

Notes

Estimation of Three-Body Recombination Rate Constants*

BENJAMIN J. WOZNICK AND JAMES C. KECK

Avco-Everett Research Laboratory, Everett, Massachusetts 02149

(Received 14 October 1963)

IT is the purpose of this note to provide curves (Fig. 1) displaying the value of the function, $\phi = \frac{1}{4}[F_p + F_l]$, that appears in the basic rate equation [Formula (45)] of Ref. 1. This equation gives the recombination rate constant as

$$k = (g_{12}/g_1g_2)8\pi(2\pi\mu_{12}kT)^{1/2}(z_2 - z_1)z_2^2[1 - \exp(-B_M/kT)] \\ \times \{M_1^{-1}\{a_{1-}^2\phi(\beta r_e, \beta z_2, \beta a_{1-}) \exp(\epsilon_1/kT) \\ + a_{1+}^2\phi(\beta r_e, \beta z_2, \beta a_{1+}) [\exp(\epsilon_1/kT) - 1]\} \\ + M_2^{-1}\{a_{2-}^2\phi(\beta r_e, \beta z_2, \beta a_{2-}) \exp(\epsilon_2/kT) \\ + a_{2+}^2\phi(\beta r_e, \beta z_2, \beta a_{2+}) (\exp[\epsilon_2/kT] - 1)\}\}, \quad (1)$$

where the notation is that of Ref. 1.

Equation (1) is correct for reactions of the form $A + A + C \rightarrow A_2 + C$, where C is a repulsive catalyst. It may also be used to estimate the rate for slightly unsymmetrical systems, $A + B + C \rightarrow AB + C$, where $M_A \approx M_B$. This approximation should improve as M_A increases, and deteriorate rapidly as $(M_A - M_B)$ becomes larger.

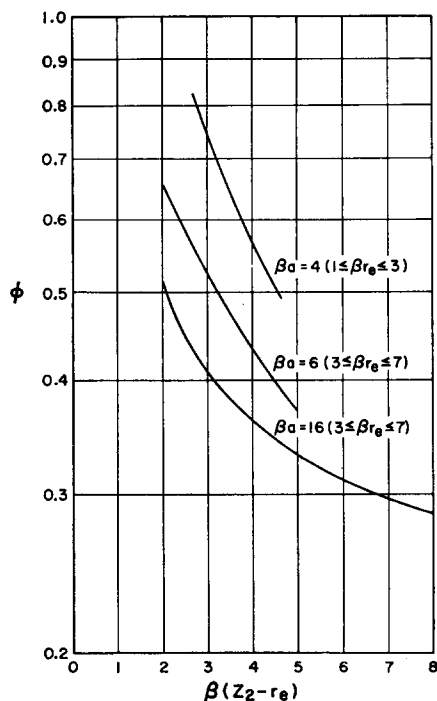


FIG. 1. The function $\phi(\beta r_e, \beta z_2, \beta a)$. The curves are accurate to about 15% for the indicated ranges of parameters.

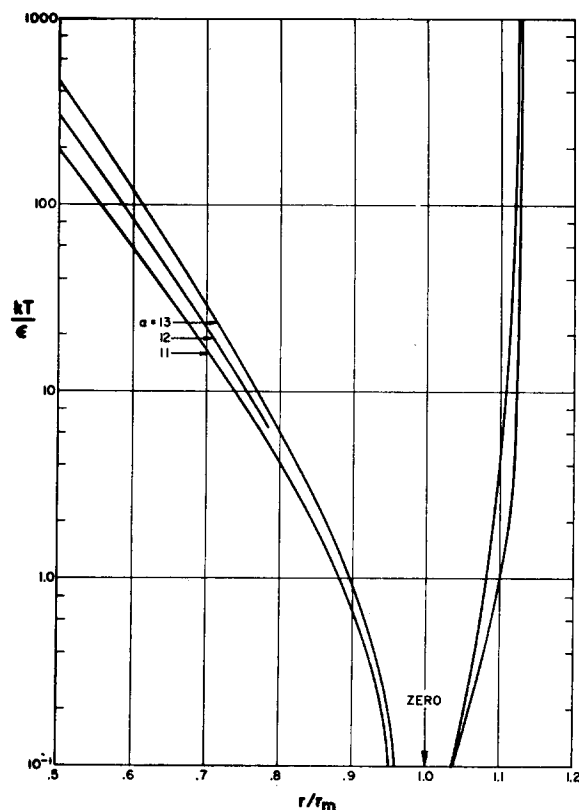


FIG. 2. Curves giving a_+ and a_- as a function of kT/ϵ for the exponential-six potential. The left branches correspond to a_- ; the right branches to a_+ .

We also suggest that the interaction between the catalyst and the recombining atoms be represented by the exponential-six potential,²

$$V(r) = \frac{\epsilon}{1 - (6/\alpha)} \left\{ \frac{6}{\alpha} \exp\left(\alpha \left[\frac{1-r}{r_m} \right]\right) - \left(\frac{r_m}{r}\right)^6 \right\}, \quad (2)$$

where ϵ is the depth of the well, r_m the internuclear separation at the minimum, and α the steepness coefficient. Use of this potential eliminates the necessity

TABLE I. Exponential-six potential parameters.

Atom	r_m (Å)	ϵ/k (°K)	α
He	2.74	9.2	13.2
Ne	3.08	38.0	13.1
Ar	3.76	123.2	11.7
Kr	4.36	158.3	11.9
Xe	4.86	231.2	11.6
N	3.0	25	13.1
O	3.0	30	13.1
Br	4.35	155	11.9
I	4.85	225	11.6

for interpolation between two expressions for a_+ and a_- . Values of a_+ and a_- are given in Fig. 2 for the parameters ϵ , α , and r_m shown in Table I. The rare-gas parameters were obtained by assuming Hirshfelder, Curtiss, and Bird's ϵ , and fitting the small r results of Mason and Vanderslice³ to the present form. The parameters for other atoms were obtained by interpolating on the atomic number.

* This work was supported jointly by Headquarters, Ballistic Systems Division, Air Force Systems Command, U.S. Air Force under Contract No. 04(694)-33, and Advanced Research Projects Agency monitored by the Army Missile Command, U.S. Army under Contract No. DA-19-020-AMC-0210.

¹ J. C. Keck, J. Chem. Phys. **32**, 1035 (1960).

² J. O. Hirshfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

³ E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **28**, 432 (1958).

Magnetic Properties of GdFe₂ and DyFe₂*

M. MANSMANN† AND W. E. WALLACE

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213

(Received 5 September 1963)

RESULTS have recently been presented¹ for the group of cubic Laves phases represented by the formula, LnFe₂, in which Ln is Sm, Tb, Ho, Er, Tm, Lu, or Y. Results were not included for GdFe₂ and DyFe₂ because at the time efforts to obtain these as pure phases had been unsuccessful. These two compounds apparently form peritectically from the melt and exist initially along with other phases. It has now been found that heat treating for seven days at 810±10°C converts the multiphase system into the well-defined LnFe₂ compound.

GdFe₂ and DyFe₂ were prepared using the usual techniques employed in this laboratory.² The iron (from Johnson Matthey) was of 99.95% purity or better and the lanthanide metals (from the Nuclear Corporation of America) had purities of 99.5%. The compound was formed by levitation melting in each case, but with DyFe₂ the component elements were first fused together in an MgO crucible. They were then sealed off *in vacuo* in quartz and heat treated as indicated above. X-ray diffraction showed well-resolved

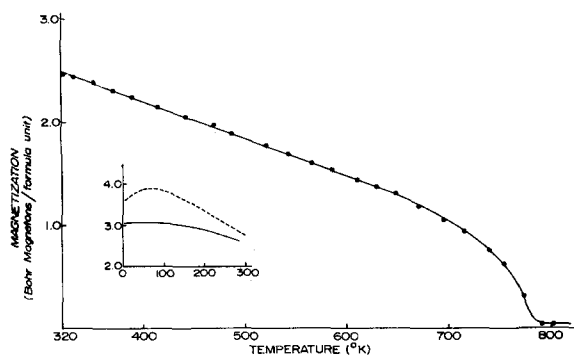


FIG. 1. Magnetization-temperature data for GdFe₂ at 2.2 kOe. Results for DyFe₂, also at 2.2 kOe, are included in the insert (dotted curve).

lines characteristic of only the C15 structure. The lattice spacing found was 7.355 and 7.285±0.004 Å for GdFe₂ and DyFe₂, respectively.

Magnetization-temperature data were obtained over the range 4.2 to 825°K and saturation magnetizations were measured at 4.2°, 77°K, and room temperature (taken to be 300°K), using techniques that have been described.^{2,3} The results obtained are largely summarized in Table I and Fig. 1. The magnetization-temperature behavior of DyFe₂ closely resembles that of GdFe₂ except at temperatures below 80°K. DyFe₂ is considerably harder magnetically than GdFe₂, and hence it is not clear as yet whether its reduced moment below 80°K is an intrinsic property or is merely due to magnetic hardness. The reduction is also suggested by the saturation moments in Table I, and it may be that in this material, as in the Y-Dy alloys recently studied in this laboratory,⁴ the Dy moments tend in the absence of a field toward partial compensation (by a spiral or some such complex structure), and this tendency is countered in part by the applied field.

The magnetization-temperature curve in Fig. 1 shows clearly that in these cases demagnetization does not follow a Brillouin function; instead for most of the temperature range the magnetization decreases almost linearly with temperature. This unusual temperature dependence and the magnitude of the observed moments strongly suggest that DyFe₂ and GdFe₂ are ferri-magnetic materials.

Results for the LnNi₂ series showed the lanthanide moments to be substantially below the free ion values.⁵ Indications are⁵ that this results from partial quenching of the orbital contribution by the crystal field. Bleaney has analyzed⁶ the results of Wallace and Skrabek for LnCo₂ compounds and has concluded that in these appreciable orbital quenching by the crystal field also occurs. Wallace and Skrabek observed¹ that the cobalt moment varied from about zero to 1.3 μ_B in the LnCo₂ compounds and Bleaney has shown⁶ that this moment varies as $(g-1)M_e/g$, where g is the Landé factor and M_e = effective moment of the lanthanide.

TABLE I. Magnetic characteristics of GdFe₂ and DyFe₂.

	Curie point (°K)	Saturation moment (Bohr magnetons/formula unit)		
		4.2°K	77°K	300°K
GdFe ₂	782	3.35	3.29	2.71
DyFe ₂	638	4.91	4.97	3.19