

$$\frac{1}{2} dC_{\text{SO}_4}/dt = k_L a C^* \quad (10.6)$$

where  $C_{\text{SO}_4}$  is the concentration of  $\text{SO}_4^{2-}$ . The factor,  $\frac{1}{2}$ , requires that  $C_{\text{SO}_4}$  and  $C^*$  be expressed in terms of moles. Oxygen solubility,  $C^*$ , is a constant dependent on medium composition, temperature, and pressure and can be measured separately. Thus,

$$k_L a = \frac{1}{2} \frac{dC_{\text{SO}_4}/dt}{C^*} \quad (10.7)$$

The sulfite method probably overestimates  $k_L a$ . The astute reader may have already noted that if the chemical reaction takes place in the liquid film around the gas bubble, the apparent oxygen transfer will be greater than that for a system with no chemical reaction in the liquid film. (An unresolved question is whether respiring organisms can enhance oxygen transfer by a similar method.)

Perhaps the best way to determine  $k_L a$  is the *steady-state* method, in which the whole reactor is used as a respirometer. Such an approach requires the accurate measurement of oxygen concentration in all gas exit streams and a reliable measurement of  $C_L$ . A mass balance on  $\text{O}_2$  in the gas allows the rate of  $\text{O}_2$  uptake, OUR, to be calculated:

$$k_L a = \frac{\text{OUR}}{C^* - C_L} \quad (10.8)$$

OUR could also be estimated with off-line measurements of a sample of the culture in a respirometer, but using information from the actual fermenter is ideal. One complication, however, in this (and other methods) is the value of  $C^*$  to use. In a large fermenter, gas is sparged under significant pressure (due at least to the liquid height in an industrial fermenter).  $C^*$  is proportional to  $p\text{O}_2$ , which depends on total pressure as well as the fraction of the gas that is oxygen. At the sparger point,  $p\text{O}_2$  will be significantly higher than at the exit, due to both higher pressure and the decrease in the fraction of the gas that is  $\text{O}_2$  because of consumption by respiration. In a bubble column, the log mean value of  $C^*$  based on  $p\text{O}_2$  at the entrance and exit would be a justifiable choice. In a perfectly mixed vessel, the composition of gas in the exit stream should be the same as bubbles dispersed anywhere in the tank, and consequently  $C^*$  would be based on  $p\text{O}_2$  at the exit. In an actual tank, a knowledge of the residence time distribution of gas bubbles is necessary to estimate a volume averaged value of  $C^*$ .

The *dynamic* method shares similarities with the steady-state method in that it uses a fermenter with active cells. It is simpler in that it requires only a dissolved oxygen (DO) probe and a chart recorder rather than off-gas analyzers as well as the DO probe required in the steady-state method. The governing equation for DO levels is:

$$dC_L/dt = \text{OTR} - \text{OUR} \quad (10.9a)$$

or

$$dC_L/dt = k_L a (C^* - C_L) - q_{\text{O}_2} X \quad (10.9b)$$

The dynamic method requires that the air supply be shut off for a short period ( $\text{eq} < 5$  min) and then turned back on. The anticipated result is shown in Fig. 10.5. Since there are no gas bubbles when the gas is off,  $k_L a$  will be zero. Hence,