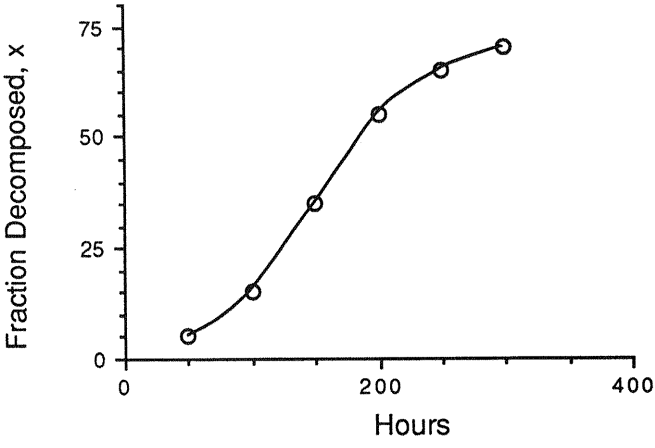

Fig. 1 Decomposition of *p*-aminosalicylic acid at 65°C in vacuo. (Figure constructed from data by Carstensen and Pothisiri, 1975.)

2. THE SOLID TO SOLID + GAS REACTION

This reaction has been investigated by Prout and Tompkins (1944) and later by Kornblum and Sciarrone (1964) and Carstensen and Pothisiri (1975). A typical example of such a reaction is that of p-aminosalicylic acid, shown in Table 1 and Fig. 1. It is noticed that the profile is S-shaped. The general explanation for this type of reaction is the following:

No solid has a smooth surface, i.e., there are always surface imperfections. These could be "steps" in the surface or they could be crystal defects. These sites are more energetic than the remaining sites. They are most likely to occur at surfaces, which in any event are populated with molecules that are unlike the molecules in the bulk of the crystal. For instance they have at least one less neighbor than bulk molecules. It is assumed that decomposition is more likely to occur at such "activated" sites (Fig. 2).

Once a molecule decomposes at an activated site it changes its geometry, and hence the neighboring molecules are more likely to decompose. There will then be a chain or plane of activated molecules forming, with a probability of a (second figure in Fig. 2). The rate of formation of activated molecules, N in number at time t, is dN/dt, and this is proportional to N. Initially this is then given by

$$\left[\frac{dN}{dt}\right]_0 = a \cdot [N + N_0] \tag{6.1}$$

Table 1 Decomposition of *p*-Aminosalicylic Acid

Time (hours)	0	50	100	150	220	260	325
Percent decomposed	0	4	18	36	60	70	77

Source: After Carstensen and Pothisiri, 1975.