and

$$q = \frac{n}{p} \tag{6.35}$$

6. TOPOCHEMICAL REACTIONS

There are theories akin to the above, which simply, empirically state that (a) decomposition starts at the surface of the solid and works inwards. If, for instance, the solid were a cube originally with side a_0 cm, then, after a given time the side length, a, would be

$$a = a_0 - kt \tag{6.36}$$

i.e., it is assumed that the decomposition "front" progresses in a linear fashion. This is akin to physical phenomena such as crystal growth (the so-called McCabe law). At time t there will, therefore, be an amount undecomposed given by

$$N\rho a^3 = N\rho[a_0 - kt] \tag{6.37}$$

where N is the number of particles in the sample and ρ is the density of the solid. The original volume of the solid was Na_0^3, so that the fraction not decomposed, x, would be given by

$$x = \frac{N\rho a^3}{[N\rho a_0]^3} = \left[\frac{a}{a_0}\right]^3 = \left[1 - \left(\frac{k}{a_0}\right)t\right]^3 \tag{6.38}$$

It is noted from Eq. 38 that the rate constant (k/a_0) is particle size dependent. This property will be touched on frequently in the following.

An example of this type of decomposition pattern is aspirin in an alkaline environment (Nelson et al., 1974). This is shown in Fig. 12.

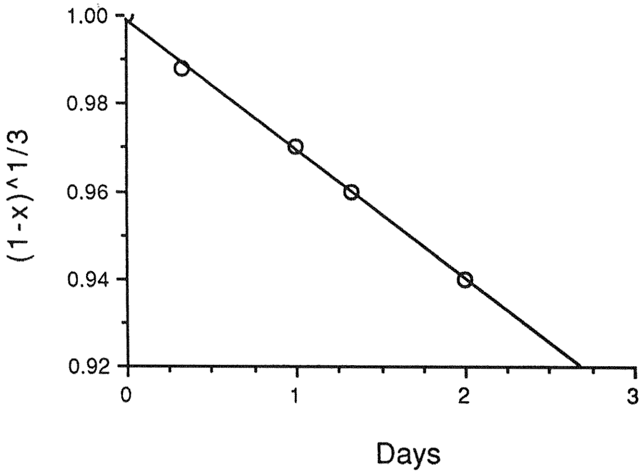

Fig. 12 Decomposition of aspirin in alkaline environment. Least squares fit: $y = 1.0 - 0.0295x$ ($R = 1.00$). (Graph constructed from data by Nelson et al., 1974.)