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ADSORPTION OF KRYPTON AND XENON BY VARIOUS MATERIALS

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The adsorptive capacities of various inorganic adsorbents and activated charcoals for krypton and xenon were determined. Columbia G activated charcoal had the highest capacity for both krypton and xenon at pressures from 0.01 to 125 mm Hg and temperatures from 2 to 85°C. If a value of 1 is assigned to the capacity of this charcoal at 28°C for krypton, other charcoals range from 0.63 to 0.84, molecular sieves (except 4A) from 0.11 to 0.20, and some silica gels from 0.05 to 0.07. Various other adsorbents, including one variety of silica gel and molecular sieve 4A, range from 0.005 to 0.032.

Molecular sieve 5A and Columbia G charcoal adsorbed 11.5 times more xenon than krypton. Adsorption of 7.5% water by either of these adsorbents lowered their capacity for krypton 25-30%, while saturating the sieve material ($\sim$15% H_2O) lowered the krypton capacity 80%.

CONTENTS

1.0 INTRODUCTION

This study was carried out to obtain basic data on the adsorption of krypton and xenon to be used in the design of off-gas systems for aqueous homogeneous reactors. For such a reactor it is desirable to continuously purge the rare gases from the fuel solution to minimize Xe-135 poisoning. However, the gases are so highly radioactive that immediate disposal is impossible and a method of storage for radioactive decay is necessary. The HRT gas disposal system was designed to use activated charcoal as an adsorbent to prevent the release of short-lived krypton and xenon radionuclides to the atmosphere. This off-gas consists largely of oxygen, and the possibility of ignition of the charcoal beds in this oxygen atmosphere as a result of fission product decay heating or other causes was recognized. In the HRT this was avoided by using a 1/2-in.-dia bed as the first of three charcoal traps in series. For the HRT operating at 5 Mw, three such assemblies are required in parallel to handle the off-gas flow without overheating. Scaleup of this design obviously requires adding additional similar parallel units, which would become prohibitively complicated for a large power reactor. A noncombustible inorganic adsorbent of suitable capacity and good heat transfer properties would therefore be attractive as an alternative for charcoal.

With a modification of an apparatus described by J. N. Burdick (1), adsorption isotherms were obtained for charcoal and various possible alternative adsorbents, including molecular sieves and silica gels in the temperature range 0-100°C. The effect of moisture on adsorption was also obtained for the better adsorbents.

2.0 EQUIPMENT

2.1 Gravimetric Determinations

The equipment used in gravimetric studies is shown in Fig. 1 and consists essentially of gas storage vessels, manifolds, adsorption vessels, McBain balance, temperature regulating system, pressure measuring devices, and evacuation systems.

Low pressure in the gas adsorption system, which was constructed entirely of glass, was maintained by a consolidated vacuum oil diffusion pump, type MCF-300, backed by a Welch Duo-Seal vacuum pump. An auxiliary mechanical pump which could be connected by way of a stopcock and ball joint to an individual adsorption chamber was used to pump down the chamber after it had been opened to the air and before the chamber was opened to the remainder of the vacuum system. This pump was also used during the early stages of degassing any adsorbent under test. With this system it was possible to maintain a pressure of 3×10^{-7} mm Hg while the pumps were operating and a pressure of 1×10^{-5} mm Hg after 18 hr isolation from the diffusion pump.

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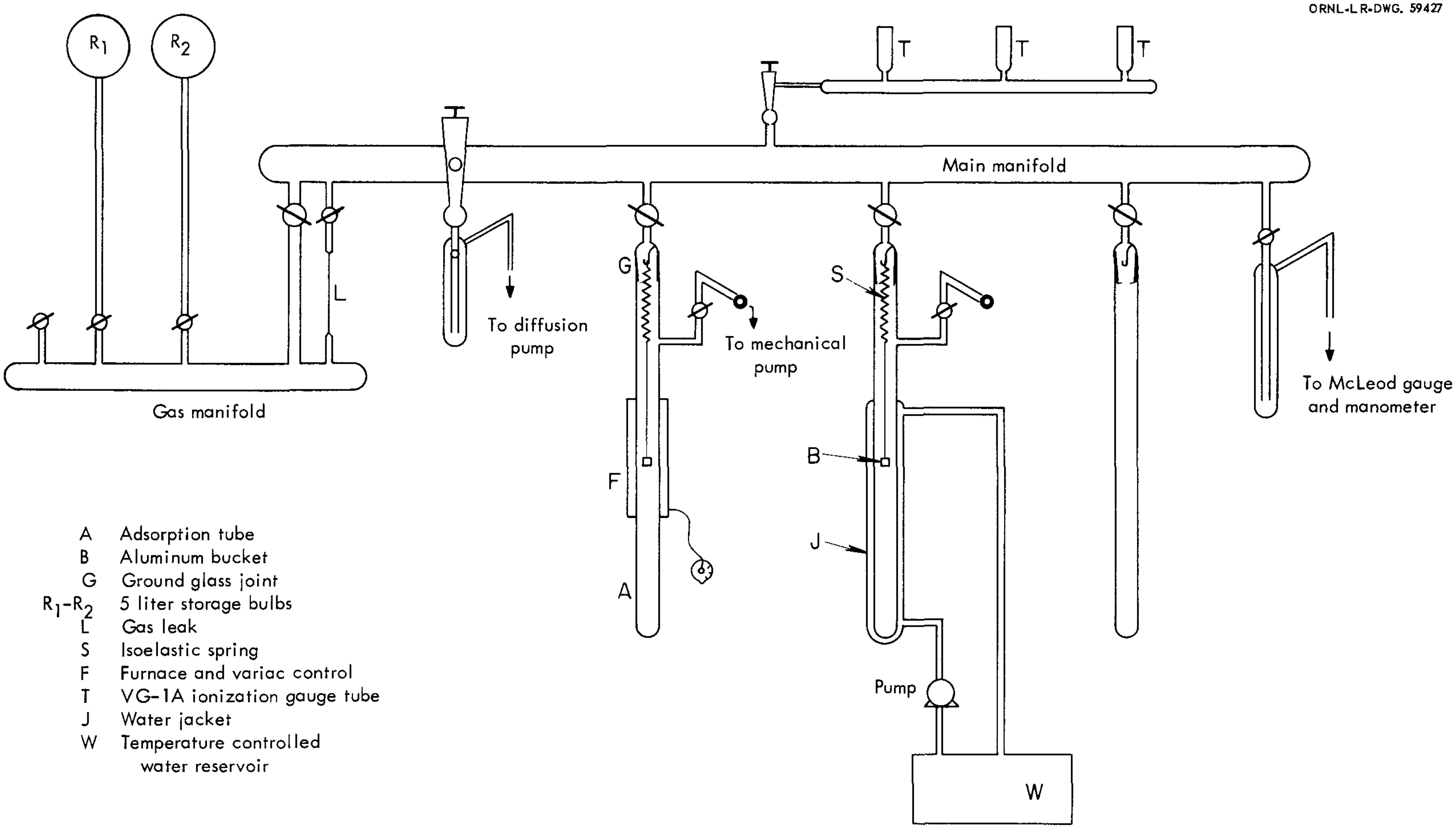

A	Adsorption tube
B	Aluminum bucket
G	Ground glass joint
R_1-R_2	5 liter storage bulbs
L	Gas leak
S	Isoelastic spring
F	Furnace and variac control
T	VG-1A ionization gauge tube
J	Water jacket
W	Temperature controlled water reservoir

Fig. 1. Experimental setup used in gravimetric determination of adsorption isotherms.

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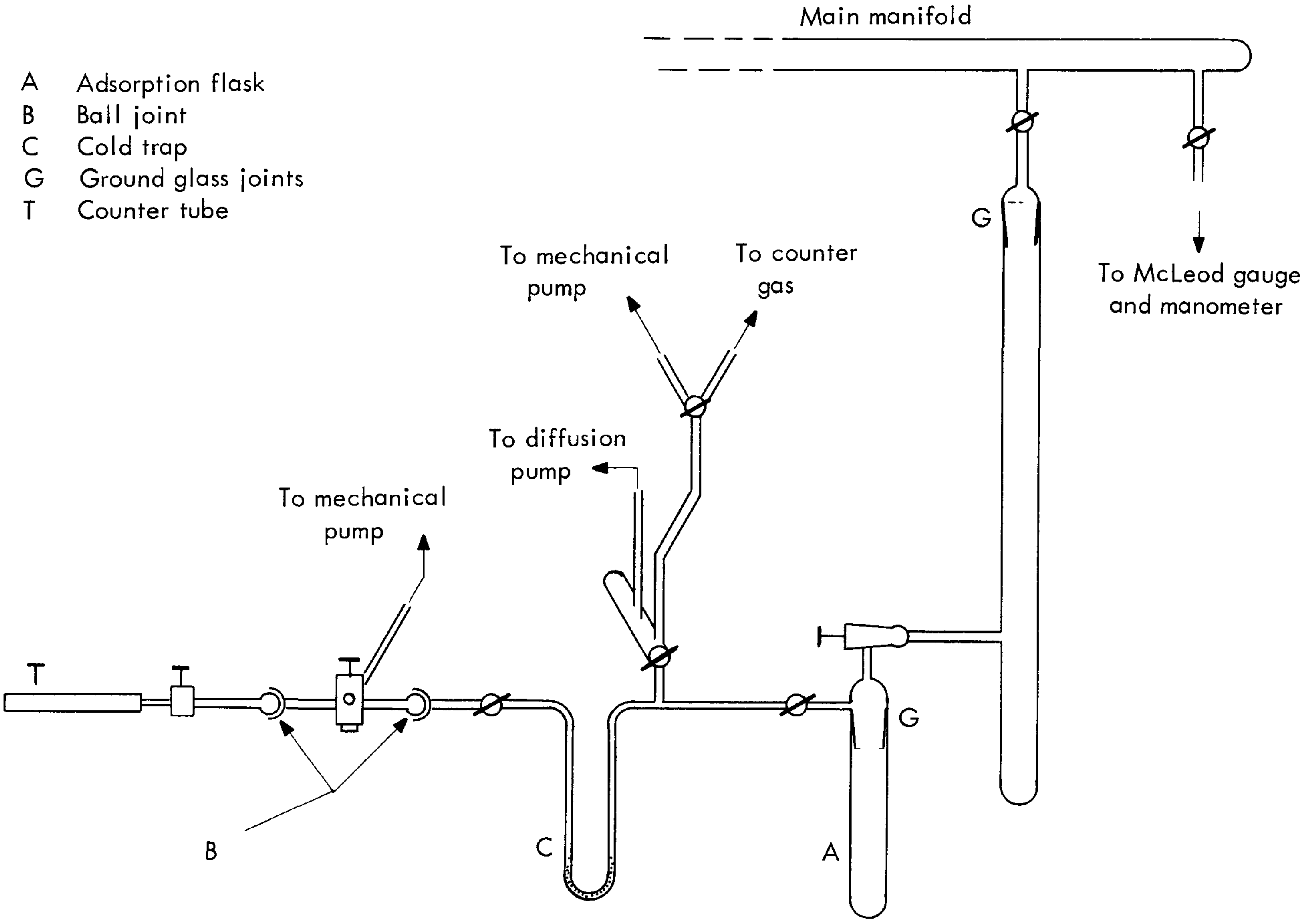

Fig. 2. Experimental setup used in determination of adsorption isotherms by tracer techniques.

Three different methods were used to measure pressure within the system. For the pressure range of 10^{-3} to 10^{-8} mm a Consolidated Vacuum DPA-38 ionization gauge with VG-1A ionization tubes was used. Experience showed that three such tubes sealed to the vacuum system were beneficial in eliminating or decreasing downtime due to a faulty or failed ionization tube. In the pressure range 10^{-3} to 5 mm a McLeod gauge was used; higher pressures up to 1 atm were measured with a closed-end manometer.

The temperature of the system during adsorption measurements was regulated by water circulating through a glass jacket surrounding the adsorption chamber, the water reservoir being cooled with ice or heated with a calrod heater controlled by a thermostat at the desired temperature. For activation of the adsorbent the glass jacket was replaced by a stainless steel tube 8 in. long wound with Chromel wire and wrapped in insulation. The temperature was controlled up to 500°C by a Variac and was measured by a thermocouple.

Weight changes in adsorbent samples in the evacuated system were measured by observing the vertical movement of the sample holder, which was suspended from helical springs. These "Iso Elastic Extension Springs" were made by John Chatillon and Sons and were rated at 0.1 mm extension per milligram of loading with a total capacity of 3 g. Each spring was calibrated by actual measurement of the extension obtained by 100-mg increments in weight from zero to 3 g loading. Vertical movements were followed with a Gaertner Scientific Company cathetometer, which read to 0.01 mm with ready estimation of 0.001 mm. The sample containers were fabricated of thin aluminum foil and suspended from the springs by a very fine wire loop. A complete sample container weighed about 100 mg.

2.2 Tracer Determination

In order to measure accurately adsorption isotherms for krypton on various materials at pressures less than 1 mm Hg, the apparatus was modified as shown in Fig. 2 to allow for use of radioactive tracer techniques. The modified system consisted of an adsorption vessel of measured capacity (99.61 ml), a cold trap, counter tube, and connections designed for quantitative transfer of gas from the adsorption tube to the counter tube. The cold trap contained activated Columbia G charcoal and could be either cooled with liquid nitrogen or heated with a calrod heater controlled by a thermostat. The counter tube was designed for use with a modified Model 117 methane proportional counter and the gas used was a 90% methane—10% argon mixture.

3.0 EXPERIMENTAL PROCEDURES

3.1 Gravimetric Method

A known quantity of adsorbent, usually about 2 g, was placed in a tared aluminum bucket and suspended from an extension spring in one of the adsorption vessels. After the position of the bucket had been determined with the cathetometer, the heating furnace was raised to surround the sample and the system was heated under vacuum to a temperature of 250 to 400°C for 30 hr or more. Heating was discontinued when there was no longer an apparent change in sample weight and when the pressure in the system could easily be lowered to 10^{-6} mm Hg. In order to avoid excessive contamination of the entire system by materials expelled from the sample during activation, the adsorption vessel was evacuated during the first several hours of heating by means of an auxiliary mechanical pump connected to the vessel through a side arm. The weight loss during activation and the resultant sample weight were determined by observing changes in spring extension during activation.

After activation of the sample was complete, the entire vacuum system was evacuated to a pressure less than 10^{-6} mm Hg and isolated from the pumps. The gas manifold was isolated from the main manifold and gas admitted to it from the gas storage system. A small amount of gas was then admitted to the main manifold and adsorption vessel through the leak valve after the sample had been brought to the desired temperature. Adsorption equilibrium was assumed to have been established when no change in gas pressure or weight increase in the sample was observable. The increase in weight in the sample due to gas adsorption at the observed pressure was noted by measuring the spring extension after which additional gas was admitted to the system and the process was repeated. With most of the adsorbents, equilibrium was established quite rapidly so that an isotherm with 10 to 15 points could be obtained in 4 to 6 hr. The same procedure was used for both krypton and xenon.

3.2 Tracer Method

In the tracer method ordinary krypton was spiked with Kr-85 so that the activity in the adsorption vessel at 0.001 mg and 28°C was about 200 cpm; at 0.60 mm Hg and 28°C the count rate was about 99,500 cpm. Prior to any isotherm measurements the amount of activity in the vessel at various pressures between these limits was determined and was found to be reproducible within the range of the counter accuracy.

The basic procedure was to admit a small amount of traced krypton to the main manifold, the McLeod gauge, and the adsorption vessel, which contained a known weight of adsorber material. After equilibrium had been established between gas and adsorber, as evidenced by no change in pressure reading, the adsorption vessel was isolated from the remainder of the system. The cold trap had meanwhile been thoroughly evacuated, isolated from the vacuum system, and then cooled with liquid nitrogen. The valve between the adsorption vessel and cold trap was then opened and the contents of the adsorption vessel were transferred to the cold trap by heating the vessel to 220°C for 20 min while keeping the cold trap at liquid nitrogen temperature. The cold trap was then isolated from the adsorption vessel, warmed to room temperature, and the valve to the counting tube was opened. The cold trap was then heated to 360°C and counter gas in small increments, 5-10 mm pressure, was flushed through the trap and into the counter tube until atmospheric pressure was reached. The counter tube was then removed from the system for counting and the process repeated.

Samples were activated in the same manner as described for the gravimetric procedure. The amount of activated solid in the adsorption vessel was determined by placing a weighed amount of solid in this vessel and a weighed amount of the same solid in the portion of the system used for gravimetric determination. Both samples were activated in an identical manner and the weight change was noted for the sample in the gravimetric portion of the apparatus. A proportionate correction was then applied to the weight of material placed in the tracer adsorption vessel. The specific gravity of the adsorber was determined by water displacement. In order to minimize effects due to the volume of adsorbent in the adsorption flask, the volume of adsorbent was held to about 1% of the vessel volume. Since the activity due to gas in the vessel had been determined experimentally, any excess activity was due to adsorbed gas and could be easily calculated from the ideal gas law.

4.0 EXPERIMENTAL DATA

By the gravimetric techniques described above, adsorption isotherms were determined for krypton on 22 different materials at 2 and 28°C (Figs. 3-5). Isotherms for krypton on two activated charcoals, Columbia Grade G and Norit RB III, were determined at 2, 28, 35, 50, and 81°C (Fig. 6). The effect of water on adsorption of krypton by Columbia G charcoal and Linde Molecular Sieve 5A is shown in Fig. 7. The adsorption of krypton on six selected materials at 28°C as determined by the tracer technique previously described is shown in Fig. 8 together with more detailed data on Columbia G charcoal at 28 and 80°C.

Adsorption isotherms were determined at 2 and 28°C for xenon on those materials which had shown the greatest capacity for krypton (Fig. 9). The capacity of Columbia G charcoal at 2, 28, and 85°C is compared in Fig. 10. Since the capacity of the materials examined is so much greater for xenon than for krypton, more precise measurements at lower gas pressures were possible for xenon. The

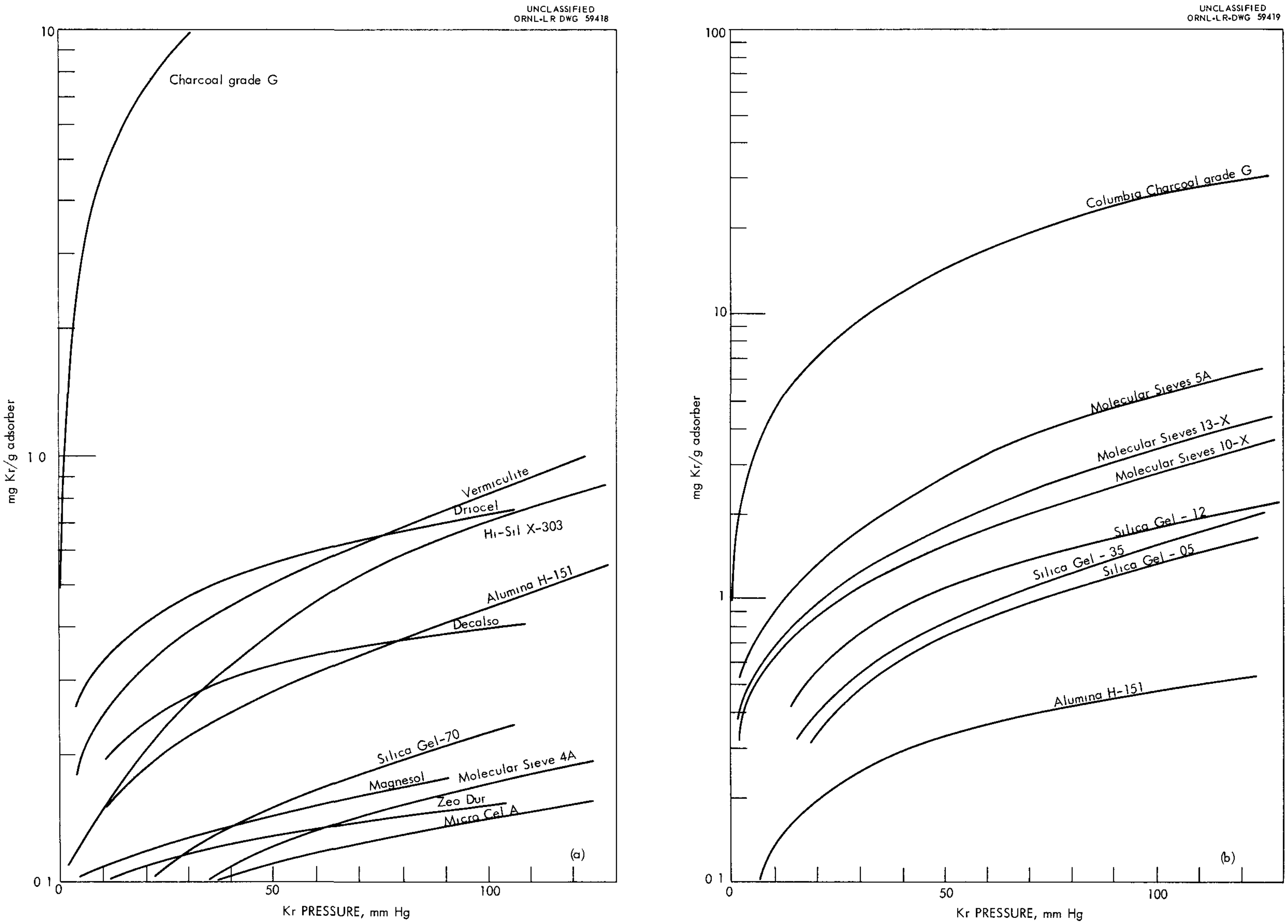

Fig. 3. Adsorption of krypton by various materials at 28°C.

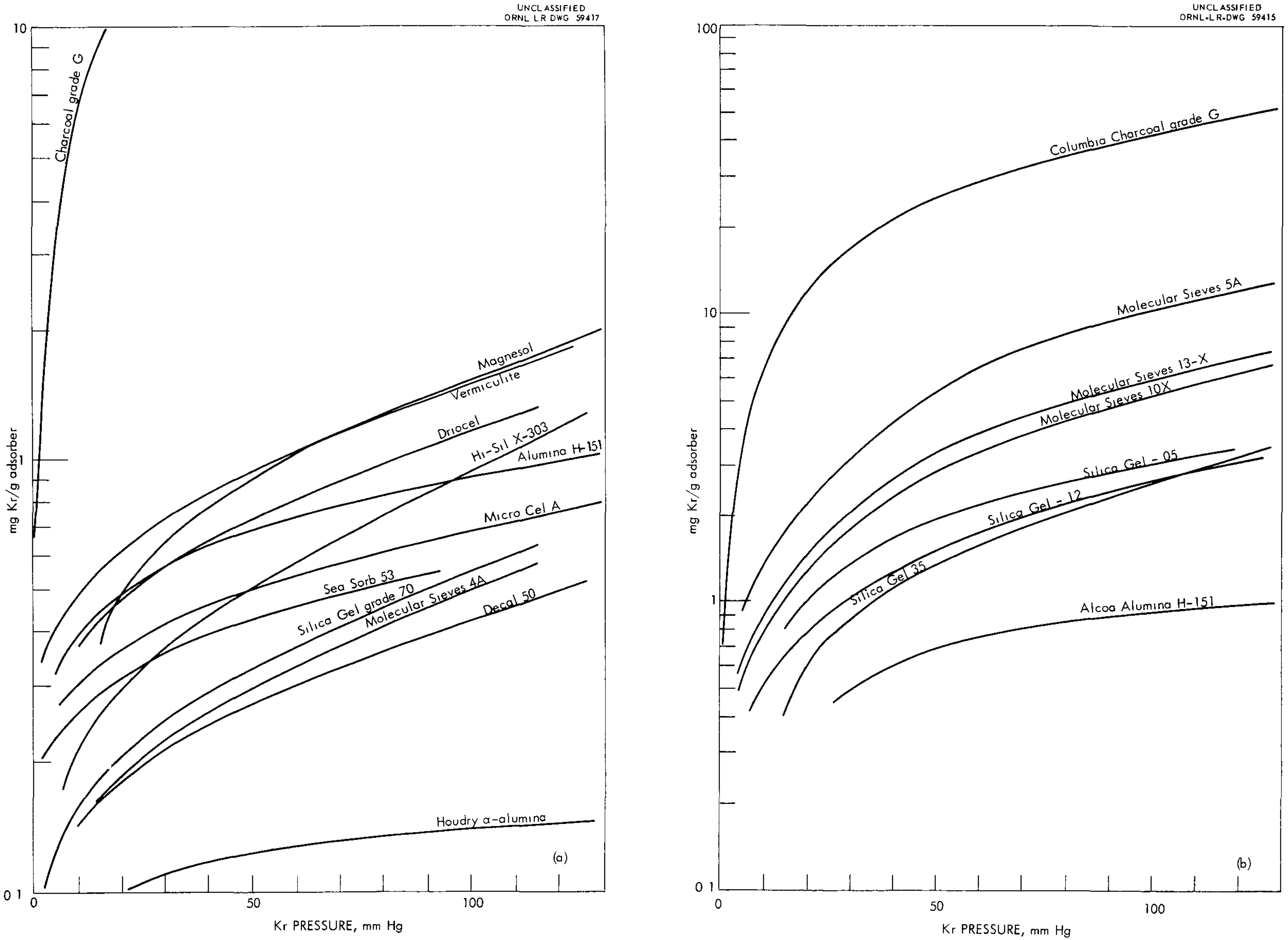

Fig. 4. Adsorption of krypton by various materials at 2°C.

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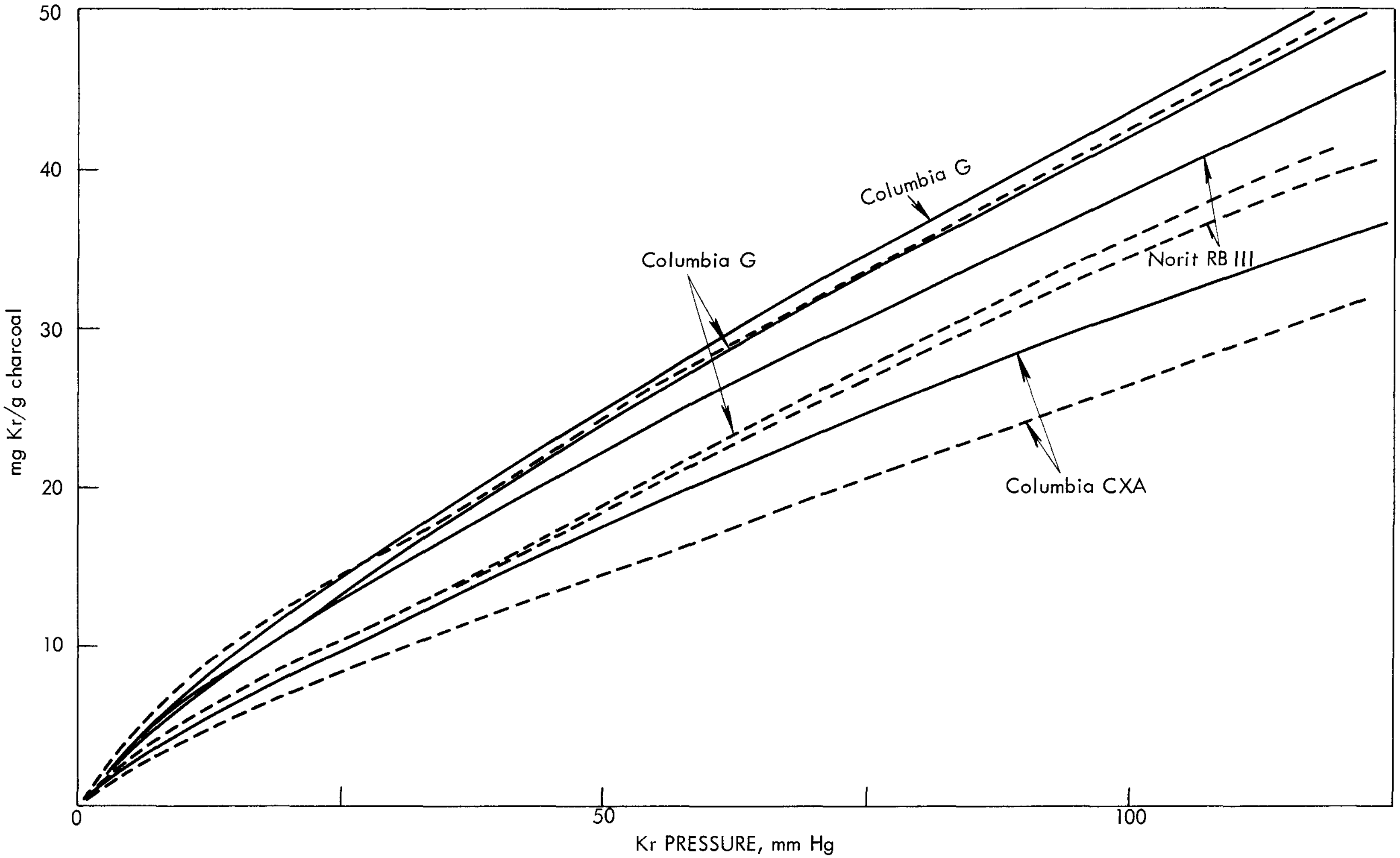

Fig. 5. Adsorption of krypton by various charcoals at 2°C (solid lines) and 28°C (dotted lines).

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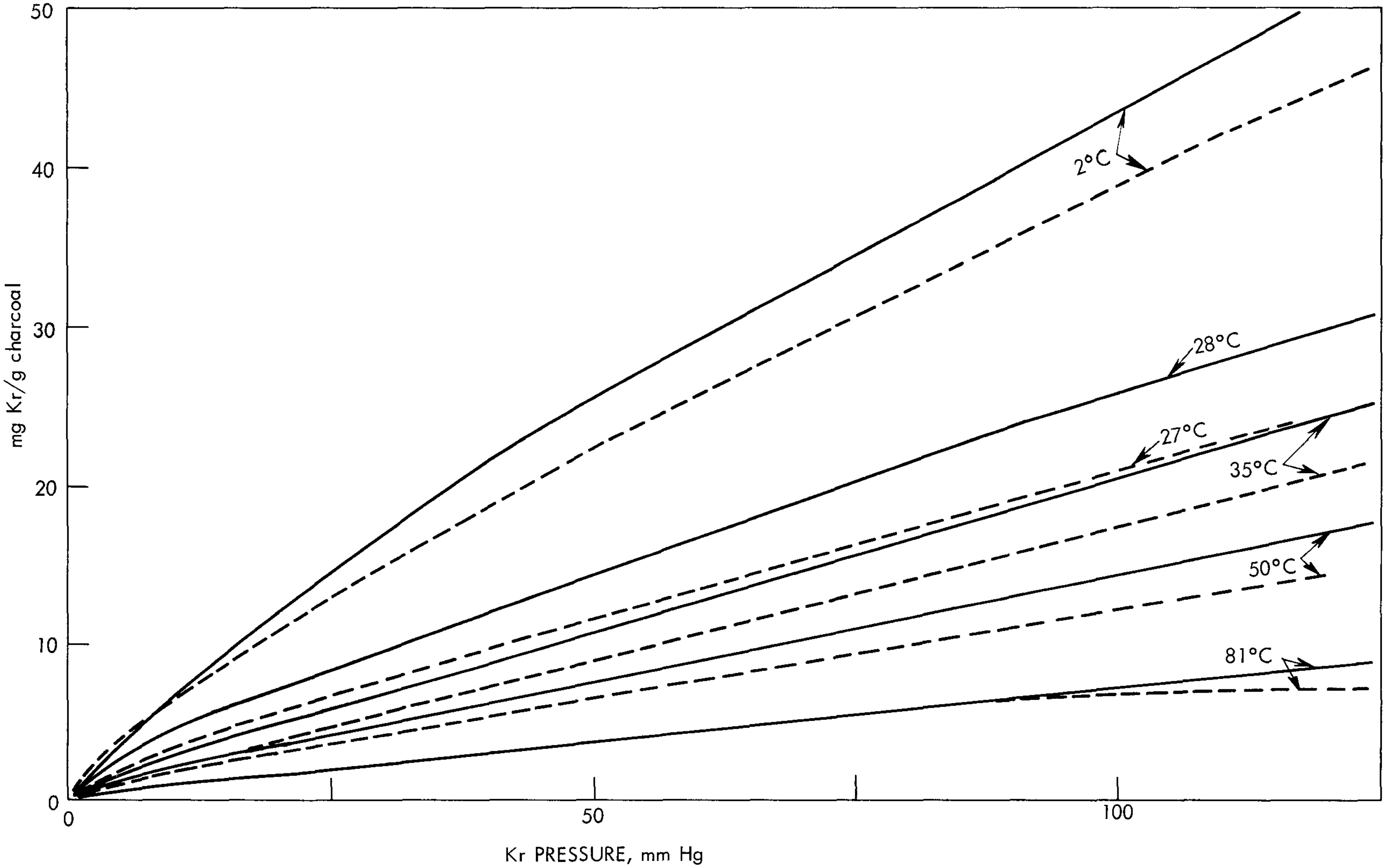

Fig. 6. Adsorption of krypton at various temperatures by Columbia G charcoal (solid line and by Norit RB-III (dotted line).

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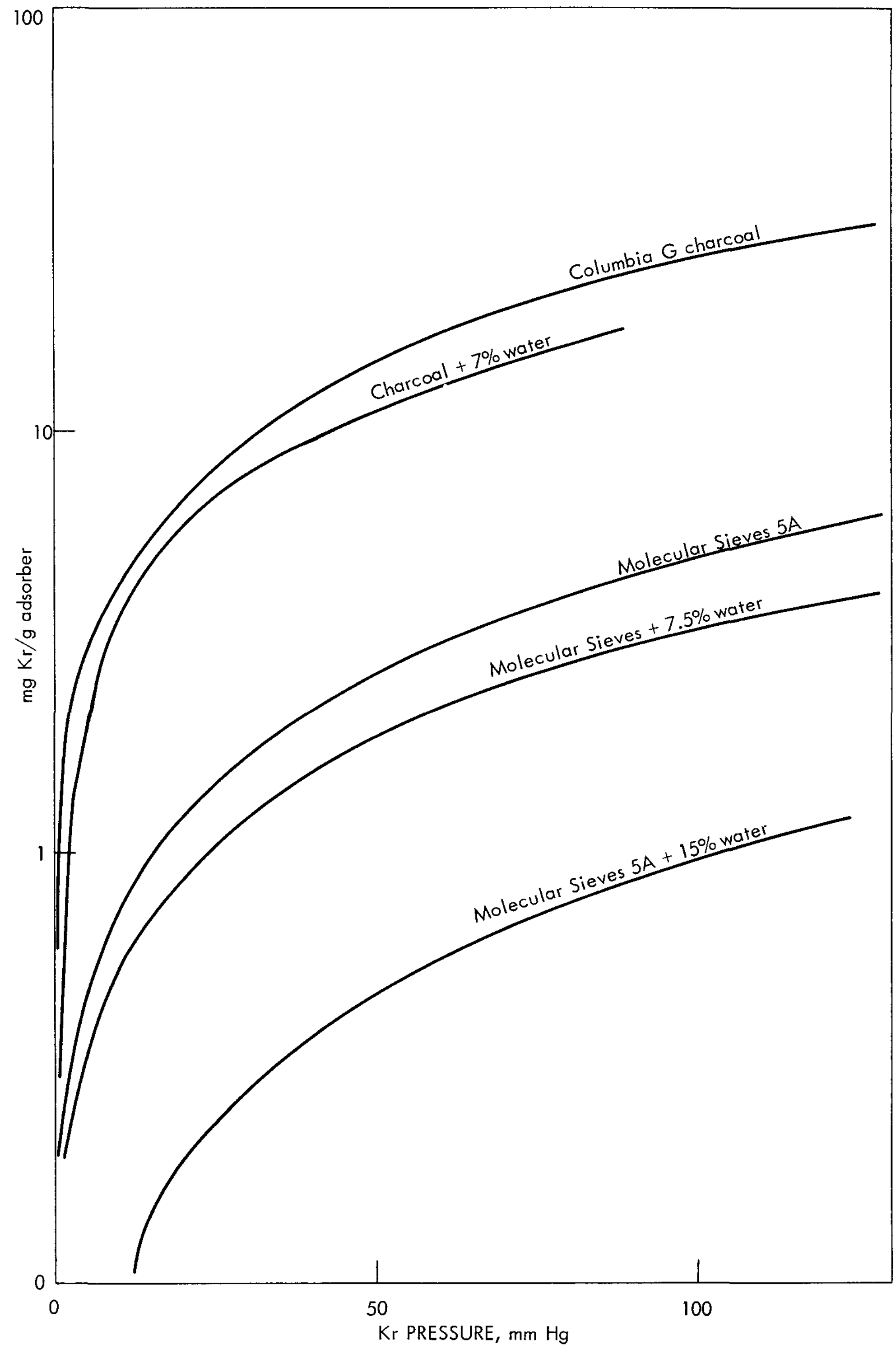

Fig. 7. Effect of water on adsorption of krypton by Columbia G charcoal and Linde molecular sieve 5A at 28°C.

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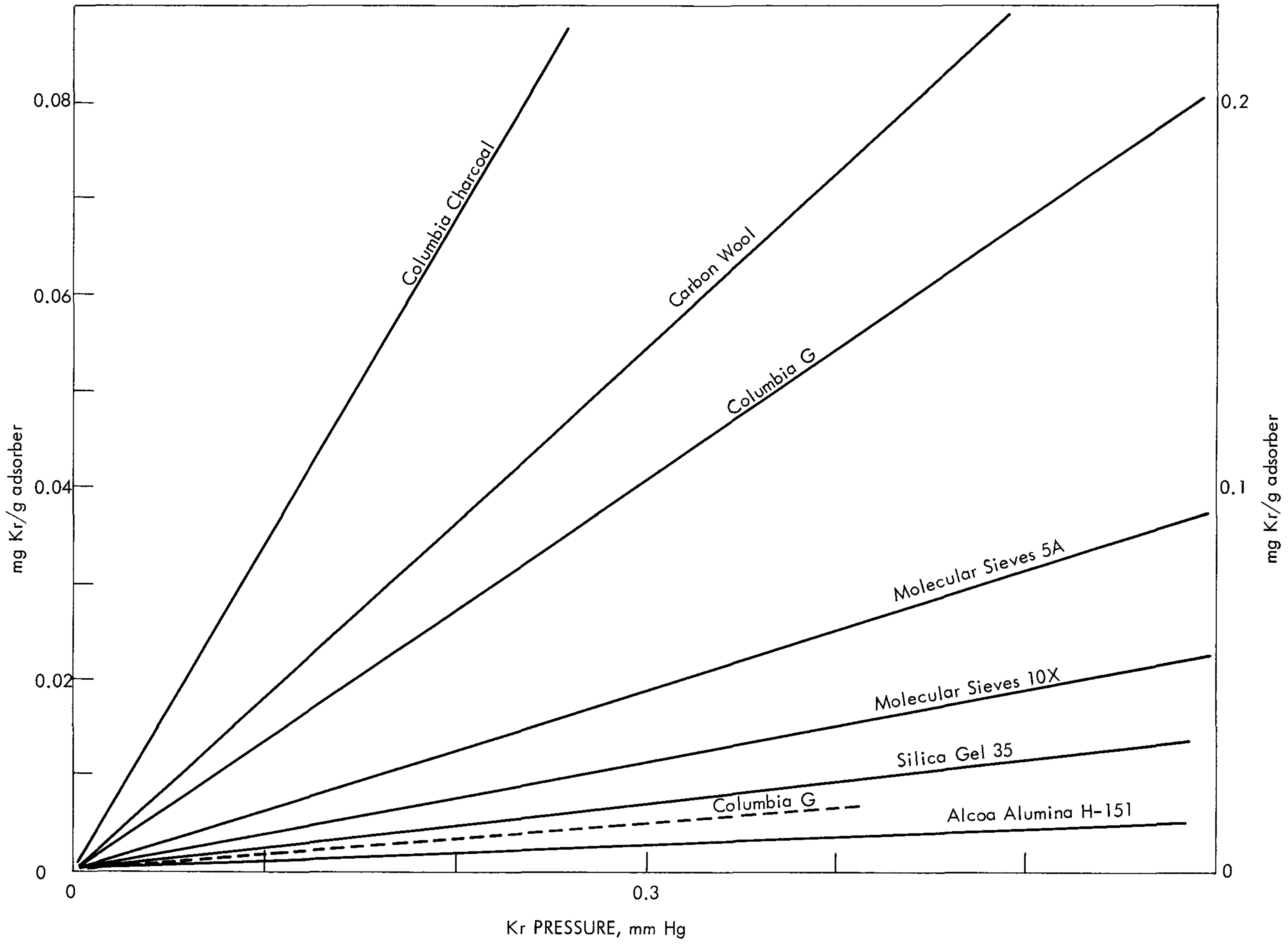

Fig. 8. Adsorption of krypton by various materials at 28°C (solid lines) and 80°C (dotted line) and low krypton pressures.

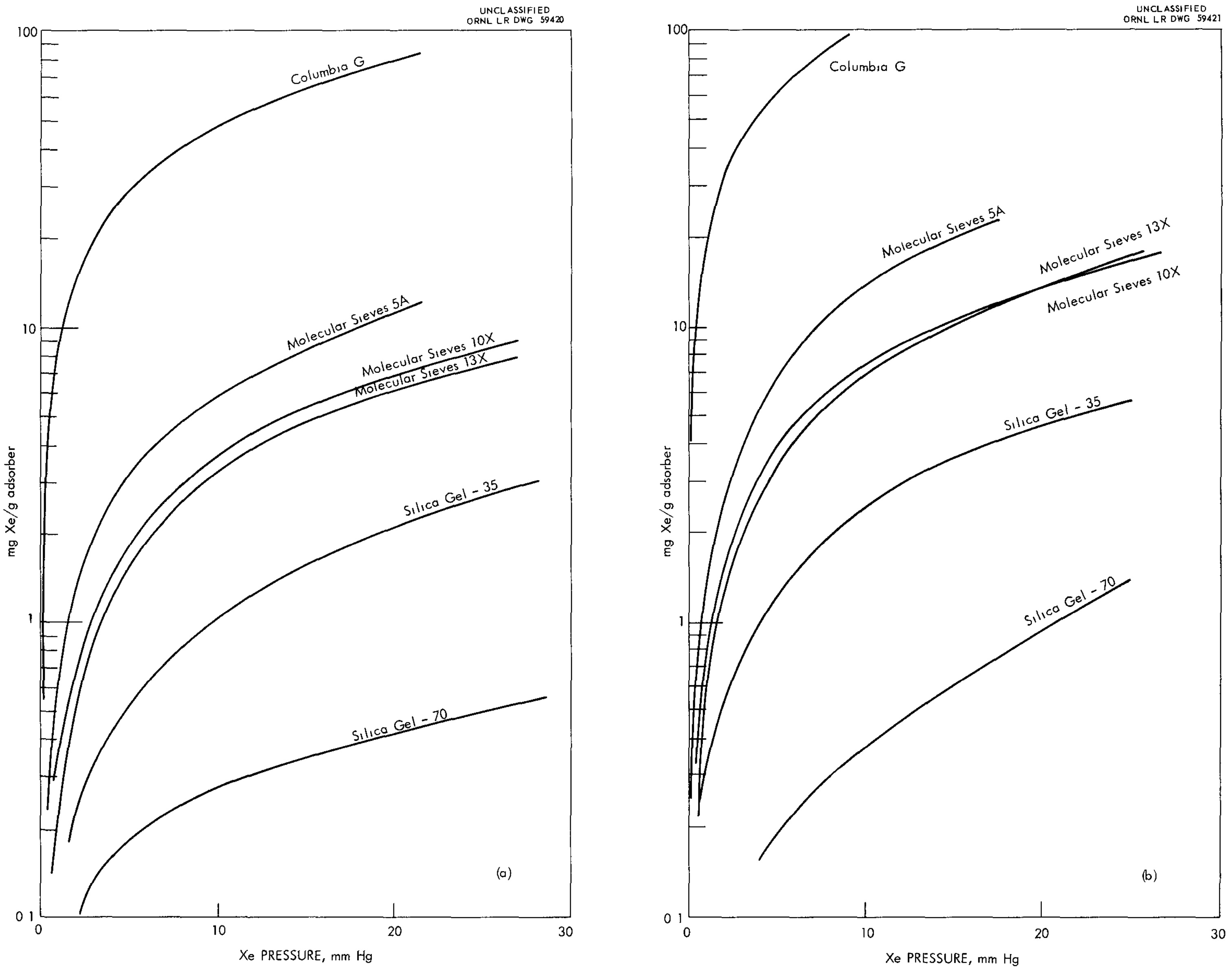

Fig. 9. Adsorption of xenon by various materials at (a) 28°C and (b) 2°C.

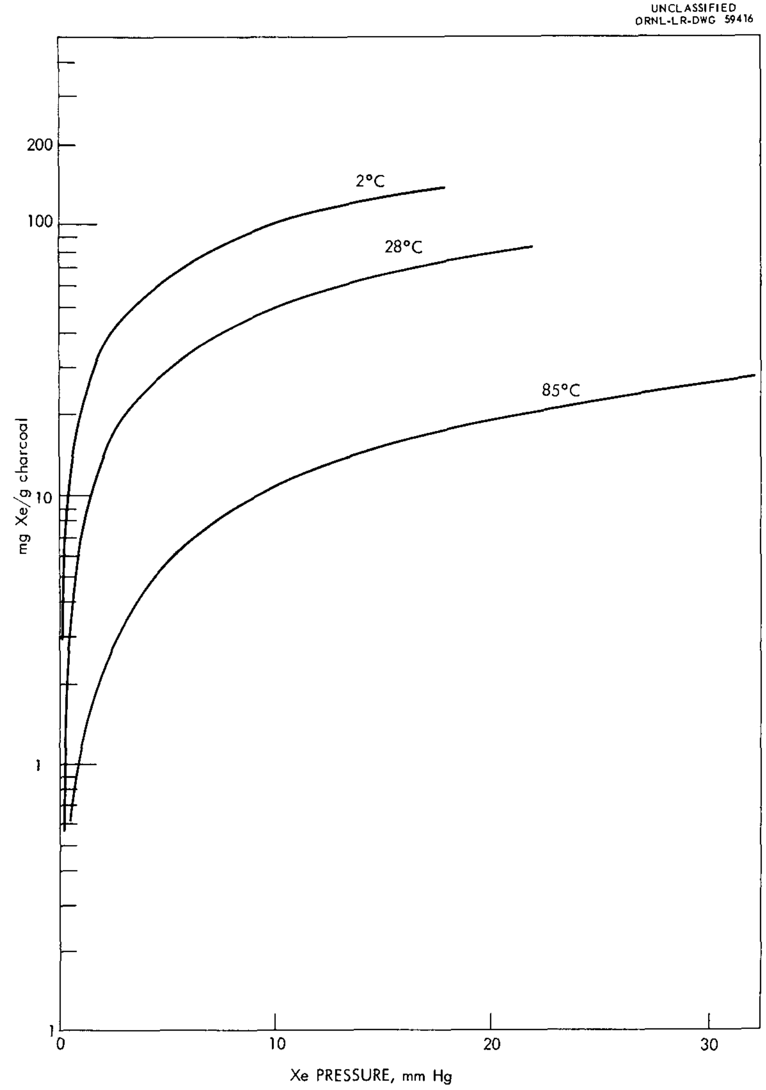

Fig. 10. Adsorption of xenon by Columbia G charcoal at 2, 28, and 85°C.

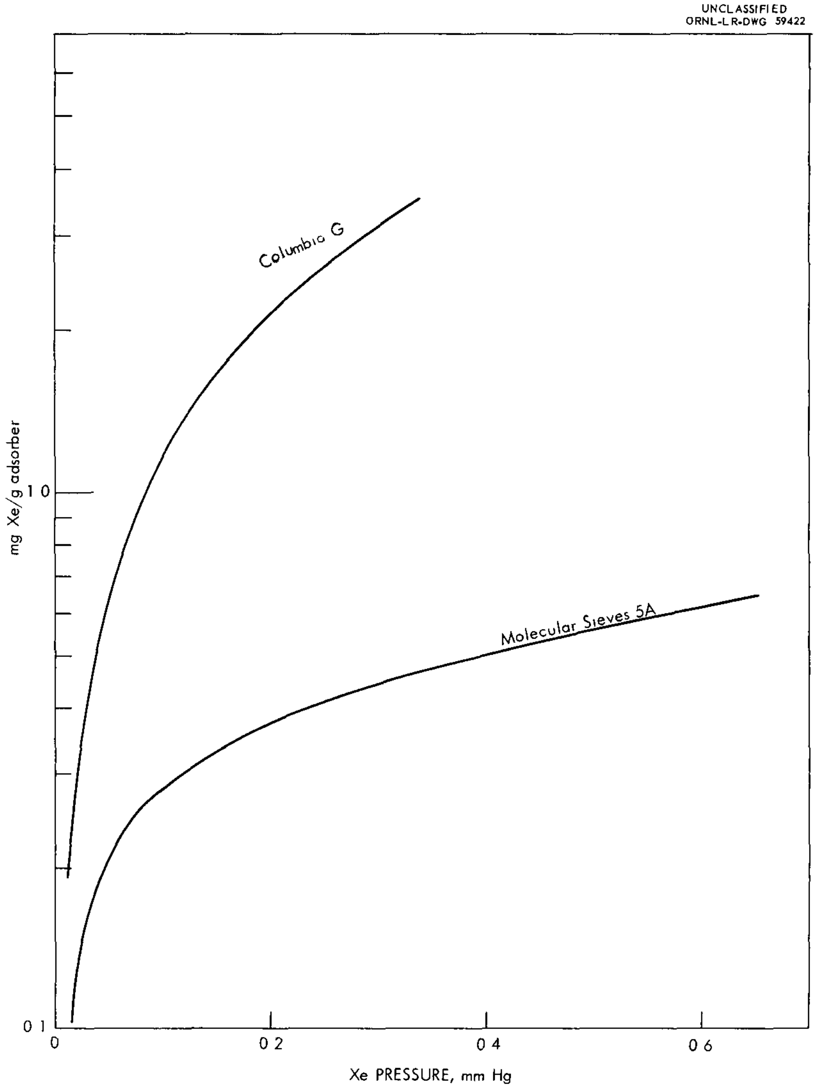

Fig. 11. Adsorption of xenon by Columbia G charcoal and Linde molecular sieve 5A at 24°C and low xenon pressure.

data obtained with Columbia G charcoal and Linde Molecular Sieve 5A at 24°C and pressures ranging from 0.012 to 0.655 mm are shown in Fig. 11.

5.0 DISCUSSION OF RESULTS

The results described above are the results of a research program directed toward ascertaining the relative effectiveness of various carbonaceous gas adsorbents compared with inorganic adsorbers of potential interest and the effect of water on the performance of the best of these materials.

The study shows that as a group carbonaceous adsorbers are significantly better adsorbers than the best inorganic adsorber. Of the various charcoals tested, Columbia G has the greatest capacity for both krypton and xenon.

Of the noncharcoal materials, the molecular sieves have the greatest adsorptive capacity followed by silica gels. However, there is a marked difference between different molecular sieves as shown by the fact that the 5A material with a nominal pore size of 5 Angstroms has 30 times the capacity of the 4A material, which has a nominal pore size of only 4 Angstroms at 28°C and 100 mm Hg pressure. Increasing the pore size to 13 and 10 Å lowers the capacity of the sieves from the value shown by the 5X material. The silica gels are less effective adsorbers than the molecular sieves and the deleterious effect of increasing pore size is shown by the decreased capacity of silica gel-70 with its 140 Å pore diameter compared with silica gel 35 with its 32 Å pore size.

The effect of adsorbed water on the krypton capacity of Columbia G charcoal was much less than the effect on Linde Molecular Sieve 5A when an excessive amount of water was present. At a water vapor pressure of 12 mm Columbia G charcoal will adsorb water to about 7% of its weight and lose about 25% of its capacity for krypton adsorption. For 7.5% water adsorption Linde Molecular Sieve 5A loses about 34% of its krypton capacity. However, the sieve material will continue to adsorb water until about 15% by weight is adsorbed if a water vapor pressure as great as 0.1 mm exists, and such a water-saturated sieve has a krypton capacity only one-fifth that of the dry material. Removal of this tightly held water under conditions existing in a large bed such as employed at the homogeneous reactor would be extremely difficult.

During these studies it was found that Columbia G charcoal at 28°C will adsorb mercury slowly over a period of 2-1/2 hr to reach an equilibrium condition of 0.6 mg of mercury per gram of charcoal. No decrease in krypton adsorption was found to result from the presence of this amount of mercury on the charcoal.

6.0 REFERENCES

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