and the experimental rate equation is:

$$v = k_{\text{obs}} S_T \tag{8.22}$$

where k_{obs} is the pseudo-first-order rate constant. Setting these equal and dividing through by S_T gives:

$$k_{\text{obs}} = k_0 f_{10} + k_{11} f_{11} \tag{8.23}$$

where f_{10} and f_{11} are the fractions of substrate present as S and SL, and can be expressed as Equation 8.24 and 8.25, respectively.

$$f_{10} = \frac{1}{1 + K_{11}[L]} \tag{8.24}$$

$$f_{11} = \frac{K_{11}[L]}{1 + K_{11}[L]} \tag{8.25}$$

The stability constant is combined with Equations 8.24 and 8.25, giving:

$$k_0 - k_{\text{obs}} = f_{11}(k_0 - k_{11}) \tag{8.26}$$

Defining:

$$\Delta k = k_0 - k_{\text{obs}} \tag{8.27}$$

$$q_{11} = 1 - \frac{k_{11}}{k_0} \tag{8.28}$$

Equation 8.26 can be rearranged as an expression of the binding isotherm.

$$\frac{\Delta k}{k_0} = \frac{q_{11} K_{11}[L]}{1 + K_{11}[L]} \tag{8.29}$$

A double reciprocal linear plot form can be easily derived.

$$\frac{1}{\Delta k} = \frac{1}{q_{11} k_{11} k_0 [L]} + \frac{1}{q_{11} k_0} \tag{8.30}$$

Equations 8.29 and 8.30 are identical in form with the isotherm and double reciprocal linear plot forms for optical spectroscopy Equations 8.15 and 8.16.

Titration Calorimetry

Titration calorimetry or thermometric titration calorimetry is a technique in which one reactant is titrated continuously into the other reactant, and either the temperature change or heat produced in the system is measured as a function of titrant added. In isoperibol titration calorimetry the temperature of a reaction vessel in a constant-temperature environment is monitored as a function of time (Figure 8.4) (Hansen et al. 1985; Winnike 1989). A single titration calorimetric experiment yields thermal data as a function of the ratio of the concentrations of the reactants.

Titration calorimetry depends on calculation of the extent of reaction from the quantity of heat evolved. Its successful application to a given system depends on (a) the equilibrium constant and the reaction conditions being such that the reaction occurs to a moderate extent (i.e., not to completion), and (b) the enthalpy of reaction being measurably different from zero.