

rather complicated experimental rate laws, but these systems can be interpreted in terms of a rather straightforward free radical chain reaction mechanism. The $\text{H}_2\text{-I}_2$ system, on the other hand, has been studied longer than any of these other systems and possesses the simplest kinetic behavior; this system, however, is the one which is the least understood and is still the subject of investigation. The hydrogen + halogen systems thus illustrate another dictum, due to Holmes rather than Benson, to the effect that “. . . strange details, far from making the case more difficult, have really had the effect of making it less so”!¹³

2.4 LAPLACE TRANSFORM METHOD

2.4.1 Introduction

The classical methods described in the preceding sections lead to the solutions of many kinetic linear differential equations, but as is plain, obtaining these solutions is not always straightforward. By contrast, using methods of *operational calculus* can lead directly to a solution satisfying given initial conditions without having to separately evaluate particular integrals or arbitrary constants. Through these methods, the calculation procedure can be both simplified and shortened considerably. The rules and operational procedures are introduced by means of a definite integral called a *transformation integral*, the general form of which is given by

$$F(p) = \int_a^b f(t)\mathcal{K}(p,t) dt \quad (2-174)$$

where $F(p)$ is the *transform* of $F(t)$ with respect to the *kernel*, $\mathcal{K}(p,t)$. For chemical kinetic systems the most commonly used transform is the Laplace transform, which is represented by the kernel $\mathcal{K}(p,t) = e^{-pt}$ and integrated over the limits $-\infty$ to ∞ . Some properties of this integral and its use in connection with solving chemical kinetic problems will be discussed in this section and also in Appendix 1 to this chapter.

2.4.2 The Laplace Transform

The transform $F(p)$ of a function $f(t)$ subjected to the Laplace transformation is defined by the integral:

$$F(p) = \mathcal{L}[f(t)] = \int_0^{\infty} e^{-pt}f(t) dt \quad (2-175)$$

in which both factors, $f(t)$ and e^{-pt} , depend on t . After integration over the limits of $t = 0$ to $t = \infty$, the integral is found to be a function of p only.

The Laplace transform of a given function may be determined by direct integration of (2-175). For example, the transform $F(p)$ of $f(t) = e^{-at}$ where a is a constant, is computed as follows:

$$\begin{aligned}
 F(p) &= \mathcal{L}[e^{-at}] = \int_0^{\infty} e^{-at} e^{-pt} dt = \int_0^{\infty} e^{-(a+p)t} dt \\
 &= -\frac{1}{a+p} [e^{-(a+p)t}]_0^{\infty} \\
 &= \frac{1}{p+a} \quad (p > -a)
 \end{aligned}
 \tag{2-176}$$

The condition $p > -a$ is required to make $e^{-(a+p)t}|_{t=\infty}$ equal to zero and to guarantee the convergence of the integral for $\mathcal{L}[e^{-at}]$.

2.4.3 Fundamental Properties of the Laplace Transform

The Laplace transform of a function has certain fundamental properties which are particularly useful in the evaluation of transforms and in the solution of chemical kinetic differential equations. Three of the most widely used properties will be mentioned here.

1. If $f(t)$ is a linear combination of known functions, i.e.,

$$f(t) = f_1(t) + f_2(t) + \cdots + f_n(t) \tag{2-177}$$

then its Laplace transform is

$$\begin{aligned}
 \mathcal{L}[f(t)] &= \int_0^{\infty} [f_1(t) + f_2(t) + \cdots + f_n(t)] e^{-pt} dt \\
 &= \int_0^{\infty} f_1(t) e^{-pt} dt + \int_0^{\infty} f_2(t) e^{-pt} dt + \cdots + \int_0^{\infty} f_n(t) e^{-pt} dt
 \end{aligned}$$

or

$$\mathcal{L}[f(t)] = F_1(p) + F_2(p) + \cdots + F_n(p) \tag{2-178}$$

This means that the Laplace transform of a linear combination of functions is the same linear combination of the transformed functions.

2. One of the most important features of the Laplace transform, especially in evaluating chemical kinetic equations, is that the Laplace transform of the derivative of $f(t)$, i.e., $f'(t)$, can be readily obtained. This is done by integrating equation (2-175):

$$\begin{aligned}
 \mathcal{L}[f'(t)] &= \int_0^{\infty} f'(t) e^{-pt} dt \\
 \mathcal{L}[f'(t)] &= \left[f(t) e^{-pt} \right]_0^{\infty} + p \int_0^{\infty} f(t) e^{-pt} dt \\
 \mathcal{L}[f'(t)] &= p \mathcal{L}[f(t)] - f(0)
 \end{aligned}
 \tag{2-179}$$

For higher order derivatives, the Laplace transform can be found by applying equation (2-179) to the second derivative of $f(t)$, as follows:

$$\begin{aligned}\mathcal{L}[f''(t)] &= p \mathcal{L}[f'(t)] - f'(0) \\ \mathcal{L}[f''(t)] &= p(p \mathcal{L}[f(t)] - f(0)) - f'(0) \\ \mathcal{L}[f''(t)] &= p^2 \mathcal{L}[f(t)] - pf(0) - f'(0)\end{aligned}\quad (2-180)$$

Higher order derivatives, $f^{(n)}(t)$, can be obtained by repeating this operation n times, i.e.,

$$\mathcal{L}[f^{(n)}(t)] = p^n \mathcal{L}[f(t)] - \sum_{i=1}^n f^{(i-1)}(0) p^{n-i} \quad (2-181)$$

3. The transform of an integral of a function $f(t)$ may be expressed as

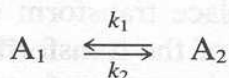
$$\mathcal{L}\left[\int_0^t f(t) dt\right] = \frac{\mathcal{L}[f(t)]}{p} \quad (2-182)$$

Additional properties of the Laplace transform are given in Appendix 1.A. A table of transforms of the functions most commonly encountered in kinetic problems is obtainable by direct integration and by using the preceding three properties. Extensive tables of Laplace transforms appear in Appendix 1.B. These tables may be used to find both the Laplace transform and the inverse Laplace transform symbolized by

$$\mathcal{L}^{-1}[F(p)] = f(t) \quad (2-183)$$

2.4.4 Solving Chemical Kinetic Problems Using the Laplace Transform Method

As we can see from the general Laplace transform properties, the method allows differential and integral equations to be converted into linear algebraic equations that include initial conditions. The procedure for solving a set of kinetic equations is illustrated for the simplest example. Consider the opposing first-order reaction discussed in Sec. 2.1.2,



The rate equations for this reaction are equations (2-3) and (2-4),

$$-\frac{d[A_1]}{dt} = k_1[A_1] - k_2[A_2]$$

and

$$-\frac{d[A_2]}{dt} = k_2[A_2] - k_1[A_1]$$

with initial conditions $[A_1] = A_0$ and $[A_2] = 0$ at $t = 0$. Laplace transformations can now be carried out on this set of differential equations to convert the equations into a set of algebraic equations.