5.9: First-order Rate Processes

First-order rate processes are ubiquitous in nature—and commerce. In chemistry we are usually interested in first-order decay processes; in other subjects, first-order growth is common. We can develop our appreciation for the dynamics—and mathematics—of first-order processes by considering the closely related subject of compound interest.

✔ Compound Interest

When a bank says that it pays 5% annual interest, ***compounded annually***, on a deposit, it means that for every \$1.00 we deposit at the beginning of a year, the bank will add 5% or \$0.05 to our account at the end of the year, making our deposit worth \$1.05. If we let the value of our deposit at the end of year n be $P(n)$, and the interest rate (expressed as a fraction) be r, with $r > 0$, we can write

$$P(1) = P(0) + \Delta P = P(0) + rP(0) = (1+r)\,P(0)$$

where we represent the first year's interest by $\Delta P = rP(0)$. If we leave all of the money in the account for an additional year, we will have

$$P(2) = (1+r)\,P(1) = (1+r)^2 P(0)$$

and after t years we will have

$$P(t) = (1+r)^t P(0)$$

Sometimes a bank will say that it pays 5% annual interest, ***compounded monthly***. Then the bank means that it will compute a new balance every month, based on $r = 0.05\ \text{year}^{-1} = (0.05/12)\ \text{month}^{-1}$. After one month

$$P(1\ \text{month}) = \left(1 + \frac{0.05}{12}\right) P(0)$$

and after n months

$$P(n\ \text{months}) = \left(1 + \frac{0.05}{12}\right)^n P(0)$$

If we want the value of the account after t years, we have, since $n = 12t$,

$$P(t) = \left(1 + \frac{0.05}{12}\right)^{12t} P(0)$$

If the bank were to say that it pays interest at the rate r, ***compounded daily***, the balance at the end of t years would be

$$P(t) = \left(1 + \frac{r}{365}\right)^{365t} P(0)$$

For any number of compoundings, m, at rate r, during a year, the balance at the end of t years would be

$$P(t) = \left(1 + \frac{r}{m}\right)^{mt} P(0)$$

Sometimes banks speak of ***continuous compounding***, which means that they compute the value of the account at time t as the limit of this equation as m becomes arbitrarily large. That is, for continuous compounding, we have

$$P(t) = \lim_{m\to\infty}\left[\left(1 + \frac{r}{m}\right)^{mt}\right] P(0)$$

Fortunately, we can think about the continuous compounding of interestinterest:continuous compounding in another way. What we mean is that the change in the value of the account, ΔP, over a short time interval, Δt, is given by

$$\Delta P = rP\Delta t$$

where P is the (initial) value of the account for the interval Δt, and r is the fractional change in P during one unit of time. So we can write

$$\lim_{\Delta t\to 0}\left(\frac{\Delta P}{\Delta t}\right)=\frac{dP}{dt}=rP$$

Separating variables to obtain $dP/P=rdt$ and integrating between the limits $P=P(0)$ at $t=0$ and $P=P(t)$ at $t=t$, we obtain

$$\ln\frac{P(t)}{P(0)}=rt$$

or

$$P(t)=P(0)\exp(rt)$$

Comparing the two equations we have derived for continuous compounding, we see that

$$\exp(rt)=\lim_{m\to\infty}\left(1+\frac{r}{m}\right)^{mt}$$

Continuous compounding of interest is an example of ***first-order*** or ***exponential growth***. Other examples are found in nature; the growth of bacteria normally follows such an equation. Reflection suggests that such behavior should not be considered remarkable. It requires only that the increase per unit time in some quantity, P, be proportional to the amount of P that is already present: $\Delta P=rP\Delta t$. Since P measures the number of items (dollars, molecules, bacteria) present, this is equivalent to our observation in Section 5.7 that a first-order process corresponds to a constant probability that a given individual item will disappear (***first-order decay***) or reproduce (***first-order growth***) in unit time. For a first-order decay we have, keeping $r>0$,

$$\Delta P=-rP\Delta t$$

In the limit as $\Delta t\to 0$,

$$\frac{dP}{dt}=-rP$$

which has solution

$$P(t)=P(0)\exp(-rt)$$

First-order growth and first-order decay both depend exponentially on rt. The difference is in the sign of the exponential term. For exponential growth, $P(t)$ becomes arbitrarily large as $t\to\infty$; for exponential decay, $P(t)$ goes to zero. If the concentration of a chemical species A decreases according to a first-order rate law, we have

$$\ln\frac{[A]}{[A]_0}=-kt$$

The units of the rate constant, k, are s^{-1}. The ***half-life*** of a chemical reaction is the time required for one-half of the stoichiometrically possible change to occur. For a first-order decay, the half-life, $t_{1/2}$, is the time required for the concentration of the reacting species to decrease to one-half of its value at time zero; that is, when the time is $t_{1/2}$, the concentration is $[A]=[A]_0/2$. Substituting into the integrated rate law, we find that the half-life of a first-order decay is independent of concentration; the half-life is

$$t_{1/2}=\frac{\ln 2}{k}$$