(3), London, 1969) p. 19.
2. R. H. JOHNSON, *Met. Rev.* **15** (1970) 115.
3. G. J. DAVIES, J. W. EDINGTON, C. P. CUTLER and K. A. PADMANABHAN, *J. Mater. Sci.* **5** (1970) 1091.
4. R. B. NICHOLSON, "Electron Microscopy and Structure of Materials", edited by G. Thomas (University of California Press, Berkeley, 1972) p. 689.
5. P. M. HAZZLEDINE and D. E. NEWBURY, "Grain Boundary Structure and Properties", edited by G. A. Chadwick and D. A. Smith (Academic Press, London, 1976) p. 107.
6. J. W. EDINGTON, K. N. MELTON and C. P. CUTLER, *Prog. Mater. Sci.* **21** (1976) 61.
7. K. A. PADMANABHAN, *Mater. Sci. Eng.* **29** (1977) 1.
8. R. K. YADAVA and K. A. PADMANABHAN, *ibid.* **37** (1979) 127.
9. K. A. PADMANABHAN, *ibid.* **40** (1979) 285.
10. G. PADMANABHAN and K. A. PADMANABHAN, *Phil. Mag.* **33** (1976) 371.
11. R. C. GIFKINS and T. G. LANGDON, *Mater. Sci. Eng.* **40** (1979) 293.
12. K. A. PADMANABHAN and G. J. DAVIES, *Phys. Stat. Sol. (a)* **18** (1973) 295.
13. K. A. PADMANABHAN, *ibid.* **22** (1974) K95.
14. P. MAULIK and K. A. PADMANABHAN, *J. Mater. Sci.* **10** (1975) 1646.
15. F. A. MOHAMED and T. G. LANGDON, *Acta Met.* **23** (1975) 117.
16. F. A. MOHAMED, S. SHEI and T. G. LANGDON, *ibid.* **23** (1975) 1443.
17. F. A. MOHAMED and T. G. LANGDON, *Phil. Mag.* **32** (1975) 697.
18. *Idem. Phys. Stat. Sol. (a)* **33** (1976) 375.
19. *Idem, Scripta Met.* **11** (1977) 575.
20. T. G. LANGDON, Proceedings of the Fifth New Zealand Science of Materials Conference, Wellington, 1977 (Department of Scientific and Industrial Research, Lower Hutt, New Zealand, 1977) p. 11.
21. S. SHEI and T. G. LANGDON, *Acta Met.* **26** (1978) 639.
22. *Idem, ibid.* **26** (1978) 1153.
23. A. K. MUKERJEE, J. E. BIRD and J. E. DORN *Trans. ASM* **62** (1969) 155.
24. A. BALL and M. M. HUTCHISON, *Met. Sci. J.* **3** (1969) 1.
25. M. F. ASHBY and R. A. VERRALL, *Acta Met.* **21** (1973) 149.
26. J. H. GITTUS, *J. Eng. Mater. Technol.* **99** (1977) 244.
27. R. B. VATSAVA and T. G. LANGDON, *Acta Met.* **27** (1979) 251.
28. K. A. PADMANABHAN and G. J. DAVIES, "Superplasticity" (Springer Verlag, Berlin, 1980).
29. A. K. MUKHERJEE, *Mater. Sci. Eng.* **8** (1971) 83.
30. T. H. ALDEN, *Acta Met.* **17** (1969) 1435.
31. R. C. GIFKINS and T. G. LANGDON, *Mater. Sci. Eng.* **36** (1978) 27.

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K. A. PADMANABHAN
Department of Metallurgy,
Indian Institute of Technology,
Madras 600036, India

Evaluation of the kinetic parameters in a reaction with a solution of the type $y = A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$

Kinetics of the type

$$y = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \quad (1)$$

are characteristic of many competitive and consecutive reactions [1]. Determination of the parameters of Equation 1 from individual experimental data points requires the solution of a system of transcendental equations which must be more than four generally, because the mean square error should be minimized. As the solution is cumbersome, a mathematical method which employs the experimental curve as a whole and not just discrete points on it, is developed here.

By using the well known integral

$$\int_0^\infty t^n \exp(-t/\tau)\, dt = n!\, \tau^{n+1}, \quad (2)$$

by multiplication of Equation 1 by $t^0 (= 1)$, t^1

TABLE I Fitted parameters using Equations 4 to 7. (The bracketted values of τ_1 and τ_2 are taken from Trieb and Veith [2])

	S (min)	M (min)^2	J (min)^3	T (°C)	A	τ_1 (min)	τ_2 (min)
Cu–15 at % Al	13.9	279.0	13.1	245	0.6	6.3 (6.2)	25.2 (25.3)
Cu–18 at % Al	−11.0	−450.4	−26.4	260	1.58	3.5 (3.7)	28.4 (28)

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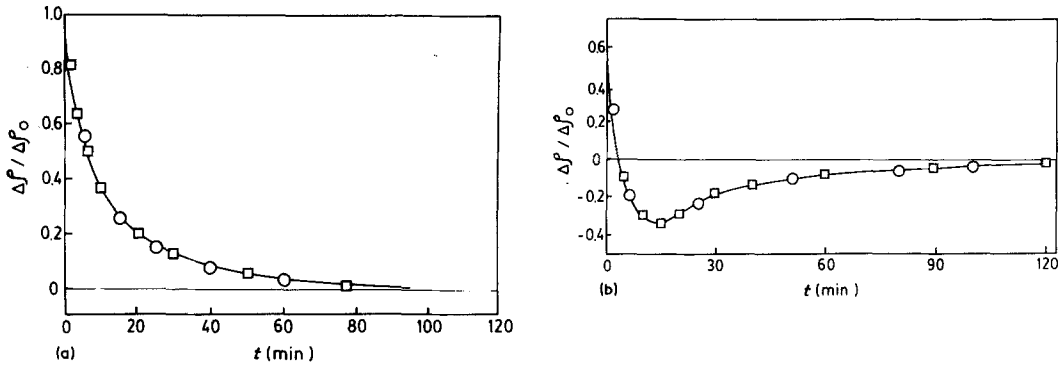

Figure 1 Normalized isotherms of ordering from Trieb and Veith [2]. (a) Cu–15 at % Al, (equilibrated at 250° C, then annealed at 245° C). (b) Cu–18 at % Al, (equilibrated at 270° C, then annealed at 260° C). The squares represent their experimental data, while the circles are some computed values for fitting Equation 1 from the present work.

and t^2, and subsequent integration from zero to infinity, the following system of equations are obtained:

$$\begin{aligned} y_0 &= A + B; \\ S &= A\tau_1 + B\tau_2; \\ M &= A\tau_1^2 + B\tau_2^2; \\ J &= 2A\tau_1^3 + 2B\tau_2^3. \end{aligned} \tag{3}$$

In the first of these equations $y_0 = y(0)$. The values $S = \int_0^\infty y\,dt$, $M = \int_0^\infty t\,y\,dt$ and $J = \int_0^\infty t^2\,y\,dt$, can easily be determined by graphic integration, for instance by weighing the areas of paper enclosed between y and $y = 0$. Eliminating τ_1 from Equation 3 yields

$$\begin{aligned} &\tau_1^4 y_0(S^2 - My_0) + \tau_1^3(MSy_0 - 2S^3 + \tfrac{1}{2}Jy_0^2) \\ &+ 3\tau_1^2 S(MS - \tfrac{1}{2}Jy_0) + \tau_1(\tfrac{1}{2}JMy_0 + JS^2 - 3M^2S) \\ &+ M^3 - \tfrac{1}{2}JMS = 0 \end{aligned} \tag{4}$$

which can be solved either algebraically or numerically. Once τ_1 is determined, the other parameters can be computed from

$$\tau_2 = \frac{M - S\tau_1}{S - y_0\tau_1}, \tag{5}$$

$$A = \frac{S - \tau_2 y_0}{\tau_1 - \tau_2} \tag{6}$$

and

$$B = \frac{S - \tau_1 y_0}{\tau_2 - \tau_1} = (y_0 - A). \tag{7}$$

The above method was successfully applied to the very precise isothermal kinetic curves for short-range ordering in Cu–15 at % Al and Cu–18 at % Al, based on the change in electrical resistivity, obtained by Trieb and Veith [2]. Trieb and Veith showed by computer fitting, that their curves were consistent with Equation 1. The values of S, M and J are shown in Table I for both alloys. Since in their curves the change in electrical resistivity is normalized, $y_0 = 1$, thus $A = (1 - B)$.

Fig. 1a and b show the Trieb and Veith curves [2]. The circles correspond to their experimental data and the squares correspond to verifications by the present method that their kinetics can be described by Equation 1. As can be seen, agreement is excellent. There is also good agreement between the τ_1 and τ_2 values obtained by the present method, which uses the entire kinetic curves, and Trieb and Veith's computer fitting method, which was presumably based on experimental points.

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References

1. R. A. FROST and R. G. PEARSON, "Kinetics and Mechanisms" (John Wiley and Sons, Inc., New York, 1953) pp. 160–99.
2. L. TRIEB and G. VEITH, *Acta Met.* **26** (1978) 185.

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P. KITTL
E. DONOSO
Departamento Ciencia de Los Materiales (IDIEM),
Universidad de Chile,
Facultad de Ciencias Fisicas y Matemáticas,
Casilla 1420, Santiago,
Chile