7. THE ARRHENIUS EQUATION

Rate constants are, of course, a function of temperature, and the data shown in Table 5 are graphed in Figs. 10A and 10B.

If rapid results are desired for a given product, it is at times a practice to store it at elevated temperatures. The purpose of this is to force sufficiently large degrees of decomposition in a short time, so that they may be assessed with accuracy. The data in Table 6 are artificially precise, and with a bit of assay error, the 25°C data would not show a discernible loss after 6 months. Is it possible to get some idea of what the loss would actually be, and what it would be after 24 months, without having to wait too long? To get an answer to this (an estimate, not a precise answer) is one of the reasons that Arrhenius plotting is carried out for drug products. The method is actually quite precise in solution systems.

The temperature dependence of a chemical reaction (as long as it is the rate-determining rate constant that is being treated) follows the so-called Arrhenius equation given by

$$\ln[k] = -\frac{E_a}{RT} + \ln[Z] \tag{2.49}$$

or its antilogarithmic form,

$$k = Z \exp\left[-\frac{E_a}{RT}\right] \tag{2.50}$$

where E_a is the activation energy, R is the gas constant, and T is the absolute temperature (°K) obtained by adding 273.15° to the degrees Celcius (Centigrade).

Often the variable $1000/T$ is used (because the numbers then are between 2 and 4 rather than between 0.002 and 0.004 and hence are easier to handle). The slope of a plot according to Eq. (2.42) is still E_a/R, but E_a will now be in kCal (rather than in cal) per degree per mole.

An example of this type of treatment of the first-order data in Fig. 10A is shown in Table 7.

A similar table may be constructed for zero-order treatment, and the graphical presentation is shown in Fig. 10A. When the rate constants are plotted according to Eq. (2.49), then Fig. 11 emerges.

Table 2.7 Least Squares Fit Parameters from Fig. 10B

Temperature °C	Temperature °K	k (mo^{-1})	$1000/T$	$\ln[k]$
15	288.15	0.00042	3.473	−7.783
25	298.15	0.0014	3.356	−6.571
37	400.15	0.0052	3.224	−5.259
45	408.15	0.0118	3.145	−4.440
55	418.15	0.031	3.049	−3.471