UCRL 3423

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

BERKELEY, CALIFORNIA

DISCLAIMER

UCRL-3423

UNIVERSITY OF CALIFORNIA

Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

THE HEATS OF FORMATION OF $AmO^{+}_{2(aq)}$ AND $AmO^{++}_{2(aq)}$ IN 1 M $HClO_4$

S. R. Gunn and B. B. Cunningham

May 22, 1956

Printed for the U.S. Atomic Energy Commission

THE HEATS OF FORMATION OF $AmO_{2(aq)}^{+}$ AND $AmO_{2(aq)}^{++}$ IN 1 M $HClO_4$ [1]

S. R. Gunn[2] and B. B. Cunningham

Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

May 22, 1956

ABSTRACT

The heats of reaction of $AmO_{2(aq)}^{+}$ and $AmO_{2(aq)}^{++}$ with $Fe_{(aq)}^{++}$ in 1 M $HClO_4$ have been measured to be -72.2 ± 1.0 and -99.1 ± 0.2 kcal respectively. From these and other thermodynamic data the heats of formation of $AmO_{2(aq)}^{+}$ and $AmO_{2(aq)}^{++}$ are calculated to be -207.8 ± 2.9 and -171.0 ± 2.7 kcal respectively. The entropy difference $S_{AmO_{2(aq)}^{++}} - S_{AmO_{2(aq)}^{+}}$ is calculated to be -16 ± 4 ev, and a self-consistent potential scheme for the various oxidation states of americium is given. A modified microcalorimeter used in the thermal measurements is described. The autoreduction of AmO_2^{+} and AmO_2^{++} and the disproportionation of AmO_2^{+} have been investigated.

---

[1] Abstracted in part from a dissertation submitted to the Graduate Division of the University of California by Stuart R. Gunn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was performed under the auspices of the U.S. Atomic Energy Commission.

[2] Present address: University of California Radiation Laboratory, Livermore, California.

THE HEATS OF FORMATION OF $AmO_{2(aq)}^{+}$ AND $AmO_{2(aq)}^{++}$ IN 1 M $HClO_4$

S. R. Gunn and B. B. Cunningham

Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

May 22, 1956

INTRODUCTION

The present investigation was undertaken to secure thermodynamic and kinetic data on the aqueous ions of the higher oxidation states of americium. Estimates of the heats and free energies of the reactions

$$Am_{(c)} + 3H^{+}_{(aq)} = Am^{+3}_{(aq)} + 3/2H_2(g) \quad (1)$$

and

$$Am^{+3}_{(aq)} + H^{+}_{(aq)} = Am^{+4}_{(aq)} + 1/2\ H_2(g) \quad (2)$$

have been reported previously.[3,4]

---

(3) H. R. Lohr and B. B. Cunningham, This Journal, 73, 2025 (1951).

(4) L. Eyring, H. R. Lohr, and B. B. Cunningham, ibid., 74, 1186 (1952).

All thermodynamic values calculated in this paper are for 298°K and all values used in the calculations are taken from the National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" unless otherwise stated. The activity coefficients of the aqueous americium ions are not known; hence our heats of formation cannot be designated as ΔH^{o} values and the potential values are "formal" rather than "standard".

EXPERIMENTAL

Preparation of Americium Solutions. -- The americium isotope used in this work was Am^{241}. Final purification was performed by oxidiation-fluoride cycles.[5] Solutions of AmO_2^{++} were prepared by

(5) S.E. Stephanou and R.A. Penneman, ibid., 74, 3701 (1952).

electrolytic oxidation in a cell consisting of three compartments separated by 1-cm Pyrex "F" sintered discs. The anode and cathode were platinum wire spirals with surface areas of 3.0 and 0.3 cm^2 respectively. The Am^{+3} in about 2 ml of either 1 M or 6 M $HClO_4$ was placed in the anode compartment and $HClO_4$ of the same concentration in the other two compartments. Electrolysis was performed at a current of 0.15 amp with the cell immersed in an ice bath; oxidation was 95% complete within 1 hour. For the calorimetric measurements the oxidized solution was then diluted to about 20 ml with distilled water or dilute $HClO_4$ and used immediately for measurements of the heat of reduction of AmO_2^{++}, or else was allowed to undergo autoreduction to AmO_2^{+} for heat measurements on this species.

Autoreduction of AmO_2^{+} and AmO_2^{++}. -- Spectrophotometric observations of the autoreduction of solutions of AmO_2^{+} and AmO_2^{++} were in reasonable agreement with the data reported by Asprey and Stephanou;[6] the rate

(6) L.B. Asprey and S.E. Stephanou, American Chemical Society, Chicago (1950).

laws are

$$-\frac{d(AmO_2^{++})}{dt} = \frac{d(AmO_2^{+})}{dt} = 0.040\,(Am_{total})\,hr^{-1}, \qquad (3)$$

and

$$-\frac{d(AmO_2^{+})}{dt} = \frac{d(Am^{+3})}{dt} = 0.020\,(Am_{total})\,hr^{-1}. \qquad (4)$$

The reduction is apparently effected mainly by hydrogen peroxide produced in the solution by the alpha radioactivity. An experiment in which extra hydrogen peroxide was added to a solution of AmO_2^+ showed the reaction to be first order with respect to (H_2O_2), the half time being about 1 hour. The reaction of H_2O_2 with AmO_2^{++} was complete before spectra could be recorded, about 5 minutes after mixing.

Solutions of AmO_2^+ thus contain an appreciable steady-state concentration of hydrogen peroxide, but solutions of AmO_2^{++} contain very little peroxide. In freshly prepared solutions of AmO_2^+, the rate of autoreduction is initially zero and increases to the limiting value given by equation 4 as the peroxide increases to its steady-state concentration. In mixed solutions of AmO_2^{++} and AmO_2^+, no AmO_2^+ is reduced to Am^{+3} until essentially all of the AmO_2^{++} has been reduced to AmO_2^+.

The Calorimeter. -- A microcalorimeter previously used in this laboratory[7] was extensively modified for the work described here. The reaction chamber was

---

(7) E. F. Westrum, Jr. and L. Eyring, This Journal, 74, 2045 (1952).

---

redesigned as shown in Fig. 1. The heater and thermometer consists of two coils of No. 42 B. and S. gage enameled copper wire of 40 and 25 ohms resistance respectively, wound bifilarly on a copper spool 0.010 inch thick. The spool is supported by four thin copper tubes through which the electrical leads are passed. All copper parts are gold plated; the chamber itself is of tantalum.

The space between the chamber and the submarine jacket was evacuated through tubing leading to an oil diffusion pump. A vacuum of about 10^{-3} mm Hg was maintained between the calorimeter reaction chamber and the enclosing submarine jacket. A thin aluminum radiation shield was placed midway between the chamber and submarine. The thermal leakage modulus obtained with this assembly was 5×10^{-3} minute^{-1}.

Operation of the calorimeter was checked by measuring the heat of solution of magnesium metal in 1.00 M HCl saturated with H_2. The results of these test measurements are shown in Table I.

Table I

Heat of Solution of Mg in 1.00 M HCl		
Sample Weight (mg)	Heat Evolved (cal)	ΔH (kcal)
0.2280	1.039	-111.1
0.1294	0.591	-111.4
0.2192	1.002	-111.4

The values agree well with that of -111.322 ± 0.041 determined by Shomate and Huffman.[8] The same correction for volatilized water has been applied.

(8) C.H. Shomate and E.H. Huffman, ibid., 65, 1625 (1943).

The data are uncorrected for the heat of breakage of the small (~20 µl volume) Pyrex bulbs used to hold the samples, since this heat was zero within the limits of sensitivity. The reductant solutions for the americium runs were contained in similar bulbs of 100 µl volume; any heat of breakage would be eliminated from the final result on correction for the apparent heat of dilution of the reductant in blank runs.

Heat of Formation of AmO_2^{++}. --Two equal aliquots of the AmO_2^{++} solution were taken, one being reacted in the calorimeter and the other titrated to determine the AmO_2^{++} concentration. The reducing solutions were weighed samples of 75 to 100 µl of 0.88 M $Fe(ClO_4)_2$ in 1.00 M $HClO_4$; the correction for the heat of dilution was about 0.03 cal. Analysis of the americium solutions for AmO_2^{+} or AmO_2^{++} consisted of addition of a slight excess of 0.1 N $Fe(ClO_4)_2$ from a gravimetrically calibrated micropipet followed by back-titration with 0.1 N $KMnO_4$ from a microburet, using 5 µl of 0.025 M orthophenanthroline ferrous sulfate. This titration was performed as close to the time of the calorimetric reaction as possible, and the (AmO_2^{++}): (AmO_2^{+}) ratio was measured spectrophotometrically at about the same time. Appropriate corrections were made for the AmO_2^{+} present. The results of the measurements of the heat of the reaction

$$AmO_{2(aq)}^{++} + 3Fe_{(aq)}^{++} + 4H_{(aq)}^{+} = Am_{(aq)}^{+3} + 3Fe_{(aq)}^{+3} + 2H_2O_{(\ell)} \qquad (5)$$

are given in Table II.

Table II

Heat of Reduction of AmO_2^{++} By Fe^{++}

Run	AmO_2^+ (μmoles)	AmO_2^{++} (μmoles)	$HClO_4$ (molarity)	Heat Evolved (cal)	$-\Delta H$ (kcal)
1	1.08	14.16	1.30	1.436	95.9
2	0.49	8.06	0.42	0.832	98.9
3	0.38	6.42	1.15	0.664	99.3
4	0.58	9.31	1.28	0.967	99.0

Run No. 1 is rejected from the series to give an average value of ΔH = -99.1 ± 0.2 kcal.

Heat of Formation of AmO_2^+. -- The heat-of-reduction measurements were performed in the same manner as the preceding series except that the AmO_2^{++} solution was allowed to undergo autoreduction until it was about 90% AmO_2^+. The data are presented in Table III.

Table III

Heat of Reduction of AmO_2^+ By Fe^{++}

Run	AmO_2^+ (μmoles)	AmO_2^{++} (μmoles)	$HClO_4$ (molarity)	Heat Evolved (cal)	$-\Delta H$ (kcal)
1	9.09	0.98	1.19	0.7507	71.9
2	9.33	0.96	0.84	0.7719	72.5
3	9.21	0.90	0.9	0.7673	73.6
4	9.58	0.82	0.92	0.7621	71.0

The average value of ΔH for the reaction

$$AmO_2^+ + 2Fe^{++} + 4H^+ = Am^{+3} + 2Fe^{+3} + 2H_2O \qquad (6)$$

is - 72.2 ± 1.0 kcal.

The method of analysis eliminates errors from chemical impurities except for substances such as Cr or Mn which would be oxidized with the americium and reduced by Fe^{++}, and these would be effective only so far as their heats of reduction per equivalent differed from that of AmO_2^{++} or AmO_2^+. Spectrographic analysis of the americium gave upper limits of 0.2 wt. % each of Cr and Mn.

The spectrophotometric determination of the (AmO_2^{++}) : (AmO_2^+) ratio is accurate only to about 3%, but the error introduced is small since the heats of reduction per equivalent of the two species differ by only 10%.

Disproportionation of AmO_2^+. -- The estimated potentials derived from thermal data indicate that AmO_2^+ should disproportionate in 1 M $HClO_4$ according to the reaction

$$3AmO_2^+ + 4H^+ = 2AmO_2^{++} + Am^{+3} + 2H_2O. \qquad (7)$$

This disproportionation of AmO_2^+ has been observed previously in 6 M and 3 M $HClO_4$,[9] but is not seen in 1 M $HClO_4$. In the present work two series of

(9) S.E. Stephanou, L.B. Asprey, and R.A. Penneman, American Chemical Society, Chicago (1950).

spectrophotometric observations of the disproportionation of solutions of AmO_2^+ in 5.70 and 5.97 M $HClO_4$ gave rate data in agreement with the earlier measurements by Stephanou, Asprey, and Penneman.[9] The rate law is

$$\frac{d(AmO_2^+)}{dt} = - 0.04 (AmO_2^+)^2 (HClO_4)^4 \text{ moles liter}^{-1} \text{ hr}^{-1} . \qquad (8)$$

The data indicate that the disproportionation follows the stoichiometry of reaction 5 within the limits of experimental error. The most probable mechanism would seem to be the rate-determining step

$$2AmO_2^+ + 4H^+ = AmO_2^{++} + Am(IV) + 2H_2O \qquad (9)$$

followed by the rapid reaction

$$AmO_2^+ + Am(IV) = AmO_2^{++} + Am^{+3} \; . \qquad (10)$$

Detectable amounts of Am(IV) have not been found in aqueous solution.

Since AmO_2^{++} is undergoing autoreduction to AmO_2^+ whenever it is present in solution, the actual variation with time of the various species is as follows:

$$\frac{d(AmO_2^{++})}{dt} = 0.027\,(AmO_2^+)^2\,(H+)^4 - 0.040\,(Am_{total}) \; , \qquad (11)$$

$$\frac{d(AmO_2^+)}{dt} = -0.04\,(AmO_2^+)^2\,(H^+)^4 + 0.040\,(Am_{total}) \; , \qquad (12)$$

$$\frac{d(Am^{+3})}{dt} = 0.013\,(AmO_2^+)^2\,(H^+)^4 \; . \qquad (13)$$

In an initially pure solution of AmO_2^+, no AmO_2^{++} will appear unless the concentration of AmO_2^+ is greater than $1.5\,(H^+)^{-4}$ mole liter^{-1}.

DISCUSSION

Using the value of $\Delta H = +9.95$ kcal[10] for the heat of oxidation

(10) R. E. Connick and W. H. McVey, This Journal, 73, 1798 (1951).

of Fe^{++},

$$Fe^{++}_{(aq)} + H^{+}_{(aq)} = Fe^{+3}_{(aq)} + 1/2\ H_{2(g)}\ , \qquad (14)$$

the heats of oxidation of Am(III) to Am(V) and Am(VI) may be calculated:

$$Am^{+3}_{(aq)} + 2H_2O_{(l)} = AmO^{+}_{2(aq)} + 2H^{+}_{(aq)} + H_{2(aq)}\ , \qquad (15)$$

$$\Delta H = +92.1 \pm 1.0 \text{ kcal.}$$

$$Am^{+3}_{(aq)} + 2H_2O_{(l)} = AmO^{++}_{2(aq)} + H^{+}_{(aq)} + 3/2\ H_{2(g)}\ . \qquad (16)$$

$$\Delta H = +129.0 \pm 0.3 \text{ kcal.}$$

These data, in combination with earlier values for the heats of reactions 1 and 2 ($\Delta H = -163.2 \pm 2.7$ kcal and $\Delta H = +47$ kcal respectively), give the heats of formation summarized in Table IV.

Table IV

Heats of Formation of the Aqueous Ions of Americium

Am^{+3}	-163.2 ± 2.7 kcal
Am^{+4}	-116 ± 6
AmO_2^+	-207.7 ± 2.9
AmO_2^{++}	-170.8 ± 2.7

The free energies and oxidation potentials of the various couples may be calculated from the data of Table IV by making use of estimated entropies; however, in view of the large discrepancies between the entropies given by Latimer[11] for the MO_2^+ type of actinide ion and the values found by Cohen and Hindman[12] for the corresponding neptunium ion, we shall use our value of $\Delta H = +36.9 \pm 1.0$ kcal for the reaction

$$AmO^+_{2\,(aq)} + H^+_{(aq)} = AmO^{++}_{2(aq)} + 1/2\ H_{2(g)}\ , \qquad (17)$$

in combination with the value of -1.60 v reported by Penneman and Asprey[13] for this couple, to calculate $S_{AmO^{++}_{2(aq)}} - S_{AmO^{+}_{2(aq)}}$.

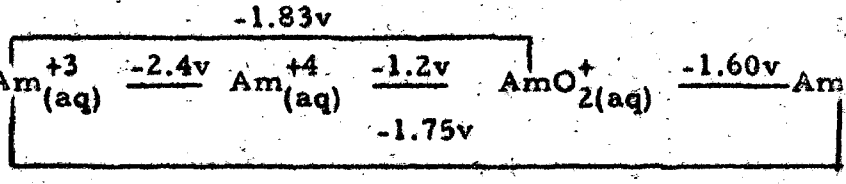
(11) W.L. Latimer, "Oxidation Potentials", second edition, Prentice-Hall, Inc., New York, N.Y., 1952, pp. 302-306.

(12) D. Cohen and J.C. Hindman, This Journal, 74, 4682 (1952).

(13) R.A. Penneman and L.B. Asprey, American Chemical Society, Chicago, Illinois (1950).

Straightforward manipulation of the data yields -16 ± 4 e.u. for this difference. We then adopt, for the entropy of $AmO_{2(aq)}^{++}$, -18 e.u., the value given by Connick and McVey[10] for PuO_2^{++}, to obtain -2 for the entropy of $AmO_{2(aq)}^{+}$. We also adopt for $Am_{(aq)}^{+4}$ the entropy of -77 e.u. given by Connick and McVey for $Pu_{(aq)}^{+4}$ and take the difference in entropy $S_{Am_{(aq)}^{+4}} - S_{Am_{(aq)}^{+3}}$ to be -47 e.u., the same value as for $S_{Np_{(aq)}^{+4}} - S_{Np_{(aq)}^{+3}}$ found by Cohen and Hindman.[12] Finally the entropy of Am^0 is assumed to be 12 e.u., the same as that of U^0.

These entropy values in combination with the heat data of Table IV yield the following self-consistent potential scheme:



The more reliable values are given to the nearest 0.01v and the less reliable to 0.1v. At best, however, the potentials are uncertain by 0.05v and those involving $Am_{(aq)}^{+4}$ by 0.2v.

It is recognized that differences in ground-state multiplicities of analogous actinide ions will lead to variations in entropy of 1 to 2 entropy units, and that the contraction in ionic radius with increasing atomic number will cause the entropies to become more negative along the series. At present, however, it is not possible to evaluate these effects adequately. It does seem most probable, however, that the entropy values assigned by Latimer to the MO_2^+ type of actinide ions are too positive by some 15 to 20 entropy units. The linear structure and high formal charge on the MO_2^+ type of ion should permit close approach and marked ordering of water of hydration, as compared with the large alkali cations, to which Latimer's entropy values correspond.

Use of the longer-lived isotope Am^{243} in studies on the disproportionation of AmO_2^+ in 1 M H^+ may yield equilibrium values that will define the ratio of the potentials of the 3-5 and 3-6 couples more precisely than is possible from the present data. In solutions of Am^{241} of conveniently realizable concentrations the disproportionation in 1 M acid is completely masked by autoreduction.

ACKNOWLEDGMENTS

We wish to express our appreciation to Mr. Herman Robinson for assistance in the design and maintenance of the apparatus and to Mrs. Winifred Heppler and Miss Lily Goda for technical assistance in some parts of the work. Spectrographic analyses were performed by Mr. John G. Conway and Mr. Ralph W. McLaughlin.

LEGEND

Fig. 1. Microcalorimeter reaction chamber.

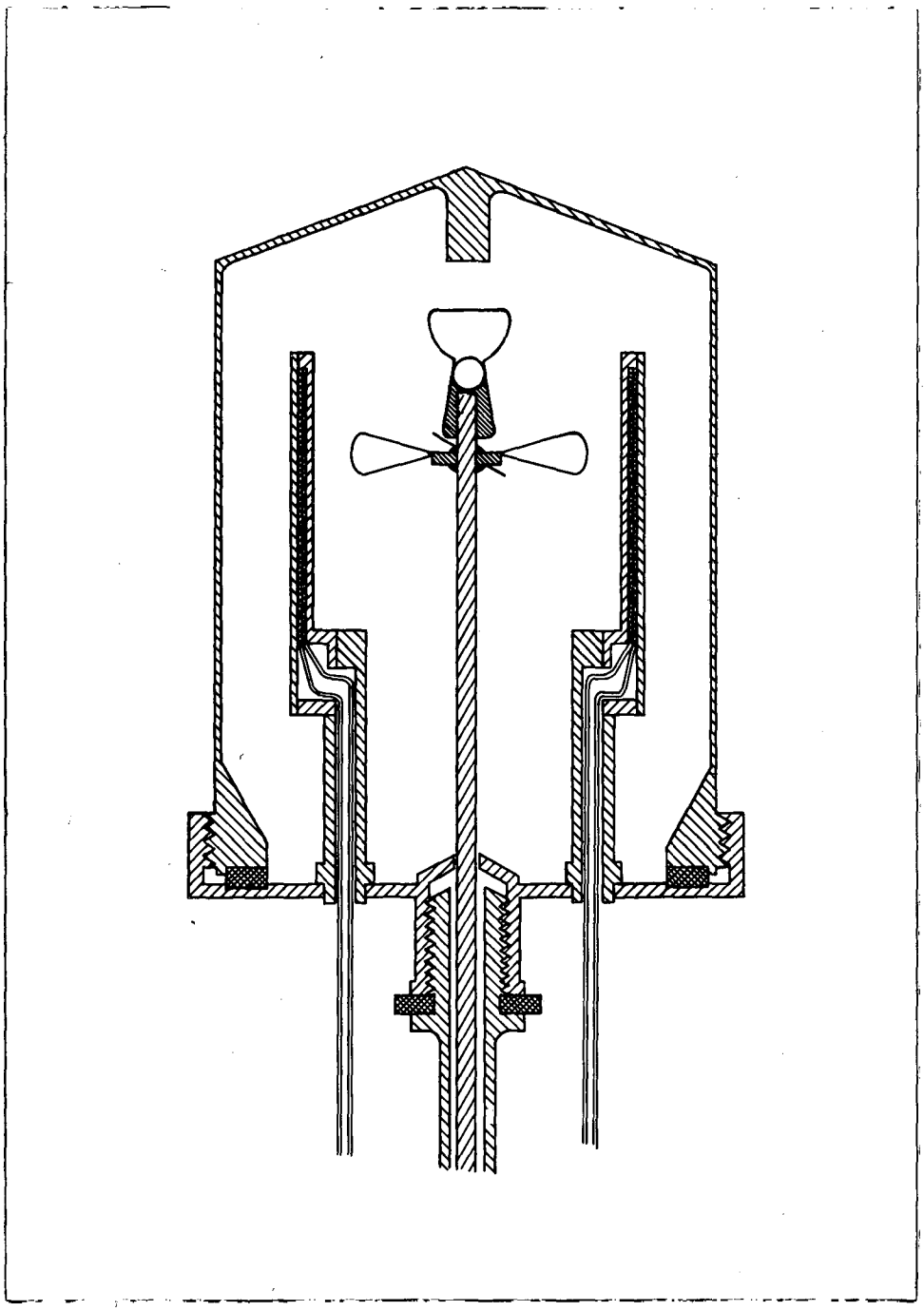
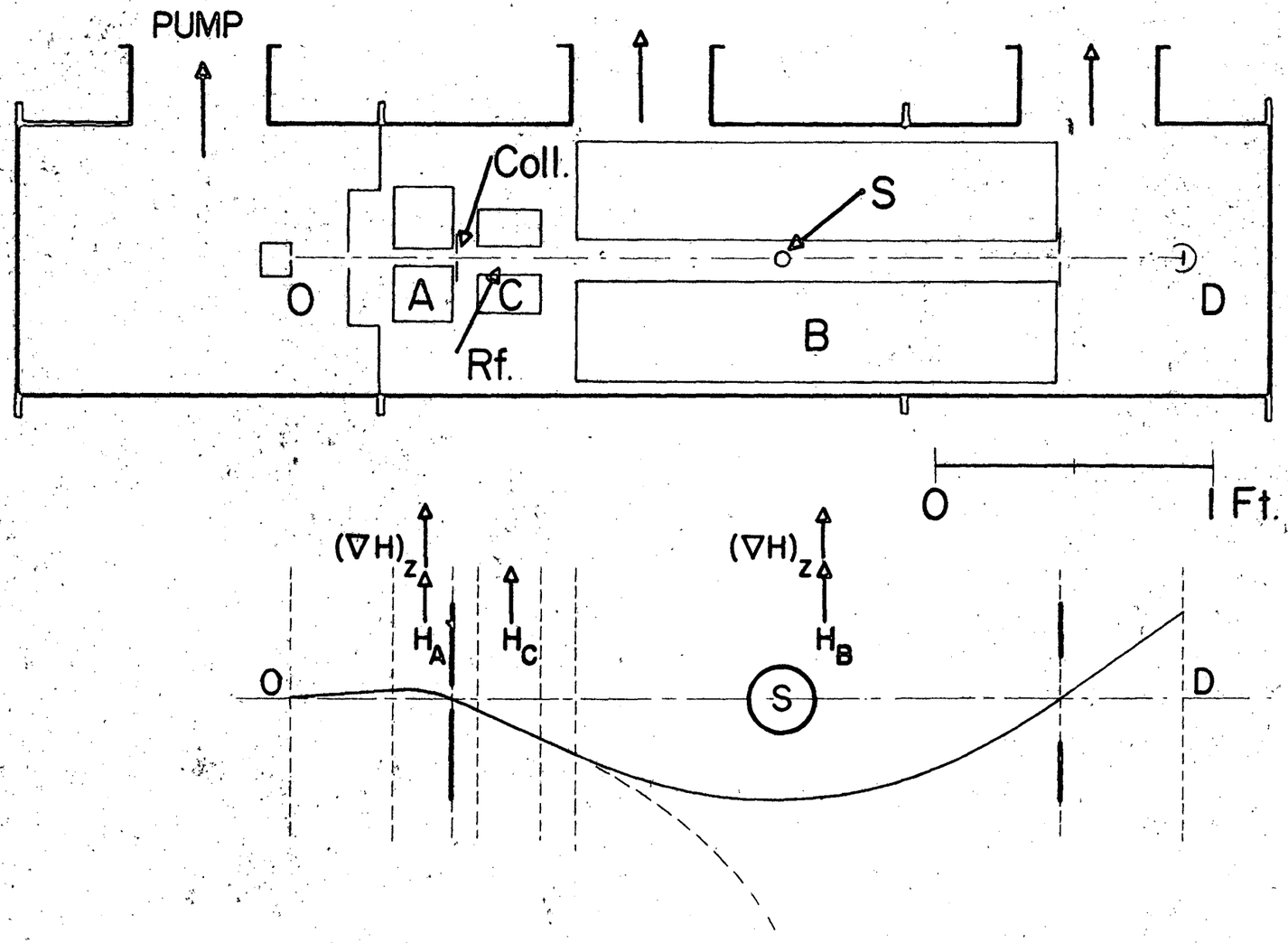


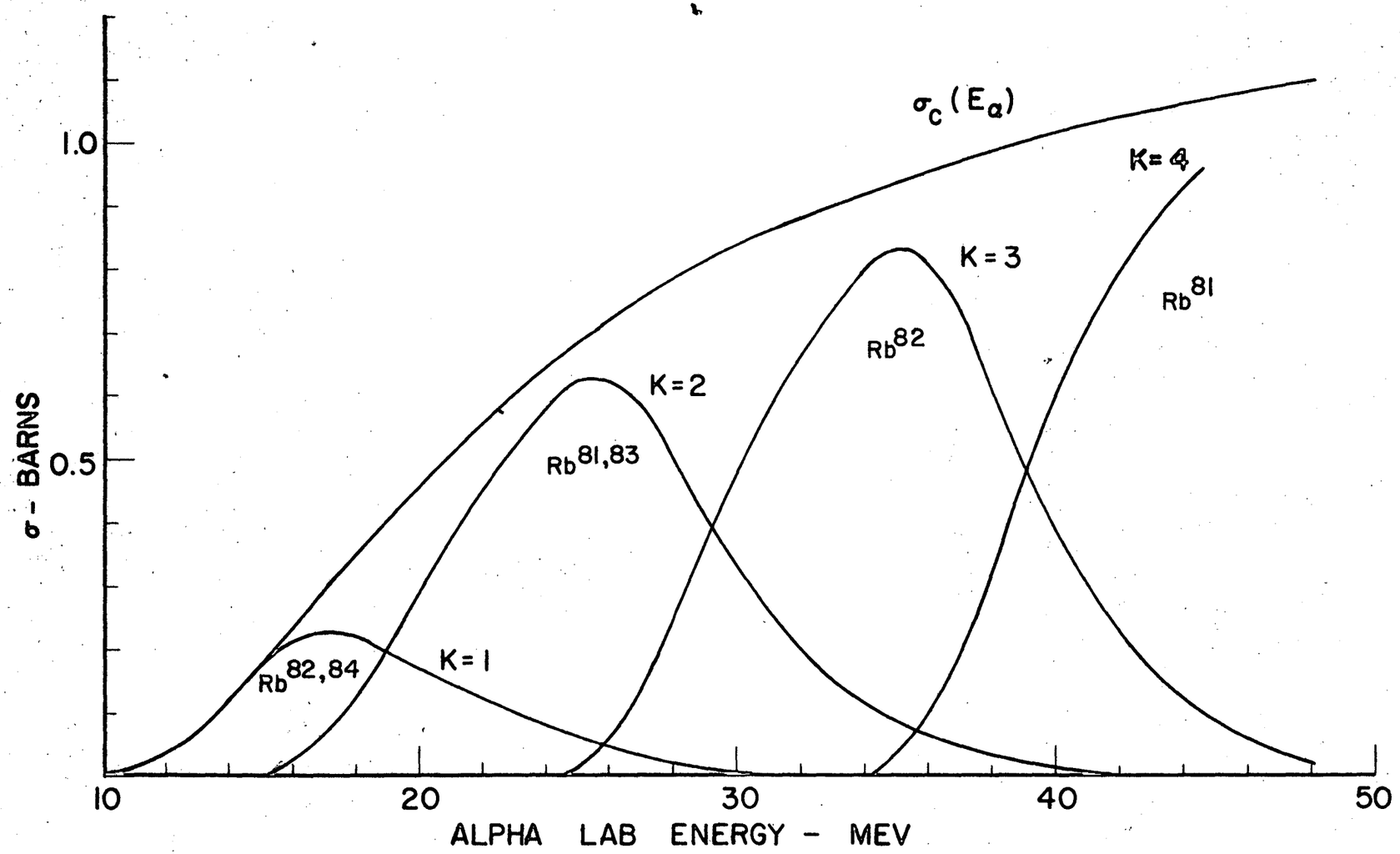
Fig. 1



SCHEMATIC ARRANGEMENT AND TRAJECTORY IN AN ATOMIC BEAM, FLOP-IN APPARATUS

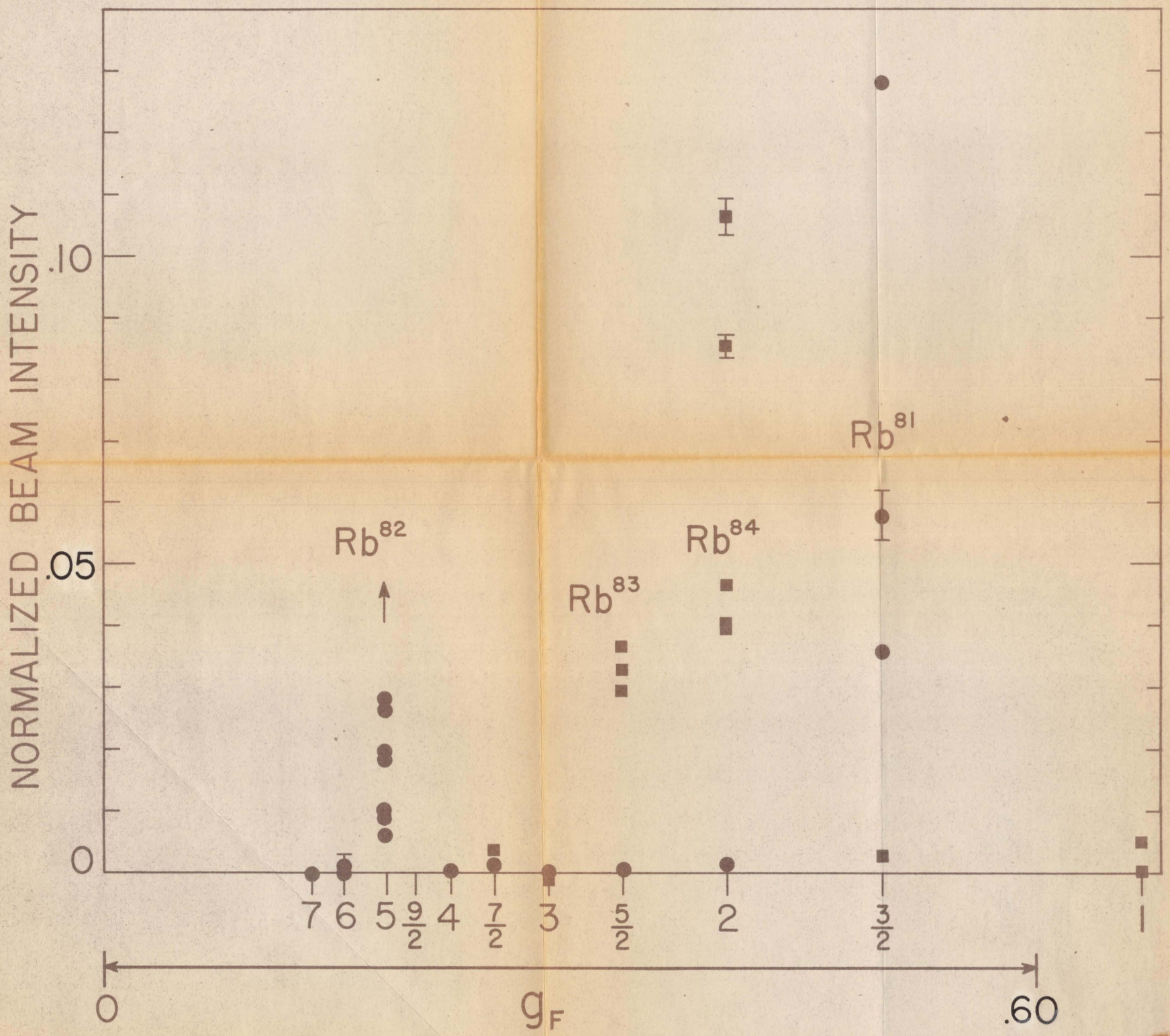
Fig 1

Fig 1



CALCULATED EXCITATION FUNCTIONS Br (α, kn) Rb

Fig 2

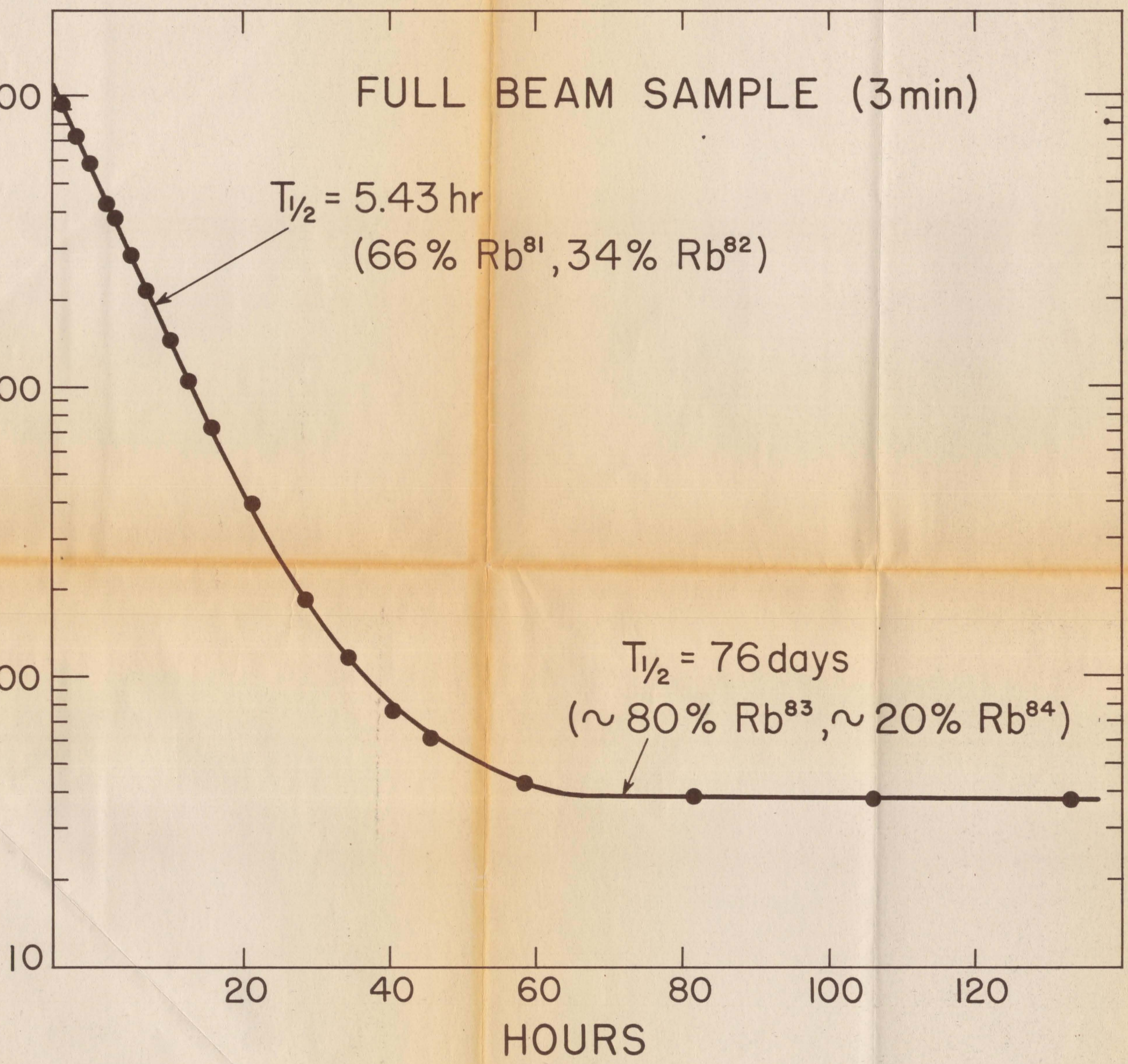


MU-11397

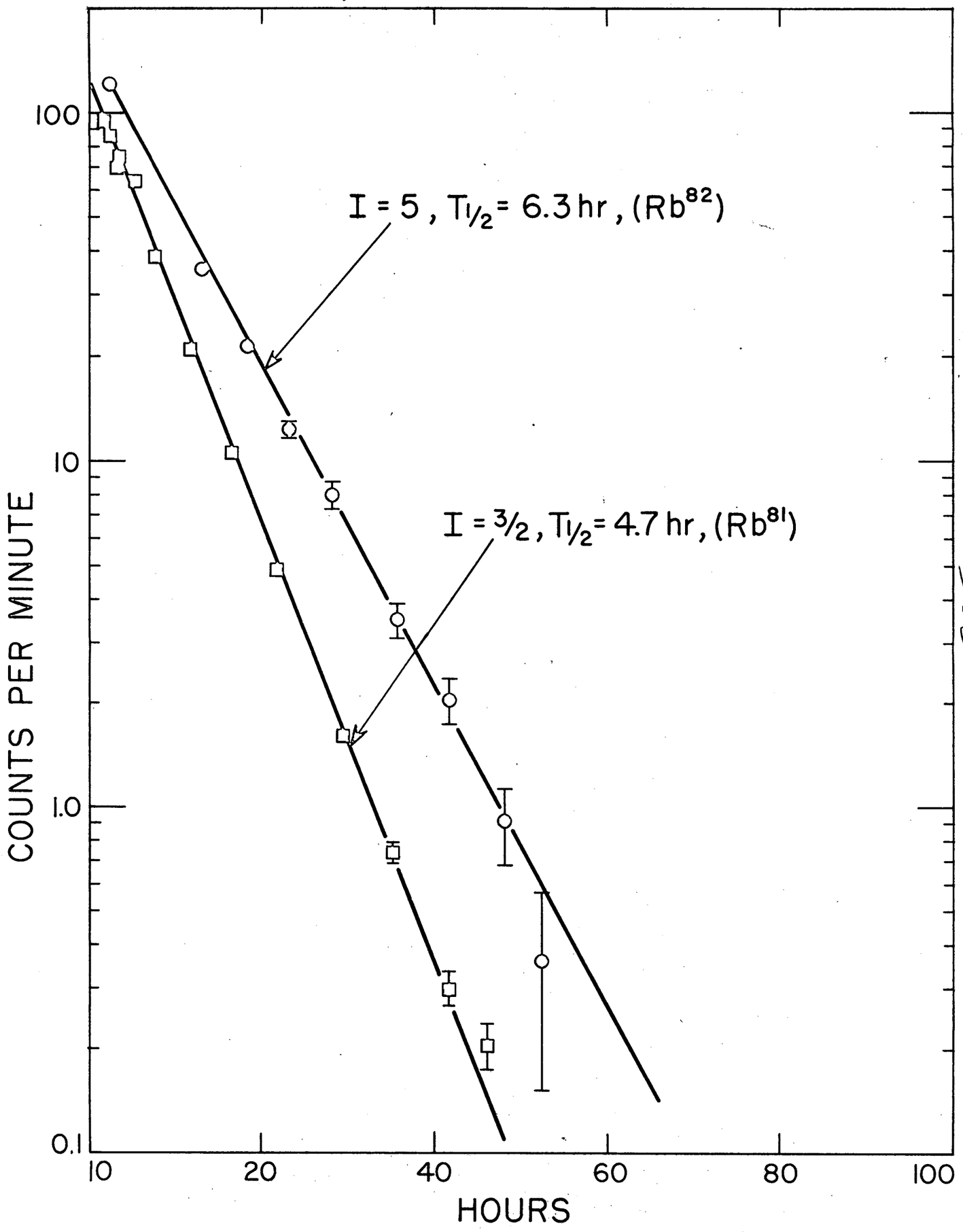
Feath

mu-11398

24499-3


FULL BEAM SAMPLE (3min)
$T_{1/2}$ = 5.43 hr
(66% Rb^{81}, 34% Rb^{82})
$T_{1/2}$ = 76 days
(~80% Rb^{83}, ~20% Rb^{84})
COUNTS PER MINUTE
10,000
1,000
100
10
20
40
60
80
100
120
HOURS

24498-3



Figs

Fig 5

24496-2

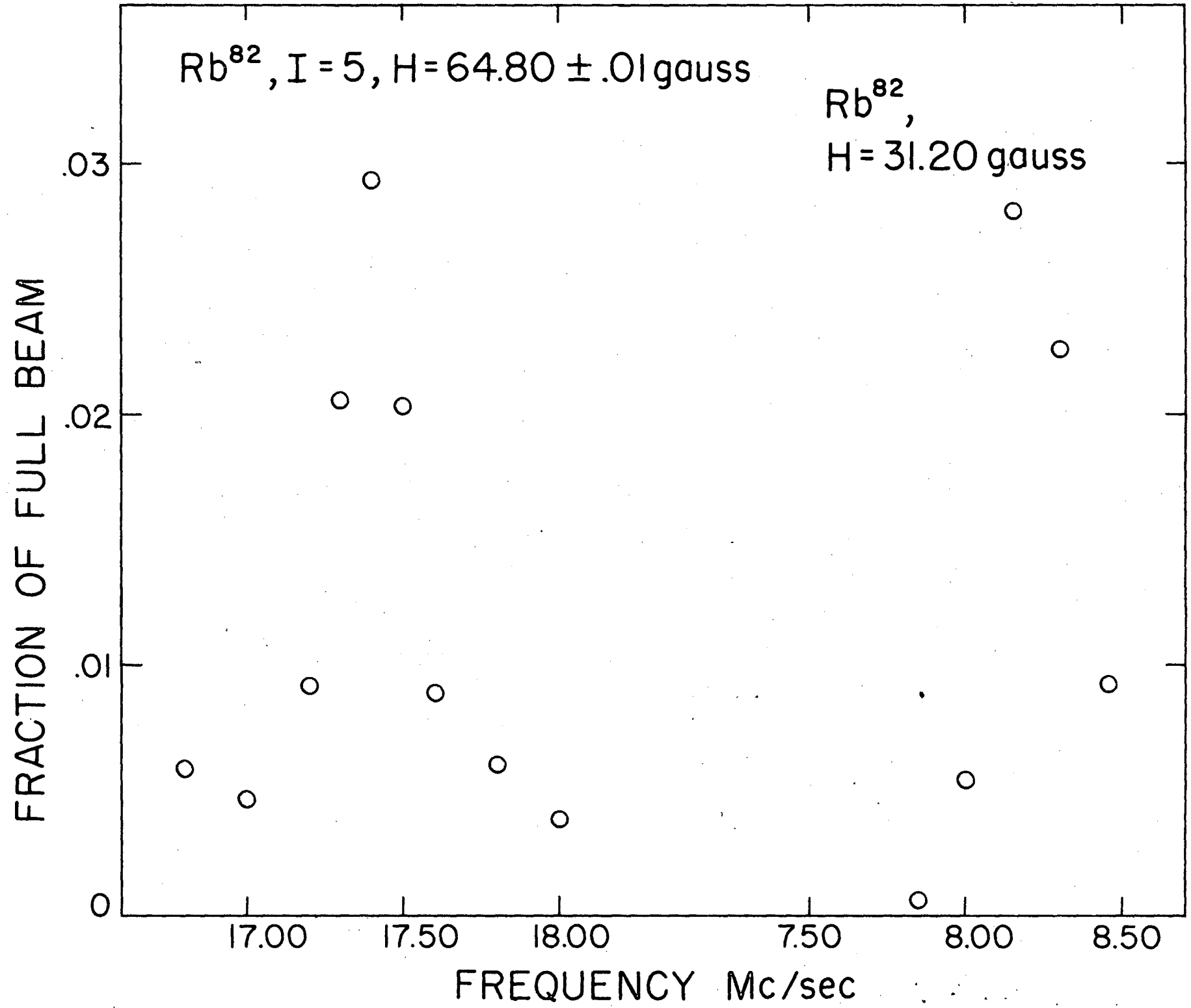
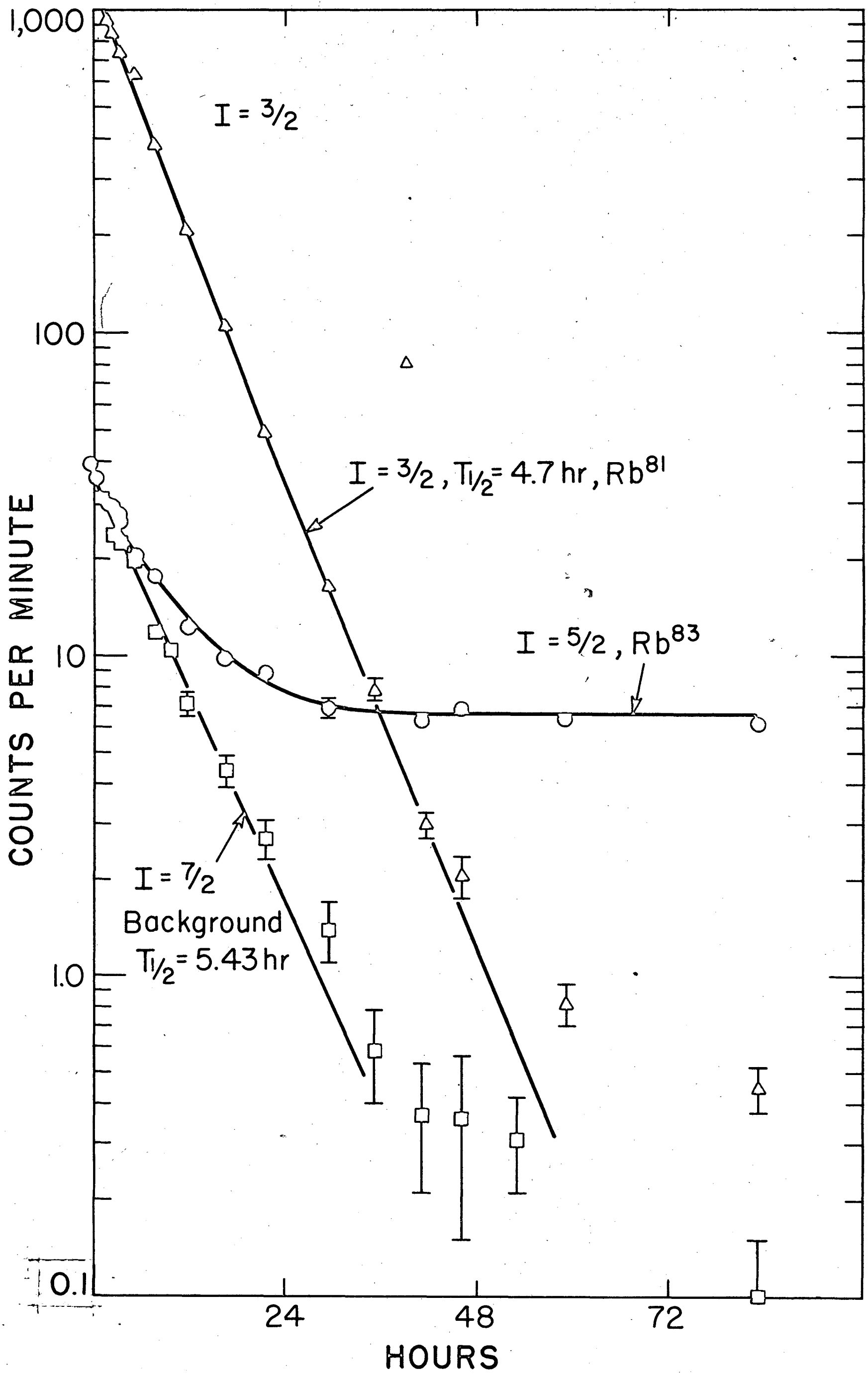

Rb^{82}, I = 5, H = 64.80 ± .01 gauss
Rb^{82},
H = 31.20 gauss
FRACTION OF FULL BEAM
.03
.02
.01
0
17.00
17.50
18.00
7.50
8.00
8.50
FREQUENCY Mc/sec

Fig 6

Fig 7


1,000
100
10
1.0
0.1
COUNTS PER MINUTE
I = 3/2
I = 3/2 , T1/2 = 4.7 hr , Rb81
I = 5/2 , Rb83
I = 7/2
Background
T1/2 = 5.43 hr
24
48
72
HOURS

24494-2

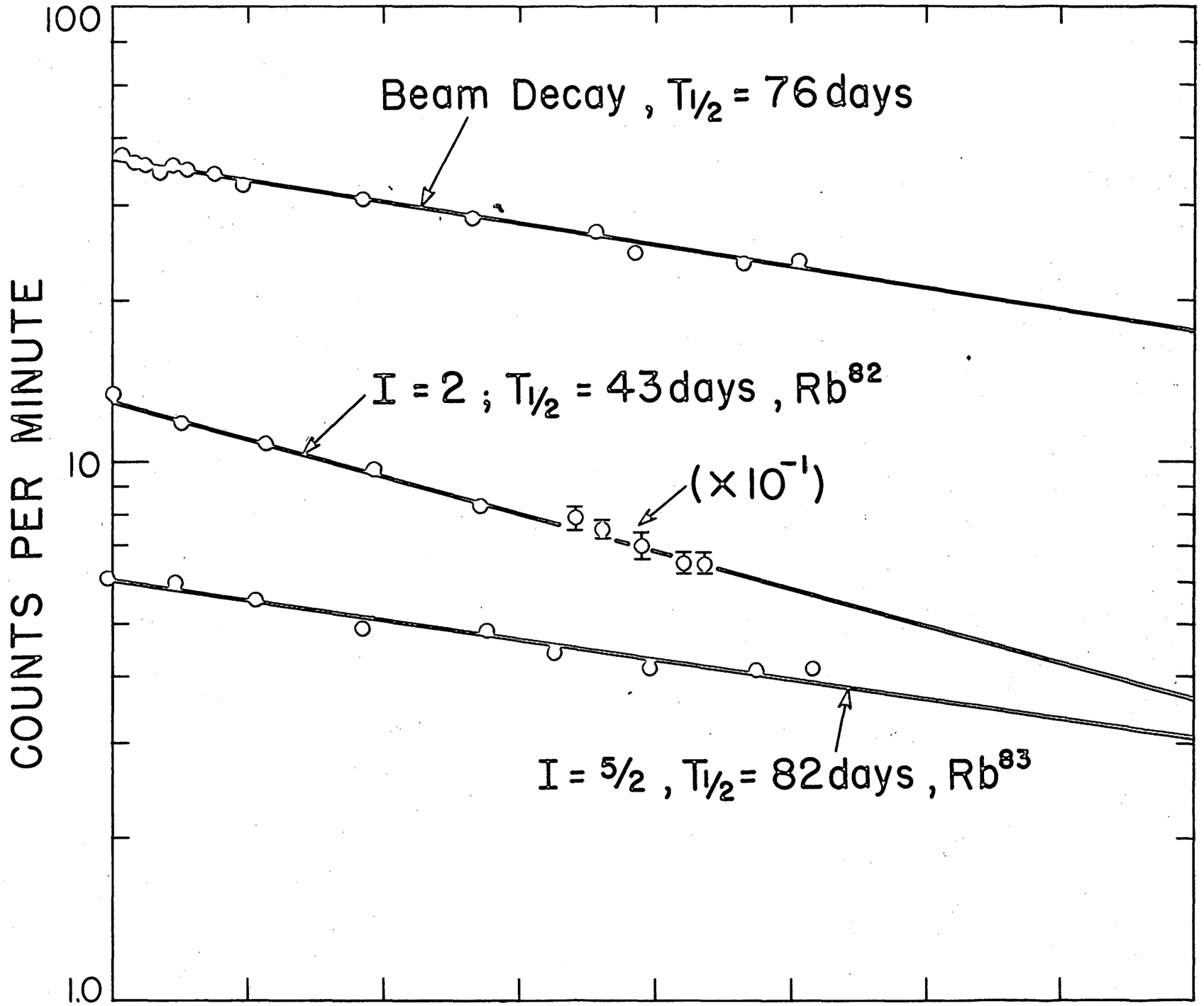


Fig 8.

Fig 8

24497-2

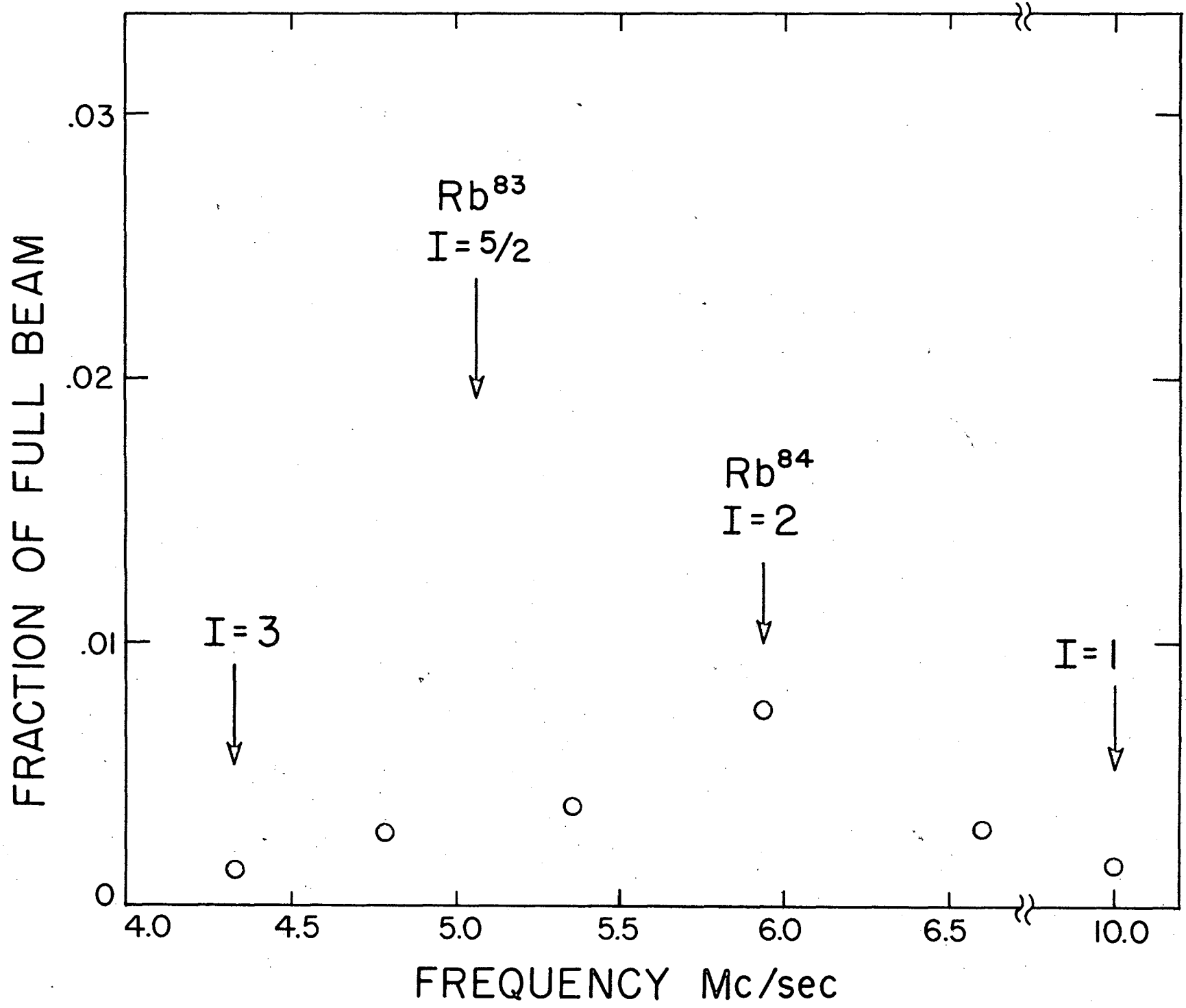

FRACTION OF FULL BEAM
.03
.02
.01
0
Rb83
I = 5/2
Rb84
I = 2
I = 3
I = 1
4.0
4.5
5.0
5.5
6.0
6.5
10.0
FREQUENCY Mc/sec

Fig 8

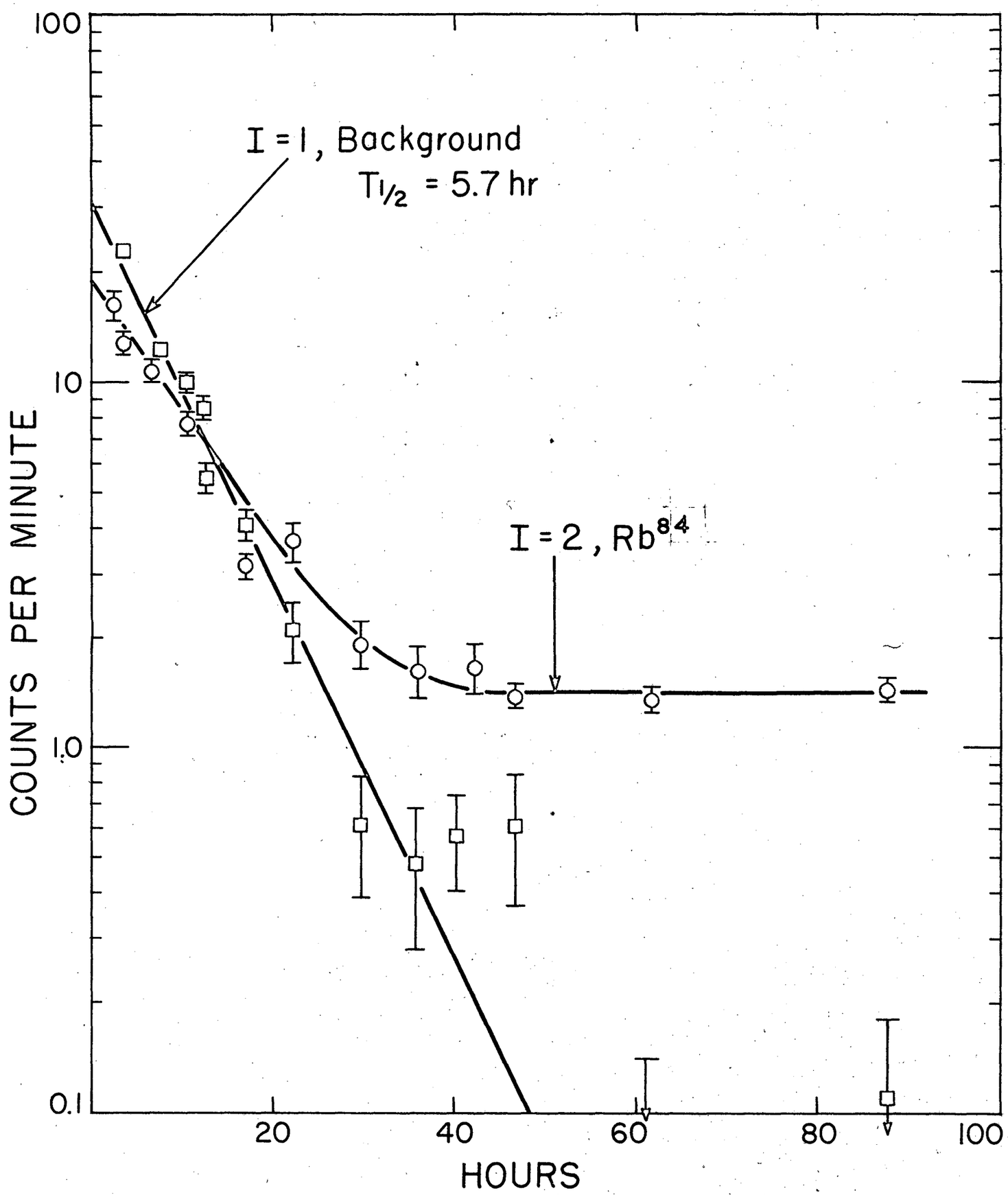


Fig 1C

24495-2