

TRN127600592

NRCN-402



הועדה לאנרגיה אטומית, קריה למחקר גרעיני-נגב
ISRAEL ATOMIC ENERGY COMMISSION, NUCLEAR RESEARCH CENTRE - NEGEV

UPTAKE OF VAPORIZED MOLYBDENUM AND CESIUM TRACERS BY MOLTEN
OXIDE MIXTURES AS FUNCTION OF FREE OXYGEN ION ACTIVITY

B. Carmon

The experimental part of this work was carried out at the Dept. of Chemistry, Boston College, Chestnut Hill, Mass., USA, in cooperation with I.J. Russel. It was supported by the U.S.A.E.C. as part of the project "Fundamental Studies of Fallout Formation Processes" Contract No. AT(30-1)-3756.

Abstract

Molten mixtures of oxides containing Ca, Fe, Al, Na and Si were exposed to vaporized Mo-99 and Cs-137 tracers at 1100 and 1300°C. Uptake values at 1300°C were extrapolated to short heating times. The obtained "attachment coefficients" for that temperature are shown to have the relationship $(Mo) = (Cs)^{-1/2}$. The chemical composition of the melts and their oxygen to metal ratio found to affect the uptake of both tracers. This is associated with the cationic field strengths and the free oxygen ion activities in the mixtures. Molybdenum and cesium apparently behave like glass-network forming and glass-network modifying species, respectively.

November 1975



Uptake of Vaporized Molybdenum and Cesium Tracers by Molten Oxide Mixtures
as Function of Free Oxygen Ion Activity

INTRODUCTION

The relative uptake of several vaporized tracer species in various molten oxides was investigated [1]. The tracers were radiisotopes of Mo, Sn, Ru, Sb, Cs and Rb whose oxides and chlorides are known to vaporize rapidly in the 1100 to 1300 centigrade range. Calculations based on the Henry's Law Constant for these tracers over various molten silicates [2] yielded very low values for their respective equilibrium vapor pressures. Consequently, if the tracers are evaporated inside a sealed chamber that contains oxide melt mixtures, then at conditions near equilibrium most of the activity should be concentrated in these melts. Similar phenomenae probably occur during the formation of radio-active fallout. The present study investigates the importance of the chemical composition of the substrates as a major parameter affecting fission product fractionation [3]. The uptake behaviour of the molybdenum and cesium tracers described here are interpreted in terms of their "relative attachment coefficients" for certain substrate combinations. These coefficients were found to be related to the cationic field strengths and to the free oxygen ion activities in these substrates.

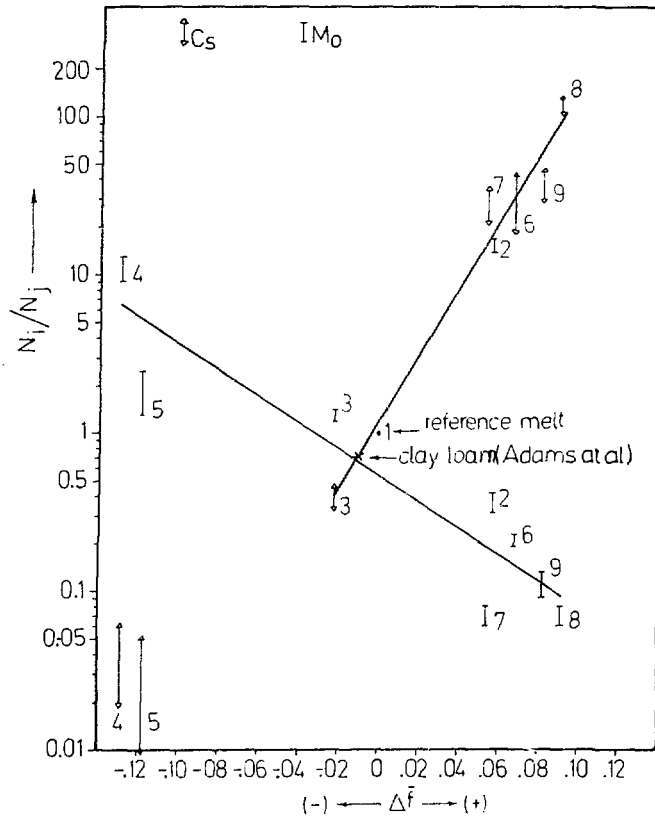


Fig.1: Uptake of Cs and Mo Values vs. field Strength for 2 hrs at 1300°C.

EXPERIMENTAL

Method

The experiments were conducted in sealed quartz chambers under an ambient pressure of one atmosphere of air at the operating temperature. The substrates, in the form of spherical beads of about 2.3 mm in diameter and weighing 20-30 mg each, were suspended from hooks inside the vessel on short platinum loops. They were prepared from stoichiometrically mixed oxides of Ca, Fe, Na, Al and Si, which are the most common elements in nature [4]. The composition of the substrates varied in each run. The carrier-free or high specific activity tracers were uniformly deposited on a quartz plate at the bottom of the chamber. The chambers were sealed and heated either for 2 or for 12 hours in a calibrated high-temperature furnace. The chambers were then cooled, opened and their content assayed by high resolution gamma-spectrometry on a 30 cm^3 Ge(Li) detector in fixed 2π geometry. Each component (melts, platinum loops, container) was measured separately.

The Radioactive Source

Mo-99 and its inactive carrier in the form of $(\text{NH}_4)_2\text{MoO}_4$, when vaporized, did not exceed 2.6×10^{-10} atoms per cm^3 for air. Under these conditions the monomer MoO_3 is the most prominent gaseous species at the experimental condition in this work [5,6]. The carrier free Cs-137 tracer however, was introduced in its chloride form which is known to be very stable even in the vapor phase [7]. The Cs tracer concentration used was about 10 orders of magnitude less than the oxygen concentration in the chamber. It is therefore, quite possible that most of the cesium converted to oxide before reacting with the

melts [6]. Both nuclides were assayed by measuring their gamma photopeaks at 140.5 (Tc-99 m) and 662 KeV respectively.

Theoretical Aspects

During the heating time, millimole amounts of the substrates reacted with less than 10^{-10} (gram) moles of tracer. Therefore first order kinetics were assumed to occur during the uptake. The absorption of tracer is proportional to the number of impacts ϕ per cm^2 of substrate, the attachment coefficient α in $\text{cm}^{-2} \text{min}^{-1}$ per molecule of tracer and the area s of the substrate. Similarly the release of the absorbed tracer is governed by the rate constant β which is however only approximately proportional to the atoms absorbed. The overall uptake factor k_1 and the overall release rate constant k_2 for the whole system, including the melt i , the reference melt j , the silica container and the platinum loop can be summarized as

$$k_1 = \phi_i (\alpha_i s_i + \alpha_j s_j + \alpha_{\text{Si}} s_{\text{Si}} + \alpha_{\text{Pt}} s_{\text{Pt}}) \quad (1a)$$

$$k_2 = \beta_i s_i + \beta_j s_j + \beta_{\text{Si}} s_{\text{Si}} + \beta_{\text{Pt}} s_{\text{Pt}} \quad (1b).$$

The term for platinum will be omitted henceforth as it did not contain any detectable Mo-99 or Cs-137 activities. The relation between the rate of disappearance of the tracer from the gas phase and its uptake by the melts is extensively treated elsewhere [1]. This includes also the relation between the measured relative uptake N_i/N_j and the relative attachment coefficient α_i/α_j . If the evaporation rate from the source and the uptake rate by the melt are short, compared to the release rate and the duration of the experiment

t, then the relative uptake is [1].

$$N_i/N_j = \frac{\alpha_i/\beta_i}{\alpha_j/\beta_j} \left\{ \frac{[(\beta_i s_i/k_2) - 1] \exp(-\beta_i s_i t) + 1}{[(\beta_j s_j/k_2) - 1] \exp(-\beta_j s_j t) + 1} \right\} \quad (2)$$

RESULTS

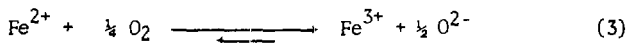
The attachment rate at the surface of the substrate is probably the most important process in these experiments. The N_i/N_j values for Mo-99 and Cs-137 are shown in tables I and II. The data for 1300°C are accurate to about $\pm 10\%$. At 1100°C much higher errors occurred ($\sim \pm 25\%$), due probably to phase separation below the melting points of the various substrates [8]. The uptake of Mo-99 was almost entirely in the melts. Cs-137 however was absorbed considerably also by the quartz chambers. This secondary reaction tends to increase with the decreasing SiO_2 content of the melts.

Table III presents the α_i/α_j data as calculated from eq. (2) using experimentally determined N_i/N_j values and release rate constants. These relative attachment coefficients follow the approximate relationship $(\alpha_i/\alpha_j)_{\text{Mo}} \approx (\alpha_i/\alpha_j)^{-1/2}_{\text{Cs}}$. Table III also shows the dependence of the release rates on substrate composition. The release rates for the melts were obtained by repeated reheating and assaying by gamma spectrometry. Quartz plates with a thin layer of an evaporated tracer solution were used to estimate β_{Si} . The plates were assayed on a low-background beta counter. All the release rate constants were estimated from nearly exponential curves which expressed residual activity vs. heating time. The release rate curves for silica were preceded by rapidly decreasing components which probably indicates the evaporation rate of the radioactive tracers.

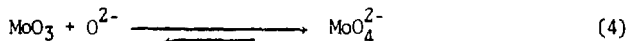
DISCUSSION

Relationship between uptake and melt composition

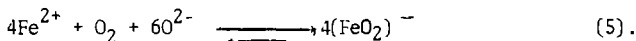
X-ray analysis showed most of our silicate melts to be glassy *amorphous* substances. The random network of such glasses does not contain any discrete oxide molecules [9,10,11,12] but is rather made up of large oxygen ions, small network-forming (such as Si^{4+} , Al^{3+} , Fe^{3+} , P^{5+}) and large modifying cations (like Ca^{2+} , Na^+ , K^+ , (S^+)) which fill the lattice holes [13]. The latter have weak ionic field strengths and when introduced as oxides into the glass structure, release additional oxygen ions to the SiO_2 -chains to form silicate anions. This induces additional depolymerization in the remaining tetrahedral silica network [12]. The lower the cationic field strength the greater is the degree of depolymerization. This is evidently a function of the competition between Si^{4+} and the cation for oxygen [14,15]. The uptake pattern by the four calcium iron silicates in Tables I and II shows that addition of silica suppresses the Mo and enhances the Cs uptake, while an excess of iron oxide produces the opposite effect. Toop and Samis [14] have shown that the free oxygen ion activity in calcium ferrous silicate melts increases with increasing iron content. This is probably due to the reaction



which occurs in soda-lime silicate glasses [16,17]. These oxygen ions in turn favour the reaction

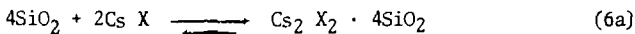


which results in a higher relative uptake N_i/N_j of Mo-99. The very low uptake in melt VI as compared to melt III (in Table I) is evidently due to a lower O^{2-} activity in the former. This in turn is due to the different field strengths of Na^+ and Ca^{2+} , 0.19 and 0.33, respectively [12]. The weak interaction between Na^+ and O^{2-} in Na_2O leads, at temperatures above $1200^\circ C$ [17,18], to the preemption of the oxygen ion by iron according to the reaction



This should leave a very low oxygen ion activity in melt VI, probably not much different from that of $Na_2O \cdot SiO_2$ [19]. However at $1100^\circ C$ eq (4) appears to be predominant even for melt VI (see Table I and [20]).

Cesium is known to form only two silicates: $Cs_2O \cdot 4SiO_2$ and the less stable $Cs_2O \cdot 2SiO_2$ [21,22]. As a network modifier, its uptake pattern was opposite to that of molybdenum. The formation of tetrasilicate in the melts can be expressed as follows:



where X refers to O^{2-} , $(O^{2-})_{\frac{1}{2}}$ or Cl^- in a noncommittal fashion. Thus, the greater the degree of polymerisation of the available tetrahedral silica-chain, the higher will be the cesium uptake (melts I to IV in table II).

This also explains the high uptake rate of the container.

Al_2O_3 and Fe_2O_3 can replace silica as glassforming oxides [23]. However the uptake behaviour of melts VIII and IX are consistent with the view that Al-containing melts are more "acidic" and have lower O^{2-} activity than those containing iron.

In equations (4) and (6b) the two glass-network forming oxides, MoO_3 and SiO_2 , are equivalent, and their reactions can be conveniently expressed in the form

$$\frac{[MoO_3][O^{2-}]}{[MoO_4]^{2-}} = C_1 \quad (7a)$$

and
$$\frac{[SiO_2][CsX]^{1/2}}{[Cs_2X_2 \cdot 4SiO_2]^{1/2}} = C_2 \quad (7b)$$

These reactions produce opposite effects and can be compared with each other by dividing eq. (7a) by (7b). This yields the relation $[MoO_3] \propto [CsX]^{-1/2}$ which is in good agreement with the observed $(\alpha_i/\alpha_j) Mo \propto (\alpha_i/\alpha_j)^{-1/2} Cs$ in table III.

Correlation with the field-strength parameter

The field-strength parameter $\frac{z}{r_c + r_a}$ [12] is apparently also a measure of the force which binds the free oxygen ion to the cations. Dietzel's [12] denominator is the sum of the cation and anion radii, while z is the charge on the cation. For any melt containing n_1 cation atoms of field-strength f_1 and m oxygen atoms, the average field-strength factor per

one oxygen atom would be

$$\bar{f} = \frac{\sum n_i \cdot f_i}{m} \quad (8).$$

Another quantity, $\Delta\bar{f}$, is defined as $(\bar{f} - f_s)$, where f_s is the value for standard reference melt $\text{CaO} \cdot 1/2 \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$. Calculated values of $\Delta\bar{f}$ for the various substrates are presented in the appendix [1]. The relative uptake of a two hour experiment is plotted against $\Delta\bar{f}$ in figure 1. The two straight lines were obtained by a least square calculation for the Mo and Cs data (the 12 hour data yielded a similar graph). The $\Delta\bar{f}$ values are apparently a crude measure of the free oxygen ion activity in binary and ternary oxide mixtures with similar cation composition.

Correlation with free oxygen ion activity

The values in table IV were taken from the free oxygen ion activity data for ion-containing slag and alkali silicates at 1600°C, calculated by Toop and Samis [14] and Charles [19] respectively. The former interrelated the bridging (O°), nonbridging (O^-) and free oxygen ions per mole of binary silicate using the equation

$$\frac{(\text{O}^\circ) (\text{O}^{2-})}{(\text{O}^-)^2} = \text{const.}$$

They claim that this relationship is common to all silicate compounds or oxide mixtures. They also calculated O^{2-} activities for the CaO-FeO-SiO_2

system, which can exist only in absence of oxygen. In the present work, at 1300°C, Fe^{2+} was probably no more than 4% of the total iron content [24]. However, comparison of the various oxide mixtures in table IV reveals that the greater the calculated O^{2-} activity in a CaO-FeO-SiO_2 combination, the higher is the Mo and the lower the Cs uptake in the similar calcium iron silicate substrate. (Tables I, II, and III).

REFERENCES

1. CARMON B. and RUSSEL, I.J., "Investigation of a Sealed Chamber Technique for the Determination of Relative Uptake Factors for Trace Vapor Levels of Elements in Contact with Oxide Melts", prelim. report NYO-3756-2; Sect. F (1968), final report, COO-3015-11 (1974).
2. NORMAN, J.H., "Henry's Law Constants for Dissolution of Fission Products in Silicate Fallout Particle Matrix", General Atomic Report (1966) No. GA-7058
3. FREILING, E.C., Science 133, 3469 (1961).
FREILING, E.C., *ibid.* 139, 3539 (1963).
EDVARDSON, K., LOW, K., and SISEFSKY, Y., Nature 184, 1771 (1939)
RAO, M.N., YOSHIKAWA, K., THEIN, M., CLARK, R.S., and KURODA, P.K., Health Phys. 14, 135 (1968).
MOORE, D.T., BECK, J.N., MILLER D.K., and KURODA, P.K., J. Geophys. Res. 78, 7039 (1973).
4. ROEDDER, E., Physics and Chemistry of the Earth, Vol. III, p. 239, Pergamon Press, N.Y. 1959.
5. ADAMS C.E., BALKWELL W.R., and QUAN, J.T., "High Temperature Measurements of the Rate of Uptake of MoO₃ Vapor by Selected Oxides", USNRDL-Tr-67-98 (1967).
6. BEDFORD R.G., and JACKSON, D.D., "Volatilities of the Fission Product and Uranium Oxides", USAEC rep. No. UCRL-12314 (1965).
7. VILLA, H., J. Soc. Chem. Ind. (London), 69, suppl. no. 1, 59 (1950).
8. LEVIN, E.M., McMURDIE, H.F., and HALL, F.P., "Phase Diagrams for Ceramics", Amer. Ceramic Soc., 1964.

9. ZACHARIASEN, W.H., Phys. Rev. 39, 195 (1935).
ZACHARIASEN, W.H., J. Amer. Chem. Soc. 54, 3841 (1932).
10. WEYL, W.A., and MARBOE, E.C., "The Constitution of Glasses", Vol. 11., part 1, Interscience John Wiley and Sons. New York, 1964.
11. BISCOE, J., and WARREN, B.E., J. Amer. Ceram. Soc. 21, 259 (1938).
12. DIETZEL, A., Glasstechnische Berichte 22, pp. 41-50, 81-85, 212-224 (1948-1949).
13. NARRAY-SZABÓ, I., "Structure and Physical Properties of Glass", Proc. VII Conf. Silicate Ind., Budapest 1965, Publ. House Hung. Acad. Sci.
14. TOOP, G.W., and SAMIS, C.S., Trans. Met. Soc. AIME, 224, 878 (1962).
15. YOKOKAWA, T., and NIWA, K., Trans. Japan Inst. Metals, 10, 3 (1969).
16. DOUGLAS, R.W., NATH, P., and PAUL, A., Physics Chem. Glasses 6, 216 (1965).
17. BUDD, S.M., Physics Chem. Glasses 7, 210 (1966).
18. PEARCE, M.L., and BEISLER, J., J. Amer. Ceram. Soc. 49, 547 (1966).
19. CHARLES, R.J., J. Amer. Ceramic Soc. 50, 631 (1967).
20. MITROFANOV, K.P., and SIDOROV, T.A., Chem. Abstr. 78, no. 33296 q, p. 220 (1973)
21. ALEKSEEVA, Z.D., Russian J. Inorg. Chem. 11 (5) 626 (1966) (translated from Russian).
22. REY, M., Disc. Faraday Soc. 4, 257 (1948).
23. KURKJIAN, C.R., and SIGETI, E.A., Physics Chem. Glasses 9, 73 (1968).

24. PHILLIPS, B., and MUAN, A., J. Amer. Ceram. Soc. 42, 421 (1959).

TABLE I

The relative uptake N_i/N_j of vaporized Mo-99 tracer species in cpm per cm^2
(j = standard melt No. I)

Substrate No.	Composition	heating at 1300°C		heating at 1100°C	
		for 2 hrs	for 12 hrs	for 2 hrs	for 12 hrs
I	CaO.1/2Fe ₂ O ₃ .SiO ₂	1.00	1.00	1.00	1.00
II	CaO.1/2Fe ₂ O ₃ .2SiO ₂	0.37	0.32	1.0	1.4
III	CaO.Fe ₂ O ₃ .SiO ₂	1.26	0.99		0.95
IV	CaO.Fe ₂ O ₃	11.0	18.0	216.	242.
V	CaO.3/2Fe ₂ O ₃	1.9	4.4		
VI	Na ₂ O.Fe ₂ O ₃ .SiO ₂	0.21	0.13	8.0	2.9
VII	Na ₂ O.SiO ₂	0.07	0.14	1.2	1.2
VIII	3CaO.Al ₂ O ₃ .7SiO ₂	0.07	0.16	4.4	5.6
IX	3CaO.Fe ₂ O ₃ .7SiO ₂	0.13	0.29		
	silica containers	0.0015	0.0015	very low	very low
	source on silica plates	0.04	0.04		
	clay loam*	0.7*	0.025*		

*) Calculated for comparison using data from ref. [5].

TABLE II

The relative uptake N_i/N_j of vaporized Cs-137 tracer species in cpm per cm^2
(j = standard melt I)

No.	Substrate composition	heating at 1300°C		heating at 1100°C	
		2 hrs	12 hrs	2 hrs	12 hrs
I	CaO.1/2Fe ₂ O ₃ .SiO ₂	1.00	1.00	1.00	1.00
II	CaO.1/2Fe ₂ O ₃ .2SiO ₂	16.0	12.0	1.8	0.89
III	CaO.Fe ₂ O ₃ .SiO ₂	0.41	0.45	0.22	0.70
IV	CaO.Fe ₂ O ₃	0.04	0.1	1.7	2.6
V	CaO.3/2 Fe ₂ O ₃	0.03	0.02		
VI	Na ₂ O.Fe ₂ O ₃ .SiO ₂	31.	47.	98.	113.
VII	Na ₂ O.SiO ₂	27.	66.	36.	89.
VIII	3CaO.Al ₂ O ₃ .7SiO ₂	122.	49.	28.	43.
IX	3CaO.Fe ₂ O ₃ .7SiO ₂	37.	9.7		
	silica containers for the melts:				
	II, III,	0.24	0.39	0.38-0.47	0.24-0.58
	IV	0.94	1.3	0.69	1.9
	VI to IX	0.01-0.2	0.01-0.15		

TABLE II1

Estimated relative attachment coefficients and release rates at 1300°C

substrates	(α_i/α_j)		$(\alpha_i/\alpha_j)^{-1/2}$	$6\text{cm}^{-2}\times\text{min}^{-1}\times 10^{-2}$	
	Mo-99	Cs-137	Cs-137	Mo-99	Cs-137
CaO.1/2Fe ₂ O ₃ .SiO ₂	1.0	1.0	1.0	2.1	4.2
CaO.1/2Fe ₂ O ₃ .2SiO ₂	0.26±0.06	16.0±1.0	0.25	1.5	5.4
CaO.Fe ₂ O ₃ .SiO ₂	2.5 ±0.1	0.10±0.02	3.2	5.1	0.8
CaO.Fe ₂ O ₃	5.2 ±0.7	0.14±0.04	2.6	0.5	8.9
Na ₂ O.Fe ₂ O ₃ .SiO ₂	0.05±0.01	66.0±15.0	0.12	7.8	8.8
Na ₂ O.SiO ₂	0.25±0.09	19.0± 5.0	0.23	4.2	2.1
3CaO.Al ₂ O ₃ .7SiO ₂	0.09±0.03	41.0±18.0	0.16	0.8	0.2
3CaO.Fe ₂ O ₃ .7SiO ₂	0.16±0.05			1.5	
silica				0.24	0.07

TABLE IV

Calculated free oxygen ion activity data taken from the literature

DATA from refs. (14) and (19)

melt composition	$[O^{2-}]$ for 1600°C	relative $[O^{2-}]$ for 1600°C
------------------	--------------------------	-----------------------------------

CaO.FeO.SiO₂

0.2

1.0

CaO.FeO.2SiO₂

0.08

0.4

CaO.2FeO.SiO₂

0.5

2.5

CaO.2FeO

1.

5.0

Na₂O.SiO₂

5×10^{-6}

2.5×10^{-5}

3CaO.2FeO.7SiO₂

0.04

0.2

Appendix

The field strength parameter $\bar{f} = \frac{\sum f_i n_i}{m}$ of the substrates

SUBSTRATES

No.	composition	atomic ratio	\bar{f}	$\Delta\bar{f}$
I	CaO.1/2Fe ₂ O ₃ .SiO ₂	Ca Fe Si O _{4.5}	0.569	0
II	CaO.1/2Fe ₂ O ₃ .2SiO ₂	Ca Fe Si ₂ O _{6.5}	0.653	+0.057
III	CaO.Fe ₂ O ₃ .SiO ₂	Ca Fe ₂ Si O ₆	0.574	-0.022
IV	CaO.Fe ₂ O ₃	Ca Fe O ₄	0.467	-0.129
V	CaO.3/2Fe ₂ O ₃	Ca Fe ₃ O _{5.5}	0.478	-0.118
VI	Na ₂ O.Fe ₂ O ₃ .SiO ₂	Na ₂ Fe ₂ O ₄ + + SiO ₂ *	0.475 0.785	-0.121 +0.189
VII	Na ₂ O.SiO ₂	Na ₂ Si O ₃	0.650	+0.054
VIII	3CaO.Al ₂ O ₃ .7SiO ₂	Ca ₃ Al ₂ Si ₇ O ₂₀	0.687	+0.091
IX	3CaO.Fe ₂ O ₃ .7SiO ₂	Ca ₃ Fe ₂ Si ₇ O ₂₀	0.687	+0.082
	clay loam**	-----	0.586	-0.01

} +0.068

* see ref. [18]

** estimated from the data published by C.E. Adams et al, ref. [5].

בחזקת מחיל - פרטומים