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GASEOUS ION RECOMBINATION RATES. III

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Rept. submitted for pub. in the
Journal of Chemical Physics.

UCRL-11134

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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November 1963

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Abstract

The rate constants for the bimolecular recombination of gaseous ions in three different systems have been determined. The results suggest that the recombination rate constant is not particularly sensitive to the chemical identity of the ions, and that complexes between ions and neutral atoms are important even at pressures below 10 mm Hg.

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In an earlier publication, Mahan and Person[1] presented evidence that the mechanism of the mutual neutralization of gaseous ions involves two parallel processes. One of these is a bimolecular electron transfer reaction:

$$A^+ + B^- \xrightarrow{k_o} \text{neutrals}$$

The other is essentially J. J. Thomson's[2] three body ion recombination reaction:

$$A^+ + B^- \xrightarrow{k_1} (A^+B^-)^*$$

$$(A^+B^-)^* \xrightarrow{k_2} A^+ + B^-$$

$$(A^+B^-)^* + M \xrightarrow{k_3} (A^+B^-) + M \longrightarrow \text{neutrals}$$

Here $(A^+B^-)^*$ represents a pair of unbound ions close enough to each other so that a collision of either of them with a neutral molecule M leads to formation of a bound ion pair (A^+B^-) and eventual charge neutralization. If we make the usual definition of the ion recombination coefficient α by the equation

$$-\frac{d(A^+)}{dt} = \alpha(A^+)(B^-)$$

then the steady state approximation for $(A^+B^-)^*$ gives

$$\alpha = k_o + \frac{k_1 k_3 (M)}{k_2 + k_3 (M)} \qquad (1)$$

The decision[1] that a bimolecular neutralization process exists was based on the fact that for the ions NO^+, NO_2^-, an extrapolation to zero pressure of a plot of α as a function of the pressure of M gave a finite intercept whose value was

independent of the nature of M, within experimental error. We would expect that the magnitude of k_o should depend on the nature of the recombining ions, and it is of interest to investigate this dependence. In this paper we present measurements of k_o for three different ion systems, and a more precise evaluation of the possible dependence of k_o on the nature of the inert gas.

Experimental

The apparatus and techniques used to determine the ion recombination rate constants were essentially the same as those described previously.[1] Photoionization was accomplished with a Kr resonance lamp whose principal ionizing radiation is the 1236 Å (10.03 ev) line. The helium, argon and xenon were Air Reduction Company reagent grade, used directly from their Pyrex bulbs. The nitric oxide and sulfur hexafluoride were taken from cylinders supplied by the Matheson Company. The nitric oxide was purified by trap to trap sublimation with retention of the middle fraction only. Reagent grade benzene, thiophene free, was vacuum distilled three times, and repeatedly degassed by freezing and pumping. Mass spectral examination of NO, SF_6, and benzene showed only innocuous impurities. Reagent grade iodine was vacuum sublimed into a storage tube, and always degassed immediately before use.

The pressures of NO, SF_6, and benzene were measured either with a McLeod gauge or a calibrated thermocouple gauge. The pressure of iodine was not measured directly, but estimated from

tabulated vapor pressure data. The iodine was allowed to sublime into the reaction vessel as the temperature of the storage tube was raised from -16°C to -10°C. Although this operation lasted 20 minutes, it is well known that iodine attains its equilibrium vapor pressure very slowly, so its pressure may have been less than the equilibrium value at -10°C, 0.011 mm.

The pressures of NO employed were between 60 and 150 μ, and for benzene the pressures ranged from 4 to 13 μ. The pressures of SF_6 used in the NO-SF_6 experiments were between 70 and 170 μ, and in the benzene-SF_6 experiments ranged from 44 to 125 μ except as noted in the tabulated results.

Results

The rate data collected for the NO-SF_6, benzene-SF_6, and I_2 systems are contained in Tables I-III and shown in Figures 1-3. The pressure dependence of α is similar to that found previously for the NO^+-NO_2^- system.

A major purpose of this work was the careful evaluation of k_o for different ion systems and different inert gases. The most obvious way to evaluate k_o from the experimental data is to realize that at low pressures $k_3(M) \ll k_2$, and Eq. (1) becomes

$$\alpha \simeq k_o + \frac{k_1 k_3}{k_2} (M) \qquad (2)$$

Thus a linear extrapolation of the low pressure data should give the value of k_o as the zero pressure intercept. Since α varies linearly with (M) only in the limit of very low pressures, this

method strictly should give an upper limit for k_o. For the $NO-SF_6$ and $C_6H_6-SF_6$ systems, the data obtained at inert gas pressures less than 100 mm seem to follow Eq. (2). For the iodine system, the plot of α vs. [M] is curved even at the lowest pressures.

Another way of evaluating k_o is to convert Eq. (1) to

$$\frac{1}{\alpha-k_o} = \frac{1}{k_1} + \frac{k_2}{k_1 k_3}\left(\frac{1}{M}\right) \tag{3}$$

and then choose k_o such that a plot of $1/(\alpha-k_o)$ vs. $1/(M)$ is a straight line. The linearity of such a graph is quite sensitive to the value of k_o. On the other hand, the procedure has the difficulty that the fractional uncertainty in $1/(\alpha-k_o)$ becomes most extreme at the lowest pressures, and it is these points that are most important in determining the linearity of the plot.

It can also be argued that the use of Eq. (3) even with data of excellent precision will not lead to the true value of k_o. That is, it is quite possible that the simple collisional mechanism given above should be replaced with a more detailed description:

$$A^+ + B^- \xrightarrow{a_i} (A^+B^-)_i^*$$

$$(A^+B^-)_i^* \xrightarrow{b_i} A^+ + B^-$$

$$(A^+B^-)_i^* + M \xrightarrow{c_i} (A^+B^-) + M \longrightarrow \text{neutrals}$$

$$\alpha - k_o = \sum_i \frac{a_i c_i (M)}{b_i + c_i (M)} \tag{4}$$

Here the subscript i denotes a particular state of energy and angular momentum for the colliding ions. Even more detailed decompositions of the recombination process are possible. If the successive terms on the right side of Eq. (4) are different, as is very probable, a plot of $1/(\alpha-k_o)$ vs. $1/(M)$ will not be linear, and any k_o obtained by forcing it to be linear will be incorrect. It is not possible to evaluate how serious this objection is, but because of the rather limited pressure range covered in our experiments, it is doubtful that the error in k_o incurred by fitting the data to Eq. (3) is appreciably more than the experimental uncertainty.

Since there is no clearly superior way of obtaining k_o, we give in Table IV values derived both from linear extrapolations according to Eq. (2) and parameter fitting to Eq. (3). We do not expect these two procedures to lead to exactly the same results, since Eq. (2) is equivalent to Eq. (3) only if $1/k_1 = 0$. Nevertheless, Table IV shows that the two methods give values of k_o which are the same within experimental uncertainty in most cases.

Discussion

In the NO-SF_6 system, photolysis by 1236 Å radiation produces NO^+ in one of three vibrational levels,[3] and a photoelectron whose energy may be 0.77, 0.47, or 0.17 ev. The attachment of low energy electrons to SF_6 leads principally[4] to SF_6^- and lesser amounts of SF_5^- under conditions where the negative ion is collision free. It is likely that the principal negative ion in the NO-SF_6

system was SF_6^-, but we cannot exclude the possible presence of other negative ions. Table IV shows that for this system, essentially the same value of k_o is obtained when He or Ar are used as inert gases, but the result determined from the Xe mixtures is definitely lower.

In the C_6H_6-SF_6 system, photolysis produces $C_6H_6^+$ in an unknown vibrational state, and electrons with a maximum kinetic energy of approximately 0.8 ev. Once again it is likely that the principal negative ion formed by electron attachment is SF_6^-. When Eq. (2) is used to determine k_o, the values for this system are the same within experimental error when He and Ar are the inert gases, but the value of k_o obtained from the Xe mixtures is lower than the others. If Eq. (3) is used, the possible ranges of k_o for the three gases overlap, but the rate constant found using Xe is less than the other two.

The primary process in the photolysis of I_2 at 1236 Å produces I_2^+ and an electron[5] with energy as great as 0.74 ev. There should be little I^+ present, since it is not produced in quantity by 10.0 ev. photons, and in any case would be neutralized by charge exchange with I_2. Heavier positive ions such as I_3^+ cannot be excluded, and have in fact been observed[6] in the high pressure mass spectrum of I_2.

The direct reaction[7] of an electron with I_2 can produce I^-, but it is also possible that I_2^- can be formed by a three body electron attachment to I_2. In addition, there is the possibility that I_3^- may be formed by

$$I^- + I_2 + M \longrightarrow I_3^- + M$$

The iodide-tri-iodide equilibrium in aqueous solution has been carefully studied.[8] By using the equilibrium constant determined in aqueous solutions we can estimate that under our conditions the concentration ratio of I^- to I_3^- should be approximately 10^4. We do not expect the equilibrium constant for the gaseous reaction to differ by more than two orders of magnitude from that of the aqueous reaction, so it is possible that I_3^- is in relatively low concentration. On the other hand, I_3^- and I^- appeared with comparable intensities in the mass spectrum[6] of I_2.

Because of the curvature of the α vs. P plots for the I_2 system, the values of k_o are quite uncertain. However, the values of k_o obtained from the He and Ar mixtures agree with the results of Yeung,[9] which were obtained by quite a different method. The value of k_o determined from the Xe mixtures is lower than the other two results. The reason for the curvature of the α vs. P plots is not clear, but it may be that the nature of the recombining ions changes as the pressure is altered.

It is evident that for each of the systems investigated, the values of k_o obtained using He and Ar as inert gases are approximately the same, and that value obtained using Xe is always lower than the other two. It is possible that this apparent dependence of k_o on the nature of the inert gas is caused by a diffusional contribution to the ion loss rate. However, if this were the case we would expect the values of k_o determined in He and Ar to exhibit the greatest differences, for the diffusion coefficient

of an ion increases very rapidly as the mass of the atmospheric molecules decreases. This expectation is contrary to the observations. Moreover, the linearity of the 1/n vs. t plots used to determine α suggest that diffusional loss of ions is not of great importance in most of our experiments. Thus it seems unlikely that diffusional effects can account for the dependence of k_o on the nature of the inert gas.

It is possible that the nature of the inert gas can affect the identity of the negative ions produced by electron attachment. The energy dependence of the cross sections for producing SF_6^- and SF_5^- from SF_6^- are different,[4] and thus the ability of the inert gas to thermalize the photoelectrons could control the realtive amounts of these two ions. However, of the three inert gases He has the largest collision cross section for 0.7 ev electrons and Ar the smallest. Thus there is no obvious correlation between the cross section for electron collisions and the trend in the values of k_o.

Inert gases can affect the value of k_o by forming clusters or complexes with the ions. If the ions are largely in the form $A^+(M)_m$, $B^-(M)_n$ at the lowest pressures investigated, then the value of k_o derived by extrapolation may depend on the nature of M and the extent to which the ions are complexed. If the binding energy in these complexes arises mostly from ion-induced dipole forces, complexing should be most extreme with small ions and polarizable neutrals. A calculation of the equilibrium constant for the reactions

$$NO^+ + He = NO^+He$$

$$NO^+ + Xe = NO^+Xe$$

following the procedure described by Fueno et al.[10] shows that the equilibrium constant of the latter reaction is nearly 800 times that of the former. The same calculation shows that at 10 mm pressure of Xe, 3% of the NO^+ should be complexed. These calculations involve an estimate of the ion-neutral binding energy by adding an ion induced dipole term to the usual Lennard-Jones expression for the interaction energy of two spherical neutral molecules. Consequently the calculated equilibrium constants are very unreliable, since an error of 1.4 kcal in the binding energy makes a factor of 10 error in the equilibrium constant. The binding energies estimated by the procedure of Fueno et al. are generally not greater than 0.2 ev, whereas the directly measured[11] bond energy for Xe_2^+ is 0.91 ev. Thus it is possible that virtually all ions are complexed even at pressures near 10 mm. Despite the quantitative uncertainty in the extent of complex formation, the qualitative fact remains that of all the gases, Xe should be the most likely to form complexes. This idea is consistent with the observed differences in k_o for Xe and the other two gases, for an increase in ion mass caused by the bound neutrals should lower the value of k_o. It appears then that complex ion formation is a plausible explanation for the influence of the nature of the inert gas on k_o, but this argument is of course speculative until the species present in these ionized gases are examined mass spectrometically.

Acknowledgements: This work was supported by the U. S. Atomic Energy Commission, and by the California Research Corporation. T.S.C. wishes to acknowledge fellowship support received from the National Science Foundation.

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Table I. Recombination Coefficients for NO-SF_6.[a,b]

He			Ar			Xe		
Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit	Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit	Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit
177.5	3.55	3.50	13.0	2.42	2.36	15.7	2.64	2.56
28.5	2.28	2.21	25.7	2.67	2.34	4.6	1.83	1.77
53.1	2.52	2.39	13.1	2.46	2.42	31.7	3.64	3.46
355.8	4.73	4.49	38.3	3.27	3.27	9.1	2.15	2.07
99.1	2.98	2.63	30.6	3.18	2.86	64.6	6.45	5.00
36.4	2.33	2.27	77.4	4.53	4.28			
68.5	2.46	2.38	122.8	5.45	5.24			
236.5	3.44	3.28	288.6	8.74	8.15			
			51.1	3.70	3.55			

a. Results in each column are listed in the order in which the experiments were performed.

b. Units of α are $cm^3\ sec^{-1}$.

Table II. Recombination Coefficients for C_6H_6-SF_6.[a]

He			Ar			Xe		
Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit	Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit	Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit
34.1	2.46	2.34	34.9	3.04	2.98	14.9	3.10	3.10
164.0	4.10	3.87	305.3	9.48	8.32	29.8	4.83	4.41
351.1	6.36	5.38	18.2	2.67	2.61	9.3	2.38	2.32
77.5	3.25	2.82	63.5	4.50	4.28	21.9	3.66	3.26
19.6	2.22	2.03	23.6	3.06	2.88			
56.6	2.52	2.42	104.9	6.90	6.32			
			51.4	4.55	4.11			
			198.6	9.68	8.88			
			39.8[b]	3.54	2.96			

a. Notation and units as in Table I.

b. In this run the SF_6 pressure was only 4μ.

Table III. Recombination Coefficients for I_2.[a]

He			Ar[b]			Xe		
Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit	Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit	Pressure (mm)	$\alpha \times 10^7$ Upper Limit	$\alpha \times 10^7$ Lower Limit
47.4	1.86	1.77	7.1	1.62	1.31	13.0	2.00	2.00
118.8	2.44	2.37	34.4	2.70	2.54	34.6	2.88	2.82
434.0	3.58	3.47	45.4	2.98	2.77	19.1	2.38	2.17
259.5	3.07	2.99	116.2	4.36	4.20	9.7	1.78	1.68
72.6	1.98	1.86	70.4	3.15	3.06	6.8	1.50	1.50
			241.9	5.38	5.09			
			28.4	2.34	2.29			
			159.7	4.27	4.05			

a. Notation and units as in Table I.

b. In these runs, the pressure of I_2 may have deviated from 0.01 mm to the greatest extent.

Table IV. Bimolecular rate constants.

System	$k_o \times 10^7$	
	By Eq. (2)	By Eq. (3)
$NO-SF_6-He$	1.95 ± 0.1	1.85 ± 0.05
$NO-SF_6-Ar$	2.0 ± 0.1	1.96 + 0.04
$NO-SF_6-Xe$	1.5 ± 0.15	1.46 ± 0.06
$C_6H_6-SF_6-He$	1.8 ± 0.2	1.82 ± 0.12
$C_6H_6-SF_6Ar$	1.75 ± 0.15	1.50 ± 0.25
$C_6H_6-SF_6Xe$	1.35 ± 0.15	1.25 ± 0.15
I_2-He	1.5 ± 0.2	1.25 ± 0.15
I_2-Ar	1.2 ± 0.2	1.2 ± 0.7
I_2-Xe	1.0 ± 0.2	0.55 ± 0.25

Figure Captions

Fig. 1. Recombination coefficient α as a function of inert gas pressure for the $NO-SF_6$ system. Only points for which the total pressure is less than 100 mm are plotted.

Fig. 2. Recombination coefficient α as a function of inert gas pressure for the $C_6H_6-SF_6$ system. Only points for which the total pressure is less than 110 mm are plotted.

Fig. 3. Recombination coefficient α as a function of inert gas pressure for the I_2 system. The line for He was drawn with the aid of 3 points at higher pressures. Otherwise only points for which the total pressure is less than 100 mm are shown.

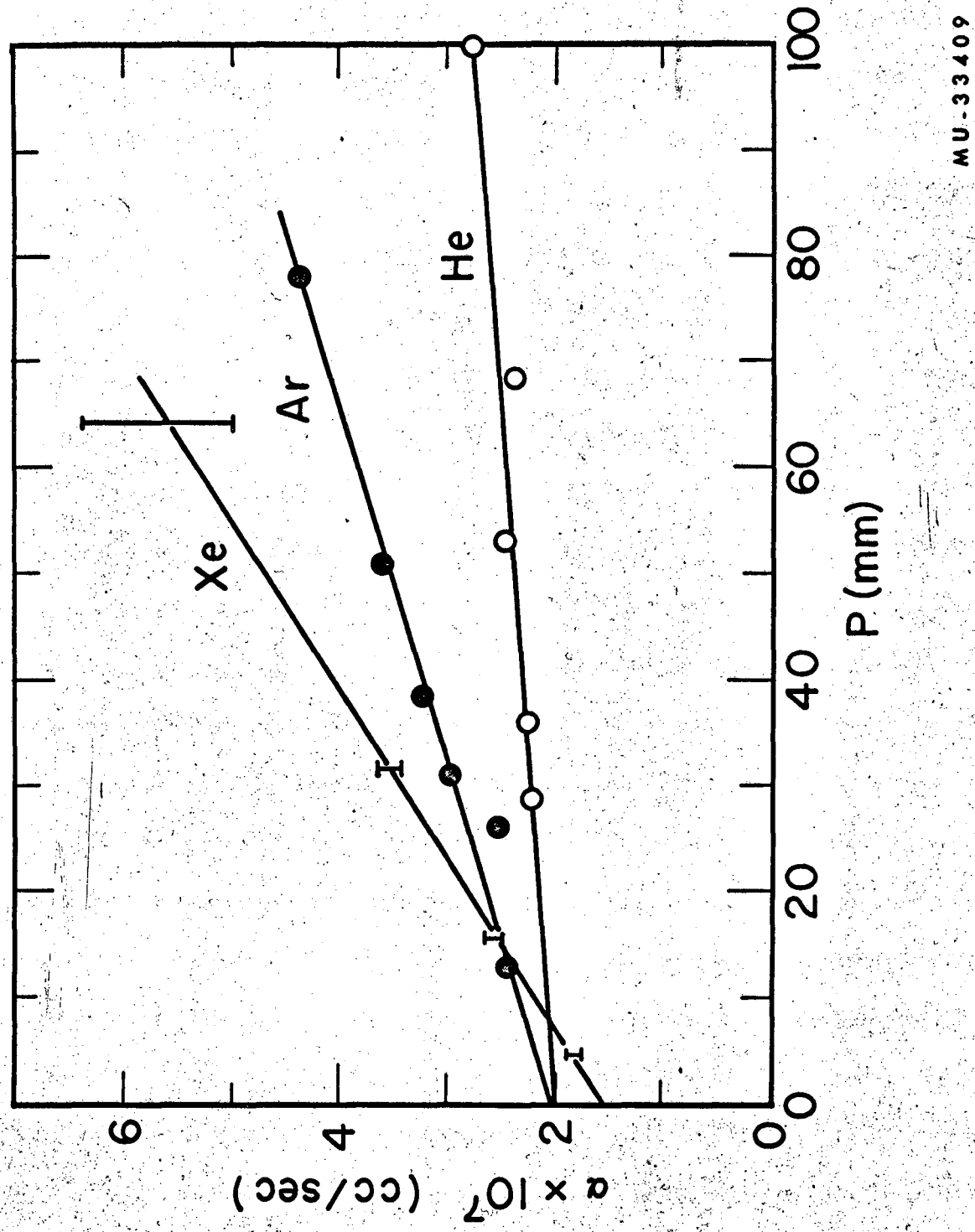


Fig. 1.

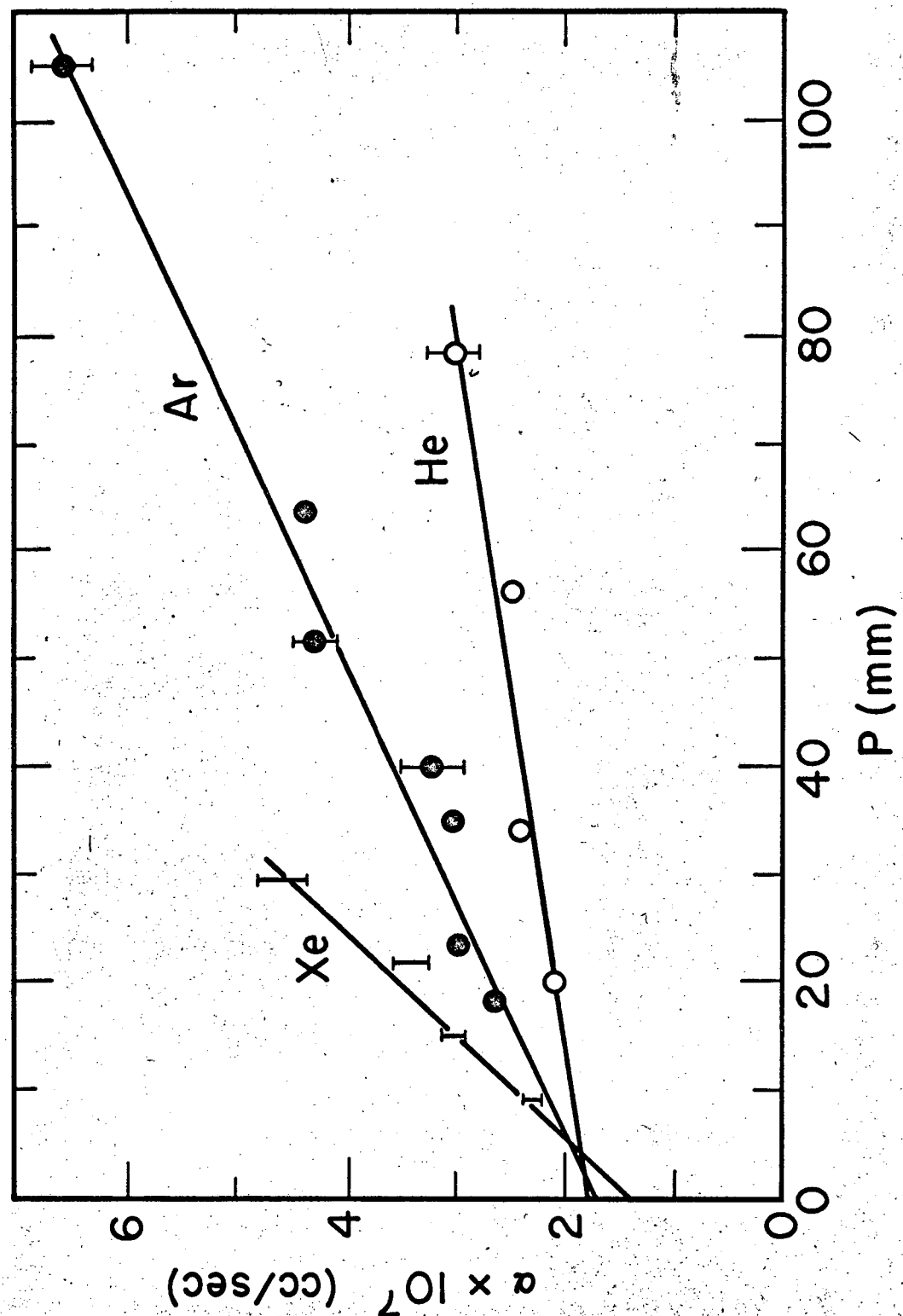
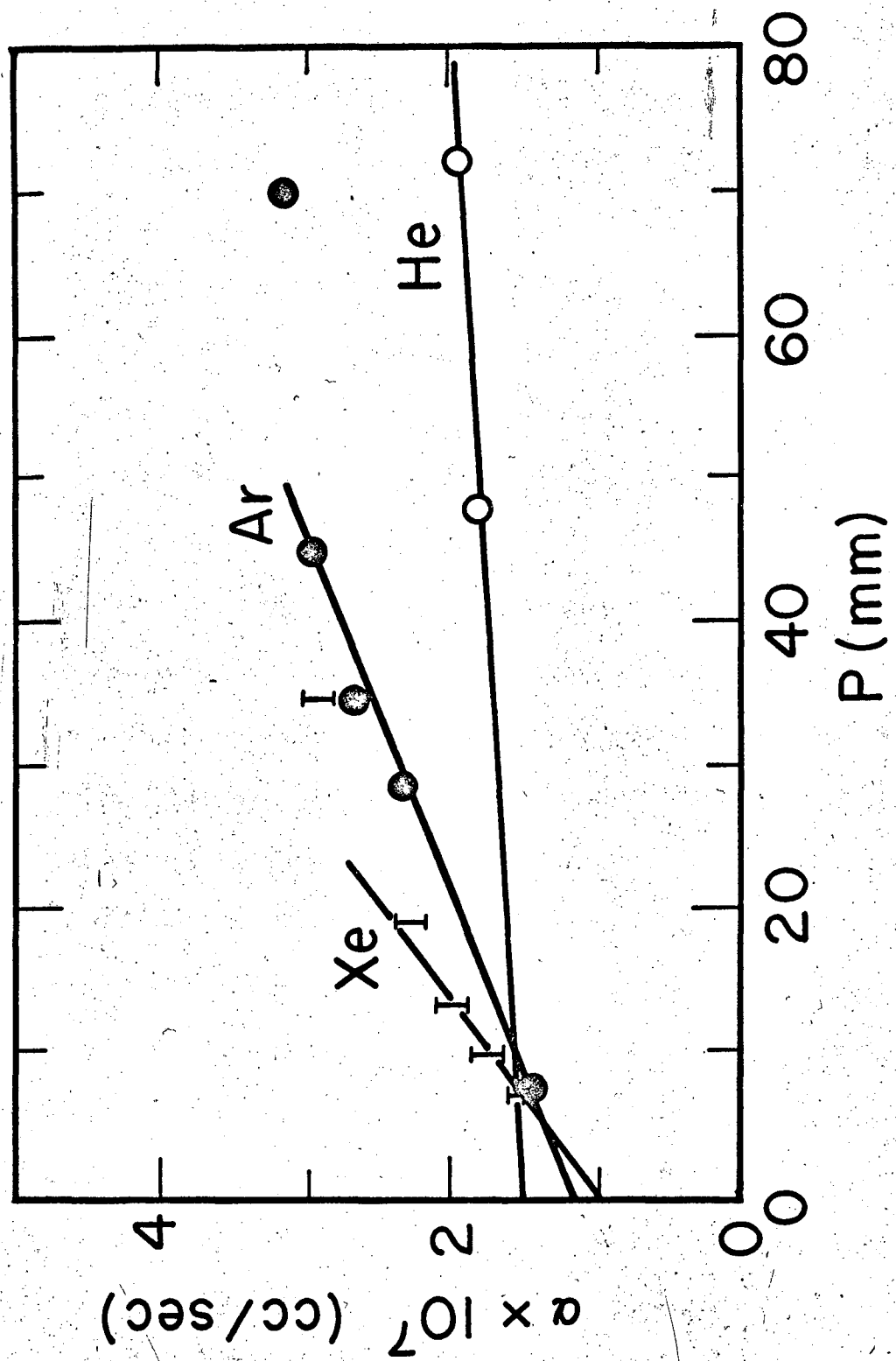


Fig. 2.



MU-33411

Fig. 3.

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