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Louis E. Toth and Alan W. Searcy

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ABSTRACT

A modification of Le Claire's microscopic model for self-diffusion is developed in a form suitable for prediction of activation energies for diffusion in disordered substitutional solutions as well as in pure metals. Bonding is considered as a localized interaction, and the energy of bonding between atoms of different types is taken as the arithmetic mean of the energies in the pure elements. The activation energies for vacancy formation and migration in substitutional alloys are shown to depend on the empirical constants developed for self-diffusion when the equations are adjusted for the mole fractions of the two elements. The calculated results for alloy diffusion usually agree with the experimental values to within the experimental errors.

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INTRODUCTION

Many different correlations have been proposed for use in predicting activation energies for self-diffusion or diffusion in dilute alloys. Usually theories for self-diffusion cannot be applied to alloys nor can theories for dilute alloys be satisfactorily adapted to self-diffusion. We present here a correlation scheme which can approximate activation energies for diffusion, vacancy formation, and atom migration in substitutional-alloy systems of any concentration.

The activation energy for self-diffusion Q_D has been correlated to the melting temperature T_m ,^{1,2} the sublimation energy L_s ,¹ the heat of fusion L_f ,³ and valence.⁴ Working with mechanical parameters Le Claire⁵ proposed that the activation energy for vacancy migration Q_m could be related to appropriate shear moduli. He also proposed that the activation energy for vacancy formation Q_v is proportional to L_s .

THEORY

We consider that Le Claire's expression for Q_v is satisfactory. But an alternate expression for Q_m in terms of the bulk modulus is just as satisfactory from a theoretical point of view for the prediction of the energy of vacancy migration in pure metals and can more easily be used for alloys.

In order for Q_m to be a minimum, not only the moving atom but also adjacent and nearby atoms must undergo distortions. These distortions

are neither isotropic as is implied by a correlation with the bulk modulus nor unidirectional as implied by a correlation with a shear modulus, but are complex and multidirectional. A complete analysis in terms of the bulk modulus and all the shear moduli is not yet available. In a first approximation in which only one parameter is used, there is no obvious theoretical reason to prefer the shear modulus over the bulk modulus.

The bulk modulus is a much more convenient parameter for use in predicting Q_m . Shear moduli are known for less than half of metallic elements while bulk moduli are usually available. Furthermore, because of the directional dependence of shear moduli, their estimation for alloys appears inherently more difficult than is the estimation of bulk moduli.

We assume that the bulk modulus B_s reflects an average value of the shear moduli such that the strain energy at the point of maximum distortion of the lattice during vacancy migration can be expressed as

$$Q_m = cB_s V_0 \sum_{ij} e_{ij}^2$$

Here V_0 is the atomic volume, c is a proportionality constant, and e_{ij} is a strain component. The summation is taken over all atoms involved in the diffusion process. Since in this approximation e_{ij} depends only on crystal structure, we can replace this expression by

$$Q_m = k_2 B_s V_0, \quad (1)$$

where k_2 is a proportionality constant dependent only on crystal structure.

Many of the correlations^{1,2,3} of the activation energy for vacancy movement with thermodynamic parameters can be related to this physical

model since Leibfried⁶ has shown that the product $B_s V_o$ is proportional to T_m , while, by Richards' rule, $L_f = 2.3 T_m$ for metals where L_f is the heat of fusion in cal/g atom. No matter whether $B_s V_o$, T_m , or L_f is correlated with Q_m , the physical interpretation given to the diffusion process can remain independent of the choice. We will verify the proportionality by calculating Q_D both from an equation that uses B_s as a parameter and from one that uses T_m as a parameter.

The expressions for Q_D are

$$Q_D = k_2 B_s V_o + k_1 L_s \quad (2)$$

and

$$Q_D = k_2' T_m + k_1 L_s \quad (3)$$

When possible, average values of k_1 , k_2 , and k_2' were determined from experimental values of Q_v and Q_m . The best available experimental values are listed in Table I. From the ratio of the experimental value of Q_v/L_s , a mean value of 0.27 is found for (fcc) and (hcp) elements treated as one class; and the same value is found for the (bcc) elements treated as a separate class. Similarly, a mean value of 16.0 for k_2' in fcc elements is found. Average experimental values of the ratios of $\frac{Q_D - 0.27 L_s}{B_s V_o}$ and $\frac{Q_D - 0.27 L_s}{T_m}$ were used for the values of k_2 and k_2' in crystal structure classes where the experimental data for Q_m are insufficient to determine k_2 and k_2' .

The equations for Q_D are

$$\text{fcc (hcp)} \quad Q_D = 22.6 B_s V_o + 0.27 L_s \quad (4a)$$

$$\text{bcc} \quad Q_D = 23.8 B_s V_o + 0.27 L_s \quad (4b)$$

$$\text{fcc (hcp)} \quad Q_D = 16.0 T_m + 0.27 L_s \quad (5a)$$

$$\text{bcc} \quad Q_D = 14.7 T_m + 0.27 L_s \quad (5b)$$

Here V_0 , the atomic volume is expressed in units cm^3/mole and B_s in $\text{kg}/\text{cm}^2 \times 10^{-7}$. The ratio of k_2'/k_2 in fcc metals is slightly larger than the one Leibfried found.

Table I compares the experimental data for Q_m and Q_v with those calculated. Figures 1 and 2 compare the values of Q_D calculated from Eqs. (4) and (5), respectively, with the most reliable experimental values available. Values for zirconium, for which the diffusion mechanism may be other than a vacancy exchange,⁷ have not been included.

ALLOYS

Previous work in this area has been largely restricted to predicting Q_D for diffusion in dilute solutions. The parameters that have been used are the difference in valence,⁸ the shear moduli of the solvent and the bulk modulus of the solute,⁹ and the partial heat of mixing.¹⁰ To extend the self-diffusion equations for application to alloy diffusion, we consider bonding as a localized interaction between nearest neighbor atoms.

For an alloy in which X_A and X_B are the mole fractions of A and B atoms, respectively, and Z is the coordination number of any atom, the number of A-A bonds for the average A atom will be ZX_A , and the number of A-B bonds will be ZX_B . Similarly the number of B-B bonds for the average B atom will be ZX_B and the number of A-B bonds, ZX_A . The assumption is made here that the number of vacancies in the solution resulting from removing A atoms from the interior of the crystal and placing them on the surface is proportional to X_A and likewise, that the number of vacancies due to removal of B atoms is proportional to X_B . Taking the bond energies as proportional to the sublimation energy L_s , we find that the total energy for vacancy formation is proportional to

$$X_A (Z X_A L_s^A + Z X_B L_s^{AB}) + X_B (Z X_B L_s^B + Z X_A L_s^{AB}),$$

where L_s^{AB} is the arithmetic mean of L_s^A and L_s^B . Using the same proportionality constant that we used for vacancy formation in self-diffusion, 0.27, we find

$$Q_v = 0.27 (X_A^2 L_s^A + 2 X_A X_B L_s^{AB} + X_B^2 L_s^B). \quad (6)$$

When an A atom exchanges places with a vacancy, the number of A-A bonds distorted is $X_A(Z-1)$ and the number of A-B bonds distorted is $X_B(Z-1)$. By analogy with our discussion of self-diffusion, we may correlate the distortion in the A-A bonds during movement with $(B_s V_o)_A$ or equivalently with T_m^A and the distortion of A-B bonds with $(B_s V_o)_{AB}$ or T_m^{AB} , the arithmetic mean of these quantities for the pure metals A and B. The activation energy for vacancy migration in fcc metals can then be expressed for A as

$$Q_m^A = 22.6 (X_A (B_s V_o)_A + X_B (B_s V_o)_{AB}) \quad (7a)$$

or

$$Q_m^A = 16.0 (X_A T_m^A + X_B T_m^{AB}), \quad (7b)$$

where the constants are the same as were used in the self-diffusion equations. Analogous equations, of course, describe Q_m^B . The activation energy for diffusion of A is the sum of Q_v and Q_m^A .

In the above equations the compressibility and the melting temperatures were used as parameters. But whenever experimental values for Q_m^A , Q_m^B , Q_v^A , and Q_v^B in the pure metals are available, these values should be utilized in preference to the other parameters. In addition, Q_m^{AB} and Q_v^{AB} should be corrected for deviations from ideality when heats of mixing

are known. Since experimental values for Q_m and Q_v are generally not yet available, we shall calculate all values exclusively from the compressibility and melting temperature data.

In Table II we apply Eqs. (6) and (7) to a large number of concentrated alloy systems in which the activation energies have been determined experimentally. In these concentrated alloy systems correlation effects have been neglected. We also express the results in the form $\Delta Q_D^A = Q_D^A - Q_D^{A \text{ pure}}$, where $Q_D^{A \text{ pure}}$ refers to the calculated diffusion heat for pure A. This form is used because we are mainly interested in the effect of solution formation on the diffusion rates and some errors in the calculation of $Q_D^{A \text{ pure}}$ would not be reflected in ΔQ_D^A .

We also have calculated $\Delta Q_D^{\text{impurity}}$ for dilute solutions of metals in Ag, Cu, Au, Ni, and Fe. We used the correlation factor proposed by Le Claire¹¹ and we evaluated the parameters in it with the aid of local bonding considerations of the form shown above. In Table III we show the results of impurities in Ag. The experimental data are taken from Shewmon.¹² More complete results may be found elsewhere.¹³

DISCUSSION

For most of the substitutional alloys for which we have data the activation energies for diffusion are predicted to within the probable errors in the experimental determination. In view of the assumptions made, that solutions are ideal and that the bond strengths are an average, the excellent quantitative agreement is somewhat surprising. Agreement should not be expected when the solutions deviate from ideality, as when ordering occurs.

The generally consistent agreement between the values calculated with the parameter $B_s V_0$ and those calculated with T_m support the Leibfried relation in pure metals and alloys. Only for Au and Pt do the two approaches yield significantly different values. For these two metals, the use of the parameter $B_s V_0$ gives poor agreement with experiment while the parameter T_m gives good agreement.

Among other correlations, the methods of Sherby and Simnad⁴ and Le Claire⁵ yield as good agreement for self-diffusion as does the present approach. Both correlations have several restrictions, however, that the present approach avoids. Our method uses only parameters that have been determined experimentally for nearly all metals. The shear moduli, used by Le Claire, have been determined for less than half of the known elements, and valence, used by Sherby and Simnad, is an arbitrary parameter when applied to metals. The approaches of Le Claire and of Sherby and Simnad do not appear to be readily adapted to prediction of activation energies in alloys; the approaches outlined in this paper not only permit prediction of good first approximations to the activation energies for diffusion in substitutional alloys, but also permit prediction of activation energies for vacancy formation and for atom movements both for pure metals and for substitutional alloys. The method may serve as a useful guide to prediction of the results of diffusion experiments and to the development of more sophisticated theories.

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Table I. Comparison of experimental and calculated values
of Q_v and Q_m (all values in kcal)

Element	Q_v experimental	Q_v 0.27 L_S	Q_m experimental	Q_m 16.0 T_m
Li	9.3 ^{a, b}	9.6		
Na	9.1 ^b 6.0 ^c 4.6 ^d	6.5		
K	9.1 ^b 9.0 ^a 5.5 ^c	5.4		
Al	17.5 ^e	19.4	15.0 ^f	14.9
Cu	21.9 ^g	20.2	24.9 ^h	21.7
Ag	24.4 ⁱ 25.1 ^j	17.1	20.3 ^h	19.7
Au	23.5 ^k	21.8	19.1 ^h	21.4
Pt	32.6 ^l	33.3	31.2 ^l	32.7

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Table II. Comparison of theoretical and experimental values for ΔQ in alloy systems of varied composition (all energies in units kcal/mole)

At.% solvent	At.% solute	Ref.	Tracer	ΔQ calc. with $B_S V_0$	ΔQ calc. with T_m	ΔQ exptl.
90.5 Ag	9.5 Al	a	Ag ¹¹⁰	- 0.3	- 0.5	- 1.2
93.5 Ag	6.5 Cd	b	Ag ¹¹⁰	- 1.4	- 1.1	- 1.5
			Cd ¹¹⁵	- 6.1	- 6.2	- 3.6
72.0 Ag	28.0 Cd	b	Ag ¹¹⁰	- 4.9	- 4.6	- 6.8
			Cd ¹¹⁵	-10.0	- 9.7	- 8.2
98.2 Ag	1.8 Cu	a	Ag ¹¹⁰	- 0.3	+ 0.1	+ 0.7
98.5 Ag	1.5 Ge	a	Ag ¹¹⁰	- 0.1	+ 0.2	- 0.1
95.6 Ag	4.4 In	b	Ag ¹¹⁰	- 1.4	- 0.4	- 1.5
			In ¹¹⁴	- 5.1	- 6.9	- 3.8
83.3 Ag	16.7 In	b	Ag ¹¹⁰	- 1.5	- 1.2	- 7.9
			In ¹¹⁴	- 6.0	- 8.0	- 7.5
99.3 Ag	0.7 Pb	a	Ag ¹¹⁰	- 0.3	0.0	+ 0.6
99.5 Ag	0.5 Pb	a	Pb ²¹⁰	- 3.3	- 5.1	- 5.4
90.2 Ag	9.8 Pd	c	Ag ¹¹⁰	+ 1.1	+ 1.1	- 0.4
99.1 Ag	0.9 Sb	d	Ag ¹¹⁰	- 0.4	0.0	- 1.6
			Sb ¹²⁴	- 4.3	- 4.3	- 5.8
70.0 Ag	30.0 Zn	e	Ag ¹¹⁰	- 4.8	- 4.3	- 8.1
			Zn ⁶⁵	-10.5	- 8.6	- 8.9
69.0 Cu	31.0 Zn	f	Cu ⁶⁴	- 5.6	- 5.8	- 6.2
			Zn ⁶⁵	-10.6	-10.0	- 7.4

Table II. (Cont.)

At.% solvent	At.% solute	Ref.	Tracer	ΔQ calc. with $B_s V_0$	ΔQ calc. with T_m	exptl.
52.0 Cu	48.0 Zn	g	Cu ⁶⁴	- 8.8	- 8.9	{ -26.1* -11.1 -12.1
			Zn ⁶⁵	-13.7	-13.3	
50.0 Au	50.0 Cd	h	Au	-14.2	-10.5	-13.8
			Cd	-20.9	-16.8	-13.7

*The activation energy is strongly dependent upon the amount of ordering.

The values 26.1 and 29.3 refer to complete disordering.

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Table III. Comparison of experimental and calculated values of ΔQ_D^{imp} for dilute solutes in Ag (all energies in units kcal/mole)

Dilute solutes in Ag $Q_D^{\text{Ag}} = 44.1 \pm 2$ $D_o = 0.44$			
Impurity	ΔQ_D^{imp} (experimental)	ΔQ_D^{imp} (bulk modulus)	ΔQ_D^{imp} (melting temp)
Pb	- 6.0	- 2.1	- 2.8
Sb	- 5.8	- 2.9	- 2.2
Sn	- 4.8	- 1.5	- 3.2
In	- 3.5	- 2.2	- 2.7
Zn	- 2.4	- 2.2	- 2.1
Hg	- 6.0	- 5.1	- 5.6
Cd	- 2.4	- 2.3	- 2.3
Te	- 4.2	- 4.4	- 3.5
Cu	+ 2.0	- 0.6	+ 1.0
Au	+ 1.4	+ 8.0	+ 0.8
Ru	+21.7	+13.6	+11.7

The experimental errors are approximately ± 2 kcal.

FIGURE LEGEND

Fig. 1 -- Values of $Q_D = k_2 V_0 B_s + k_1 L_s$ are plotted against the experimental values of Q_D .

Fig. 2 -- Values of $Q_D = k_2 T_m + k_1 L_s$ are plotted against the experimental values of Q_D .

Fig. 1

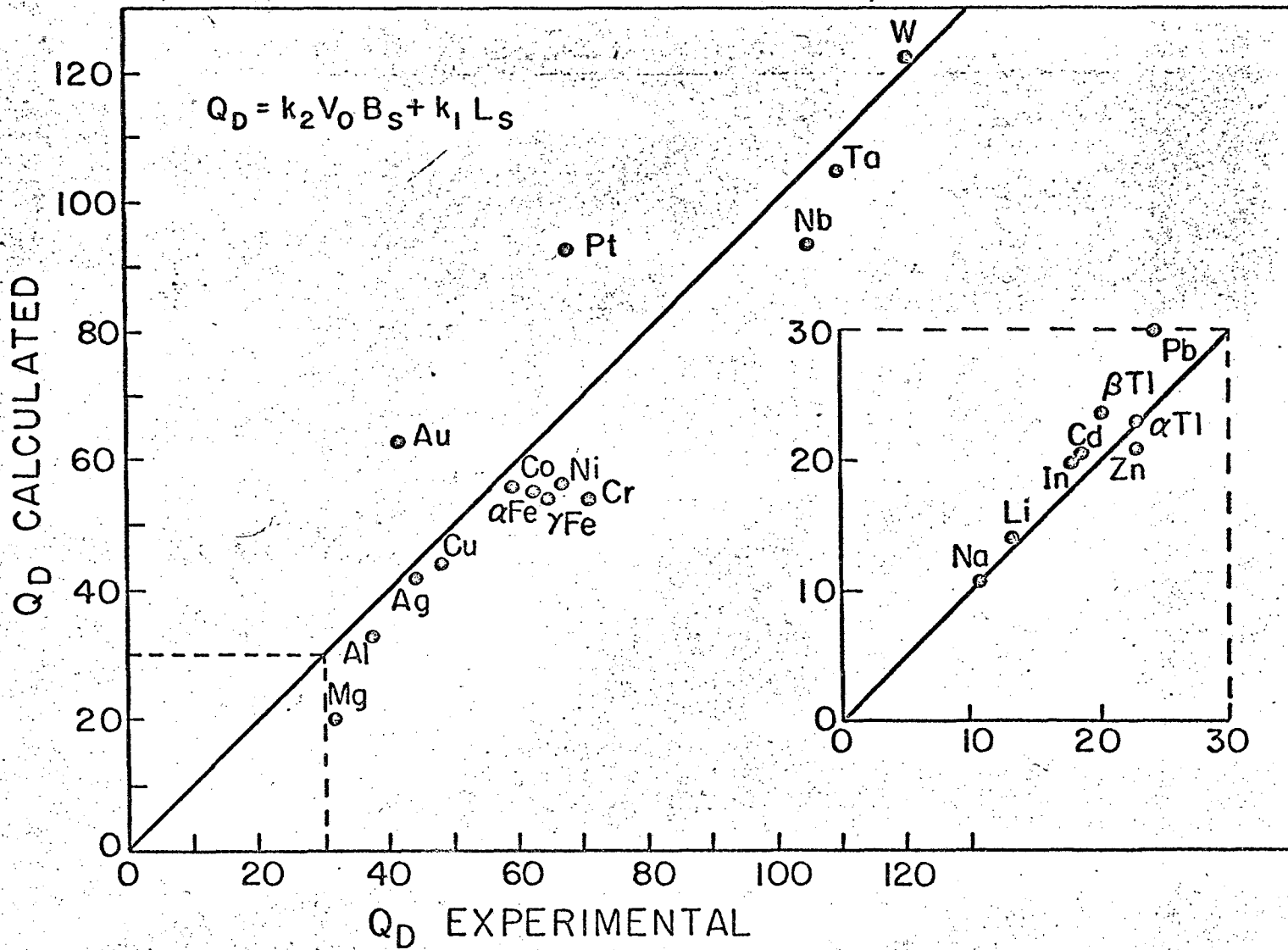


Fig. 1

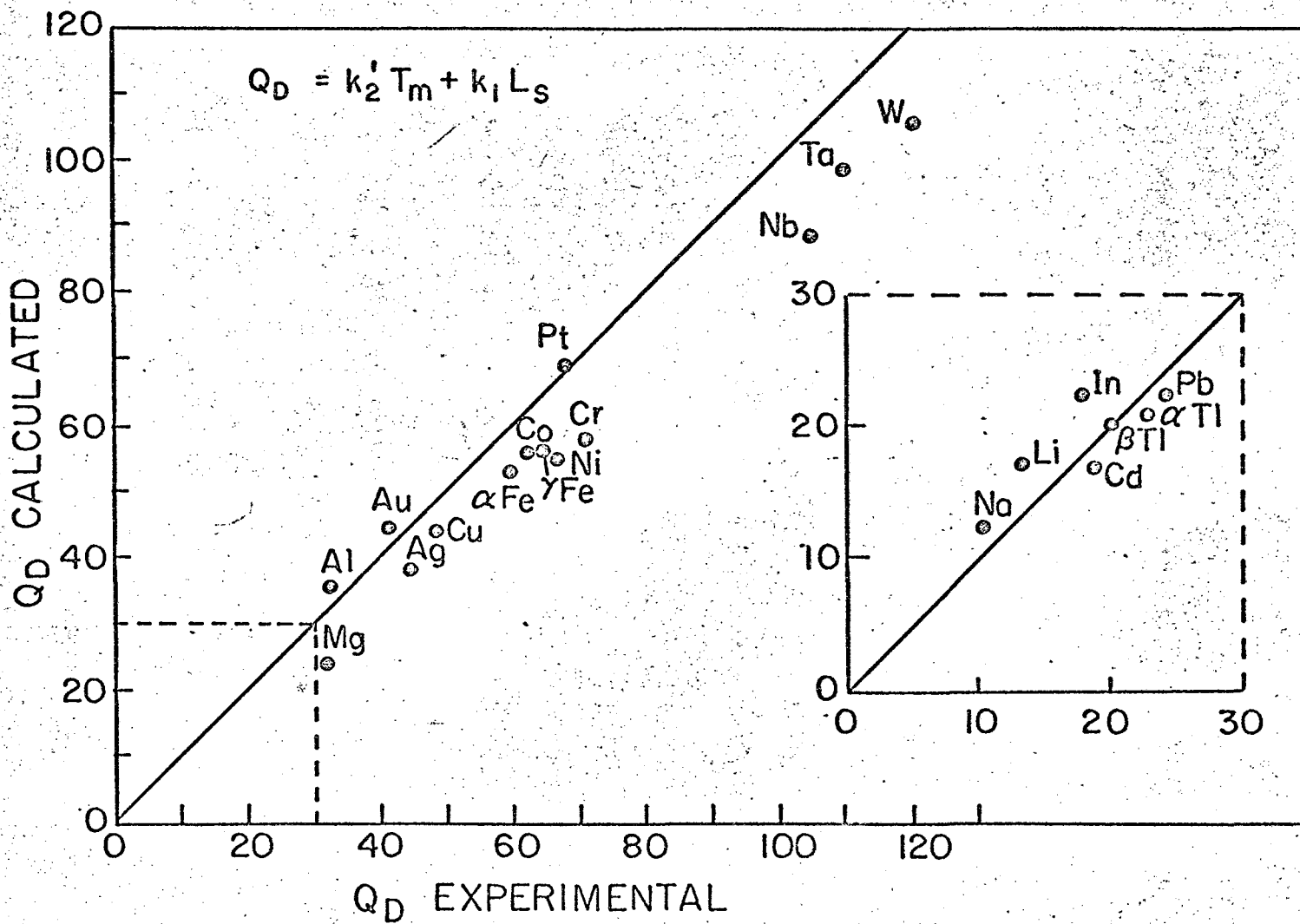


Fig. 2

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