute from the column, the flow was diverted through valves 12 and 13. The charcoal trap was cooled to −190°C. The helium from the charcoal trap was exhausted through valve 11.

When the krypton was completely eluted, valve 11 was closed and the helium pumped from the charcoal trap through valves 14 and 15. The helium was pumped to less than 10 μ Hg. The temperature of the charcoal trap was then slowly raised to 200°C and the krypton was condensed into the krypton cold trap at −195°C. From the krypton cold trap, the krypton product was evaporated to the storage tank.

Xenon Purification

The gases which remained on the column after the krypton elution were xenon, a small percentage of CO_2, approximately 0.1% krypton, and the eluting gas, helium.

The bulk of the eluting gas was removed by pumping the helium from the column through the xenon trap, which was cooled to −195°C. The column temperature was then slowly raised to 300°C and the xenon was condensed in the xenon trap. The xenon trap was pumped periodically to remove any accumulated helium. The condensed xenon was then evaporated into the xenon storage tank. The column was regenerated by purging with helium at 300°C and then cooling to −40°C.

The xenon in the storage tank was passed through the charcoal-bed reactor at 900°C and adsorbed on the A section of the column. The xenon remaining in the tank at equilibrium pressure was condensed into the xenon cold trap and evaporated through the charcoal-bed reactor to the column. The remaining xenon in the cold trap was discarded.

The impurities in the xenon (CO, Kr) were then eluted from the column to the off-gas line. The removal of the impurities was monitored with the activity monitor and thermal conductivity analyzer.

The pure xenon fraction which remained on the column was condensed and evaporated to the storage tank as previously described.

DATA

Effect of Temperature

The constants K and 1/n in the Freundlich isotherm equation are dependent on temperature and must be determined experimentally at each temperature. The constants also depend on the quality of the activated charcoal being used.

These constants were determined by static adsorption at 0, 8.5, and 23°C. The adsorption data are shown in Table 1 and Fig. 4. Also plotted in Fig. 4 are the isotherms for krypton as reported by Sangster.[20] There is good agreement with Sangster's data since charcoal of similar characteristics was used in both cases. The values of K and 1/n as determined from these isotherms (using the Freundlich equation) are plotted in Figs. 5 and 6. Also shown for comparison are the data of Peters and Weil.[21,22]

[20] D. F. Sangster, The Isotherm for the Adsorption of Krypton on Charcoal, AERE C/M 280 (1956).

[21] K. Peters and K. Weil, Z. angew. Chem. 43, 608 (1930).

[22] K. Peters and K. Weil, Z. physik. Chem. A148, 1 (1930).

Table 1. Adsorption of Krypton on Coconut Charcoal

T = 0°C		T = 8.5°C		T = 23°C	
Pressure (mm Hg)	Volume Adsorbed (cc/g)	Pressure (mm Hg)	Volume Adsorbed (cc/g)	Pressure (mm Hg)	Volume Adsorbed (cc/g)
5	0.6	58	6.3	102	2.8
8	1.0	91	8.3	153	4.2
11	1.7	110	9.7	184	5.6
18	2.6			216	7.1
25	3.5			252	8.5
33	4.5			291	9.9
38	5.2			331	11.3
47	6.4			341	11.8
84	10.0				

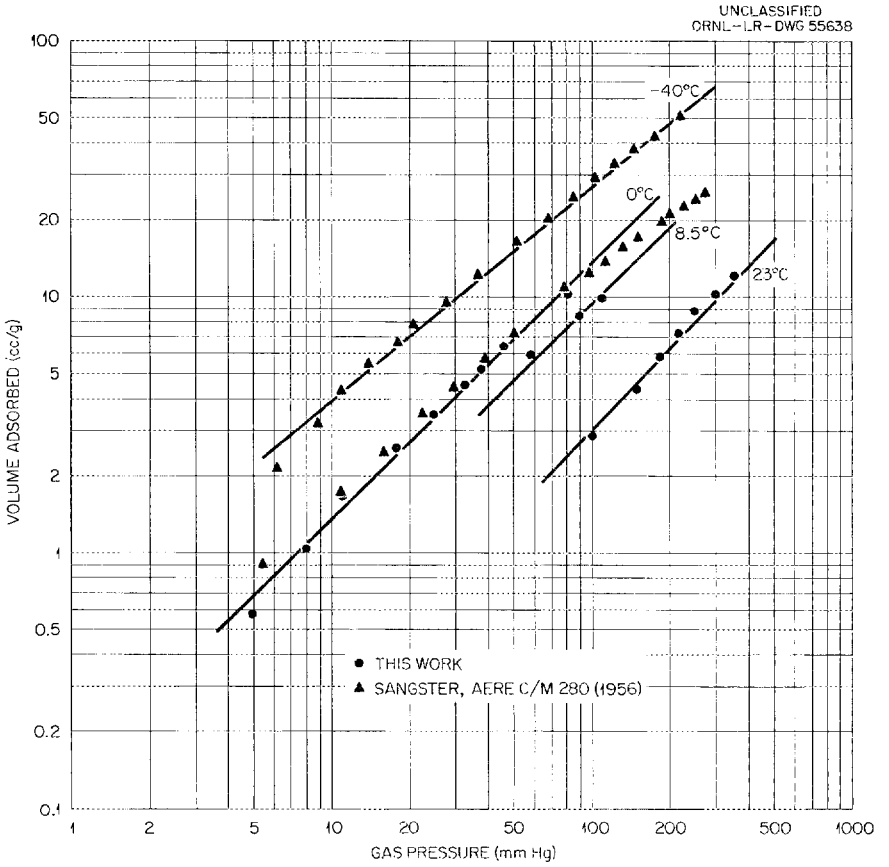

Fig. 4. Freundlich Isotherms for Krypton.

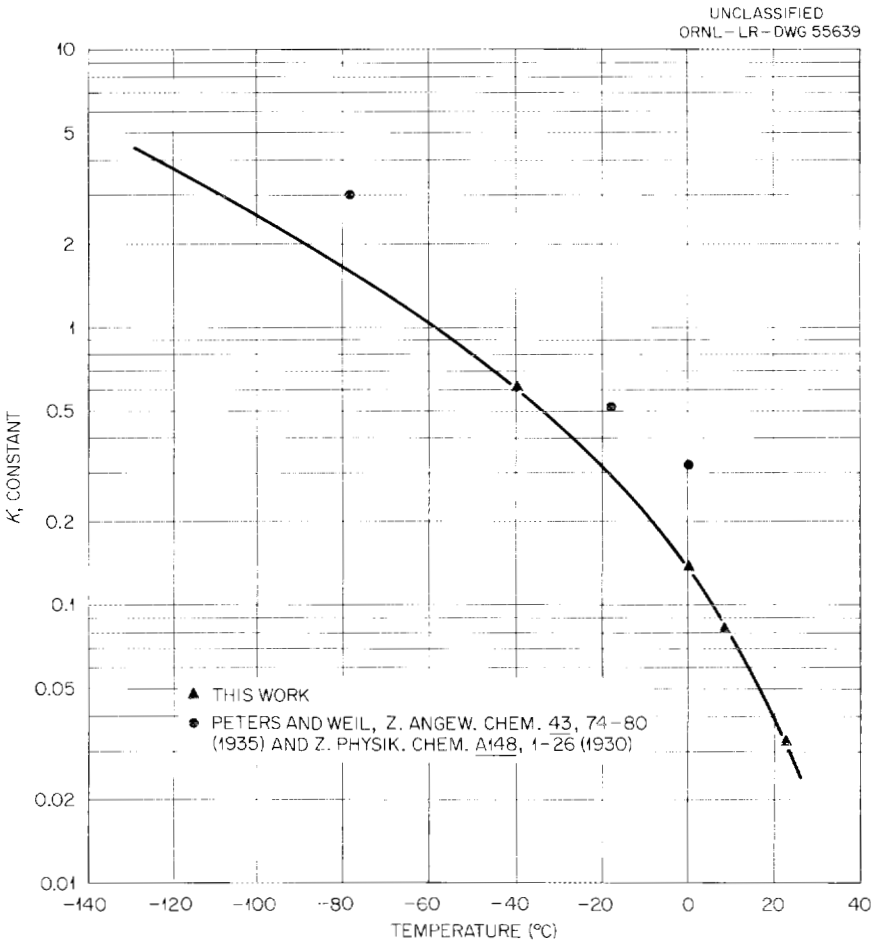

Fig. 5. Value of the Constant K as a Function of Temperature.

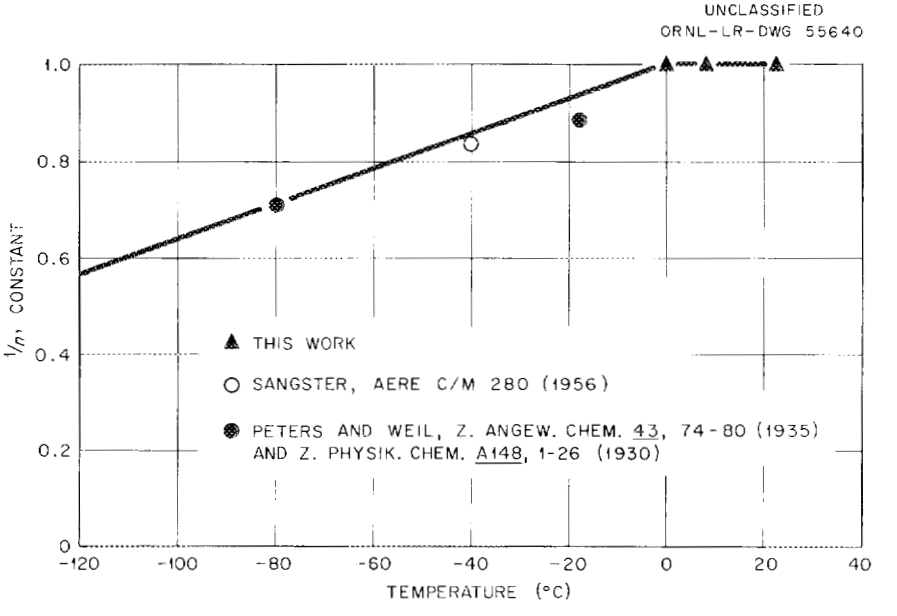

Fig. 6. Value of the Constant 1/n as a Function of Temperature.

The extrapolated line below −40°C was drawn so as to fit Eq. (6) as will be seen later.

Charcoal-Bed Reactor

The effectiveness of the charcoal-bed reactor[23] in destroying the oxides of nitrogen was essentially 100%. No detectable amount of the oxides of nitrogen was found in the xenon product when analyzed by infrared absorption or mass spectrometer analysis.

The reaction products of the oxides of nitrogen and carbon are nitrogen, carbon monoxide, and carbon dioxide. The ratio of CO_2 to CO at 900°C in the presence of carbon at equilibrium is 0.022 (ref 24). For two passes through the reactor, the theoretical ratio of initial CO_2 to final CO concentration should be less than 0.00048. If xenon and N_2O were initially present in equal quantities, the final xenon product would contain less than 0.04% CO_2. In actual runs, equilibrium values were not obtained; however, the CO_2 concentration was less than 0.5%.

Elution Time and Flow Rates

The volume of eluting gas required to move an adsorbed gas a fixed distance on a column at a given temperature is approximately constant. For a short elution time a high flow rate is desired. However, at high flow rates the number of theoretical plates obtainable is decreased.

The maximum theoretical plates are obtained at a flow velocity which is just sufficient to eliminate longitudinal diffusion in the gas phase as a factor. This maximum is obtained at a flow velocity of about 1 cm/sec (ref 25).

In a column which is to be used to separate large amounts of material, a compromise must be made between elution time and column length. With the column described in this report, the mean flow velocity was 23 cm/sec.

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[23] J. C. Posey, Removal of Oxides of Nitrogen from Inert Gases by Reaction with Carbon, unpublished report, ORNL.

[24] J. F. Thorpe and M. H. Whitely, Dictionary of Applied Chemistry, vol II, p 348, Longman Green, New York, 1946.

[25] C. Phillips, Gas Chromatography, p 76, Academic Press, New York, 1956.

This flow velocity gave a reasonable elution time and sufficient theoretical plates to accomplish the required separation.

Raw Material Composition

The process raw material from which the krypton and xenon were separated was a fission gas concentrate obtained from the gases released by dissolution of uranium fuel elements.

The concentrates were received in cylinders containing 100 to 1400 liters of gas (STP). The composition of the material in the cylinders varied over a wide range. In Table 2 are listed the approximate composition ranges of the gases which were processed. Table 3 shows the average isotopic composition of the xenon and krypton present in the gases.

Table 2. Composition of Process Raw Material

Component	Concentration Range (%)
Hydrogen	0–1
Nitrogen	5–96
Oxygen	0–8
Argon	0–2
Nitrous oxide	2–60
Nitrogen dioxide	0–2
Carbon dioxide	0–1
Krypton	0.5–40
Xenon	5–55

Production Runs

The data from a number of production runs at various temperatures are shown in Table 4. During processing, the gases are passed through the charcoal-bed reactor[21] which converts CO_2, N_2O, and NO_2 to N_2 and CO. A small amount of CO_2 remains in the gas. Since N_2 and CO have similar adsorption characteristics and the impurities other than N_2 and CO are small, all the constituents of the process raw material, other than krypton

Table 3. Average Isotopic Composition of Krypton and Xenon

Mass	Concentration (%)
	Xenon
131	10.17
132	16.35
134	29.20
136	44.25
	Krypton
82	0.78
83	13.42
84	29.41
85	6.32
86	49.87

and xenon, are listed as nitrogen in the third column of the table. Most of these runs required several cylinders of raw gas to load the column, and these cylinders were of different compositions. For this reason the composition values listed are average values for that particular run and could be a source of error in the data.

The values for the observed krypton capacity as given in the sixth column of the table were based on the krypton analysis and the volume of the feed gas entering the column prior to the appearance of krypton in the effluent. Runs 5, 6, 8, 11, 12, and 15 were terminated before 100% loading of the charcoal was reached. However, in these runs, it was possible, by means of valves along the section, to monitor gas samples and make an estimate of the extent of loading reached. The observed capacity values in the table for these runs have been adjusted to 100% loading based on the estimates. Loading was also incomplete in runs 21, 22, 25, and 27, but here it was not possible to estimate the degree of loading and therefore the actual observed values are given.

Table 4. Column Capacities

Run No.[1]	Column Temperature (°C)	Feed Gas Composition (%)			Krypton Capacity (cc)	
		Nitrogen[2]	Krypton	Xenon	Observed	Calculated
		Section A Filled with 5500 g of Charcoal				
2	−30	99.5	0.48	0	3,650	4,409
3	−30	99.1	0.95	0	8,300	8,064
5	−30	83.7	2.54	13.7	20,500[3]	15,982
6	−30	86.8	5.4	7.8	28,500[3]	34,598
7	−30	74.3	4.9	20.8	27,000	25,850
8	−30	78.9	15.0	6.1	42,700[3]	82,431
9	−30	81.9	6.7	11.4	37,000	40,157
10	−30	68.2	2.9	29.0	21,000	13,790
11	−30	58.5	7.6	33.9	34,400[3]	30,678
12	−30	66.8	7.8	25.4	41,200[3]	36,972
13	−30	76.7	5.8	17.5	35,500	32,132
14	−30	81.6	4.2	14.2	31,900	24,970
15	−30	47.7	17.8	34.6	40,300[3]	60,135
16	−30	82.1	3.7	15.5	22,500	21,641
		Section A Filled with 9400 g of Charcoal				
17	−30	51.9	11.4	36.7	61,600	72,936
18	−30	61.0	6.7	32.3	43,000	48,011
19	−30	22.6	13.4	64.0	33,900	36,837
20	−60	86.9	6.2	6.9	115,000	106,808
21	−50	85.1	4.2	10.7	50,000[4]	66,834
22	−70	56.2	5.2	38.6	58,600[4]	59,305
23	−125	69.7	4.2	26.1	143,000	142,572
24	−80	60.2	9.0	30.8	122,000	122,000
25	−90	40.0	7.0	53.0	59,000[4]	57,885
27	−110	56.2	5.4	38.4	90,000[4]	86,292

[1]Feed gas analysis was not available for runs 1 and 4. Run 26 was stopped due to a leak in the equipment.

[2]Includes all gases other than krypton and xenon (see text).

[3]Column not completely loaded. Value given is based on estimate of extent of loading.

[4]Column not completely loaded. Value given is that observed.

As was shown in Table 2, the major impurities in the krypton-xenon concentrates are nitrogen, oxygen, and nitrous oxide. In only five runs (Nos. 5, 7, 10, 11, and 12) was the nitrous oxide content more than a few per cent, but in these runs, the nitrous oxide concentration was approximately equal to the nitrogen concentration.

Using the observed column capacities, the values for K shown in Fig. 5, and the values for 1/n shown in Fig. 6 it was possible to calculate values for k_1 and k_2 of Eq. (6). Below −40°C it was necessary to use extrapolated values for K (Fig. 5); however, the agreement between the observed and calculated column capacities indicates that a reasonable choice was made. The values for the constants used in Eq. (6) for the capacity calculations are given in Table 5. From the table it appears that at least over the range of conditions in the production runs the values of k_1 and k_2 are not temperature dependent.

Some typical elution curves for the production runs are shown in Fig. 7.

Table 5. Constants for Equation (6)

Temperature (°C)	K	1/n	k_1	k_2
−30	0.42	0.88	0.390	1.176
−50	0.79	0.81	0.390	1.176
−60	1.01	0.77	0.390	1.176
−70	1.27	0.84	0.390	1.176
−80	1.60	0.71	0.390	1.176
−90	1.95	0.67	0.390	1.176
−110	3.00	0.60	0.390	1.176
−125	3.90	0.55	0.390	1.176

Product Analysis

The chemical purity of the krypton product was greater than 99%. The impurities were traces of helium and nitrogen. The limits on impurities are determined by the thoroughness of the krypton cold trap cleanup, leakage of air into the system, and the completeness of helium removal from

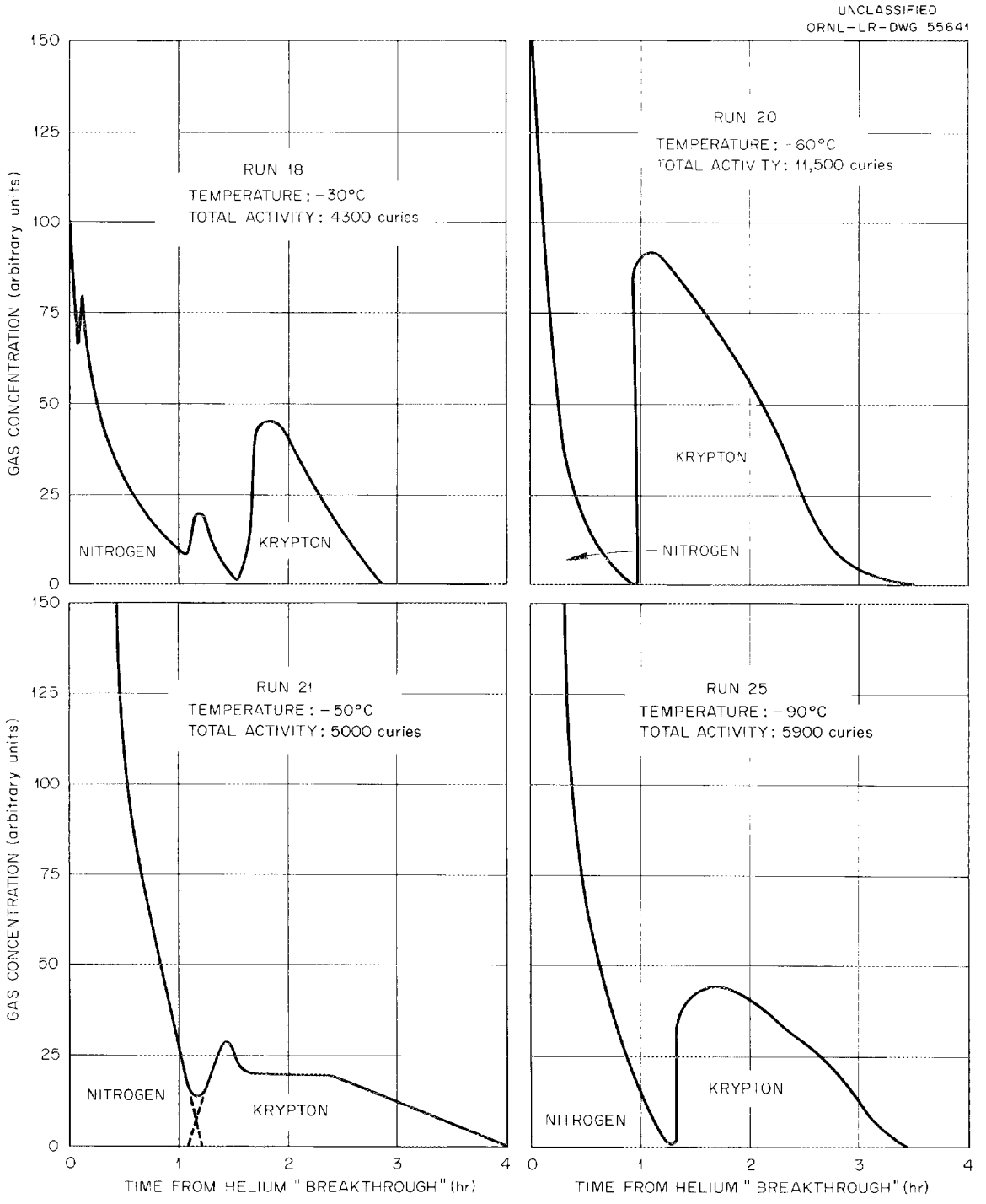

Fig. 7. Some Typical Elution Curves.

the krypton cold trap. The radiochemical purity of the Kr^{85} was essentially 100%.

The xenon product purity was greater than 98%. The major impurity was carbon dioxide. Decontamination factors for xenon through one complete process cycle were approximately 1×10^5, or approximately one curie of Kr^{85} per 1000 liters of xenon product. The limits on decontamination of the xenon are determined by the practical limit of the column decontamination between cycles. Additional recycle of the xenon on the column which had been grossly contaminated reduced the Kr^{85} by a factor of 10.

CONCLUSION

Krypton and xenon can be effectively separated from gross amounts of impurities and from each other with negligible loss of either krypton or xenon by a gas chromatographic method. The method makes use of a combined displacement and elution technique from an activated charcoal column.

The capacity of an activated charcoal column for total krypton and xenon is highly dependent on the temperature of the column and the concentration of krypton and xenon in the gas process stream. The capacity also depends on the nature of the diluting gas. Column capacities as calculated by an empirical equation agree reasonably well with the experimentally determined capacities.

The method described is not advantageous for use in removing krypton and xenon from a gas stream where the concentration of rare gas is less than 1%. It is most effective for final processing of rare gases that have been enriched by other processes.

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