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CORRELATIONS FOR DIFFUSION CONSTANTS

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Abstract—Correlations for the melting-point diffusivity (D_{T_M}), the activation energy (Q), and the activation volume (V^*) for diffusion are re-examined, using the best available diffusion data for metals and ceramics. The data support the postulates that, for a given crystal structure and bond type

$$D_{T_M} = A$$

$$\frac{Q}{RT_M^0} = B$$

and

$$V^* = \frac{Q^0}{T_M^0} \left(\frac{dT_M}{dp} \right)^0$$

where A and B are constants which, to first order, are independent of pressure, p ; T_M^0 is the melting-point at atmospheric pressure; and R is the gas constant. Mean values of the constants A and B , and values for V^* , are evaluated for twelve crystal structures and bond types. For each such class the diffusion behaviour can be written

$$D = \frac{A}{\exp - B} \exp - \left\{ \frac{B \cdot T_M^0}{T} \left(1 + \frac{p}{T_M^0} \frac{dT_M^0}{dp} \right) \right\}$$

Such equations are useful in estimating approximate rates of transport, or creep, or sintering, in materials for which little or no diffusion data are available.

Résumé—Nous avons examiné de nouveau les corrélations de la diffusivité au point de fusion (D_{T_M}), de l'énergie d'activation (Q) et du volume d'activation (V^*) pour la diffusion, en passant en revue les meilleures données concernant la diffusion, dont on peut disposer pour les métaux et les céramiques. Ces données confirment l'hypothèse selon laquelle, pour un cristal et un type de liaison donnés:

$$D_{T_M} = A$$

$$\frac{Q}{RT_M^0} = B$$

et

$$V^* = \frac{Q^0}{T_M^0} \left(\frac{dT_M}{dp} \right)^0$$

où A et B sont des constantes qui sont indépendantes au premier ordre de la pression p ; T_M^0 est la température de fusion à la pression atmosphérique et R est la constante des gaz parfaits. Nous évaluons la valeur des constantes A et B et de V^* pour douze structures cristallines et types de liaison. Pour chacune de ces classes, on peut décrire le comportement de diffusion par:

$$D = \frac{A}{\exp - B} \exp - \left\{ \frac{B \cdot T_M^0}{T} \left(1 + \frac{p}{T_M^0} \frac{dT_M^0}{dp} \right) \right\}$$

Ce type d'équation est utile dans l'estimation des vitesses de transport, de fluage ou de frittage, dans les matériaux pour lesquels on ne dispose que de peu d'informations sur la diffusion, voire même d'aucune information.

Zusammenfassung—Anhand der besten verfügbaren Diffusionsdaten für Metalle und Keramiken werden die Korrelationen zwischen der Diffusivität beim Schmelzpunkt (D_{T_M}), der Aktivierungsenergie (Q) und dem Aktivierungsvolumen (V^*) für Diffusion nochmals überprüft. Die Daten stützen die Forderung, daß für gegebene Kristallstruktur und Bindungstyp folgendes gilt:

$$D_{T_M} = A$$

$$\frac{Q}{RT_M^0} = B$$

$$V^* = \frac{Q^0}{T_M^0} \left(\frac{dT_M}{dp} \right)^0$$

A und B sind Konstanten, die in erster Näherung nicht vom Druck abhängen; T_M^0 ist der Schmelzpunkt bei Atmosphärendruck, R ist die Gaskonstante. Für zwölf Kristallstrukturen und Bindungstypen wurden Mittelwerte der Konstanten A und B und Werte für V^* ermittelt. Für eine jede solche Klasse kann das Diffusionsverhalten beschrieben werden als:

$$D = \frac{A}{\exp - B} \exp - \left\{ \frac{B \cdot T_M^0}{T} \left(1 + \frac{p}{T_M^0} \frac{dT_M^0}{dp} \right) \right\}$$

Solche Gleichungen sind nützlich für die näherungsweise Abschätzung von Transport-, Kriech- oder Sinterraten in Materialien, für die keine oder nur begrenzte Diffusionsdaten bekannt sind.

1. INTRODUCTION

In this paper we re-examine three old and useful correlations for the material constants which describe lattice diffusion and grain boundary diffusion in metals and ceramics. All three correlations must be regarded as empirical (even though qualitative physical explanations can be used to justify them), and so their usefulness rests on their ability to describe known diffusion data. We have collected more data than was available to earlier authors seeking to test these correlations, and find that they appear to hold remarkably well when applied to materials with the same structure and bond-type.

2. THE CORRELATIONS

2.1 The melting point diffusivity

Let the lattice self-diffusion coefficient for an element, or for the slowest moving species in a compound, at temperature T and pressure p be given by

$$D = D_0 \exp - \left(\frac{Q}{RT} \right) \quad (1)$$

where

$$Q = Q^0 + pV^* \quad (2)$$

and Q^0 is the activation energy at atmospheric pressure ($p \approx 0$), V^* the activation volume, R the gas constant, and D_0 the pre-exponential factor (which we assume to be independent of pressure and temperature). Then at the melting point, T_M ,

$$D_{T_M} = D_0 \exp - \frac{(Q^0 + pV^*)}{RT_M} \quad (3)$$

The observation that the rate of diffusion at the melting point, D_{T_M} , is roughly constant, is an old one [1] dating from 1935. But it was not until the mid-1950's that enough data of sufficient precision were available for it to become clear that D_{T_M} is roughly constant only for a given crystal structure: the b.c.c. and f.c.c. metals, and diamond and cubic elements, all differ significantly [2, 3]. As data became better, additional refinements were added: the b.c.c. metals were subdivided into two groups, each with a characteristic D_{T_M} [4] and alkali halides were seen to have a characteristic D_{T_M} for anion diffusion [5]. The constancy of D_{T_M} reflects the fact that for a given crystal structure and bond-type, D_0 and Q/RT_M are roughly constant, for reasons which can be supported by physical arguments (see Sections 2.2 and 2.3).

In Section 3.1 we re-examine this postulate that, for a given crystal structure and bond-type,

$$D_{T_M} = A \quad (4)$$

[†] The author's attention has been drawn to a not yet published paper by Sammis, Smith and Schubert [15] assessing methods of estimating activation volume. They make a thorough assessment and comparison of a number of alternative equations for V^* [including those given here as equations (9), (11) and (12)].

where A is a constant. We find that the data support it, with some scatter. We evaluate a mean and standard deviation for A , for twelve classes of crystalline solids.

2.2. The Activation Energy

When diffusion is by a vacancy mechanism, the pre-exponential, D_0 , is roughly $10^{-4} \text{ m}^2/\text{s}$. If D_{T_M} is a constant (for a given class of solid) then it follows that, at atmospheric pressure (superscript 0),

$$\frac{Q^0}{RT_M^0} = B \quad (5)$$

where B is a constant. This empirical relation (or an extension of it to include the effect of crystal structure) appears first in the literature about 20 years ago [3, 6] and has since been investigated, for pure metals, in some detail [7].

Physically, D_0 is almost constant because it depends only on an atomic vibration frequency, v , the lattice parameter, a , and the entropy of diffusion ΔS .

$$D_0 = \phi a^2 v \exp - \frac{\Delta S}{R} \quad (6)$$

where ϕ is a geometric constant. For solids with the same crystal structure and bond type, and not too widely separated in atomic mass (which influences v , a , ϕ , a , v and ΔS are all about equal [8]).

The physical arguments for the constancy of Q^0/RT_M^0 are less clearcut. One helpful line of argument is to note that the formation of a vacancy, like the process of sublimation, involves breaking half the bonds that link an atom in the interior of a crystal to its neighbours; the enthalpy required to do so should scale as H_{vap} (the heat of sublimation). The motion of an atom into a vacancy involves a temporary loss of positional order—it is like local melting [7]—and might reasonably involve an energy which scales with the heat of melting, H_{melt} . We therefore expect

$$Q^0 = \alpha H_{\text{vap}} + \beta H_{\text{melt}}$$

or

$$\frac{Q^0}{RT_M^0} = \alpha \frac{H_{\text{vap}}}{RT_M^0} + \beta \frac{H_{\text{melt}}}{RT_M^0} \quad (7)$$

where α and β are constants.

The first term on the right-hand side contains the entropy change on sublimation at $T = T_M$; the second contains the entropy change on melting (both in units of R). These changes of entropy are roughly constant for a given crystal structure and bond-type; it follows that Q^0/RT_M^0 , too, should be constant.

In Section 3.2 we re-examine the postulate that Q^0/RT_M^0 is constant [equation (5)]. The data support it, with some scatter. We evaluate a mean and standard deviation for B , for twelve classes of crystalline solids.

2.3 The Activation Volume[†]

There exist data, derived by direct measurement of D at a variety of pressures, that D_{T_M} is independent of

pressure. Nachtrieb and his co-workers, studying the lattice self-diffusion of lead [9] and tin [10], observed that the diffusion coefficient decreased with increasing pressure, but that the increased melting point resulted in a constant rate of diffusion at the same homologous temperatures (T/T_M). If we postulate that D_{T_M} is independent of pressure, that is, that

$$\frac{d(\ln D_{T_M})}{dp} = 0 \quad (8)$$

then it follows from equation (3) that, for modest pressures (which we define as $p/K < 10^{-1}$, where K is the bulk modulus):

$$V^* = \frac{Q^0}{T_M^0} \cdot \left(\frac{dT_M}{dp} \right)^0 \quad (9)$$

where the superscript (0) means at atmospheric pressure.

This correlation, too, is an old one: equation (9) first appeared over 20 years ago [9]. Physically, it can be partly understood if the process of melting and that of diffusion are closely related. Equation (9) states that the pressure dependence of the average energy-per-atom at melting ($d(RT_M)/dp$) is the same as that for diffusion (dQ/dp), when scaled by the ratio of the two energies (Q^0/RT_M^0).

In Section 3.3 we assemble data for the physical constants that appear on the right-hand-side of equation (9), and compare values of V^* calculated in this way with those measured experimentally. The results support those of an earlier, more limited, analysis of Weertman [11]: equation (9) is a good empirical description of the data.

The correlation we have tested (equation 9) is very closely related to that investigated by Sherby and co-workers [12], namely:

$$V^* = R(k_0 - v)(X/\Delta S_m)\Omega \quad (10)$$

where R is the gas constant, k_0 a crystal-structure factor, v the valence, X the fractional volume change on melting, ΔS_m the entropy of melting and Ω the molar volume. (If this equation is combined with equations (9) and (12) of their paper, our equation (9) is obtained.) They then calculated V^* by using data for the material properties which appear in equation (10) and demonstrated good agreement between these calculated values and those measured in diffusion or creep experiments. They did not attempt to test equation (9) directly; but our test and theirs must be regarded as complementary; both point to the same underlying physical mechanism.

Other correlations for the activation volume have been proposed. Lawson [13] suggests

$$V^* \simeq \frac{\beta S}{\alpha} \quad (11)$$

where β is the isothermal compressibility, S the activation entropy and α the volumetric thermal expansion coefficient. Keyes [14] proposes

$$V^* \simeq 4\beta Q^0 \quad (12)$$

The first is hard to test or use (because there are almost no data for S) and the second is dubious because it does not allow negative values of V^* .

3. TESTS OF CORRELATIONS USING LATTICE DIFFUSION DATA

3.1 Melting-point diffusivities at atmospheric pressure

Table 1 lists diffusion data, and values of D_{T_M} , for lattice self-diffusion in elements and for lattice diffusion of the slowest-diffusing components (the anion in most alkali halides; the oxygen atom in most oxides). Data of dubious quality, or for which extrinsic diffusion was suspected, were rejected.[†]

The table classifies materials by crystal structure and bonding, and ranks the classes in order of decreasing D_{T_M} . It lists diffusion coefficients, and their source, the melting point diffusivity, and the dimensionless activation energy Q^0/RT_M^0 . When a class has several members, the arithmetic mean and standard deviation of Q^0/RT_M^0 , and the geometric mean and standard deviation of D_0 and D_{T_M} , are also listed.

The values and ranges of D_{T_M} are plotted in Fig. 1, which illustrates how each crystal structure and bond type has a characteristic value of D_{T_M} (equation 4). One class, the b.c.c. metals, has been subdivided because the data clearly indicate three sub-classes: the alkali metals (Na, K, Li, etc.), the transition-metals (Ta, V, Nb, etc.) and the transuranium metals (Pu, Yb, La, etc.). One would expect that oxides should show several such subdivisions, but at present the only clear division is that between simple oxides and silicates.

3.2 The activation energy at atmospheric pressure

Values of Q^0 and Q^0/RT_M^0 are listed in Table 1. There is a clear correlation with a characteristic value of Q^0/RT_M^0 associated with each crystal structure and bond type (Fig. 2). Means and standard deviation for each class are listed in Table 1.

3.3 The activation volume V^*

Tables 2 and 3 list crystallographic, diffusion and thermal data. The data are grouped by the type of bonding and crystal structure. The melting temperatures listed are those at atmospheric pressure ($p = 0$). Values of $(dT_M/dp)^0$ are taken from the initial slope of the fusion curve, again at $p = 0$. The activation energies listed are for intrinsic bulk diffusion of the slowest species. For some materials creep activation energies are listed. (Creep and diffusion activation energies are comparable, because creep is frequently diffusion-controlled.) Two values of activation volume, V^* , are listed: that measured by intrinsic dif-

[†]We have noted, for oxides, that for intrinsic diffusion $Q^0/RT_M^0 \approx 23 \pm 2$ whereas, when extrinsic diffusion is suspected, $Q^0/RT_M^0 \approx 11 \pm 3$. (The ranges are \pm one standard deviation.)

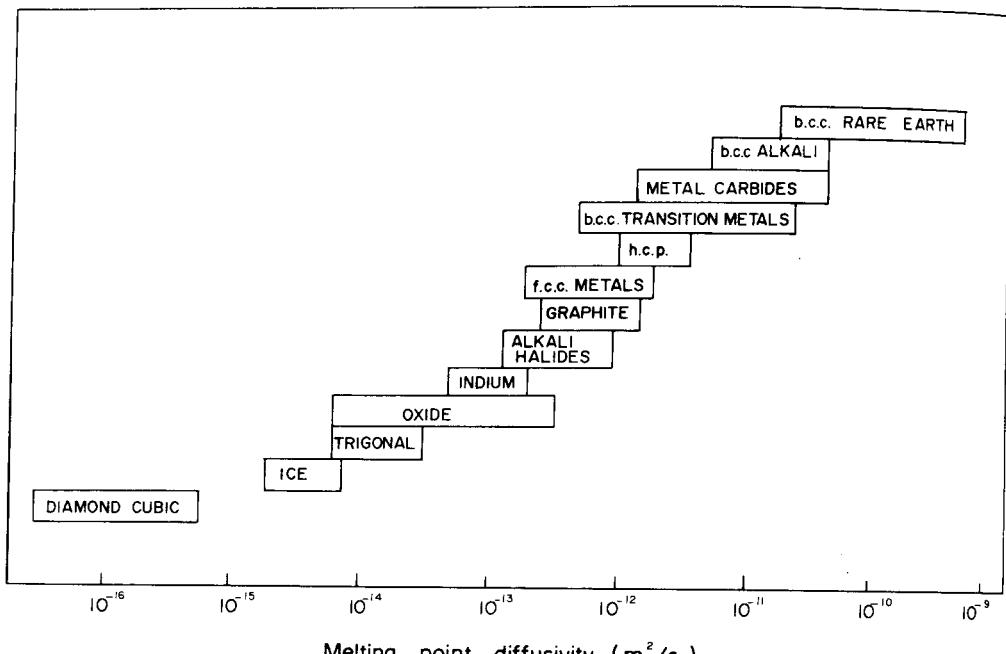


Fig. 1. Melting-point diffusivities for classes of crystalline solids. The width of the bar is either twice the standard deviation of the geometric mean, or a factor of four, whichever is greater. Data for the solidus diffusivities for b.c.c. and the f.c.c. alloys coincide with the range shown for the pure metals.

fusion experiments or creep tests, and that calculated from equation (9). The striking agreement between the two can be seen in Fig. 3.

3.4 Solidus diffusivities of alloys

Table 1 also lists thermal and diffusion data for several binary alloys. The solidus temperature, T_s^0 ,

has been used to calculate the dimensionless activation energy $Q^0/R T_s^0$ and the diffusivity at the solidus temperature, $D T_s$, for the alloys. The solidus diffusivities of the b.c.c. and f.c.c. alloys are within the standard deviation bounds of the melting point diffusivities of the b.c.c. and f.c.c. metals shown in Fig. 1.

We have tried normalising the data in other ways.

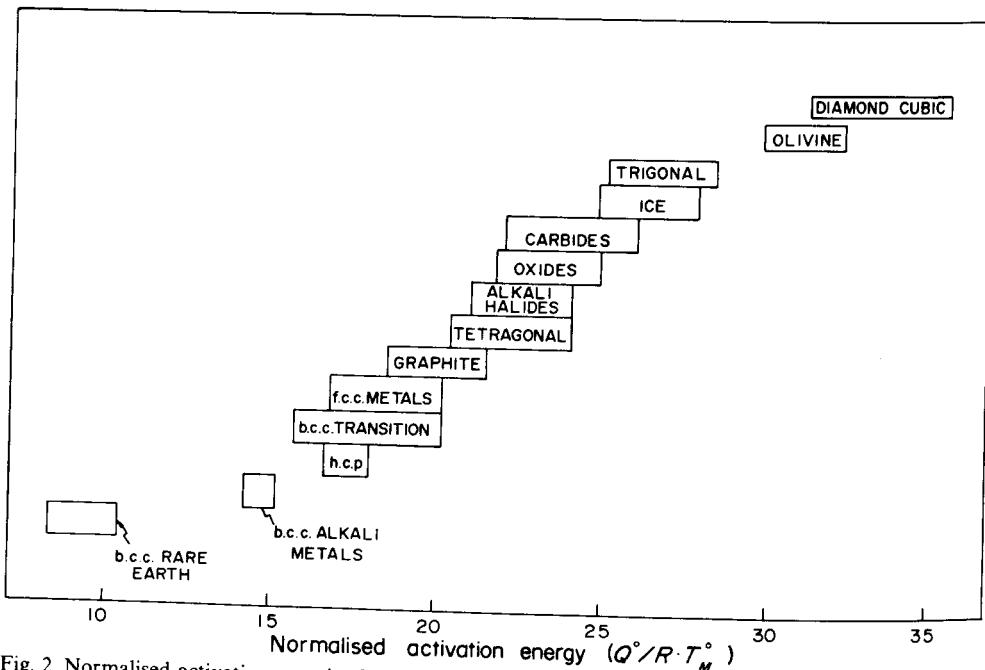


Fig. 2. Normalised activation energies for classes of crystalline solids. The width of the bar is twice the standard deviation of the arithmetic mean. Data for alloys, normalised by using the solidus temperature in place of the melting point, coincide with the range shown for the pure metals.

Table 1

Class -	Material -	T_M^* (K)	D_o (m^2/sec)	Q° (kJ/mole)	$Q^\circ/R \cdot T_M^\circ$ -	D_{TM} (m^2/sec)	ref. -
CARBIDES	UC	2623	-	528.6	24. 25	-	1
	SiC	2973	-	523.4	21. 19	-	2
	TiC	3413	4. 4	738.6	26. 04	2.16×10^{-11}	3
	ZrC	3530	0.103	720.2	24. 55	2.24×10^{-12}	4
	MEANS	-	0.673	-	24. 01	6.95×10^{-12}	
BCC	ϵ -Pu	914	3.0×10^{-7}	65.7	8. 65	5.25×10^{-11}	5
	δ -Ce	1071	1.2×10^{-6}	90.0	10. 11	4.87×10^{-11}	6
	γ -La	1193	1.3×10^{-6}	102.6	10. 35	4.16×10^{-11}	7
	γ -Yb	1796	1.2×10^{-5}	121.0	8. 11	3.62×10^{-9}	8
	MEANS	-	1.54×10^{-6}	-	9. 31	1.4×10^{-10}	
BCC	Rb	312	2.3×10^{-5}	39.4	15. 20	5.78×10^{-12}	9
	K	337	3.1×10^{-5}	40.8	14. 57	1.46×10^{-11}	10
	Na	371	2.42×10^{-5}	43.8	14. 21	1.64×10^{-11}	11
	Li	454	2.3×10^{-5}	55.3	14. 66	9.91×10^{-12}	12
	MEANS	-	2.5×10^{-5}	-	14. 66	1.08×10^{-11}	
BCC	β -Ti	577	4.0×10^{-5}	94.6	19. 72	1.08×10^{-13}	13
	Eu	1095	1.0×10^{-4}	143.5	15. 77	1.42×10^{-11}	14
	Er	1795	4.51×10^{-4}	302.4	20. 27	7.08×10^{-13}	15
	β -Ti	1933	1.09×10^{-4}	251.2	15. 64	1.76×10^{-11}	16
	β -Zr	2125	1.34×10^{-4}	273.5	15. 49	2.52×10^{-11}	17
	Cr	2130	2.0×10^{-5}	308.6	17. 43	5.36×10^{-13}	18
	V	2163	2.38×10^{-5}	309.2	17. 20	9.74×10^{-13}	19
	Nb	2741	1.24×10^{-3}	439.6	19. 30	5.15×10^{-12}	20
	Mo	2890	1.8×10^{-4}	460.6	19. 18	8.43×10^{-13}	21
	Ta	3269	1.24×10^{-4}	413.3	15. 21	3.06×10^{-11}	22
	W	3683	4.28×10^{-3}	641.0	20. 94	3.43×10^{-12}	23
	MEANS	-	1.60×10^{-4}	-	17. 83	2.88×10^{-12}	
			$\frac{x}{4.97}$	-	$\pm 2. 12$	$\frac{x}{6.45}$	
HCP	Cd	594	6.8×10^{-5}	86.3	17. 48	1.74×10^{-12}	24
	Zn	692	1.8×10^{-5}	96.3	16. 75	9.60×10^{-13}	25
	Mg	922	10^{-4}	134.8	17. 59	2.29×10^{-12}	26
	MEANS	-	4.97×10^{-5}	-	17.27	1.56×10^{-12}	
			$\frac{x}{2.46}$	-	± 0.46	$\frac{x}{1.56}$	

Table 1 (continued)

Table 1 (*continued*)

Class -	Material -	T_M° (K)	*	D_o (m^2/sec)	Q° (kJ/mole)	$Q/R.T_M^\circ$ -	D_{TM} (m^2/sec)	ref. -
FCC	Pb	601		1.37×10^{-4}	109.1	21. 84	4.46×10^{-14}	27
	Al	933		$1. 7 \times 10^{-4}$	142.0	18. 31	1.89×10^{-12}	28
	Ag	1234		$4. 0 \times 10^{-5}$	184.6	18. 00	6.08×10^{-13}	29
	Au	1336		1.07×10^{-5}	176.9	15. 93	1.29×10^{-12}	30
	Cu	1356		$3. 1 \times 10^{-5}$	200.3	17. 78	5.91×10^{-13}	31
	Ni	1726		$1. 9 \times 10^{-4}$	279.7	19. 50	6.45×10^{-13}	32
	β -Co	1768		$8. 3 \times 10^{-5}$	283.4	19. 29	3.48×10^{-13}	33
	γ -Fe	1805		$4. 9 \times 10^{-5}$	284.1	18. 94	2.91×10^{-13}	34
	Pd	1825		2.05×10^{-5}	266.3	17. 56	4.85×10^{-13}	35
	Th	2023		$1. 2 \times 10^{-4}$	319.7	19. 02	6.61×10^{-12}	36
	Pt	2046		$2. 2 \times 10^{-5}$	278.4	16. 37	1.70×10^{-13}	37
	MEANS	—		5.46×10^{-5}	—	18. 41	5.50×10^{-13}	
		—		$\frac{\Sigma}{2} 2.63$	—	$\pm 1. 61$	$\frac{\Sigma}{2} 2.79$	
HEXAGONAL	Graphite	4100		$2. 4 \times 10^{-4}$	681.7	20. 01	4.91×10^{-13}	38
ALKALI HALIDES	AgBr	705		—	123.1	21. 01	5.98×10^{-14}	39
	AgCl	728		$8. 5 \times 10^{-3}$	151.2	24. 99	1.19×10^{-13}	40
	LiCl	887		—	158.9	21. 56	—	41
	CsCl	919		$7. 0 \times 10^{-5}$	150.6	19. 72	1.91×10^{-13}	42
	KI	959		—	170.5	21. 39	—	41
	RbCl	988		3.33×10^{-3}	191.6	23. 34	2.42×10^{-13}	43
	KBr	1003		—	205.6	24. 67	2.42×10^{-13}	44
	NaBr	1028		$5. 0 \times 10^{-3}$	194.5	22. 77	6.47×10^{-13}	45
	KCl	1049		$3. 6 \times 10^{-3}$	202.2	23. 20	3.04×10^{-13}	46
	NaCl	1074		$6. 2 \times 10^{-3}$	206.1	23. 09	5.80×10^{-13}	47
	LiF	1115		$6. 4 \times 10^{-3}$	211.9	22. 87	7.48×10^{-13}	48
	KF	1130		—	211.9	22. 57	—	49
	NaF	1261		—	259.5	24. 61	1.70×10^{-12}	50
	MEANS	—		2.82×10^{-3}	—	22. 75	3.21×10^{-13}	
		—		$\frac{\Sigma}{2} 5.27$	—	$\pm 1. 54$	$\frac{\Sigma}{2} 2.65$	
TETRAHEDRAL	In	430		$3. 2 \times 10^{-4}$	78.3	21. 91	9.74×10^{-14}	51
OXIDES	Fe ₂ O ₃	1663		2.04×10^{-4}	326.0	23. 59	1.16×10^{-14}	52
	CoO	2208		$5. 0 \times 10^{-3}$	397.8	21. 68	1.92×10^{-12}	53
	ZnO	2248		1.05×10^{-5}	395.1	21. 15	6.85×10^{-15}	54
	Al ₂ O ₃	2318		$2. 8 \times 10^{-3}$	477.3	24. 78	4.85×10^{-14}	55
	MgO-Al ₂ O ₃	2378		1.86×10^{-3}	485.1	24. 55	4.06×10^{-14}	56
	BeO	2803		—	607.1	26. 06	—	57
	ZrO ₂	2988		—	535.9	21. 58	—	58
	MgO	3125		—	640.0	24. 65	—	59
	ThO ₂	3323		$5. 0 \times 10^{-5}$	627.3	22. 72	6.81×10^{-15}	60
	MEANS	—		3.75×10^{-4}	—	23. 42	3.56×10^{-14}	
		—		$\frac{\Sigma}{2} 11.84$	—	$\pm 1. 72$	$\frac{\Sigma}{2} 8.43$	

Table 1 (*continued*)

Table 1 (continued)

Class -	Material -	T_M^o (K) [*]	D_o (m^2/sec)	Q^o (kJ/mole)	$Q^o/R.T_M^o$ -	D_{T_M} (m^2/sec)	ref -
OLIVINE	2MgO.SiO ₂	2171	3.0	565.2	31.33	7.43×10^{-14}	61
TRIGONAL	Sn	504	9.1×10^{-4}	105.1	25.04	1.21×10^{-14}	62
	Bi	544	-	129.8	28.71	-	63
	Sb	904	5.6×10^{-3}	201.0	26.76	1.34×10^{-14}	64
	MEANS	-	2.26×10^{-3}	-	26.84	1.27×10^{-14}	
ICE	ICE	273	10^{-3}	59.7	26.32	3.73×10^{-15}	65
DIAMOND CUBIC	Ge	1211	4.4×10^{-3}	324.5	32.25	4.36×10^{-17}	66
	Si	1683	0.9	496.0	35.46	3.57×10^{-16}	67
	MEANS	-	6.29×10^{-2}	-	33.86	1.25×10^{-16}	
		-	$\frac{x}{\ddagger} 43.1$	-	2.27	$\frac{x}{\ddagger} 4.42$	
Class -	ALLOY (atomic %)	Species -	Solidus ⁽⁶⁸⁾ (K)	D_o ⁽⁶⁹⁾ (m^2/sec)	Q^o ⁽⁶⁹⁾ (kJ/mole)	$\frac{Q^o}{R.T_s}$ -	DT Solidus (m^2/sec)
B.C.C.	Co-42 % Al	Co	1880	1.8×10^{-2}	355.9	22.78	2.3×10^{-12}
	Co-49 % Al	Co	1915	3.3	427.1	26.84	7.3×10^{-12}
	MEAN		-	0.24	-	24.81	4.1×10^{-12}
	S.D.		-	$\frac{x}{\ddagger} 39.8$	-	$\frac{x}{\ddagger} 2.87$	$\frac{x}{\ddagger} 2.26$
Tetragonal	Cr-16 % Fe	Cr	1940	3.8×10^{-5}	268.8	16.67	2.2×10^{-12}
	Cr-31 % Fe	Cr	1850	2.5×10^{-3}	316.1	20.56	2.9×10^{-12}
	Cr-49 % Fe	Cr	1790	4.0×10^{-3}	293.1	19.70	1.1×10^{-11}
	MEAN		-	7.2×10^{-4}	-	18.98	4.1×10^{-12}
CsCl Structure	S.D.		-	$\frac{x}{\ddagger} 13.0$	-	$\frac{x}{\ddagger} 2.04$	$\frac{x}{\ddagger} 2.36$
	Au-47.5 % Cd	Cd	897	1.4×10^{-4}	129.8	17.41	3.8×10^{-12}
	Au-49 % Cd	Cd	898	1.5×10^{-4}	130.6	17.50	3.8×10^{-12}
	Au-50 % Cd	Cd	900	2.3×10^{-5}	117.2	15.67	3.6×10^{-12}
	Au-50.5 % Cd	Cd	898	2.2×10^{-5}	113.5	15.21	5.5×10^{-12}
	Mg-42.8 % Ag	Ag	1050	5.1×10^{-6}	120.2	13.78	5.3×10^{-12}
	Mg-47.2 % Ag	Ag	1085	3.3×10^{-5}	153.7	17.05	1.3×10^{-12}
	Ag-41.1 % Mg	Ag	1065	9.5×10^{-6}	139.0	15.71	1.4×10^{-12}
	Ag-43.6 % Mg	Ag	1080	1.5×10^{-5}	147.8	16.47	1.1×10^{-12}
	Ag-48.5 % Mg	Ag	1085	3.7×10^{-5}	165.4	18.34	4.0×10^{-13}
CsCl Structure	Ag-48.7 % Mg	Ag	1087	3.9×10^{-5}	166.2	18.40	4.0×10^{-13}
	MEAN		-	2.9×10^{-5}	-	16.55	1.9×10^{-12}
	S.D.		-	$\frac{x}{\ddagger} 2.90$	-	$\frac{x}{\ddagger} 1.47$	$\frac{x}{\ddagger} 2.71$

Table 1 (continued)

Table 1 (*continued*)

Class -	ALLOY (atomic %)	Species -	Solidus ⁽⁶⁸⁾ (K)	D ₀ ⁽⁶⁹⁾ (m ² /sec)	Q° ⁽⁶⁹⁾ (kJ/mole)	Q° R T _s -	DT Solidus (m ² /sec)
F.C.C.	Al-4.3 % Zn	Zn	900	3.5 × 10 ⁻⁵	118.0	15.78	4.9 × 10 ⁻¹²
	Al-9.2 % Zn	Zn	850	2.0 × 10 ⁻⁵	113.0	16.00	2.3 × 10 ⁻¹²
	Al-16.7 % Zn	Zn	800	1.0 × 10 ⁻⁵	104.7	15.75	1.4 × 10 ⁻¹²
	Al-36.9 % Zn	Zn	745	1.6 × 10 ⁻⁵	100.9	16.30	1.3 × 10 ⁻¹²
	Al-49.4 % Zn	Zn	720	4.8 × 10 ⁻⁶	91.7	15.33	1.1 × 10 ⁻¹²
	Ag-2.05 % Al	Ag	1228	2.5 × 10 ⁻⁵	177.9	17.43	6.7 × 10 ⁻¹³
	Ag-9.47 % Al	Ag	1135	8.3 × 10 ⁻⁵	179.6	19.04	4.5 × 10 ⁻¹³
	Ag-14.1 % Al	Ag	1075	7.3 × 10 ⁻⁵	172.5	19.31	3.0 × 10 ⁻¹³
	Ag-0.9 % Cd	Ag	1228	1.8 × 10 ⁻⁵	173.8	17.03	7.2 × 10 ⁻¹³
	Ag-1.09 % Cd	Ag	1227	1.3 × 10 ⁻⁵	167.1	16.39	1.0 × 10 ⁻¹²
	Ag-2.8 % Cd	Ag	1222	6.0 × 10 ⁻⁶	160.4	15.80	8.3 × 10 ⁻¹³
	Ag-5.13 % Cd	Ag	1210	3.0 × 10 ⁻⁶	154.9	15.41	6.1 × 10 ⁻¹³
	Ag-6.5 % Cd	Ag	1205	3.1 × 10 ⁻⁵	178.4	17.82	5.7 × 10 ⁻¹³
	Ag-13.6 % Cd	Ag	1165	2.3 × 10 ⁻⁵	171.5	17.72	4.7 × 10 ⁻¹³
	Ag-28 % Cd	Ag	1075	1.6 × 10 ⁻⁵	156.0	17.46	4.2 × 10 ⁻¹³
	Au-6 % Ag	Au	1330	9.0 × 10 ⁻⁶	176.2	15.94	1.1 × 10 ⁻¹²
	Au-17 % Ag	Au	1320	1.2 × 10 ⁻⁵	180.3	16.44	8.7 × 10 ⁻¹³
	Au-34 % Ag	Au	1300	1.7 × 10 ⁻⁵	186.4	17.25	5.5 × 10 ⁻¹³
	Cu-21.5 % Ni	Ni	1400	6.3 × 10 ⁻⁶	208.1	17.89	1.1 × 10 ⁻¹³
	Ni-10 % Cr	Ni	1705	3.3 × 10 ⁻⁴	293.9	20.74	3.2 × 10 ⁻¹³
	Ni-19.9 % Cr	Ni	1675	1.6 × 10 ⁻⁴	285.6	20.52	2.0 × 10 ⁻¹³
	Ni-29.7 % Cr	Ni	1665	2.9 × 10 ⁻⁴	295.2	21.34	1.6 × 10 ⁻¹³
	Co-10 % Al	Co	1720	2.7 × 10 ⁻⁴	282.6	19.77	7.0 × 10 ⁻¹³
	Ni-5.3 % W	W	1745	1.7 × 10 ⁻³	337.1	23.25	1.4 × 10 ⁻¹³
	Ni-9.2 % W	W	1765	1.4 × 10 ⁻⁴	311.9	21.27	8.1 × 10 ⁻¹⁴
	Ni-4.3 % Co	Co	1727	4.9 × 10 ⁻⁵	261.3	18.19	6.2 × 10 ⁻¹³
	Ni-10.8 % Co	Co	1730	6.6 × 10 ⁻⁵	263.8	18.35	7.1 × 10 ⁻¹³
	Ni-21.1 % Co	Co	1734	3.3 × 10 ⁻⁵	255.8	17.25	6.4 × 10 ⁻¹³
	Ni-43.3 % Co	Co	1744	5.2 × 10 ⁻⁵	262.1	18.09	7.3 × 10 ⁻¹³
	Ni-48.6 % Co	Co	1746	1.2 × 10 ⁻⁵	252.1	17.38	3.4 × 10 ⁻¹³
	Ni-49.4 % Co	Co	1746	1.8 × 10 ⁻⁵	250.4	17.26	5.8 × 10 ⁻¹³
	Co-6.2 % Ni	Ni	1765	5.4 × 10 ⁻⁴	302.3	20.61	6.0 × 10 ⁻¹³
	Co-10.9 % Ni	Ni	1763	1.7 × 10 ⁻⁵	262.5	17.92	2.8 × 10 ⁻¹³
	Co-11 % Ni	Ni	1763	6.4 × 10 ⁻⁴	304.0	20.75	6.2 × 10 ⁻¹³
	Co-19.4 % Ni	Ni	1760	1.9 × 10 ⁻⁴	285.6	19.53	6.3 × 10 ⁻¹³
	Co-20.1 % Ni	Ni	1759	4.1 × 10 ⁻⁵	275.1	18.82	2.7 × 10 ⁻¹³
	Co-27.4 % Ni	Ni	1756	1.6 × 10 ⁻⁴	281.4	19.28	6.7 × 10 ⁻¹³
	Co-30.1 % Ni	Ni	1755	6.7 × 10 ⁻⁵	271.3	18.60	5.6 × 10 ⁻¹³
	Cu-9.8 % Pt	Pt	1410	9.3 × 10 ⁻⁶	220.2	18.79	6.4 × 10 ⁻¹⁴
	Cu-24.6 % Pt	Pt	1525	1.9 × 10 ⁻⁶	215.2	16.98	8.0 × 10 ⁻¹⁴
	Cu-49.4 % Pt	Pt	1770	6.6 × 10 ⁻⁶	249.1	16.94	2.9 × 10 ⁻¹³
	Pt-25.5 % Cu	Pt	1950	2.2 × 10 ⁻⁶	252.5	15.58	3.8 × 10 ⁻¹³
	MEAN		-	3.3 × 10 ⁻⁵	-	18.04	4.8 × 10 ⁻¹³
	S.D.		-	±4.90	-	±1.83	±2.40

In particular, we have normalised them by using liquidus temperatures and by using the melting points of adjacent pure phases on the phase diagram. Neither method is as successful as bringing the data into uniformity.

4. APPLICATION TO BOUNDARY DIFFUSION

If the three correlations work well for lattice diffusion, there is no obvious reason why they should not

also work for grain-boundary diffusion. Data for boundary diffusion are too sparse and inaccurate to allow a detailed check; but if we assume the correlations hold, then useful generalisations can be made.

4.1 Boundary diffusion at the melting point

Let the rate of grain boundary diffusion be described by

$$\delta D_b = \delta D_{0b} \exp - \left(\frac{Q_b}{RT} \right) \quad (13)$$

Table 2

Class	Material	$T_M^\circ *$ (K)	$(dT_M^\circ / dp)^\circ$ (K/Kbar) [†]	Reference
BCC	Cs	302	20.0	1
	Rb	312	18.4	1
	K	337	15.3	1
	Na	371	8.0	1
	Li	452	2.1	1
	β -Tl	577	6.9	2
	ϵ -Pu	914	-4.4	3
	Ba	1002	4.0	4
	Sr	1042	20.0	5
	Ce	1071	-4.7	6
	Eu	1095	15.0	7
	Ca	1112	17.0	5
	La	1193	2.5	8
	Pr	1204	0.1	8
	Nd	1283	3.5	8
	Sm	1345	11.5	8
	Mn	1517	3.9	9
	Gd	1584	6.5	8
	Tb	1633	9.0	8
	Dy	1682	12.0	8
	Ho	1743	15.0	8
	Er	1795	15.0	8
	Yb	1796	19.0	7
	Tm	1818	12.0	8
	Lu	1929	8.5	8
HCP	Cd	594	6.4	10
	Zn	692	5.4	11
	Mg	922	7.3	11
FCC	Pb	601	7.8	2
	Al	933	5.9	12
	Ag	1234	5.2	11
	Cu	1356	4.2	13
	Ni	1726	4.2	14
	γ -Fe	1805	3.8	15
	Pt	2046	7.3	14
	Rh	2239	6.25	14
Hexagonal	Graphite	~4100	9.5	16
Alkali halides	LiCl	887	24.2	17
	CsCl	919	17.0	17
	RbI	920	33.0	18
	NaI	924	32.7	17
	KI	959	64.6	19
	RbBr	965	32.0	18
	RbCl	988	24.9	17
Alkali halides (cont.)	KBr	1003	37.9	19
	NaBr	1028	28.7	17
	KCl	1049	26.5	17
	RbF	1068	15.0	18
	NaCl	1074	23.8	17
	KF	1130	22.6	19
	NaF	1261	16.1	17
Tetragonal	In	430	5.2	2
Orthorombic	Ga	303	-2.0	12
Silicates	Na ₂ Al ₂ Si ₃ O ₈	1391	14.0	20
	CaO·MgO·2SiO ₂	1663	9.6	20
	MgO·SiO ₂	1940	7.5	21
	2MgO·SiO ₂	2171	4.8	22
Trigonal	Hg	234	5.1	23
	Se	494	21.3	24
	Sn	505	3.4	24
	Bi	544	-3.4	2
	Sb	904	-0.57	11

$$+ 1 \text{ } ^\circ\text{K}/\text{Kbar} = 10^{-8} \text{ } ^\circ\text{K}/\text{N m}^{-2}$$

Table 2 (continued)

Class	Material	T_M^o (K)	$(dT_M^o/dp)^o$ (K/Kbar) [†]	Reference
Hexagonal	Ice	273	-7.38	25
Cubic	CO_2	194	14.3	26
Diamond Cubic	Ge Si	1210 1683	-3.8 -5.8	27

$$+ 1^\circ \text{K}/\text{Kbar} = 10^{-8} \text{ }^\circ \text{K/N m}^{-2}$$

Table 3

Class	Material	T_M^o $^\circ \text{K}$	Q^o kJ/mole	$(dT_M^o/dp)^o$ $^\circ \text{K}/\text{Kbar}$	Ω^+ m^3/mole	V^* meas. m^3/mole	V^* calc. m^3/mole	V^*/Ω	Ref.
BCC	Rb	312	39.4	18.4	5.58×10^{-5}	-	2.23×10^{-5}	0.40	-
	K	337	40.8	20.0	4.55×10^{-5}	2.5×10^{-5}	2.42×10^{-5}	0.55	1
	Na	371	43.8	8.0	2.37×10^{-5}	9.8×10^{-6}	9.44×10^{-6}	0.41	2
	Li	454	55.3	2.1	1.30×10^{-5}	3.4×10^{-6}	2.56×10^{-6}	0.26	3
	β -Tl	577	94.6	6.9	1.72×10^{-5}	9.54×10^{-6}	1.13×10^{-5}	0.55	4
	ϵ -Pu	914	65.7	-4.4	1.45×10^{-5}	-4.9×10^{-6}	-3.16×10^{-6}	-0.34	5
	δ -Ce	1071	90.0	-4.7	2.07×10^{-5}	-1.9×10^{-6}	-3.95×10^{-6}	-0.09	6
	Eu	1095	143.5	15.0	2.90×10^{-5}	-	1.97×10^{-5}	0.68	-
	γ -La	1193	102.6	2.5	2.25×10^{-5}	2.2×10^{-6}	2.15×10^{-6}	0.10	7
	Er	1795	302.4	15.0	1.83×10^{-5}	-	2.53×10^{-5}	1.39	-
γ -Yb	1796	121.0	19.0	2.66×10^{-5}	1.57×10^{-5}	1.28×10^{-5}	0.59	8	
	β -Ti	1933	251.2	-	1.06×10^{-5}	4.0×10^{-6}	-	0.38	9
HCP	Cd	594	86.3	6.4	1.30×10^{-5}	8.2×10^{-6}	9.3×10^{-6}	0.63	10
	Zn	692	96.3	5.4	9.16×10^{-6}	5.96×10^{-6}	7.51×10^{-6}	0.65	10
	Mg	922	134.8	7.3	1.40×10^{-5}	-	1.07×10^{-5}	0.77	-
FCC	Pb	601	109.1	7.8	1.83×10^{-5}	1.46×10^{-5}	1.42×10^{-5}	0.80	11
	Al	933	142	5.9	9.99×10^{-6}	8.7×10^{-6}	8.98×10^{-6}	0.87	12
	Ag	1234	185	5.2	1.03×10^{-5}	8.8×10^{-6}	7.8×10^{-6}	0.86	13
	Au	1336	176.9	-	1.02×10^{-5}	8.7×10^{-6}	-	0.85	14
	Cu	1356	200.3	4.2	7.11×10^{-6}	6.4×10^{-6}	6.2×10^{-6}	0.90	15
	Ni	1726	279.7	4.2	6.59×10^{-6}	5.3×10^{-6}	6.81×10^{-6}	0.80	16
	γ -Fe	1805	284.1	3.8	7.11×10^{-6}	5.5×10^{-6}	5.98×10^{-6}	0.77	17
	Pd	1825	266.3	-	9.33×10^{-6}	9.43×10^{-6}	-	1.01	18
	Pt	2046	278.4	7.3	9.09×10^{-6}	-	9.93×10^{-6}	1.09	-
ALKALI HALIDES	AgBr	705	123.1	-	1.40×10^{-5}	4.4×10^{-5}	-	3.15	19
	AgCl	728	151.2	-	1.09×10^{-5}	2.14×10^{-5}	-	1.96	20
	LiCl	887	158.9	24.2	1.17×10^{-5}	-	4.34×10^{-5}	3.69	-
	CsCl	919	150.6	17.0	1.47×10^{-5}	-	2.79×10^{-5}	1.90	-
	KI	959	170.5	64.6	1.99×10^{-5}	(1.7×10^{-4})	1.15×10^{-4}	(0.86)	21
	RbCl	988	191.6	24.9	1.11×10^{-5}	-	4.83×10^{-5}	4.34	-
	KBr	1003	205.6	37.9	1.42×10^{-5}	3.9×10^{-5}	7.77×10^{-5}	2.74	9
	NaBr	1028	194.5	28.7	1.40×10^{-5}	3.1×10^{-5}	5.43×10^{-5}	2.22	9
	KCl	1049	202.2	26.5	1.09×10^{-5}	6.7×10^{-5}	5.11×10^{-5}	6.13	22
	NaCl	1074	206.1	23.8	1.07×10^{-5}	4.3×10^{-5}	4.57×10^{-5}	4.01	22
	LiF	1115	211.9	-	4.25×10^{-6}	5.1×10^{-5}	-	12.00	23
	NaF	1261	259.5	16.1	3.94×10^{-6}	-	3.31×10^{-5}	8.41	-
TRIGONAL	Sn	505	105.1	3.4	1.63×10^{-5}	5.31×10^{-6}	7.08×10^{-6}	0.33	24
	Bi	544	129.8	-3.2	2.13×10^{-5}	-	-7.64×10^{-6}	-0.36	-
	Sb	904	201	-0.57	1.82×10^{-5}	-	-1.27×10^{-6}	-0.07	-
DIAMOND CUBIC	Ge	1211	324.5	-3.8	1.36×10^{-5}	-	-1.02×10^{-5}	-0.75	-
	Si	1683	496	-5.8	1.21×10^{-5}	-	-1.71×10^{-5}	-1.42	-
HEXAGONAL	H_2O	273	59.7	-7.4	1.31×10^{-5}	-1.08×10^{-5}	-1.61×10^{-5}	-0.83	25
CUBIC	P	317	-	-	6.81×10^{-5}	3.0×10^{-5}	-	0.44	26
TETRAGONAL	In	430	78.3	5.2	1.57×10^{-5}	1.20×10^{-5}	9.47×10^{-6}	0.76	27
HEXAGONAL	Graphite	4100	681.7	9.5	1.59×10^{-5}	-	1.58×10^{-5}	0.99	-
OLIVINE	$2\text{MgO} \cdot \text{SiO}_2$	2171	565.2	4.8	4.38×10^{-5}	1.34×10^{-5}	1.25×10^{-5}	0.31	28

(N.B. () indicates conductivity experiment).

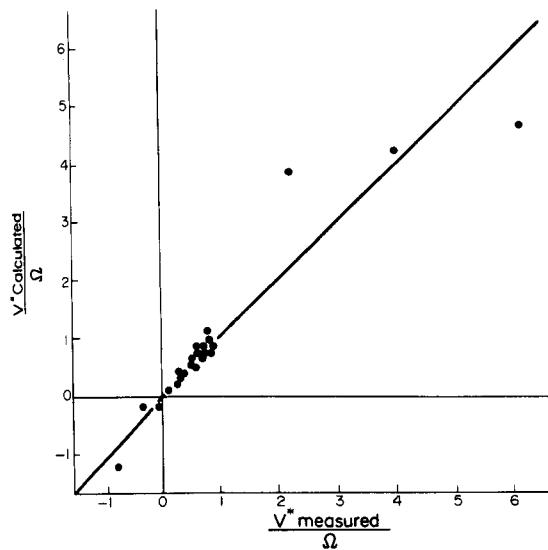


Fig. 3. Comparison of activation volumes as determined by experiment and activation volumes calculated by equation 9. Activation volumes for ionic conduction (faster species) have not been used.

where

$$Q_b = Q_b^0 + pV_b^* \quad (14)$$

and δ is the boundary thickness. Then at the melting point,

$$(\delta D_b)_{T_M} = \delta D_{ob} \exp - \left(\frac{Q_b^0 + pV_b^*}{RT_M} \right) \quad (15)$$

Table 4 lists data for δD_{ob} , Q_b^0 and the melting-point diffusivity, $(\delta D_b)_{T_M}$, which we take to be constant for a solid with a given crystal structure and bond type.

4.2 The activation energy for boundary diffusion at atmospheric pressure

The pre-exponential for boundary diffusion (δD_{ob}), like that for lattice diffusion, is expected to be independent of T and p . It follows that

$$\frac{Q_b^0}{RT_M^0} = B_b \quad (16)$$

where B_b is a constant. Values of Q_b^0 and Q_b^0/RT_M^0 are

Table 4

Class	Material	T_M^0 K	δD_{ob} m^3/sec	Q_b^0 kJ/mole	$\frac{Q_b^0}{R \cdot T_M^0}$	$\frac{Q_b^0}{Q^0}$	$(\delta D_b)_{T_M}$ m^3/sec	V^{*b} calculated $m^3/mole$	Ref.
METAL CARBIDES	SiC	2973	7.0×10^{-14}	305.7	12.37	0.58	2.96×10^{-19}	-	1
B.C.C. (1) RARE EARTH METALS	γ -U	1405	1.0×10^{-11}	178.8	15.31	-	2.23×10^{-18}	-	2
B.C.C. (3) TRANSITION METALS	Cr	2130	-	192.6	10.88	0.63	-	-	3
	W	3683	3.35×10^{-13}	385.2	12.59	0.60	1.16×10^{-18}	-	4
	MEANS	-	3.35×10^{-13}	-	11.74	-	1.16×10^{-18}	-	-
	-	-	-	-	± 1.21	-	-	-	-
H.C.P. METALS	Cd	594	5.0×10^{-14}	54.4	11.03	0.63	8.13×10^{-19}	5.86×10^{-6}	5
	Zn	692	1.5×10^{-14}	60.7	10.56	0.63	3.90×10^{-19}	4.74×10^{-6}	6
	MEANS	-	2.74×10^{-14}	-	10.80	-	5.63×10^{-19}	-	-
	-	$\frac{x}{2} 2.34$	-	-	± 0.33	-	$\frac{x}{2} 1.68$	-	-
F.C.C. METALS	Pb	601	8.1×10^{-14}	65.7	13.16	0.60	1.57×10^{-19}	8.53×10^{-6}	7
	Ag	1234	8.55×10^{-16}	74.5	7.27	0.40	5.98×10^{-19}	3.14×10^{-6}	8
	Au	1336	1.9×10^{-16}	111.7	10.06	0.63	8.11×10^{-21}	-	9
	Cu	1356	-	108.9	9.64	0.54	-	3.37×10^{-6}	10
	Ni	1726	3.5×10^{-15}	114.7	8.00	0.41	1.18×10^{-18}	2.79×10^{-6}	11
	β -Co	1768	2.0×10^{-13}	163.3	11.12	0.58	2.98×10^{-18}	-	12
	γ -Fe	1805	7.7×10^{-14}	159.1	10.61	0.56	1.91×10^{-18}	3.35×10^{-6}	13
	MEANS	-	9.44×10^{-15}	-	9.98	-	4.15×10^{-19}	-	-
	-	$\frac{x}{2} 17.13$	-	-	± 1.97	-	$\frac{x}{2} 8.89$	-	-
OXIDES	MgO	3125	-	439.6	16.93	0.69	-	-	14
	UC ₂	3151	7.05×10^{-16}	339.2	12.95	-	1.67×10^{-21}	-	15
	ThO ₂	3323	3.15×10^{-14}	393.6	14.25	0.63	2.03×10^{-20}	-	16
	MEANS	-	4.71×10^{-15}	-	14.71	-	5.8×10^{-21}	-	-
	-	$\frac{x}{2} 14.68$	-	-	± 2.03	-	$\frac{x}{2} 5.85$	-	-
TRIGONAL	Sn	505	3.0×10^{-15}	40.0	9.53	0.38	2.18×10^{-19}	2.69×10^{-6}	17
	Sb	904	2.5×10^{-13}	94.2	12.54	0.47	8.96×10^{-19}	-5.94×10^{-7}	18
	MEANS	-	2.74×10^{-14}	-	11.04	-	4.41×10^{-19}	-	-
	-	$\frac{x}{2} 22.82$	-	-	± 2.13	-	$\frac{x}{2} 2.72$	-	-

Table 5. Archetypal diffusion equations

CLASS OF SOLID	LATTICE DIFFUSION COEFFICIENT m^2/s	BOUNDARY DIFFUSION COEFFICIENT m^3/s
METAL CARBIDES	$D = 0.2 \exp - \{24.0 \frac{T_M^0}{T} C\}$	$\delta D_b = 7 \times 10^{-14} \exp - \{12.4 \frac{T_M^0}{T} C\}$
B.C.C. (1) RARE EARTHS	$D = 1.5 \times 10^{-6} \exp - \{9.3 \frac{T_M^0}{T} C\}$	$\delta D_b = 1 \times 10^{-11} \exp - \{15.3 \frac{T_M^0}{T} C\}$
B.C.C. (2) ALKALI METALS	$D = 2.5 \times 10^{-5} \exp - \{14.7 \frac{T_M^0}{T} C\}$	-
B.C.C. (3) TRANSITION METALS	$D = 1.6 \times 10^{-4} \exp - \{17.8 \frac{T_M^0}{T} C\}$	$\delta D_b = 3.4 \times 10^{-13} \exp - \{11.7 \frac{T_M^0}{T} C\}$
H.C.P. METALS	$D = 4.9 \times 10^{-5} \exp - \{17.3 \frac{T_M^0}{T} C\}$	$\delta D_b = 2.7 \times 10^{-14} \exp - \{10.8 \frac{T_M^0}{T} C\}$
F.C.C. METALS	$D = 5.4 \times 10^{-5} \exp - \{18.4 \frac{T_M^0}{T} C\}$	$\delta D_b = 9.4 \times 10^{-15} \exp - \{10.0 \frac{T_M^0}{T} C\}$
HEXAGONAL (GRAPHITE)	$D = 2.4 \times 10^{-4} \exp - \{20.0 \frac{T_M^0}{T} C\}$	-
ALKALI HALIDES	$D = 2.8 \times 10^{-3} \exp - \{22.8 \frac{T_M^0}{T} C\}$	-
TETRAGONAL (In)	$D = 3.2 \times 10^{-4} \exp - \{21.9 \frac{T_M^0}{T} C\}$	-
SIMPLE OXIDES	$D = 5.3 \times 10^{-4} \exp - \{23.4 \frac{T_M^0}{T} C\}$	$\delta D_b = 4.7 \times 10^{-15} \exp - \{14.7 \frac{T_M^0}{T} C\}$
SILICATES (OLIVINE)	$D = 3.0 \exp - \{31.3 \frac{T_M^0}{T} C\}$	-
TRIGONAL ELEMENTS	$D = 5.8 \times 10^{-3} \exp - \{26.8 \frac{T_M^0}{T} C\}$	$\delta D_b = 2.7 \times 10^{-14} \exp - \{11.0 \frac{T_M^0}{T} C\}$
ICE	$D = 1 \times 10^{-3} \exp - \{26.3 \frac{T_M^0}{T} C\}$	-
DIAMOND CUBIC ELEMENTS	$D = 6.3 \times 10^{-2} \exp - \{33.9 \frac{T_M^0}{T} C\}$	-

D = Lattice-diffusion coefficient ($m^2.s^{-1}$)
 δD_b = Boundary diffusion coefficient times thickness ($m^3.s^{-1}$)
T = Absolute temperature at atmospheric pressure (K)
 T_M^0 = Melting temperature at atmospheric pressure (K)
C = $1 + \frac{P}{T_M^0} \left(\frac{dT_M^0}{dp} \right)$
P = Pressure (N.m⁻²)
 $\left(\frac{dT_M^0}{dp} \right)$ = Pressure dependence of the melting temperature (K.N⁻¹.m²)

listed in Table 4, which also shows the ratio

$$\frac{B_b}{B} = \frac{Q_b^0}{Q^0} \quad (17)$$

4.3 The activation volume for boundary diffusion

If the rate of boundary diffusion at the melting point is independent of pressure, then, following the reasoning of Section 2.3,

$$V_b^* = \frac{Q_b^0}{T_M^0} \left(\frac{dT_M^0}{dp} \right)^0 \quad (18)$$

where (as before) the superscript (0) means at atmos-

pheric pressure. No experimental data for V_b^* are available. Values calculated from equation (18) are listed in Table 4; they are smaller than those for lattice diffusion (because Q_b^0 is smaller).

Physically, this can be understood as follows. Removing an atom from within a crystal and placing it (on a ledge) on the free surface initially increases the volume of the crystal by one atomic volume; subsequent local relaxation at the vacancy result in an elastic field which extends to the surface of the crystal and results in a further volume change, usually a shrinkage. Removing an atom from a grain-boundary does the same thing; but the possible relaxations are

more numerous; and the subsequent volume decrease is greater than before: so the volume of formation of a boundary vacancy is smaller than that of a lattice vacancy. Further, when a diffusive jump occurs in the boundary plane, the excess volume which is permanently associated with the boundary should make the jump possible with less local dilation than that required within the crystal; so the volume of motion of a boundary vacancy, too, should be smaller than that of a lattice vacancy.

5. CONCLUSIONS

5.1 The melting point diffusivity, D_{T_M}

Our survey confirms earlier studies which concluded that

$$D_{T_M} = A$$

where A is a constant, independent of pressure. The results are listed in Table 1 and shown in Fig. 1. Based on this, we anticipate that, for boundary diffusion,

$$(\delta D_b)_{T_M} = A_b$$

is a constant. Data are assembled in Table 4. Values of A_b spread less than values of A between classes of material, probably because grain boundaries in solids differ less in atom-packing density than crystals do.

5.2 The activation energy, Q^0

We have assembled data for the quantities

$$\frac{Q^0}{RT_M^0} = B$$

and

$$\frac{Q_b^0}{RT_M^0} = B_b$$

and find (as others have done) that the quantities B and B_b are constants for solids of a given crystal structure and body type. The data are listed in Tables 1 and 4, and shown in Fig. 2.

5.3 The activation volume, V^*

We find that the activation volume, V^* , is well described by

$$V^* = \frac{Q^0}{T_M^0} \left(\frac{dT_M}{dp} \right)^0$$

Data are given in Table 3 and plotted in Fig. 3. We anticipate that, for boundary diffusion,

$$V_b^* = \frac{Q_b^0}{T_M^0} \left(\frac{dT_M}{dp} \right)^0$$

Data are listed in Table 4.

5.4 Archetypal diffusion equations

Combining equations (1) and (9) gives

$$D = D_0 \exp - \frac{Q^0}{RT} \left[1 + \frac{p}{T_M^0} \left(\frac{dT_M}{dP} \right)^0 \right]$$

The data survey has shown that, for solids of a given crystal structure and bond type, $D_{T_M} = A$ and $Q^0/RT_M^0 = B$, where A and B are constants, we may therefore define an archetypal diffusion equation for each class of solid:

$$D = \frac{D_{T_M}}{\exp - (B)} \exp - \left[B \frac{T_M^0}{T} \left(1 + \frac{p}{T_M^0} \left(\frac{dT_M}{dp} \right)^0 \right) \right]$$

Table 5 lists archetypal diffusion equations for each of the classes of solid we have studied. The uncertainty involved in their use can be calculated from the standard deviations listed in the Tables.

5.5 Use of these correlations

The obvious value of correlations such as these is that they allow diffusion rates to be estimated for solids for which little or no data are available, and that they suggest a close relationship between the process of diffusion and that of melting. They should be used with a clear appreciation of the possible errors involved (given in the Tables); but in some instances this is small, and as more data becomes available a more detailed classification of solids, and more precise equations, should become available.

It is common practice to plot data for the mechanical behaviour of materials against the homologous temperature T/T_M . This paper shows that, when diffusion controls the mechanical behaviour, this procedure is a proper way of comparing the strength of members of a given class of pure solid. For alloys, T/T_s should be used (where T_s is the solidus temperature).

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