

DIFFUSION COEFFICIENTS OF Br₂, HNO₃, and PdCl₂ IN GRAPHITE

M. B. Dowell

 Union Carbide Corporation, Carbon Products Division
 Parma Technical Center, Parma, Ohio 44130

Bromine, nitric acid, and palladium dichloride react, at sufficiently high vapor pressures, with graphite to form second-stage C₁₈Br₂⁽¹⁾, second-stage C₄₈+NO₃·3HNO₃⁽²⁾ and third-stage C_{10,7}PdCl₂⁽³⁾. Kinetics of bromination of graphite have been studied in some detail⁽⁴⁻⁵⁾, but rates of intercalation of HNO₃ and PdCl₂ have not yet been studied from the same kinetic point of view. Comparative studies of rates of intercalation might be expected to clarify mechanisms of intercalation and to permit useful generalizations. Nitric acid, palladium chloride, and bromine were chosen for study because they intercalate respectively as a two-dimensional liquid-like layer⁽⁶⁾, a disordered two-dimensional solid, and an ordered solid⁽⁷⁾. Higher-stage intercalates of bromine and nitric acid are also known, and it is of interest to know whether changes in rate of diffusion attribute to the formation of discrete stages can be observed.

Cylindrical wafers of stress-annealed, highly oriented pyrolytic graphite used in these experiments have mosaic spreads (FWHM) ≤ 2 deg. Weight gains of graphite wafers suspended in HNO₃ and Br₂ vapors are monitored continuously by a recording microbalance, and rates of weight gain in HNO₃ vapor are monitored using a derivative computer. Temperature of the wafer is maintained ~3 deg higher than that of the intercalant reservoir by which the vapor pressure of intercalant is fixed. Graphite wafers are exposed to PdCl₂ vapor by packing them in PdCl₂ powder in a quartz boat and heating in flowing Cl₂.

Weight gains M_t at time, t, during intercalation are plotted as fractions of the ultimate weight gain M_∞ corresponding to formation of the lowest-stage compound for Br₂ and PdCl₂ in Figure 1 and for HNO₃ in Figure 2. Figure 1 shows an initial "induction period" during which little weight gain occurs, and a region in which M_t/M_∞ increases linearly with t^{1/2} as expected for a diffusion process. The "induction period" region has been omitted for clarity's sake from Figure 2, which shows a third region, during which M_t/M_∞ increases more slowly with time than in the second region. Diffusion coefficients, D, calculated from the expression⁵

$$(1) \frac{M}{M_{\infty}} = \frac{4}{\pi^2} \frac{Dt}{r^2} - \frac{Dt}{r^2} - \frac{1}{3\pi^2} \frac{Dt}{r^2}^{3/2}$$

where r is the radius of the wafer, are shown in Table I. Rates of intercalation increase linearly with t^{-1/2} when the contribution of t^{1/2} is small, as expected from the time derivative of Equation 1 and as shown in Figure 3 for a typical bromination reaction. Nitration can thus be attributed to a process characterized by a single diffusion coefficient up to M_t/M_∞ = 0.50, a weight gain corresponding to formation of Stage III graphite nitrate, and bromination can be characterized by a single diffusion coefficient at least up to M_t/M_∞ = 0.25.

X-ray diffraction scans of graphite wafers exposed to PdCl₂ vapor until M_t/M_∞ ≈ 0.5 and then quenched show only the (00l) reflections of Stage III C_{10,7}PdCl₂. No higher-stage compound is observed; indeed, none is known. Electron microprobe analysis of the cleavage surface of such a wafer yields the plot of Cl₂ intensity versus radial distance shown in Figure 4. The pronounced reaction front and absence of lower-stage compounds shown here, and the linearity of M_t/M_∞ shown in Figure 1, are expected for a process characterized by a single diffusion coefficient.

The diffusion coefficient of HNO₃ in graphite at 30°C increases with increasing HNO₃ vapor pressure as shown in Table I, and seems in fact to be proportional to vapor pressure. The diffusion coefficient of PdCl₂ increases with increasing vapor pressure of PdCl₂ and with increasing temperature. Values of log D_{PdCl₂} fall closely on a straight line when plotted versus 1/T. The activation energy for diffusion calculated from the slope of this line is approximately 35 kcal/mole. For comparison, the activation energy for diffusion of Br₂ in graphite is approximately 6 kcal/mole.⁽⁷⁾

References

1. T. Sasa, Y. Takahashi and T. Mukaibo, Carbon 9, 407 (1971).
2. A. R. Ubbelohde, Proc. Roy. Soc. (London) A304, 25 (1968).
3. Yu. N. Novikov, V. A. Postnikov, Ya. V. Salyn, V. I. Nefedov and M. E. Volpin, Izv. Akad. Nauk. SSSR, Ser. Khim (1973) 1689. [Bull. Acad. Sci. SSSR, Ser. Chem. (1973) 1653.]
4. J. G. Hooley, Canadian J. Chem. 40, 749 (1962).
5. J. G. Hooley and J. L. Smee, Carbon 2, 135 (1964).
6. J. G. Hooley, W. P. Garby and J. Valentin, Carbon 3, 7 (1965).
7. T. Mukaibo and Y. Takahashi, Bull. Chem. Soc. Japan 36, 625 (1963).
8. D. E. Dixon, G. S. Parry, and A. R. Ubbelohde, Proc. Roy Soc. 291A, 324 (1966).

Table I
 Diffusion of Intercalants into Highly-Oriented
 Pyrolytic Graphite

Intercalant	Vapor Pressure, Torr	Intercalation Temperature °C	D, cm ² /min.	
Br ₂	258	30	1.47 × 10 ⁻⁶	
		HNO ₃	81	203 × 10 ⁻⁶
PdCl ₂	2.10 × 10 ⁻⁴	40	133 × 10 ⁻⁶	
		37	85 × 10 ⁻⁶	
		416	0.16 × 10 ⁻⁶	
PdCl ₂	1.04 × 10 ⁻³	450	0.52 × 10 ⁻⁶	
		8.82 × 10 ⁻³	500	2.46 × 10 ⁻⁶

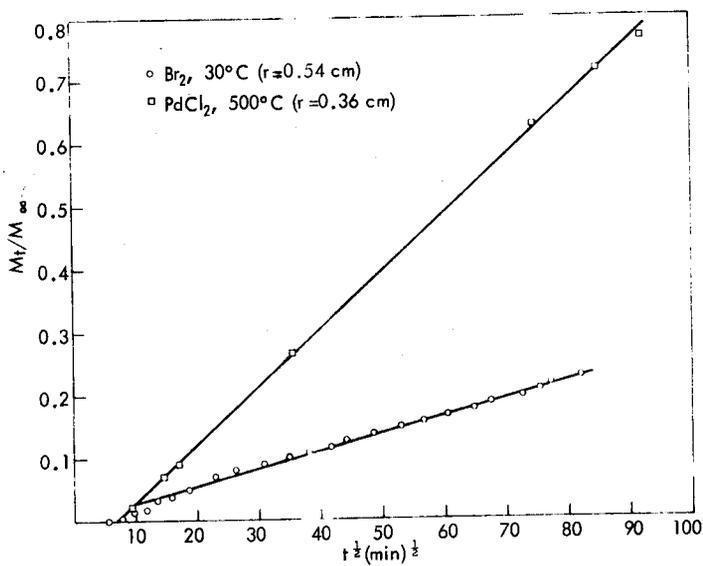


Figure 1. Increases of Br_2 and PdCl_2 with $t^{1/2}$.

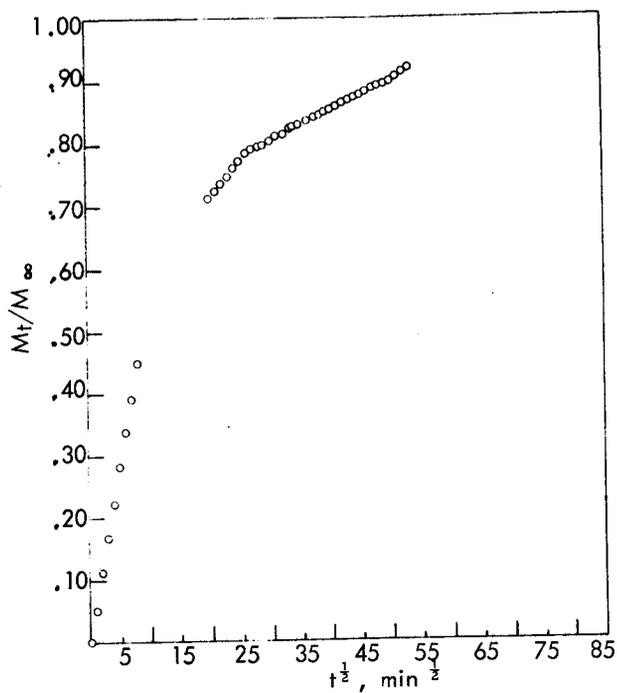


Figure 2. Increases of HNO_3 with $t^{1/2}$.

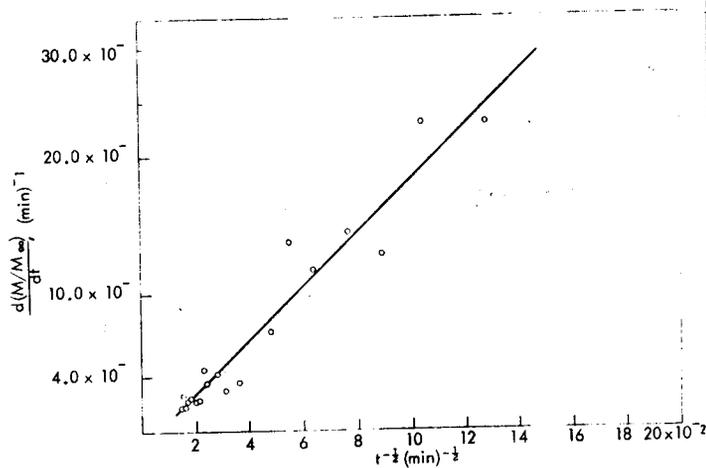


Figure 3. Rate of bromination at 30°C as a function of $t^{1/2}$.

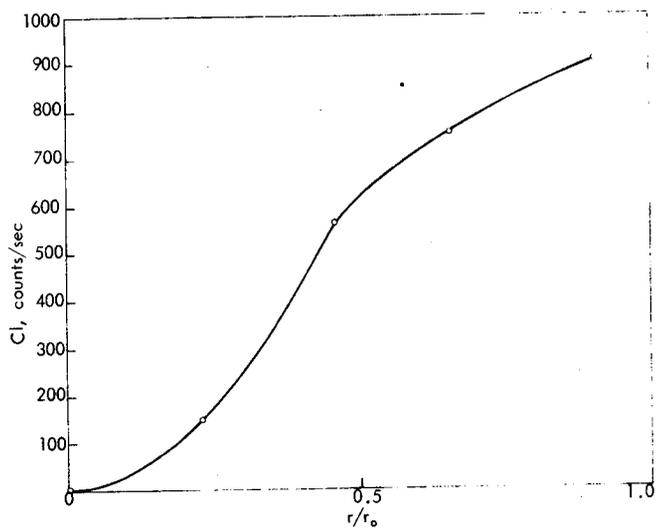


Figure 4. Chlorine concentration of a graphite wafer exposed to PdCl_2 until $M_t/M_\infty \approx 0.50$ then quenched, as a function of fractional distance r/r_0 from the center of the wafer.