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SUBJECT: Equilibrium Adsorption of Krypton and Xenon on Activated Carbon and Linde Molecular Sieves

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Abstract

Equilibrium krypton and xenon adsorption isotherms were obtained for four varieties of charcoal and for Linde Molecular Sieves Types 4A and 5A, generally at 0, 25, and 60°C. Such data are of interest in connection with design and evaluation of adsorbers for radioactive noble gas fission products. The isotherms were fitted, by linear regression analysis, to straight-line forms of the Freundlich and Langmuir equations. The Freundlich linear equation gave the better fit and the parameters of this equation are presented for each of the isotherms. Also presented are the constants for an equation representing the temperature dependence of arbitrary adsorption coefficients, the coefficients having been calculated from the Freundlich isotherm parameters. Some aspects of the applicability and accuracy of these results are discussed.

Introduction

Charcoal traps (adsorbers) have extensive application in removing the radioactive fission-product gases krypton and xenon from various carrier gases associated with nuclear operations. A number of studies pertaining to dynamic adsorption of these noble gases have been performed at ORNL (1, 2, 3, 4). The experimental data most generally utilized are elution curves obtained with radioactive Kr-85 and/or Xe-133 as tracers. To interpret the elution curves, a theoretical plate treatment was developed for the particular case of a linear isotherm (1); this case is practically applicable in the majority of situations encountered. The most important parameter of this theory is the dynamic adsorption coefficient k since, when the void volume of the adsorbent is negligible and carrier gas velocities are not too extreme, the holdup time for the noble gas being considered is very close to being directly proportional to its k-value (for a given quantity of adsorbent and a given flow rate). The dynamic adsorption coefficient k may be identified theoretically with the slope of the equilibrium linear adsorption isotherm for krypton or for xenon in the presence of the carrier gas; the linear isotherm is commonly written as $V = kP$ where V is volume adsorbed, k is the isotherm slope, and P is adsorbate pressure.

Equilibrium (or static) krypton and xenon adsorption data would thus appear to be of considerable value both as a means of independently checking dynamic adsorption measurements and theory and as a convenient means for obtaining information regarding xenon adsorption characteristics since the Xe-133 tracer used in dynamic measurements is not as readily available as Kr-85. Consequently, krypton and xenon adsorption isotherms were obtained on four activated carbons and on one type of Linde Molecular Sieves at 0, 25, and 60°C. Less extensive measurements were also made on another type of Sieves. These data on carbons and Sieves have already been summarized in a semi-quantitative fashion in progress reports (5, 6).

In several instances comparable dynamic and equilibrium adsorption coefficients were available and, except in one case as is to be noted later, good agreement was observed. Subsequently, a more quantitative treatment of the data was considered to be worthwhile and was performed as described below. The main purpose of this memo is to present the detailed results of the more recent calculations.

Calculation Procedures and Results

Each of the isotherms was statistically analyzed by means of a digital computer (ORACLE) linear regression code. Linear forms of both the Freundlich and the Langmuir equations were employed for fitting the data. The basic data were pairs of values of V (cm^3(STP)/g) and P(mm Hg). The Freundlich linear form used was $\log V = \log k + (1/n) \log P$ and that for the Langmuir equation was $P/V = a + bP$. Weighting factors of unity were used for log V and log P and for P/V and P. On this basis and as judged by the correlation coefficient squared, also called the coefficient of determination*, the Freundlich linear form gave the better fit for every isotherm. Therefore, the constants obtained for the Freundlich equation are presented herein while those for the Langmuir equation are not. After the Freundlich constants were evaluated, an arbitrary adsorption coefficient in units corresponding to those customarily employed for the dynamic adsorption coefficient was calculated as follows: for each isotherm the volume adsorbed in cm^3 (STP)/g was calculated for a pressure of 0.1 mm (Hg) using the Freundlich constants k and 1/n; this quantity was then multiplied by 7600 to give an artificial coefficient for the artificial equation $V = k_{arb}P$ where P is in atmospheres. This equation would tend to lose validity at fission gas pressures in excess of 0.1 mm (Hg) and a predicted V and holdup time might be higher than the actual; however, the

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*Ideally, the coefficient of determination represents the fraction of variance of the dependent variable due to the effect of the independent variable. If there are no experimental errors and correlation is perfect, the coefficient is one, the coefficient being reduced by experimental errors (7, 8).

pressures of usual interest are of the order of 0.1 mm (Hg) or less and at pressures lower than 0.1 mm the artificial equation would tend to yield low or pessimistic holdup times.

The results of fitting the data, by the method outlined, to the Freundlich equation,

$$V\ \left(\frac{\mathrm{cm}^3(\mathrm{STP})}{\mathrm{g}}\right) = k\ \left(\frac{\mathrm{cm}^3(\mathrm{STP})}{\mathrm{g}(\mathrm{mm\ Hg})^{1/n}}\right)\ P^{1/n}(\mathrm{mm\ Hg})^{1/n}, \tag{1}$$

where V is volume of gas adsorbed measured at 0°C and 760 mm (Hg) per gram of adsorbent, P is krypton or xenon pressure, and k and 1/n are constants, are given in Table I. Also included are the numbers of isotherm points, the coefficients of determination, and the derived values of k_{arb}. The pretreatment of the adsorbents was evacuation for four hours at 150°C for the charcoals and evacuation for 2-4 hours at 600°F for the Sieves. A representative pressure range for the isotherms is 0.1-2 mm (Hg).

An analytical expression for the variation of the adsorption coefficient, for a given adsorbate-adsorbent system, with temperature is of value for purposes of interpolation and limited extrapolation and, also, for use in computer calculations, as, e. g., in the estimation of temperature profiles in an adsorber. The sets of values for k_{arb} in Table I were fitted using $\ln k_{arb} = \ln A + B/T$, the linear form of

$$k_{arb}\ (\mathrm{cm}^3(\mathrm{STP})/\mathrm{g\ atm}) = A\ (\mathrm{cm}^3(\mathrm{STP})/\mathrm{g\ atm})\ e^{B(^\circ\mathrm{K})/T(^\circ\mathrm{K})}, \tag{2}$$

where T is absolute temperature and A and B are evaluated constants. The results are given in Table II. Also, as indicated in the table, corresponding k_{arb} values for G and PCB and for ACC and HCC grades of charcoal were averaged and fitted to equation 2 since a comparison of k_{arb}'s in Table I provides some justification for these pairings of charcoals. These composite data are shown in Fig. 1 where the circles and squares represent the average of the k_{arb} values from Table I and the solid and dashed lines are as calculated from the last four pairs of A and B values in Table II. The results for the 5A Sieves are shown in Fig. 2.

Comments on Results

In general, the results of Table I appear fairly consistent and good precision is indicated. Minor discrepancies, however, appear to be evident. Regarding $1/n$, the more obvious expectations are that it would be lower for xenon than for krypton, that it would increase with temperature, and that it would not exceed one. The observed aberrations in $1/n$ may have resulted in part from the inherent difficulty in pretreating and maintaining adsorbent surfaces so that they are reproducible. (If the value of $1/n$ is in error, then the associated k and k_{arb} values would probably also be in error).

While these results were obtained in the absence of carrier gas, they should still be reasonably applicable when the carrier gas is not appreciably adsorbed such as is the case with helium and hydrogen at temperatures in the range of these measurements. In the case of the Homogeneous Reactor Test off-gas system, which has Columbia G charcoal, the carrier gas is oxygen which is appreciably adsorbed. The suggested approximate correction factor, based on dynamic measurements, for the data here is 0.9; i. e., the k_{arb} values and the constants A of Table II for Columbia G would all be multiplied by 0.9. Reasonably good estimates could probably be made for certain other situations when required using literature data and theory. The results for Type 4A Sieves represent the only known instance (to us) where the equilibrium or static data are in strong disagreement with dynamic measurements as the observed dynamic adsorption coefficient for this material at 25°C is approximately zero. This is obviously a result of the very low rate of adsorption of krypton on 4A Sieves. As already implied, the equilibrium results on the other adsorbents appear to be applicable under the usual dynamic conditions, provided allowance is made for the possible interference due to adsorption of the carrier gas.

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Table I. Linear Regression Analysis of Krypton and Xenon Adsorption Data (Based on the Freundlich Equation)

Adsorbent	Adsorbate	Isotherm Temp. (°C)	Freundlich Constants		No. of Isotherm Points	Coefficient of Determination	k_{arb} (cm^3(STP)/g atm)
			k (cm^3 (STP)/g(mm Hg)$^{1/n}$)	1/n			
Columbia G Activated Carbon, 8/14 mesh	Xe	0	3.7827	0.89667	15	0.9792	3647.2
	Xe	25	1.3338	0.92901	9	0.9990	1193.7
	Xe	60	0.44020	0.90350	11	0.9980	417.79
	Kr	0	0.18465	1.01149	10	0.9999	136.67
	Kr	25	0.080505	1.00334	15	0.9995	60.716
	Kr	60	0.031981	1.04785	11	0.9976	21.770
Pittsburgh PCB Activated Carbon, 12/30 mesh	Xe	0	3.0302	0.90074	16	0.9957	2894.3
	Xe	25	1.2716	0.88444	5	0.9960	1261.1
	Xe	60	0.29186	0.81650	5	0.9980	338.44
	Kr	0	0.17203	0.96261	7	0.9996	142.50
	Kr	25	0.073542	0.96874	5	0.9977	60.063
	Kr	60	0.026494	0.81051	5	0.9962	31.149
Columbia ACC Activated Carbon, 6/14X mesh	Xe	0	2.7049	0.91782	6	0.9860	2484.0
	Xe	25	1.0983	0.92820	5	0.9987	984.81
	Xe	60	0.32095	0.92631	6	0.9982	289.02
	Kr	0	0.14696	0.95395	7	0.9998	124.18
	Kr	25	0.064717	0.96635	5	0.9954	53.148
	Kr	60	0.028871	0.95799	5	0.9999	24.170
Columbia HCC Activated Carbon, 12/28X mesh	Xe	0	2.8877	1.00172	5	0.9843	2186.0
	Xe	25	1.1946	0.90211	5	0.9987	1137.5
	Xe	60	0.34275	0.96886	5	0.9982	279.86
	Kr	0	0.14621	0.93548	7	0.9984	128.92
	Kr	25	0.066833	0.97958	5	0.9993	53.238
	Kr	60	0.018836	0.93745	5	0.9942	16.532
Linde Molecular Sieves Type 5A, 1/16" pellets	Xe	0	0.21166	1.01428	7	0.9996	155.66
	Xe	25	0.094842	1.03917	8	0.9989	65.863
	Xe	60	0.032837	1.06223	5	0.9993	21.624
	Kr	0	0.025290	1.00690	6	0.9968	18.918
	Kr	25	0.013095	1.00882	6	0.9988	9.7516
	Kr	60	0.0065603	0.92787	5	0.9977	5.8866
Linde Molecular Sieves Type 4A, 1/16" pellets	Kr	25	0.0095670	0.83683	10	0.9923	10.587

NOTE: Equilibrium times of up to 4 hours were required for Type 4A Sieves.

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Table II

Temperature Dependence of Krypton and Xenon Adsorption Coefficients (According to $k_{arb} = Ae^{B/T}$ for Range of 0-60°C)

Adsorbent	Adsorbate	A $(cm^3(STP)/g\ atm)$	B (°K)	Coefficient of Determination
Columbia G	Xe	0.021454	3279.79	0.9967
	Kr	0.0050954	2790.15	0.9992
Pittsburgh PCB	Xe	0.019629	3267.79	0.9919
	Kr	0.030179	2296.10	0.9861
Columbia ACC	Xe	0.016235	3268.94	0.9983
	Kr	0.013902	2477.00	0.9963
Columbia HCC	Xe	0.024860	3139.73	0.9722
	Kr	0.0014452	3121.10	0.9984
Type 5A Sieves	Xe	0.0027178	2998.79	0.9988
	Kr	0.028579	1762.91	0.9862
G, PCB	Xe	0.020517	3275.11	0.9998
	Kr	0.013524	2518.72	0.9981
ACC, HCC	Xe	0.019921	3207.33	0.9892
	Kr	0.0049433	2771.54	0.9999

FIG. 1. TEMPERATURE DEPENDENCE OF ADSORPTION COEFFICIENTS FOR ACTIVATED CARBON (COMPOSITE DATA)

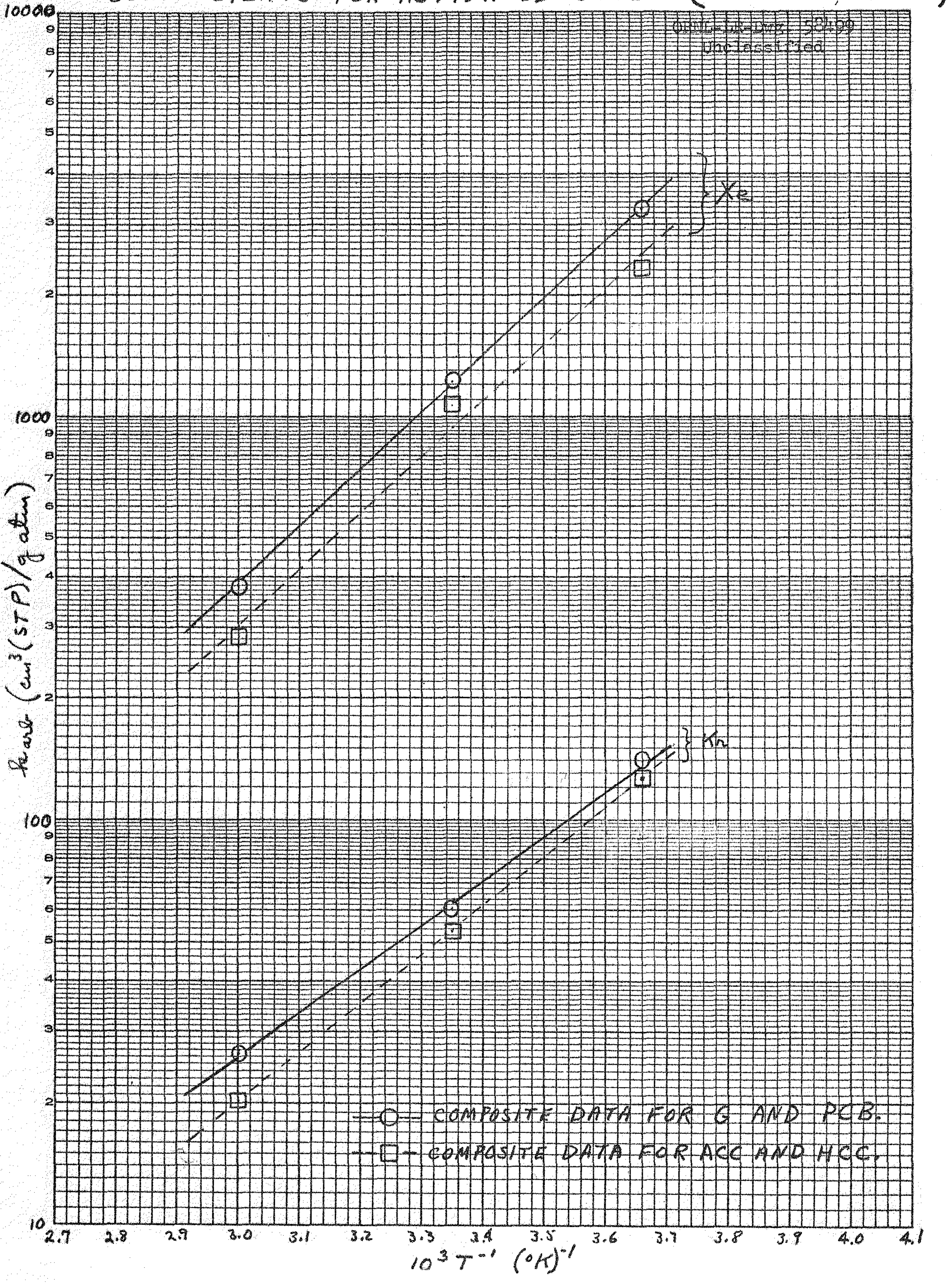

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FIG. 2 TEMPERATURE DEPENDENCE OF ADSORPTION COEFFICIENTS FOR TYPE 5A SIEVES

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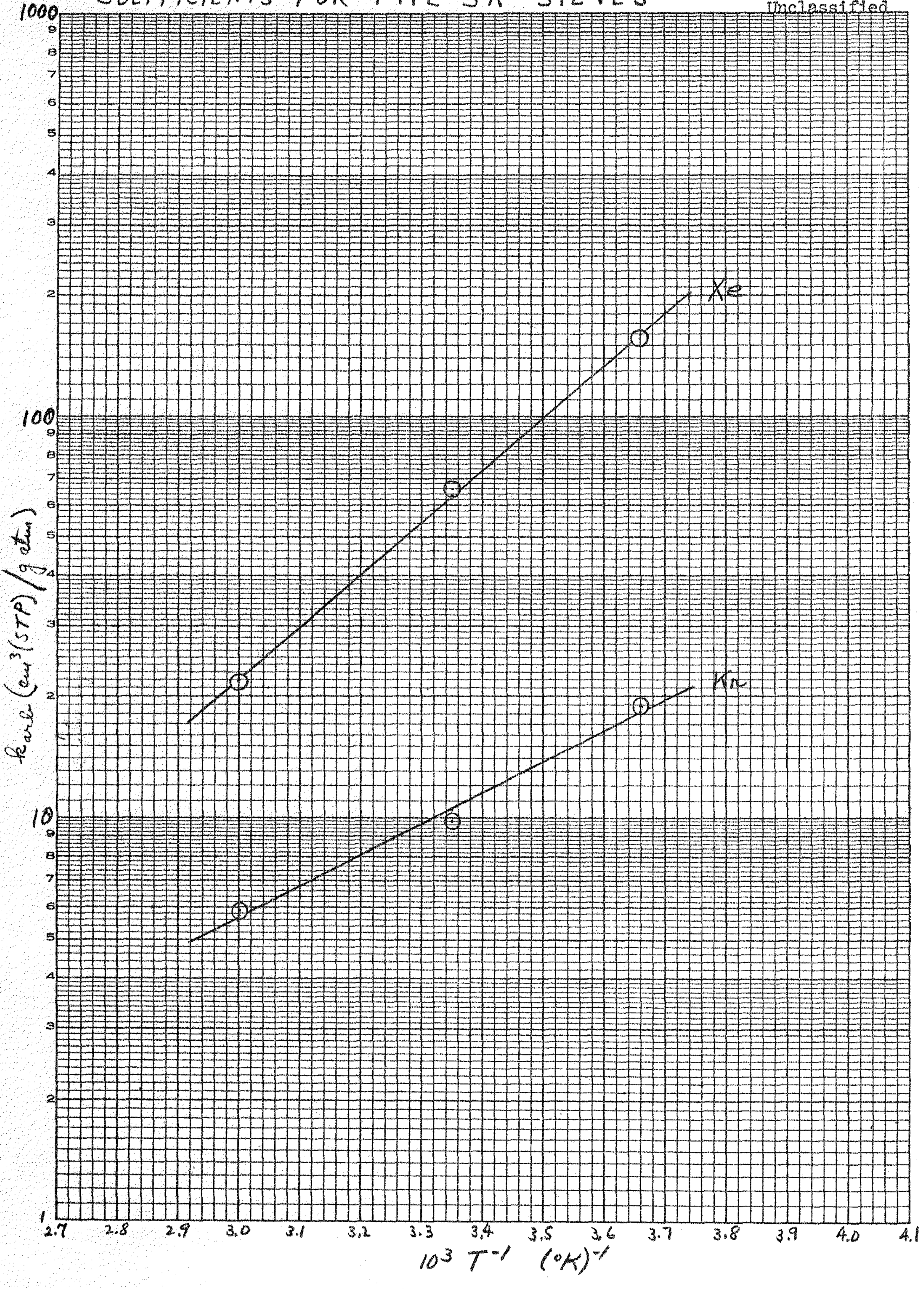

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