SGAE BER.No. 2614 CH-189/76 JUNI 1976

Berichte der
Österreichischen Studiengesellschaft
für Atomenergie Ges. m. b. H.
Forschungszentrum Seibersdorf

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Zur Veröffentlichung vorgesehen in Nuclear Technology

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Abstract

A survey of data relevant to the assessment of amoeba failure parameters is presented. The data which can be extracted from the various sources were used to derive amoeba endurance parameters which were also compared to ones from other sources. The governing mechanism is discussed.

1. Introduction

One of the phenomena occurring in coated particle fuel consists of an unidirectional movement of the fuel kernel into the coating which eventually may result in complete destruction of the latter. During this process the main fission product retaining barrier is progressively damaged and ultimately destroyed. Due to its apparence in a number of cases this phenomenon was called "amoeba effect". It is encountered in oxide and carbide as well as uranium, thorium or plutonium fuel. This work is mainly concentrated on the phenomenon in UO_2 fuel.

Already some time ago attempts were made to assess the amoeba effect empirically which resulted in a statistical evaluation methode (ref 1). Later it was recognized that not only the fraction of particles exhibiting amoeba effect was significant but also the direction and extent of the average amoeba in a particular position. The direction of amoeba attack was found to be determined by the temperature gradient (ref 2). This has been generally accepted since. There also exists much agreement on the empirical dependence of the extent on the various parameters like time, temperature, gradient and rating. But there still is much discussion on the mechanism creating amoebas in UO_2 fuel.

2. Data and Evaluation

2.1. Studsvik 18

This irradiation experiment contained UO_2 coated particle fuel in monolayer coupons of graphite. The irradiation conditions are given in ref 3. A detailed report on the data and their evaluation is given in ref 2. Metallurgical sections of the particles were prepared and the amount of amoeba displacement was measured, both axially and radially with reference to the zylindrical irradiation geometry. The gradients were taken to be represented by the external gradients created by the heat flux in the graphite bodies. The resulting data is summarized in table 1:

Table 1: Amoeba Displacements in Studsvik 18

No. of Particles Evaluated	Average Temperature (°C)	Time (d)	Temperature Gradient (°C/cm)	Average Displacement (μm)
2	1420	32	179	3.5
25	1480	96	275	10.5
19	1490	64	325	13.0
29	1550	96	110	10.1

A comparative study of this data suggested a linear dependance of displacement on time and gradient.

2.2. Dragon Charge III Centre Rods

This irradiation experiment contained UO_2 coated fuel particles in boxes. The particles were bonded together with a resin binder only. The whole experiment contained some 10^5 particles of which 10^3 were examined metallogrphically. Especially due to the very high statistical significance and the long irradiation time this experiment was selected for amoeba evaluation. The data obtained are summarized in table 2. A more detailed report is given in ref 2.

Table 2: Amoeba Displacements in Charge III C.R.

No. of Particles Evaluated	Average Temperature (°C)	Time (d)	Temperature Gradient (°C/cm)	Average Displacement (μm)
125	1184	763	110	13.7
147	1327	763	110	30.7

2.3. High Temperature Matrix Test Elements

This experiment was basically a matrix (graphite) experiment to study matrix behaviour at high temperature. It was found though that this experiment provided the first significant evidence on amoeba in anular matrixcompacted fuel-compacts. A more detailed description on its evaluation can be found in ref 4, the resultant data is contained in table 3.

Table 3: Amoeba Displacement in H.T.M.T. Elements

No. of Particles Evaluated	Average Temperature (°C)	Time (d)	Temperature Gradient (°C/cm)	Average Displacement (um)
21	1440	141	85	10
30	1540	141	90	14
66	1640	141	90	11
34	1730	141	90	18

2.4. HFR 900

This low temperature irradiation experiment examined an area which is very critical for HTGR fuel performance since most of the fuel in such a reactor will be at low temperatures. The coated particles were irradiated loose in single holes in the high flux reactor at Petten. A statistical approach which is given in ref 5 yielded the measured displacements in table 4. The gradients in this table were obtained by a two-dimensional temperature calculation by use of a quasi-finite-difference approach (ref 6). This was done to take account of the very large assymetric kernel-coating gaps encountered.

Table 4: Amoeba Displacements in HFR 900 (Type C)

No. of Particles Evaluated	Average Temperature (°C)	Time (d)	Temperature Gradient (°C/cm)	Average Displacement (um)
30	950	315	1650	48
30	950	315	1650	46

2.5. ORNL Data

ORNL reformed a specific experiment to elucidate the nature of the amoeba phenomenon and its mechanism to some extent. This experiment, H-1, was an irradiation of pitch injected fuel rods. Pitch injection together with the subsequent curing creates a rather irregular matrix resulting in a temperature and gradient distribution with large scatter. This explaines somewhat the relatively large scatter in amoeba migration distances found during P.I.E. of this experiment.(ref 7) If one places all measurements into four groups according to their temperature-gradient combination one can obtain the following data (table 5):

Table 5: Amoeba Displacements in H-1-2

Average Temperature (^{o}C)	Time (d)	Temperature Gradient (^{o}C/cm)	Average Displacement (um)
1240	97.1	180	2
1110	97.1	715	15
1000	97.1	950	9
890	97.1	1150	5

2.6. Other Data

Beside the data quoted above KFA and Belgonucleaire obtained some data in the respective experiments BR2-P15 and MOPS C01. In both these experiments the particles were matrixcompacted into a rod (refs 8 and 9). For a very similar geometry an anulus of matrix compacted fuel data was obtained during evaluation of the LET-2 experiment at the Dragon Project. All these data are given in appendix 1 together with a mathematical description of the amoeba migration.

3. Mechanisms

Three different mechanisms of mass transport across or around the oxide kernel appear feasable:

(i) solid state diffusion of a species such as carbon through the kernel.

(ii) gaseous diffusion of carbon as CO around the kernel.

(iii) gaseous diffusion of some other carbon compound.

The second and third type of carbon transport require some counter-transport mechanism. For the carbon transport by CO the oxygen has to be transported somehow up the temperature gradient to complete a cyclic transport path. This could be in the form of CO_2 by gaseous diffusion around the kernel or in the form of O^{2-} by solid state diffusion of the oxygen-ions through the kernel.

Type (i) of transport seems rather unlikely at least as long as oxide fuel is considered, but several possibilities which fall under type (iii) have been considered in the past. Especially the role of hydrogen has been investigated by various workers.

If one therefore selects transport type (ii) as the most feasable mode one can draw a schematic diagram of a number of possibly contributing transport and reaction steps which is given in fig. 1. By a suitable combination of such steps several cyclic processes can tentatively be designed. The rate of amoeba attack is governed by the slowest process in every such cycle. Depending on fuel type, irradiation conditions and the appreciability of the proposed mechanisms the following rate limiting processes were identified:

(i) gaseous diffusion of CO_2.
(ii) solid state diffusion of oxygen.
(iii) reaction rate of CO decomposition in the adsorbed state.

Steps (i) and (ii) operate in parallel or coupled, which means that the faster of them will be rate limiting. Step (iii) can operate in series with (i+ii) and could be rate limiting when the faster of (i+ii) is also faster than step (iii).

All three processes imply however that at very low free oxygen levels the amoeba attack will be suppressed due to the lack of CO as carrier for carbon (oxygen gettering !).

3.1. Gaseous Diffusion of CO_2

A well known hypothesis is the gas phase diffusion rate limited Boudouard mechanism, where carbon is transported as CO in one direction and oxygen in the opposing direction as CO_2 (process (i)). The driving forces for

diffusion are the different partial pressures of CO and CO_2, the equilibrium pressures resp. their potentials are different at the hot and cold end. A detailed description is given in ref. 10. The difficulty of this hypothesis is the necessity of assuming very low tortuosity factors for the diffusion path if one wants to match the experimental rates with the theory. This appears unrealistic especially for cases where a large kernel/coating gap exists.

This mechanism results in an amoeba dependence on the square of time. Nevertheless it is possible to calculate mean KMC (cf. app. 1) values for a given time interval for comparative reasons. Assuming an adjusted labyrinth factor for the inpore diffusion of 10^{-2}, a satisfactory agreement between observed and calculated particle behaviour can be achieved, at least for some irradiation experiments.

3.2. Solid State Diffusion of Oxygen.

Another hypothesis is the solid state oxygen diffusion mechanism which consists of oxygen transport through the UO_2 by thermodiffusion and carbon transport by CO diffusion in the opposite direction. Such a mechanism is proposed in refs. 2, 7, 11. The theoretically derived equation for such a mechanism is:

$$\frac{dy}{dt} = \frac{\Omega_c \, n_o \, Q^*}{R \, T^2} \, \text{grad } T \left[D_o \exp \left(- \frac{\Delta H}{RT} \right) \right] \qquad (1)$$

which is closely related to the one given by T. Gulden (ref. 12) for carbide amoeba migration. If one inspects equation (1) the constants in it can be expressed by:

$$K = \frac{\Omega_c \, n_o \, D_o \, Q^*}{R} \qquad (2)$$

The difficulty for a theoretical evaluation of K lies in the fact that in oxide coated particle fuel n_o and Q are not determinable with sufficient accuracy. Experimental results only permit evaluation of the

product $n_o \cdot Q$. Experimental evidence indicates that is fairly constant during irradiation. For proof of this hypothesis though it would be necessary to determine these two quantities and compare their product to the values found by amoeba rate determinations.

3.3. Reaction Rate Limited Transport (ref. 13)

The basic assumption of this mechanism is: Carbon is transported in the form of CO, the rate limiting step being the reaction between absorbed CO molecules to form CO_2 on the cold side of the particle. The main conclusions are demonstrated in Fig. 2. The experimental results from an out of pile experiment would lead to severe discrepancies in amoeba attack rate and its temperature dependence if one applied them in a gas phase diffusion limited theory to a coated particle. The model predicts that the CO pressure in a particle in-pile is not in equilibrium with the CO_2 pressure, but a steady state pressure is determined by the difference of the reaction rate terms on the hot and the cold side of the particle. The main feature is the increase of the reaction rate with increasing CO pressure up until the CO adsorption results in nearly complete coverage from where there seems to be very little dependence on CO pressure. This feature results in a mechanism which gradually switches over from gasphase diffusion characteristics to a solid state characteristic as irradiation proceeds.

The basic equation can be simplified for the range in which the coated particle CO pressures generally lie:

$$x = k \; T \; t \left(1 - \sqrt{p/\bar{p}} \right) \qquad (3)$$

The temperature dependence is given in fig. 2 by the 100 atm line and corresponds to 20 kcal/mole.

3.4. Coupled Transport

This hypothesis is based specifically on very precise experimental results on some UKAEA fuel (ref. 14). In this experiment a temperature dependence of the amoeba attack rate was found which passes through

a maximum at about $1100^{0}C$. This points to the conclusion that there are two opposing transport phenomena. One of them is assumed to be the gaseous diffusion of CO_2 the other the solid state diffusion of oxygen ions. Both these use CO as a carbontransporting species. These two oxygen diffusion paths constitute a coupled system in which the direction of the solid state diffusion can reverse at high CO pressures. This way the whole system would pass through a maximum with rising temperature and/or CO pressure.

For a certain pressure, temperature combination the equations can yield a formalism very similar to a solid state diffusion mechanism alone.

4. A Special Evaluation Technique

T. B. Lindemer (ref. 7) proposed a ratio method by which a distinction between all these mechanisms should be possible. If a metalurgical section perpendicular the axis of a fuel rod is inspected then due to the different mathematical laws applicable the amoeba displacement of the individual particles is a different function of the radial position for the different mechanisms mentioned above. By comparison of the experimentally determined function with the theoretical ones it should be possible to identify the actual mechanism. The advantage of this approach lies in the elimination of uncertainties in temperature and gradient between the particles. The type of relations obtained are shown for four different experiments in figs. 3 - 6. As one can see most of the data tend to support a solid state diffusion type of mechanism, but due to scatter and uncertainties in temperatures and gradients it cannot be considered final evidence.

5. Conclusion

The amoeba attack in UO_2 coated particle fuel is in a stage where a complete design figure set is available. It can be demonstrated that a properly designed steam raising HTGR does not suffer from particular restrictions by the amoeba phenomenon.

The theoretical explanation also seems to consolidate and if some more specific experimental material will become available it will be possible to construct a theory on the amoeba attack. The necessity of this appears to be mostly academic now but it may be very desirable for the development and construction of an advanced HTGR with very high operating temperatures.

6. List of Symbols

D_o ..... Frequency factor of oxygen self diffusion coefficient in UO_2 ($cm^2\ s^{-1}$)

ΔH ..... Enthalpy of activation for oxygen self diffusion in UO_2 ($kcal\ mole^{-1}$)

k,K ..... Proportionality constant

KMC ..... Kernel Migration Constant ($cm^2\ s^{-1}\ K$)

n_o ..... Oxygen concentration ($mole\ cm^{-3}$)

p ..... CO pressure (atm)

Q ..... Activation energy of amoeba ($kcal\ mole^{-1}$)

Q^* ..... Heat of transport for oxygen in UO_2 ($kcal\ mole^{-1}$)

R ..... Universal gas constant ($cal\ K^{-1}\ mole^{-1}$)

T ..... Absolute temperature

grad T .... Temperature gradient ($K\ cm^{-1}$)

t ..... Time (s)

x ..... rate of amoeba attack ($cm\ s^{-1}$)

y ..... migrations distance (cm)

Ω_c ..... molar volume of pyrocarbon (6 - 10 $cm^3\ mole^{-1}$)

7. References

(1) E. Formann, "A Statistical Approach to Coated Particle Endurance", DPTN/82.

(2) M. Wagner-Löffler, "A Re-Evaluation of the Amoeba Behaviour of UO_2 Coated Particle Fuel", D.P. Report 861.

(3) P. Svensson, "Dragon Charge 18, Report on Irradiation Conditions and Fission Product Release Measurements", D.P. Report 834.

(4) M. Wagner-Löffler, "Amoeba in Oxide Coated Particle Fuel" DPTN/567

(5) M. Wagner-Löffler, "Chemical Particle Endurance of HTGR Coated Particle Fuel", DPTN/742

(6) M. Wagner-Löffler and H. Nablelek, "Temperature Fine Structure in Coated Particles", DPTN/764

(7) T. B. Lindemer and H. J. DeNordwall, "An Analysis of Chemical Failure of Coated UO_2 and other Oxide Fuels in the HTGR", O.R.N.L. 4926.

(8) A. Naoumidis, R. Rotterdam and B. Thiele, "Thermische Belastungsgrenzen oxidischer Brennstofftellchen", Reactor Meeting 1975 of the Deutsches Atomforum pp 374 - 377.

(9) J. Thomson and M. Gaube, "Study of the Chemical Failure of UO_2 Low Enriched Particles", DPTN/in print.

(10) R. Rotterdam, "Influence of the CO Partial Pressure on the Performance of Low Enriched UO_2 Coated Particle Fuel", D.P. Report 742.

(11) L. W. Graham and H. Hick, Appendix to "Performance Limits of Coated Particle Fuel", BNES Conf. Nucl. Fuel Perf., London October 1973.

(12) T. D. Gulden, "Carbon Thermal Diffusion in the UC_2 - C System", J. Amer. Ceram. Soc. 55,(1972) 14 - 18.

(13) E. Glückauf, "Quantitative Discussions of the Amoeba Effect on the Basis of the Catalysed Boudouard Reaction", AERE-R 7829.

(14) G. W. Horsley, Private Communication.

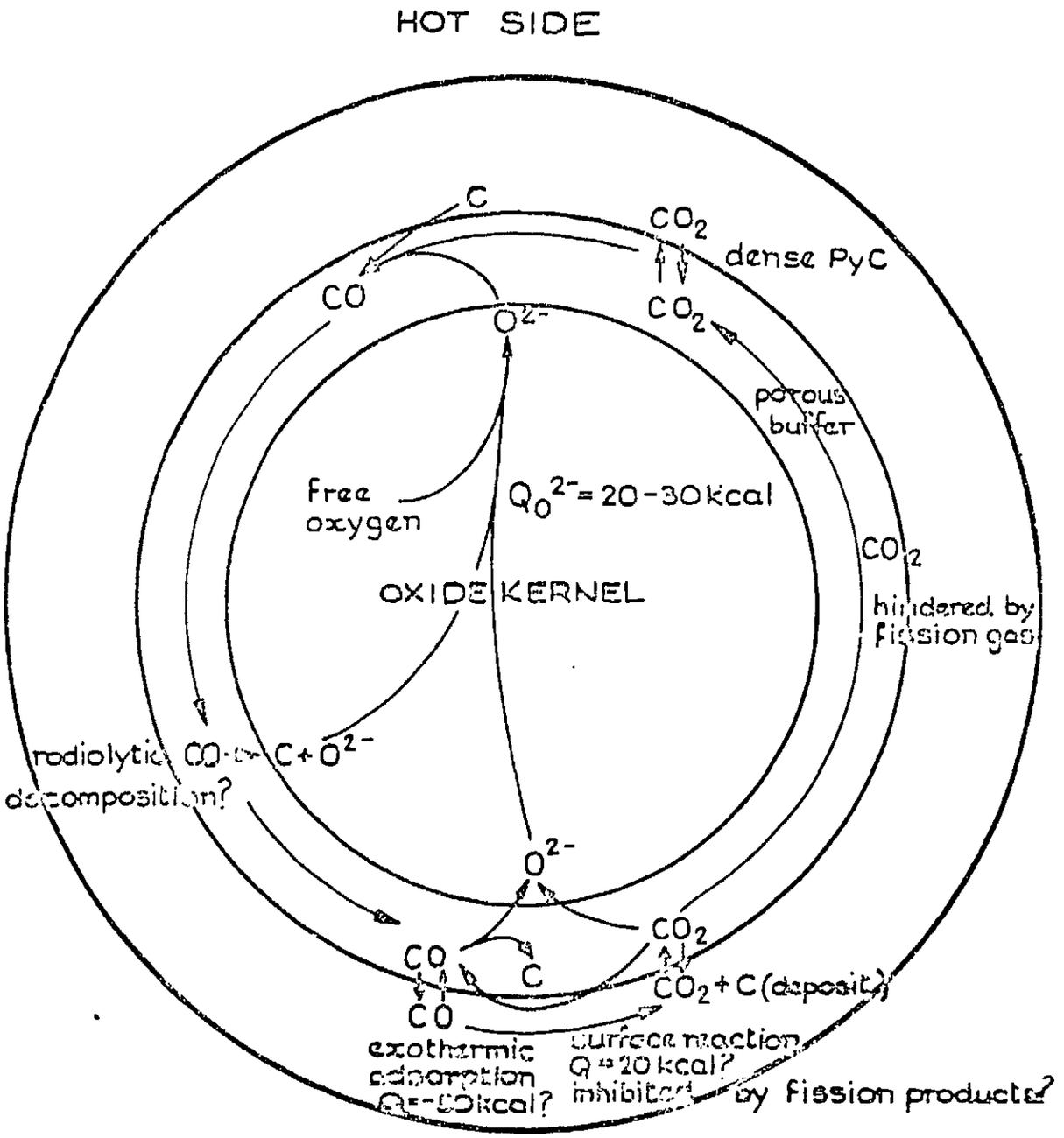

FIG 1 REACTION & DIFFUSION STEPS INVOLVED IN AMOEBA MIGRATION

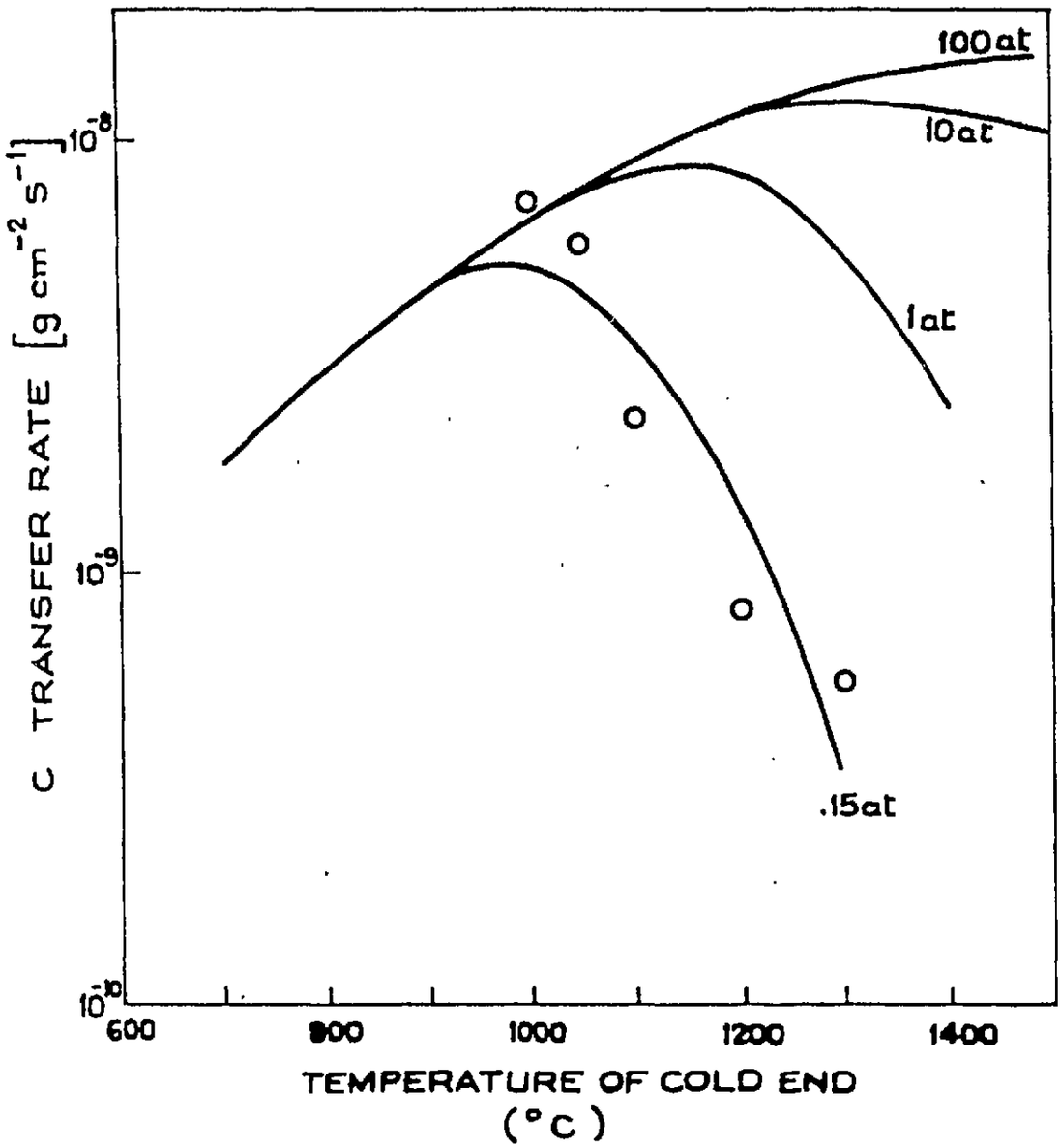

FIG. 2: OBSERVED AND CALCULATED REACTION RATES AT CONSTANT PRESSURES

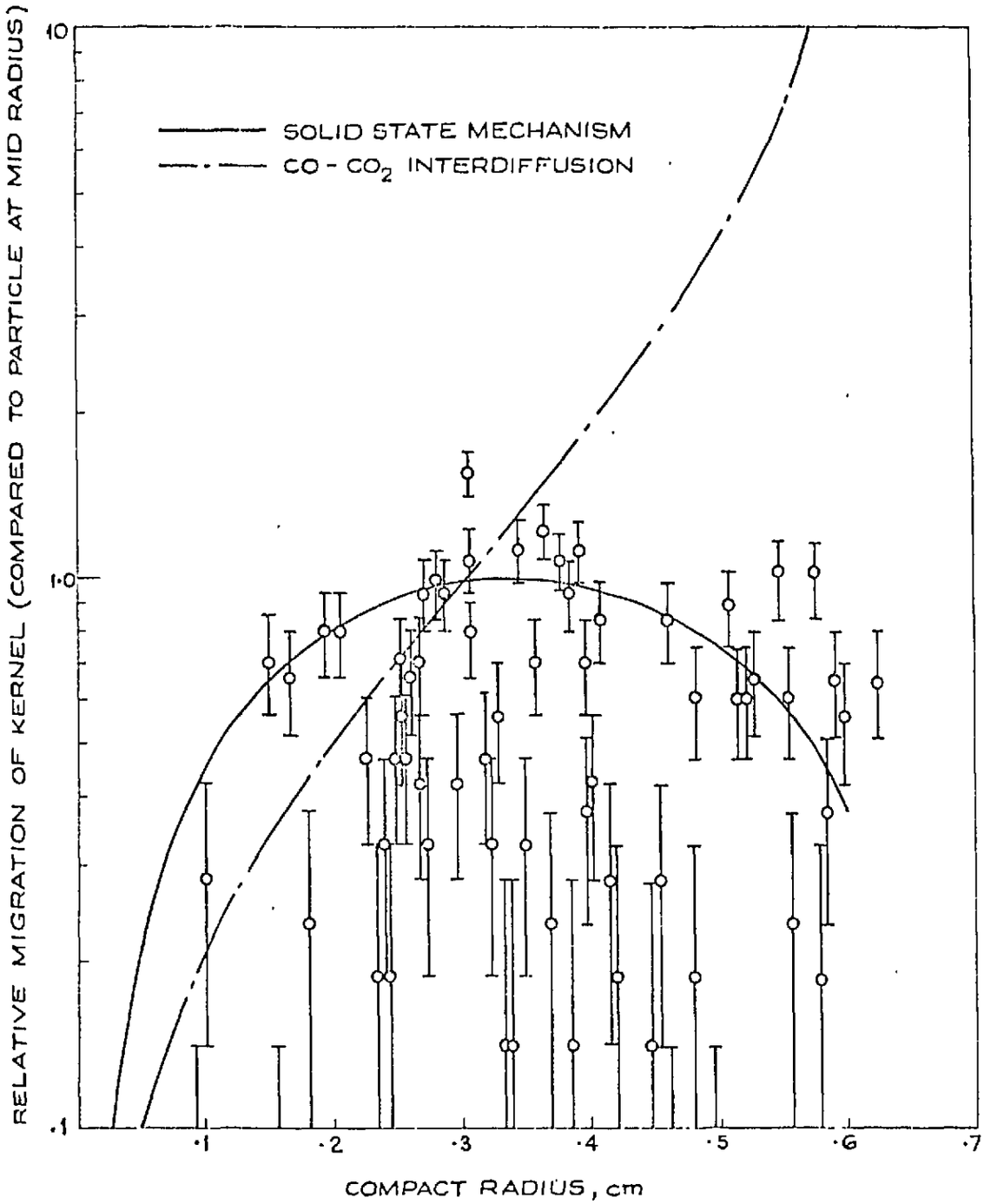

FIG.3. THEORETICAL AND MEASURED RELATIVE MIGRATION IN EXPERIMENT H-1-2

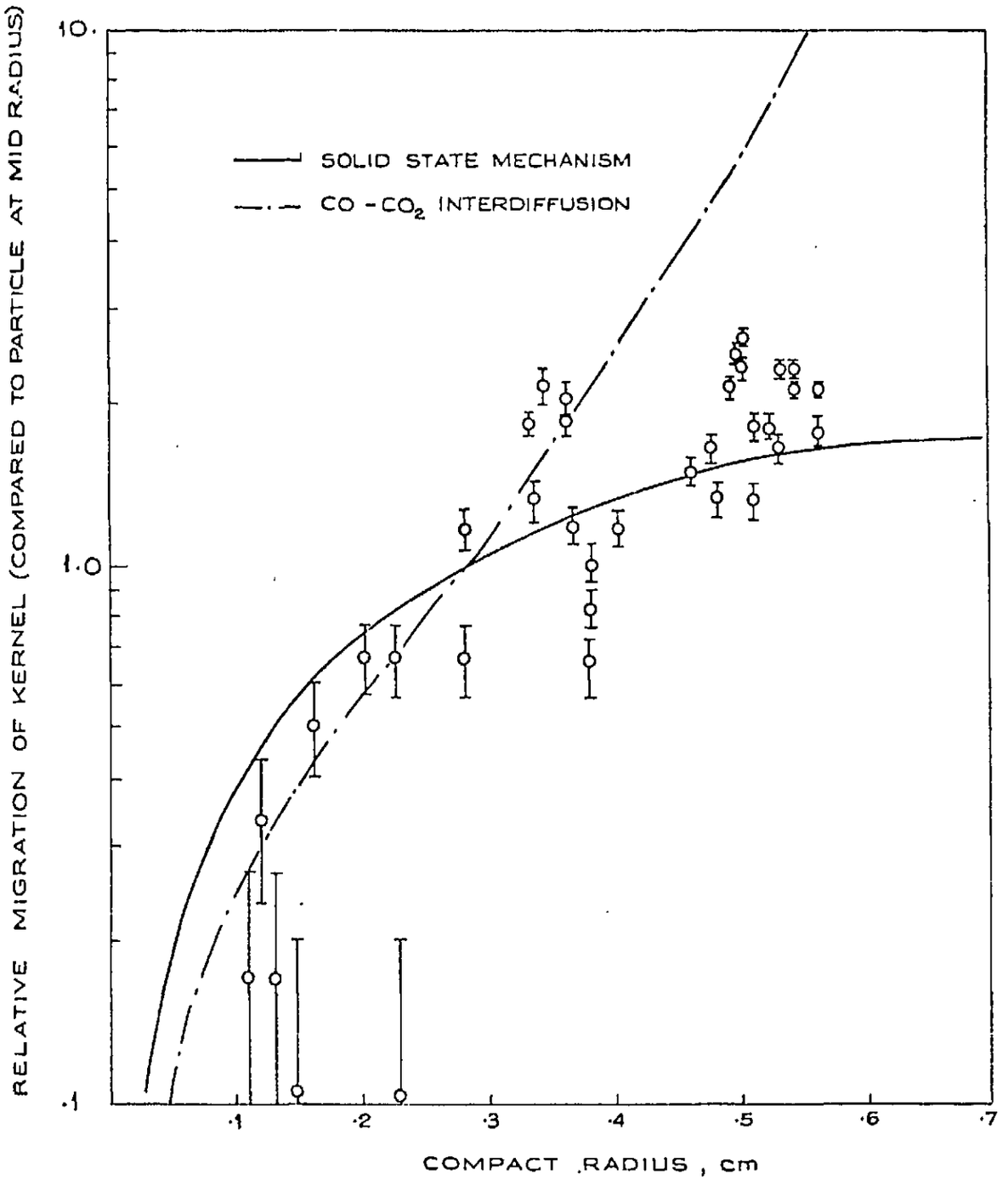

FIG. 4. THEORETICAL AND MEASURED RELATIVE MIGRATION IN EXPERIMENT BR 2 - P15

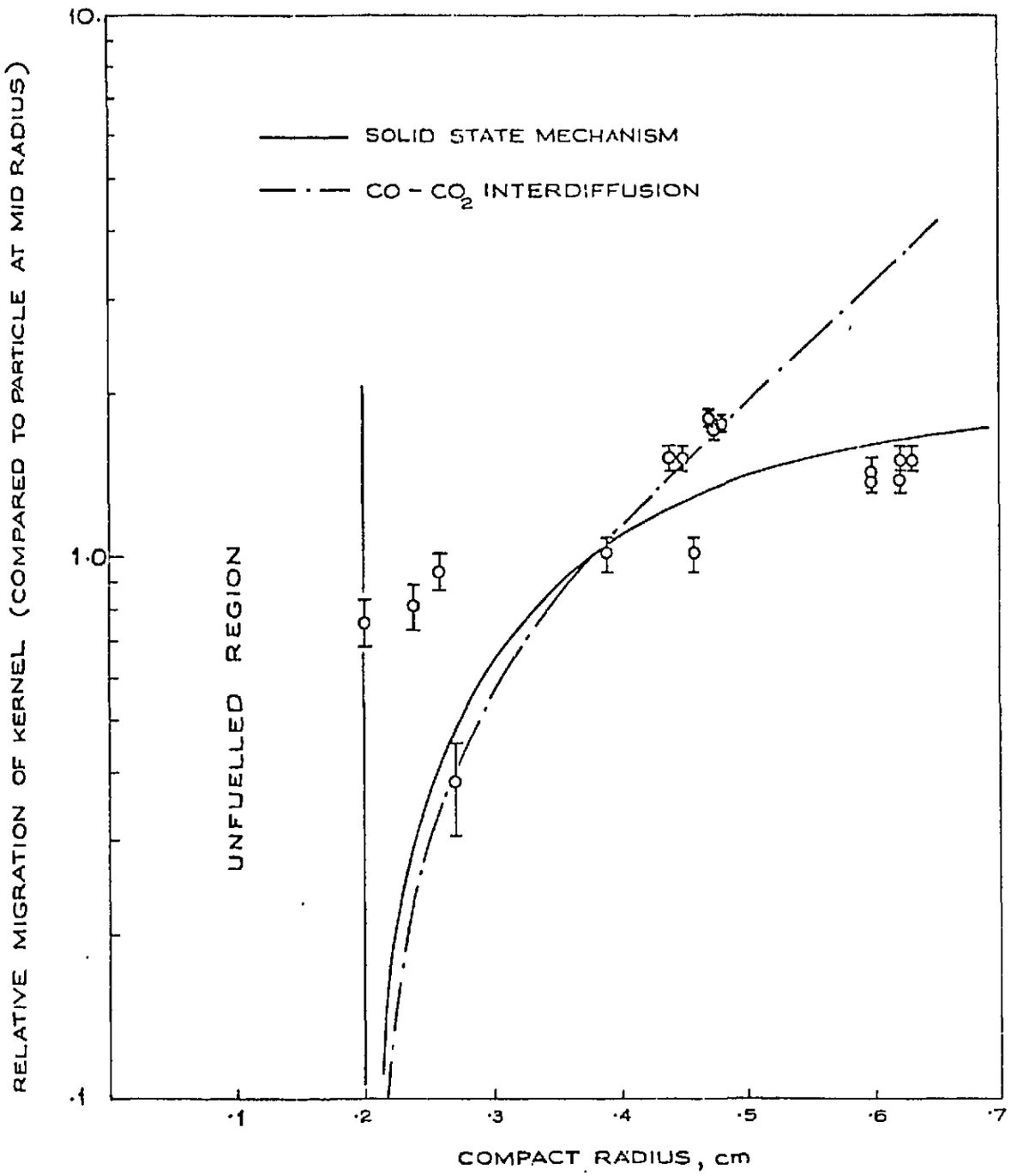

FIG. 5. THEORETICAL AND MEASURED RELATIVE MIGRATION IN EXPERIMENT MOPS CO1/VC 01

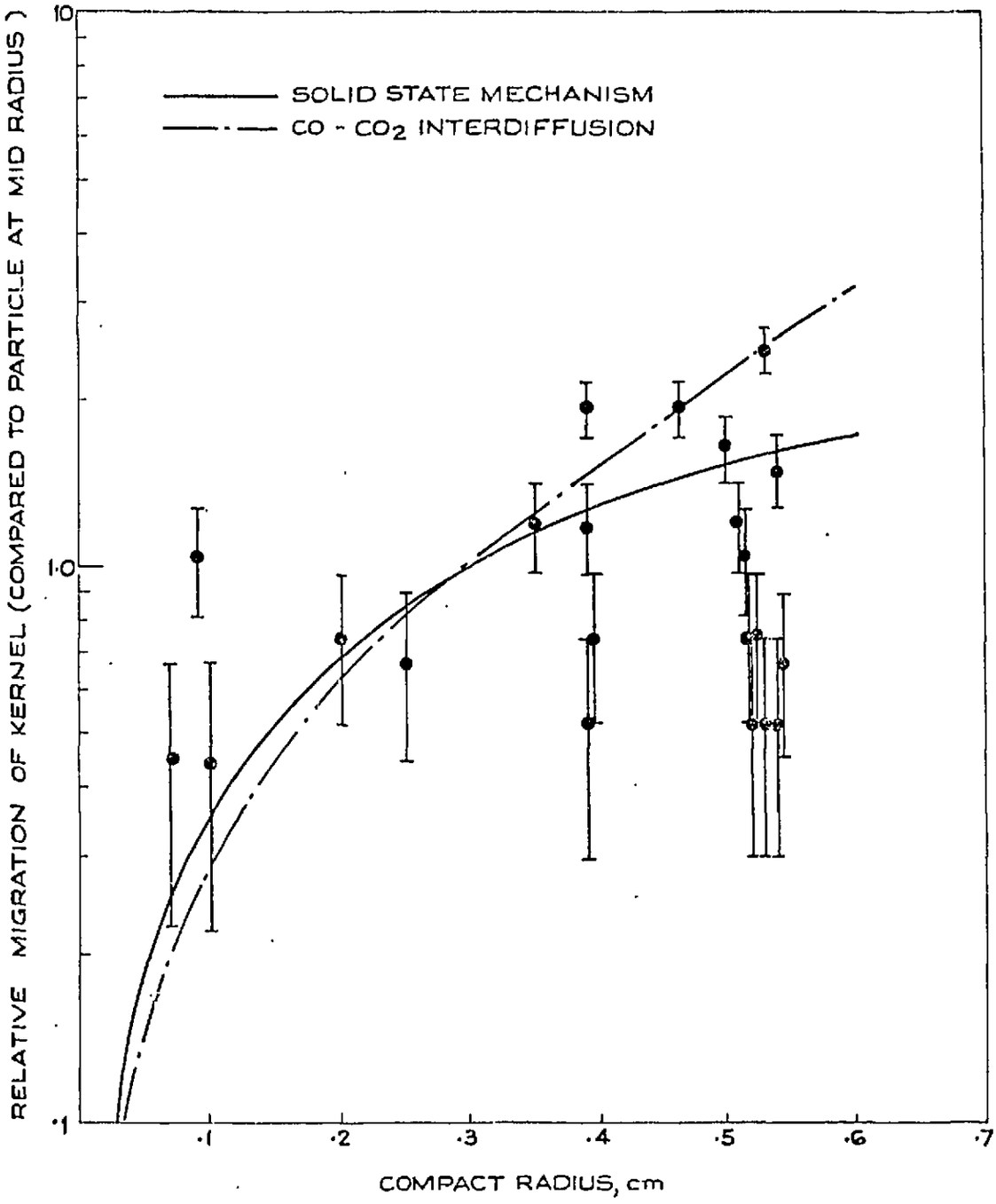

FIG.6: THEORETICAL AND MEASURED RELATIVE MIGRATION IN EXPERIMENT LET-2

Appendix 1

Mathematical Description of Amoeba Migration

For carbide fuels a cosistent explanation of the experimental results has been given by T. Gulden (ref 11) in terms of solid state carbon diffusion down the temperature gradient. The amount of carbon transported (or the amount of coating attack on the hot side of the particle) neglecting chemical potential gradients is given by solid state theory as:

$$y = K \cdot \frac{1}{T^2} \cdot \text{grad } T \cdot \exp(-Q/R.T) \cdot t \qquad (1)$$

with the symbols as they are given in the main text. This expression is rearranged to derive a KERNEL MIGRATION CONSTANT (KMC):

$$KMC = K \cdot \exp(-Q/R.T) = \left[\frac{T^2 \cdot y}{\text{grad } T \cdot t}\right]_{\text{experiment}} \qquad (2)$$

from experimental data. Plotted in an Arrhenius diagram it should yield a straight line, from which values of K and Q can be derived in usual ways.

For oxide fuel there is no real established single mechanism for the amoeba migration. For comparision and simplicity though th experimental results are usually described by the same mathemathical expressions (1) and (2). A comparison of such KMC data for UO_2 as derived indepently by several organisations is given in fig. 1. It illustrates that the important design data are largely in agreement.

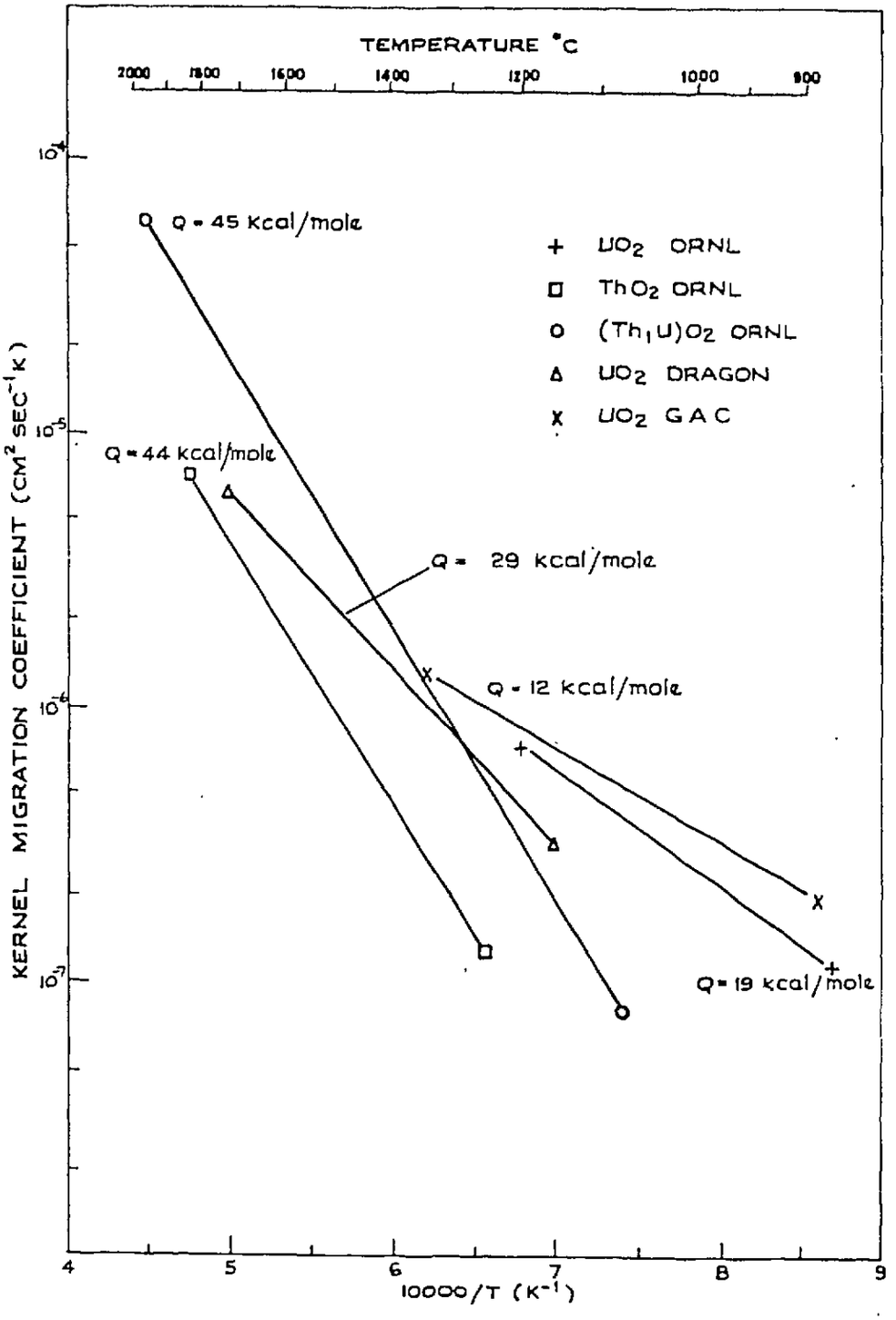

FIG. 1. KMC FOR VARIOUS MATERIALS FROM DIFFERENT SOURCES

Appendix 2

Collection of Data for Amoeba Parameter Fit

On the following pages the input data for a calculation of amoeba parameters by a least square fit are listed. They constitute a selected batch of raw data, some of the averages of which are given in the main text. The results of this particular fit were:

$$\ln K = -6.2603 \qquad \Delta H = 23 \text{ kcal mole}^{-1}$$

which are typical values. Fig 1 shows the quality of the fit by comparing recalculated and measured migration distances. Fig 2 shows the resulting endurance plot, this one with a ΔH of 28 kcal mole^{-1}.

Number	Experim.	Weight	Temperat. (°C)	Time (d)	Gradient (°C/cm)	Migration (μm)
1	Studsvik 18	4	1550	96	78	11
2		1	1525	96	191	14
3		2	1575	96	86	7
4		4	1550	96	205	25
5		2	1575	96	95	7
6		3	1550	96	230	16
7		2	1575	96	95	7
8		2	1550	96	230	16
9		4	1575	96	86	13
10		3	1550	96	205	18
11		1	1550	96	78	8
12		1	1525	96	191	15
13		2	1425	32	179	3
14		3	1600	64	116	12
15		12	1575	64	250	13
16		3	1500	64	125	5
17		7	1500	64	262	8
18		9	1475	64	331	17
19		5	1500	96	125	10
20		12	1500	96	262	17
21		8	1475	96	331	23
22	Ch. III	13	1184	763	110	13
23		15	1327	763	110	31
24	HTMT	2	1440	141	85	10
25		3	1540	141	90	14
26		7	1640	141	90	11
27		3	1730	141	90	18

Number	Experim.	Weight	Temperat. (°C)	Time (d)	Gradient (°C/cm)	Migration (um)
28		2	1300	70	765	40
29		2	1500	40	3130	67
30		2	1900	9	8944	190
31		2	1900	9	8944	172
32		2	1900	9	8944	210
33		2	1900	9	8904	152
34		2	1350	169	789	70
35		2	2000	27	1520	290
36		2	2000	27	1842	40
37		2	2000	27	1921	290
38		2	2000	27	3838	150
39	K. F. A.	2	1300	164	861	70
40		2	1300	100	1020	50
41		2	1300	100	688	50
42		2	1300	100	1726	100
43		2	1350	142	641	60
44		5	1225	358	114	7
45		3	1200	358	280	13
46		3	1175	358	380	27
47		5	1150	358	458	55
48		5	1125	358	525	29
49		1	1100	358	584	45
50		8	1075	358	638	60
51		6	1050	358	687	56
52		1	1025	358	733	60
53		1	1202	97	102	6
54		6	1177	97	312	11
55		11	1152	97	429	11
56		8	1127	97	520	18
57		8	1102	97	598	11
58		8	1077	97	667	13
59	O. R. N. L.	3	1052	97	729	9
60		4	1027	97	786	7
61		2	1002	97	839	9
62		4	977	97	890	11
63		2	952	97	937	18
64		4	927	97	982	10
65		4	902	97	1025	9
66		2	877	97	1067	11
67			1094	763	250	20
68			1130	763	290	50
69			1153	763	310	70
70			1149	763	340	40
71	A. E. R. E.		1109	763	330	25
72			1054	763	320	40
73			980	763	300	20
74			880	763	270	1
75			1200	769	153	15
76			1286	769	173	30
77			1287	769	193	40
78			1198	769	188	40

Number	Experim.	Weight	Temperat. (°C)	Time (d)	Gradient (°C/cm)	Migration (um)
79	A. E. R. E.		1128	769	175	20
80			1146	675	250	35
81			1169	675	290	55
82			1180	675	310	80
83			1166	675	320	55
84			1132	675	310	20
85			996	675	260	15
86			1168	757	95	10
87			1260	757	144	35
88			1289	757	157	35
89			1300	757	166	40
90			1285	757	167	30
91			1262	757	164	30
92			1205	757	155	35
93			1134	757	144	15
94			1060	757	128	1
95	HFR 900	10	950	315	1500	47

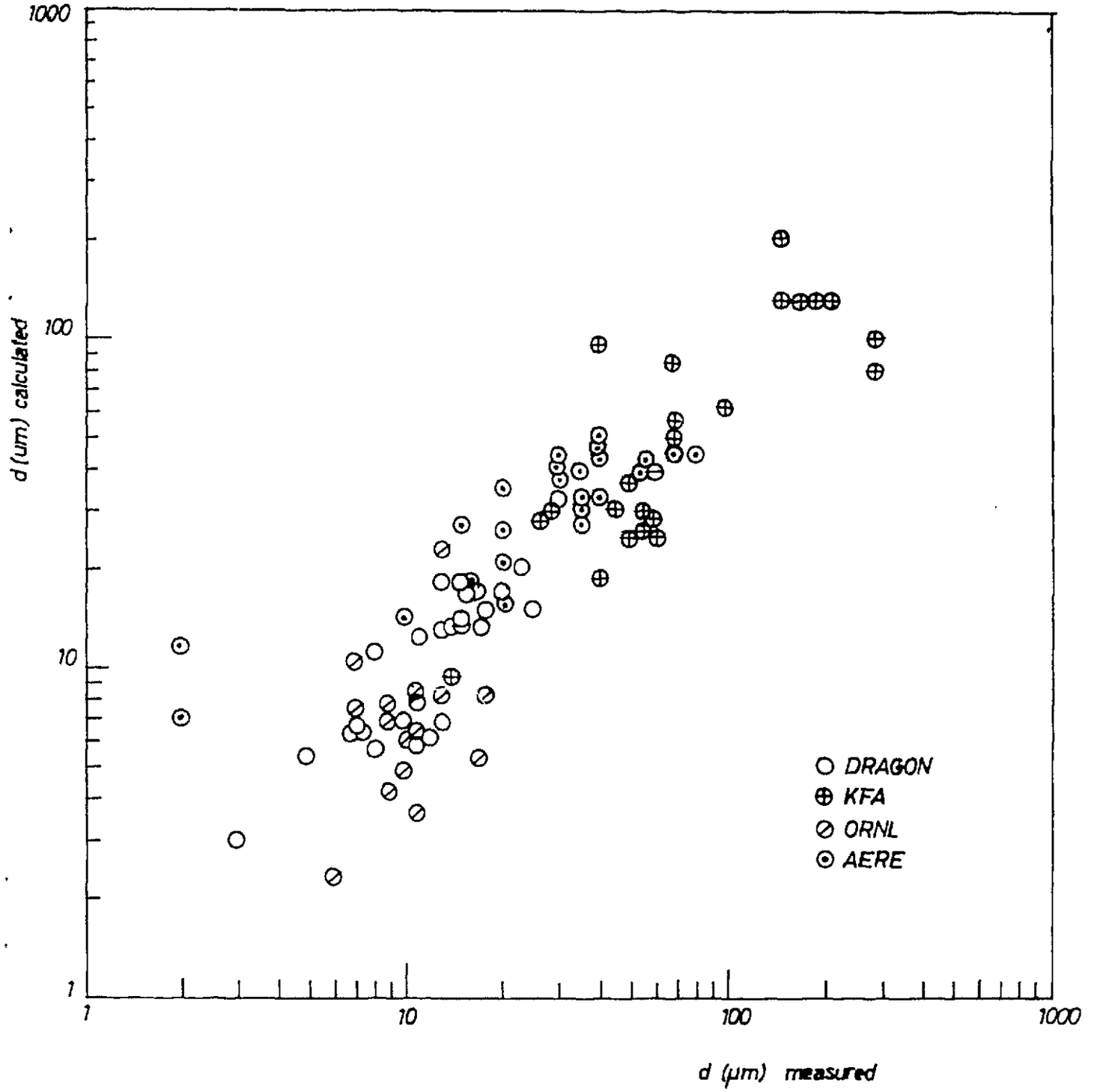

FIG.1: Quality of Amoeba Fit

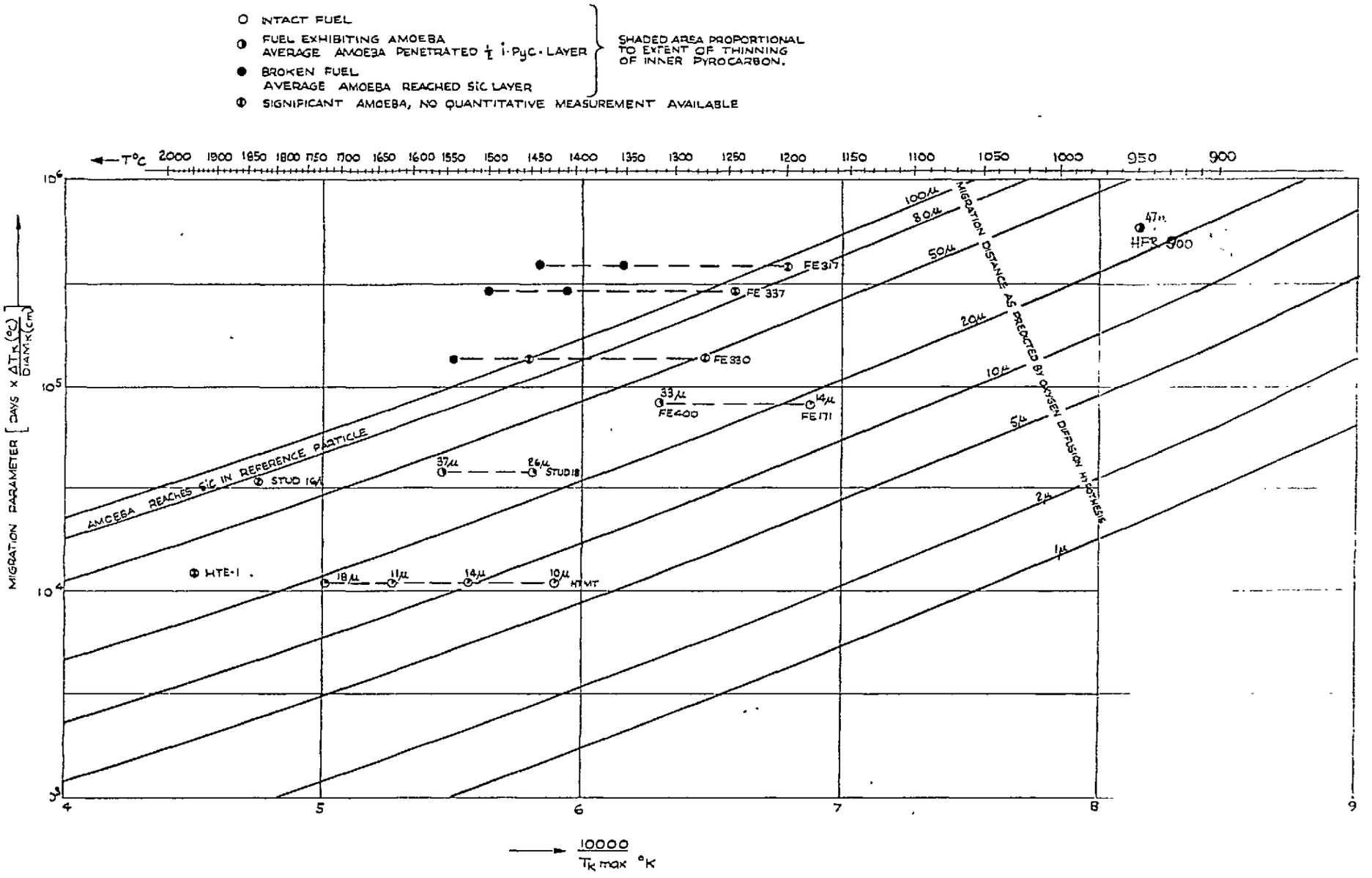

FIG. 2

AMOEBA ENDURANCE PLOT

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