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LECTURE TEXT

First-order differential equations in chemistry

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Abstract Many processes and phenomena in chemistry, and generally in sciences, can be described by first-order differential equations. These equations are the most important and most frequently used to describe natural laws. Although the math is the same in all cases, the student may not always easily realize the similarities because the relevant equations appear in different topics and contain different quantities and units. This text was written to present a unified view on various examples; all of them can be mathematically described by first-order differential equations. The following examples are discussed: the Bouguer–Lambert–Beer law in spectroscopy, time constants of sensors, chemical reaction kinetics, radioactive decay, relaxation in nuclear magnetic resonance, and the *RC* constant of an electrode.

Keywords Differential equations · Bouguer–Lambert–Beer law · Time constants · Chemical kinetics · Radioactive decay · Nuclear magnetic resonance · RC constant

Introduction

> "Differential equations are extremely important in the history of mathematics and science, because the laws of nature are generally expressed in terms of differential equations. Differential equations are the means by which scientists describe and understand the world" [1].

The mathematical description of various processes in chemistry and physics is possible by describing them with the help of differential equations which are based on simple model assumptions and defining the boundary conditions [2, 3]. In many cases, first-order differential equations are completely describing the variation dy of a function $y(x)$ and other quantities. If y is a quantity depending on x, a model may be based on the following assumptions: The differential decrease of the variable y is proportional to a differential increase of the other variable, here x, i.e. $-\mathrm{d}y \sim \mathrm{d}x$. This decrease $-\mathrm{d}y$ should depend on the function y itself: $-\mathrm{d}y \sim y\mathrm{d}x$, and together with a so far unknown constant a, results in the equation

$$\mathrm{d}y = -ay\mathrm{d}x \tag{1}$$

Thus follows the *ordinary linear homogeneous first-order differential equation*:

$$\frac{\mathrm{d}y}{\mathrm{d}x} + ay = 0 \tag{2}$$

The characteristics of an *ordinary linear homogeneous first-order differential equation* are: (i) there is only one independent variable, i.e. here x, rendering it an *ordinary* differential equation, (ii) the depending variable, i.e. here y, having the exponent 1, rendering it a *linear* differential equation, and (iii) there are only terms containing the

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variable y and its *first* derivative, rendering it a *homogeneous first-order* differential equation.

This equation can be solved when, e.g. the boundary conditions are such that y varies between y_0 and y, when x varies between 0 and x. Following a separation of variables, the integration of Eq. 2 gives:

$$\frac{\mathrm{d}y}{y} = -a\mathrm{d}x \tag{3}$$

$$\int_{y_0}^{y} \frac{\mathrm{d}y}{y} = -a \int_{0}^{x} \mathrm{d}x \tag{4}$$

$$\ln \frac{y}{y_0} = -ax \tag{5}$$

$$y = y_0 \mathrm{e}^{-ax} \tag{6}$$

Equation 6 describes the exponential decrease of y as a function of x.

This formalism will now be applied to some special cases which occur frequently in chemistry, and finally all discussed cases will be compared in a table.

The Bouguer–Lambert–Beer Law

The intensity of electromagnetic radiation (e.g. visible light), i.e. exactly the radiant flux I (unit W, watt or J s^{-1}, joule per second), diminishes along the path length x through a homogeneous absorbing medium (e.g. a coloured solution). Figure 1 depicts a cuvette and the changes in radiant flux along the optical path length.

The differential decrease $-\mathrm{d}I$ of radiant flux by passing through the differential length increment dx is supposed to be proportional to the actual value of I at x_i. To understand this, we must consider the physical background of the decrease of radiant flux: If the radiation is understood as a flux of photons, the absorption of radiation is the loss of photons due to their "capture" by absorbing particles (molecules, atoms or ions) in the cuvette. Clearly, the *effectivity* of capture must be proportional to the number of particles per volume, i.e. their concentration c in mol L^{-1}, as the *probability* that a photon hits a particle will be proportional to its concentration. However, not each hitting leads to an absorption event (capture of a photon). To take into account the probability that a collision of a photon with a particle leads to its capture, one defines an effective cross section of the particles. This cross section has the unit of an area because one may understand it as an effective target area for the photons in contrast to the geometric target area which a particle exposes to the photon flux. Instead of using the effective cross section, one may define a constant κ (Greek letter kappa) which theoretically can have values between 0 and 1, giving the fraction of successful absorption events. κ is a value specific for the particles and specific for the photon energy E_{photon}, and thus the frequency ν (Greek letter nu) of the radiation, with $\nu = E_{\mathrm{photon}}/h$ (h is the Planck constant $6.62606957(29) \times 10^{-34}$ Js), and the wavelength λ (Greek letter lambda) with $\lambda = hc_{\mathrm{light}}/E_{\mathrm{photon}}$ (c_{light} being the velocity of light in the respective medium).

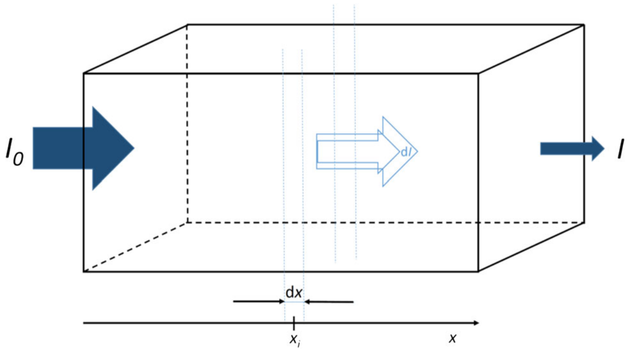


Fig. 1 Electromagnetic radiation is trespassing a cuvette filled with a homogeneous absorbing medium. I_0 is the radiant flux before entering the cuvette, I is the radiant flux leaving the cuvette, $-\mathrm{d}I$ is the differential decrease of radiant flux by passing through the differential length increment dx at x_i

From the preceding discussion follows that the differential equation

$$-\mathrm{d}I(x) = I(x)\kappa c \mathrm{d}x \tag{7}$$

adequately describes the decrease of radiation flux. Since κ is specific for the energy of absorbed photons, this equation

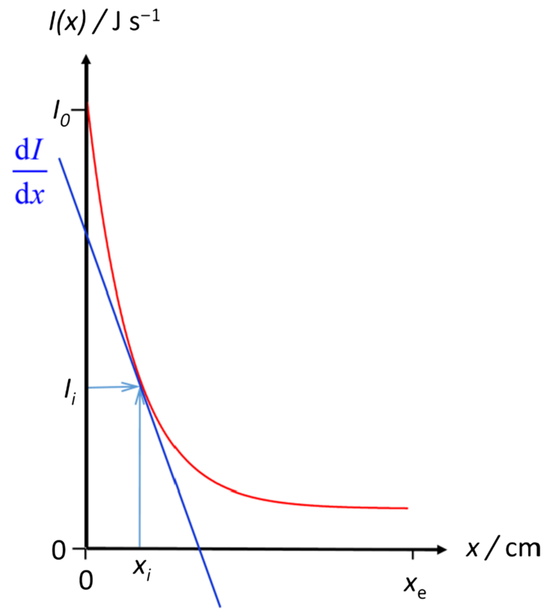


Fig. 2 The decay of radiation flux when passing through the absorbing medium

relates to monochromatic radiation (radiation with one constant frequency, i.e. photon energy). The meaning of Eq. 7 can be understood with the help of Fig. 2: If x_e marks the overall length which the electromagnetic radiation passes through the absorbing medium, and the intensity (radiation flux) of the incident light is I_0 (at $x = 0$), then at a path length x_i the intensity of light will have dropped to I_i and the slope of $I(x) = f(x)$, i.e. $\frac{\mathrm{d}I(x)}{\mathrm{d}x}$ will be proportional to I_i and κ and c.

Integration of Eq. 7 and some rearrangements have to be performed as follows:

$$-\frac{\mathrm{d}I(x)}{I(x)} = \kappa c \mathrm{d}x \tag{8}$$

$$-\int_{I_0}^{I} \frac{\mathrm{d}I(x)}{I(x)} = \kappa c \int_{0}^{x_e} \mathrm{d}x \tag{9}$$

$$-\ln\frac{I}{I_0} = \kappa c x_e \tag{10}$$

$$\ln\frac{I_0}{I} = \kappa c x_e \tag{11}$$

$$\log\frac{I_0}{I} = \frac{1}{\ln 10}\kappa c x_e \approx 0.4343\kappa c x_e \tag{12}$$

The ratio $\log\frac{I_0}{I}$ is called absorbance A, and the product 0.4343κ is called the molar absorption coefficient ε (Greek letter epsilon) or molar absorptivity. The path length of the radiation x_e is usually given the symbol l. The Bouguer–Lambert–Beer Law is thus normally written as:

$$A = \varepsilon c l \tag{13}$$

Outside of this purely mathematical analysis, it needs to be mentioned that Eq. 13 has a restricted range of validity: it is a good description of real systems only at low concentrations. At higher concentrations (sometimes already above 10^{-5} mol L^{-1}) intermolecular interactions of the absorbing particles, and chemical equilibria can lead to deviations (apparent variations of the molar absorption coefficient). Further, another contribution to the absorption coefficient depends on the refractive index n of the solution. Because the refractive index may significantly vary with the concentration of the dissolved analyte, it is not ε, which is constant, but the molar refraction and the term $\varepsilon n/(n^2+2)^2$ should be used instead of ε [4].

The time constant of a sensor

Sensors measure a physical or chemical quantity and transduce it to an output signal which is read, monitored or stored. Possible physical quantities are temperature, pressure, radiative flux, magnetic field strength, etc. Chemical quantities are mainly concentrations and activities of molecules, atoms and ions. The recorded signals are usually voltages or currents. The most typical feature of a signal is that the results are one dimensional, e.g. the output signal is a single quantity, i.e. one measures only that signal and not a dependence of that signal on another given quantity. Most devices for chemical analysis produce two-dimensional read-outs, e.g. optical spectra in which the absorbance is displayed as a function of wavelength ($E = f(\lambda)$), voltammograms in which currents are displayed as function of electrode potential or X-ray diffractograms, in which the intensity of diffracted rays is displayed as function of diffraction angle, etc. In modern instrumentation, one has even expanded the

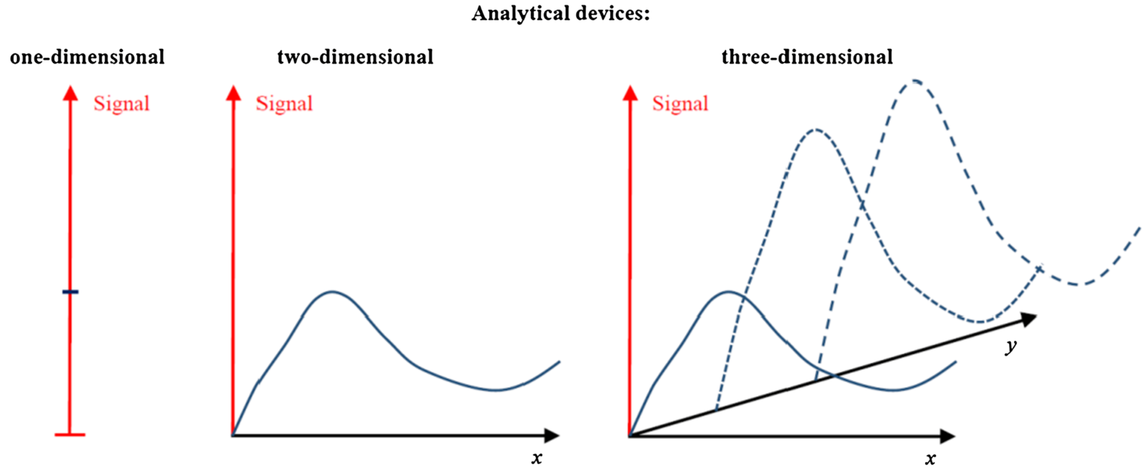
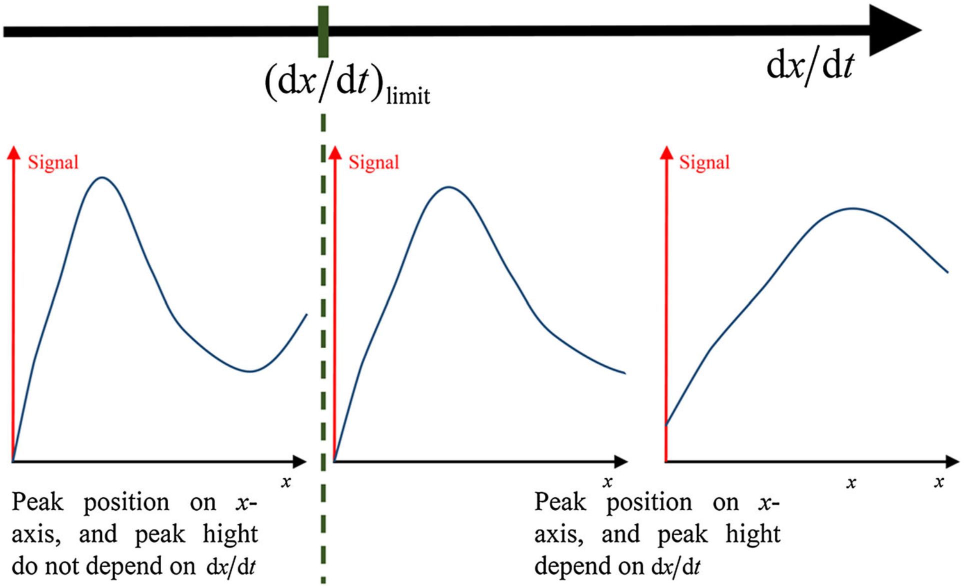


Fig. 3 A comparison of the three common dimensionalities of analytical devices

Fig. 4 Possible distortion of a spectrum when the rate of changing x with time above a limiting value $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{limit}}$



dimensionality to three, when, as an example, optical spectra ($E = f(\lambda)$) (or mass spectra, i.e. ion intensities versus the mass-to-charge ratio of ions) are displayed as a function of elution time of a chromatogram. Figure 3 gives a comparison of the common dimensionalities of analytical measurements.

Since any measurement needs time, there is nothing like an instantaneous establishment of a signal. This is easy to see when using a sensor, e.g. a pH electrode: There is always a certain time period in which the reading changes until we finally have the impression that a constant *end value* is reached. The same is true also for two- or three-dimensional measurements, but we cannot easily detect it because the variation of the measured signal (e.g. the absorbance) anyway changes as a function of the varied quantities (e.g. the wavelength) and thus with time. Normally, the wavelength is changed with the so-called scan rate $\mathrm{d}\lambda/\mathrm{d}t$ (rate of recording the spectrum), and generally (see Fig. 4), the quantity x is varied with a scan rate $\mathrm{d}x/\mathrm{d}t$ (which may be also zero). Whether we measure at each wavelength really the end value of the absorbance can be only seen if we decrease the rate at which the wavelength is changed (in the extreme even keeping the wavelength constant). Referring to Fig. 4, this means in general terms, that a variation of the scan rate $\mathrm{d}x/\mathrm{d}t$ may give a reproducible and identical response only below a certain limiting rate $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{limit}}$. If that rate is exceeded, the signal cannot establish its true value and the spectra are distorted (the signal lags behind) (cf. Fig. 4).

Figure 4 shows impressively that it is important to know the rate at which the signal is established for a given x value. In case of a sensor, i.e. a one-dimensional device where no parameters like x or y are changed, the time change of the signal can be studied following a concentration step. The introduction of the sensor into a solution can be regarded as a concentration step. Figure 5 depicts two different kinds of response of a sensor on a concentration step.

Figure 5 depicts two basic types of time responses of sensors. The different sensor behaviours shown in B and C can be modelled with the help of different differential equations. Whereas the response curve shown in B can be modelled with a first-order differential equation; the curve shown in C needs higher-order differential equations [5]. At this point, it is necessary to note that it is impossible to realize a concentration step with infinite rate of concentration rise, as shown in Fig. 5a. This means, when the temporal response properties of a sensor are studied, this concentration rise has to be much quicker than the response of the sensor. Further, also the response shown in Fig. 5b is to some extend an idealization, and in reality there may be always a sluggish response at the start, but it may be on such short time scale that it escapes our recognition. The response curve shown in Fig. 5b can be modelled as follows:

$$S = S_{\max} - z(t) \tag{14}$$

z is a time-dependent quantity for which we write the first-order differential equation

$$a_1 \frac{\mathrm{d}z}{\mathrm{d}t} + a_2 z(t) = 0 \tag{15}$$

Integration and rearrangements follow:

$$\int_{z_0}^{z} \frac{\mathrm{d}z}{z(t)} = -\frac{a_2}{a_1} \int_{0}^{t} \mathrm{d}t \tag{16}$$

$$\ln \frac{z(t)}{z_0} = -\frac{a_2}{a_1} t \tag{17}$$

$$\frac{z(t)}{z_0} = \mathrm{e}^{-\frac{a_2}{a_1}t} \tag{18}$$

$$z(t) = z_0\mathrm{e}^{-\frac{a_2}{a_1}t} \tag{19}$$

and with Eq. 14 follows:

$$S = S_{\max} - z_0\mathrm{e}^{-\frac{a_2}{a_1}t} \tag{20}$$

Obviously, z_0 should be equal to $S_{\max}$, because then we can write:

$$S = S_{\max} - S_{\max}\mathrm{e}^{-\frac{a_2}{a_1}t} = S_{\max}\left(1 - \mathrm{e}^{-\frac{a_2}{a_1}t}\right) \tag{21}$$

Since the term $\left(1 - \mathrm{e}^{-\frac{a_2}{a_1}t}\right)$ should not have a unit, it follows that the ratio $\frac{a_2}{a_1}$ must be a reciprocal time, and we may write Eq. 21 using the definition $\frac{a_1}{a_2} = \tau$ (Greek letter tau), i.e. $\frac{a_2}{a_1} = \frac{1}{\tau}$:

$$S = S_{\max}\left(1 - \mathrm{e}^{-\frac{t}{\tau}}\right) \tag{22}$$

The quantity τ is called the time constant of the sensor. At $t = \tau$, the signal S has the value

$S = S_{\max}\left(1 - \mathrm{e}^{-1}\right) = S_{\max}\left(1 - \frac{1}{\mathrm{e}}\right) \approx 0.632 S_{\max}$. In other words, after elapse of τ, the signal has reached 63.2 % of its “final value”. Equation 22 implies of course that the signal will never reach a constant value, but the increments of the function z in Eq. 14 may become meaninglessly small as the time progresses. Because of the e-function of Eq. 22, one can give simple relations between the time to reach 50, 63.2, 90, 99 % (and any other values) of $S_{\max}$:

$$t_{63.2\%} = \tau = 1.44 t_{50\%} \tag{23}$$

$$t_{50\%} = 0.69\tau \tag{24}$$

$$t_{90\%} = 2.3\tau \tag{25}$$

$$t_{99\%} = 4.6\tau \tag{26}$$

Figure 6 shows the response curve of Fig. 5b with a scale giving the response in percentage.

The time constant τ is an important parameter of a sensor. However, in practice, one is much more interested in the time necessary to reach 90 or 99 % of the final value, i.e. $t_{90\%}$ and $t_{99\%}$, as the signal reached after that time is often regarded as a good estimate of the true signal value. Thanks to the exponential dependence of the signal on time (Eq. 22), these time data can easily be calculated from the time constant τ according to the Eqs. 25 and 26.

In case of flow-through detectors, one can also calculate the so-called *response volume*, which is simply the volume of solution flowing through the detector within $t = \tau$. It can be calculated by $v_{\mathrm{response}(\tau)} = \tau \cdot f$, where f is the flow rate, e.g. in ml s^{-1} [6]. Of course, one can also calculate the response volumes relating to 90 or 99 % of the signal, i.e. $v_{\mathrm{response}(\tau)} = t_{90\%} \cdot f$ or $v_{\mathrm{response}(\tau)} = t_{99\%} \cdot f$, respectively. The response volumes of a flow-through detector can be larger or also smaller than the geometric volume of the detector. This depends on their construction and principle of function.

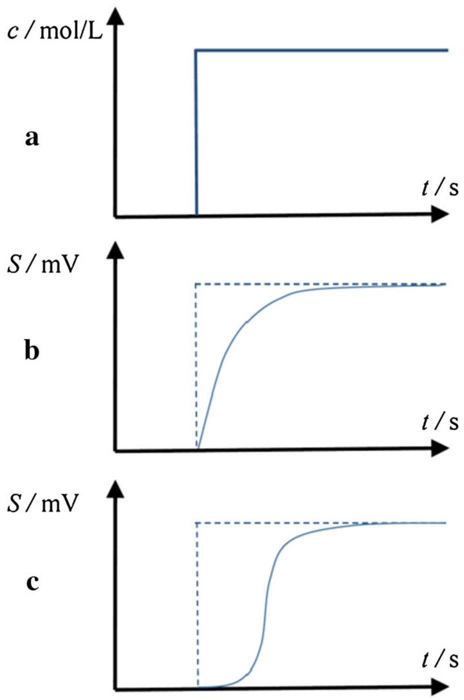


Fig. 5 **a** The concentration is stepped from zero to a constant value. **b** The signal of the detector starts to respond immediately when the step is made, and the slope of the response over time continuously decreases until it finally approaches a constant final value. The response curve has no turning point. **c** The sensor starts slowly to respond (but with *increasing rate/slope*), and after a turning point the response slows down (*decreasing slope*) until it approaches the final value

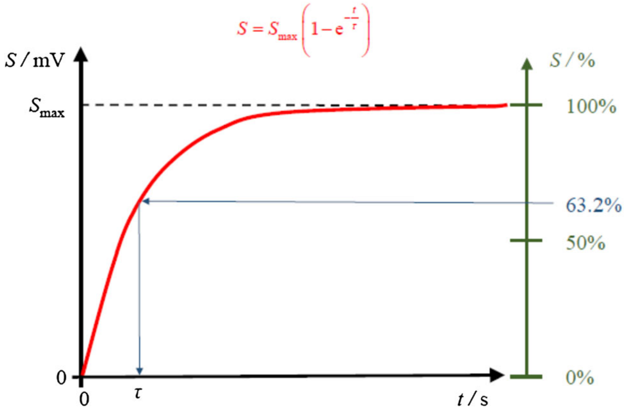


Fig. 6 Time response of a sensor when it can be modelled with a first-order differential equation

We have already mentioned that the response type shown in Fig. 5c is observed in many experimental cases.

For analytical applications, the most important information to know is, how long the sensor needs to acquire, e.g. 90 or 99 % of the final value. Thus, it is much less important to exactly describe the *complete* response curve from beginning to the end, which would be only possible by solving higher-order differential equations and characterizing the response by more than one time constant. Therefore, a frequently used approach is as follows: one analyses only the later part of the response (i.e. the part after the turning point) using Eq. 22, and introduces a delay time t_{delay} after which this equation is assumed to be followed. The response is then described by

$$S = S_{\max}\left(1 - \mathrm{e}^{-\frac{t - t_{\mathrm{delay}}}{\tau}}\right) \tag{27}$$

The response of a sensor of the type shown in Fig. 5c and in Fig. 7 can also be described with the help of two or more time constants using an equation like the following (here with two time constants):

$$S = S_1\left(1 - \mathrm{e}^{-\frac{t}{\tau_1}}\right) + S_2\left(1 - \mathrm{e}^{-\frac{t}{\tau_2}}\right) \tag{28}$$

The crucial point is that there should be a model supporting the use of two or more time constants, as otherwise the fitting of such curve may be mathematically correct but meaningless, as not supported by a model. A somewhat exotic physico-chemical example where the fitting of a response with an equation of the type of Eq. 28 is based on a physical model is the spreading of a liposome on a mercury electrode [7]: When the liposome interacts with the mercury surface, it disintegrates and forms an island of adsorbed lipid molecules. This is accompanied by a change of double layer capacity, which can be measured as a current transient. Integration of the current transient gives the charge transient following Eq. 28 and the form of the curve shown in Fig. 7.

The origin of time constants is a very complex topic needing extensive explanations. Here, it may suffice to mention some possible time depending processes which can contribute to the measured time constant: (a) diffusion of particles towards the sensing surface (e.g. in some electrochemical sensors), (b) convection, when a sensor chamber (cuvette) has to be filled with solution (e.g. in optical sensors as used in chromatography), (c) chemical reactions, esp. in biosensors where enzymatic reactions may be rather slow. Despite these chemical or physico-chemical sources of time constants, one should never forget that each part of a measuring system, from the amplifier to the recorder, has its own time constant. The modern instrumentation of chemical analysis normally have so small constants that they are irrelevant for the measurement they have been developed for, and the chemical and physico-chemical sources will dominate; however, it is good to remember that any measuring system involves time constants, which occasionally may affect the measurement. Coming back to the example of spectroscopy (Fig. 4), it should be mentioned that even modern scanning (!) optical spectrometers may come to their limits if one tries a too fast recording.

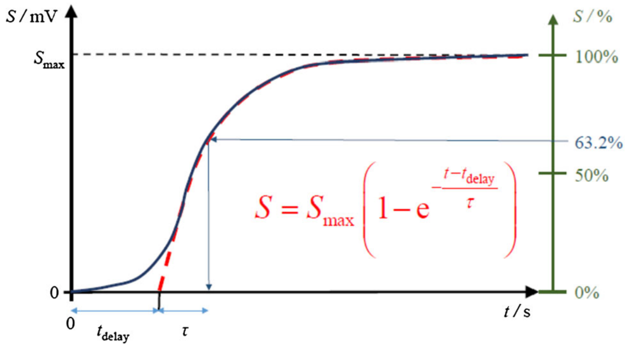


Fig. 7 Time response of a sensor which exactly has to be described by a higher-order differential equation, but which is approximated by assuming first-order behaviour after a delay time t_{delay}

Chemical reaction kinetics

Chemical reaction kinetics is the study of rates of chemical processes (reactions). The goal is to find the relations between the concentrations c of educts or products of a chemical reaction (as depending variable) and the time t (as independent variable). In general, *all* chemical reactions can be described mathematically by first-order differential equations. Their solutions, however, depend directly on the nature of the chemical reaction itself. The latter is characterized by the so-called *reaction order*, which has nothing what so ever to do with the *order of a differential equation*. The reaction order of a chemical reaction is simply defined by the sum of exponents of concentrations occurring in the rate law.

In the following, a *first-order chemical reaction*, typical for thermal decompositions or isomerization reactions, is explained in more detail.

Simple reactions like the transformation of A to B (A → B) can be described by the differential equation:

$$-\mathrm{d}c_{\mathrm{A}} = k \cdot c_{\mathrm{A}} \cdot \mathrm{d}t \tag{29}$$

This *first-order differential equation* describes also a *first-order reaction* in chemical kinetics, due to the exponent 1 of the concentration c_{A}. Following a separation of variables, the integration results in:

$$\int_{c_{\mathrm{A}_0}}^{c_{\mathrm{A}_t}} \frac{\mathrm{d}c_{\mathrm{A}}}{c_{\mathrm{A}}} = -k \int_0^t \mathrm{d}t \tag{30}$$

The result

$$\ln\frac{c_{A_t}}{c_{A_0}} = -kt \tag{31}$$

can be also written in the exponential form:

$$c_{A_t} = c_{A_0}e^{-kt} \tag{32}$$

The half-time, i.e. the time within which the concentration decreases to 50 % of the initial concentration (Eq. 33), is then given by Eq. 34:

$$c_{t_{1/2}} = \frac{1}{2}c_0 \tag{33}$$

$$t_{1/2} = \frac{\ln 2}{k}, \tag{34}$$

which is only dependent on the rate constant k.

In the majority of chemical reactions, however, more than one educt is involved, e.g.

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}. \tag{35}$$

These are second-order reactions in chemical kinetics, because the sum of exponents of concentrations of A and B in the rate law (see Eq. 36) is two. In case of a simple reaction, first-order differential equations are resulting for the math description:

$$-\frac{dc_A}{dt} = k \cdot c_A \cdot c_B \tag{36}$$

For equal initial concentrations of A and B (or also for a dimerization), Reaction 35 can be written as

$$2\mathrm{A} \rightarrow \mathrm{C} + \mathrm{D}, \tag{37}$$

with the differential equation

$$-\frac{1}{2}\frac{dc_A}{dt} = k \cdot c_A^2 \tag{38}$$

This first-order differential equation is no longer a linear one, so it will not be considered here. Moreover, in the case of unequal initial concentrations the solution of the differential equation (Eq. 36) has to be developed by expansion into partial fractions. For the latter two situations the reader is advised to consult textbooks of chemical kinetics (e.g. [8]).

The radioactive decay

Radioactive decay refers to nuclear conversions of atoms accompanied by emission of either electromagnetic radiation (gamma radiation) or particles (e.g. alpha particles, i.e. helium-4 nuclei; beta particles, i.e. electrons or positrons; protons, fission products, etc.). Although these are physical processes, they are considered here because the radioactive decay plays an important role in chemistry, e.g. in isotope dilution analysis, activation analysis, and in labelling molecules in kinetic studies, etc. There exists a variety pathways of nuclear conversions: alpha decay, beta decay, spontaneous fission, electron capture, internal conversion, etc., to name but a few. For a comprehensive overview, see [9, 10]. It is very interesting to note that among the more than 3,000 isotopes, there are only 265 stable isotopes, all others being radioactive! Here, we shall treat the simplest case, the decay of a radioactive isotope which is not produced during the decay (by another decay or by nuclear activation). The activity A of a sample containing this isotope is defined as the number of atoms disintegrating per time unit, i.e. the rate of decay. The differential expression is:

$$A = -\frac{dN}{dt} \tag{39}$$

Since each disintegration is completely independent of any other, and because it is a completely stochastic process, the rate of disintegration is simply proportional to the absolute number of radioactive atoms N:

$$-\frac{dN}{dt} = \lambda N \tag{40}$$

λ (Greek letter lambda) is a proportionality constant called the decay constant. Equation 40 is a first-order differential equation which we can also write similar to Eq. 2:

$$\frac{dN}{dt} + \lambda N = 0 \tag{41}$$

Separation of variables leads to:

$$\frac{dN}{N} = -\lambda dt \tag{42}$$

Integration of Eq. 42 should be done in the limits of N_0 (initial number of radioactive atoms) and N_f (final number of radioactive atoms), when the time runs from 0 to t:

$$\int_{N_0}^{N_f}\frac{dN}{N} = -\lambda\int_{t=0}^{t} dt \tag{43}$$

The result is:

$$\ln N_f - \ln N_0 = -\lambda t \tag{44}$$

$$\ln\frac{N_f}{N_0} = -\lambda t \tag{45}$$

$$N_f = N_0e^{-\lambda t} \tag{46}$$

Equations 39 and 40 show that generally it holds that

$$A = \lambda N \tag{47}$$

This must also hold for N_0 and N_f, so that multiplication of Eq. 46 with λ yields:

$$A_f = A_0e^{-\lambda t} \tag{48}$$

The last equation shows that the activity of a sample decays in the same way as the number of radioactive atoms.

Equation 46 can be used to calculate the so-called half-time $t_{1/2}$ of an isotope: it gives the time in which half of the initial number of radioactive atoms has decayed:

$$N(t_{1/2}) = \frac{N_0}{2} = N_0 \mathrm{e}^{-\lambda t_{1/2}} \tag{49}$$

This means that

$$\frac{1}{2} = \mathrm{e}^{-\lambda t_{1/2}} \tag{50}$$

with the result:

$$t_{1/2} = \frac{\ln 2}{\lambda} \approx \frac{0.693}{\lambda} \tag{51}$$

If an isotope decays on two different pathways, the overall decay constant is the sum of the two individual decay constants. Here is an example: ${}^{40}_{19}\mathrm{K}$ decays on two pathways:

$${}^{40}_{19}\mathrm{K} \xrightarrow{\lambda_{\mathrm{EC}}} {}^{40}_{18}\mathrm{Ar}$$

$${}^{40}_{19}\mathrm{K} \xrightarrow{\lambda_{\beta}} {}^{40}_{20}\mathrm{Ca}$$

The indices β (Greek letter beta) and EC indicate a β-decay and an electron capture decay, respectively.

The differential equation for the overall decay is:

$$-\frac{\mathrm{d}N_{\mathrm{K}}}{\mathrm{d}t} = \frac{\mathrm{d}N_{\mathrm{Ar}}}{\mathrm{d}t} + \frac{\mathrm{d}N_{\mathrm{Ca}}}{\mathrm{d}t} = \lambda_{\mathrm{EC}} N_{\mathrm{K}} + \lambda_{\beta} N_{\mathrm{K}} = (\lambda_{\mathrm{EC}} + \lambda_{\beta}) N_{\mathrm{K}} = \lambda_{\mathrm{overall}} N_{\mathrm{K}} \tag{52}$$

Relaxation in nuclear magnetic resonance

In an external magnetic field B_0, the macroscopic magnetization vector M_0 of the spin system is oriented parallel to the external field, i.e. per definition in z-direction (M_z). Starting an NMR experiment, this equilibrium state of the spin system is disturbed: By applying a 90° radio frequency pulse (B_1 in x-direction), the macroscopic magnetization is rotated on the y-axis or after a 180° pulse the magnetization is turned to $-z$ (cf. Fig. 8). As a result, the occupation numbers of the spin energy levels are changed. Switching off this perturbation by the additional field B_1, the spin system returns to its thermal equilibrium state by relaxation. Felix Bloch [11] described two different relaxation processes with (i) the spin–lattice or longitudinal relaxation time T_1, describing the relaxation in the direction of the external magnetic field B_0, and (ii) the spin–spin or transversal relaxation time T_2, describing the relaxation perpendicular to the external magnetic field B_0. For these relaxation processes, first-order mechanisms are assumed, both from the viewpoint of kinetics (cf. Chapter 4) and from the viewpoint of mathematics [12]:

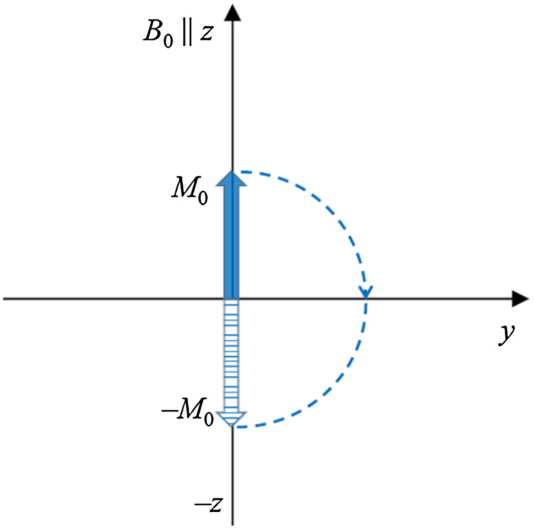


Fig. 8 Orientation of the macroscopic magnetization before ($+M_0$) and after ($-M_0$) a 180° pulse. At $t = 0$ follows that $M_z = -M_0$

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = -\frac{M_z - M_0}{T_1} \tag{53}$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = -\frac{M_y}{T_2} \tag{54}$$

and

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = -\frac{M_x}{T_2} \tag{55}$$

These equations represent the time dependence of magnetization along the three space directions with the rate constants $1/T_1$ and $1/T_2$ for the two relaxation processes mentioned.

A typical experiment for the determination of the spin–lattice (or longitudinal) relaxation time T_1 is the so-called inversion recovery experiment. Here, first a 180° pulse turns the macroscopic magnetization vector M_0 from $+z$ to $-z$ (see Fig. 8). Then, a 90° pulse is necessary to enable the signal detection in y-direction.

The quantitative description of this experiment starts from Eq. 53. Introducing a new dependent variable y as

$$y = M_z - M_0 \tag{56}$$

and

$$\mathrm{d}y = \mathrm{d}M_z \tag{57}$$

Equation 53 can be rewritten as

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -\frac{y}{T_1} \tag{58}$$

Separation of variables and integration leads to:

$$\int_{y_0}^{y} \frac{\mathrm{d}y}{y} = -\frac{1}{T_1} \int_0^t \mathrm{d}t \tag{59}$$

At $t = 0$ the definition of y in Eq. 56 gives $y_0 = -2M_0$ as initial condition. Integration and re-substitution of y result in

$$\ln\left(\frac{M_z - M_0}{-2M_0}\right) = -\frac{t}{T_1} \tag{60}$$

or in the exponential notation

$$M_0 - M_z = 2M_0 \mathrm{e}^{-t/T_1} \tag{61}$$

$$M_z = M_0(1 - 2\mathrm{e}^{-t/T_1}) \tag{62}$$

Equations 61 and 62 present explicit dependencies of the magnetization M_z in z-direction on time. This time-dependent behaviour is schematically illustrated in Fig. 9.

The mathematical solution of the differential equations (Eq. 54) for the determination of the spin–spin (or transversal) relaxation time T_2 is obvious and is exemplarily given for the time-dependent behaviour of the magnetization M_y in y-direction (cf. Eq. 54). Separation of variables and integration gives Eqs. 63–65:

$$\int_{M_0}^{M_y} \frac{\mathrm{d}M_y}{M_y} = -\frac{1}{T_2}\int_0^t \mathrm{d}t \tag{63}$$

$$\ln\frac{M_y}{M_0} = -\frac{t}{T_2} \tag{64}$$

$$M_y = M_0 \cdot \mathrm{e}^{-t/T_2} \tag{65}$$

For $t = 0$, the magnetization M_y in y-direction equals M_0, which is the initial value immediately after the 90° pulse. Equations 64 and 65 can now be used to determine the spin–spin relaxation time T_2, which is a measure how fast the transversal magnetization disappears. Experimentally, the well-known spin-echo method developed by Hahn [13] is used to determine T_2.

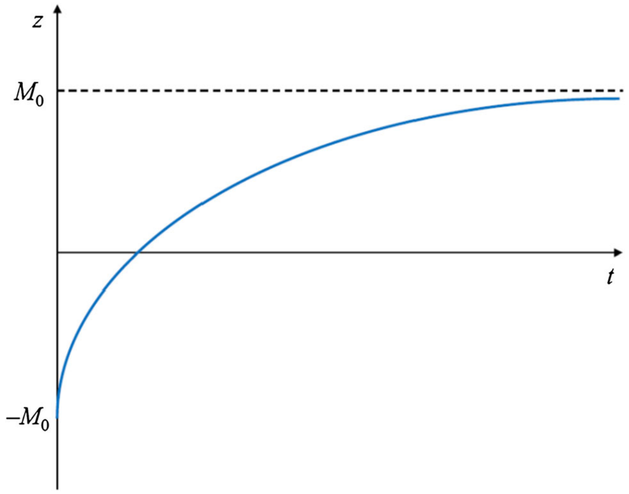


Fig. 9 Development of the macroscopic magnetization in z-direction M_z in dependence on time following a 180° pulse

The *RC* constant of an electrode

When a metal electrode is in contact with an electrolyte solution, a double layer is formed at the interface. It has a complex structure with the charged metal side and the oppositely charged solution side. The double layer has the property of a capacitor, as charge can be stored on both sides, always equal amounts with opposite signs. Of course, it is also possible that no net charge is on both sides and this situation is referred to as the *potential of zero charge* (given versus a reference potential). Most electrochemical techniques make use of a changing electrode potential (linear and non-linear) to measure the current response. Only rarely the current is deliberately changed or controlled to measure the response of the electrode potential. In the potential-controlled experiments, the double layer is always charged or discharged during the experiment, depending on the applied potentials, so that charging currents accompany the so-called faradaic currents, which result from charge *transfer* reactions at the interphase. Thus, the charging or capacitive currents are normally interfering as they may become dominating when the compounds undergo the electrochemical reaction are at very low concentration. Therefore, the double layer charging is worth to be considered, not to speak about their great importance for modern capacitors. It is also important to study capacitive currents because the double layer charging reveals information about the complex structure of the solution and metal sides of the interface. Here, we shall discuss the most simple case: two metal pieces are inserted in an electrolyte solution, e.g. of potassium nitrate in water, and there is no compound in the solution other than KNO_3 and H_2O, i.e. only the following ions and molecules are present: K^+, NO_3^-, H_2O, H_3O^+, OH^- (if we neglect more complex ions like $H_5O_2^+$, and also ion pairs, like $[KNO_3]$, which are present only in extremely small concentrations). If at each electrode in the above system the potential difference between the metal and the solution side is insufficient to perform an electrochemical reaction with all these species, i.e. insufficient to reduce the protons of water to hydrogen or oxidize the oxygen-containing species to oxygen, any change of the voltage between the electrodes can only charge or discharge the double layer of the electrodes. In electrochemistry, such electrode is called an ideally polarizable electrode. The current has thus to flow via a resistor, which is formed by the electrolyte solution into or out of the capacitor formed by the double layers. All other resistors in the circuit, e.g.

the metal wires, have a much lower resistance than the electrolyte solution. In such case, we may model the situation at one electrode by the capacitor “double layer”, and the resistor “solution” in series (see Fig. 10). (The second electrode can be treated in the same way). Let us suppose that the double layer is initially completely discharged (the electrode rests at the potential of zero charge), i.e. there is no charge separated by the two capacitor plates. In a potential step experiment (i.e. when the electrode potential is stepped from one value to another), the double layer is charged (the capacitor is loaded). At the beginning ($t = 0$), the current flows only through the resistor, and upon charging the current decays to zero, when the capacitor is charged to its potential difference ΔE.

According to Kirchhoff’s law, the overall potential difference across the resistor and capacitor is the sum of two potential drops:

$$\Delta E = \Delta E_{\text{resistor}} + \Delta E_{\text{capacitor}} \tag{66}$$

For the potential drop across the resistor follows (Ohm’s law):

$$\Delta E_{\text{resistor}} = RI \tag{67}$$

where R is the solution resistance and I the current.

The potential drop across the capacitor is:

$$\Delta E_{\text{capacitor}} = \frac{q}{C} \tag{68}$$

where q is the charge, and C the capacitance of the capacitor “double layer” (which in fact is depending on the electrode potential, what we may neglect here).

Substituting the terms from Eqs. 67 and 68 in Eq. 66 yields:

$$\Delta E - RI - \frac{q}{C} = 0 \tag{69}$$

Solving this equation for I gives:

$$I = \frac{\Delta E}{R} - \frac{q}{RC} \tag{70}$$

Since the current is the first derivative of charge over time ($I = \mathrm{d}q/\mathrm{d}t$), one can write Eq. 70 also as follows:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{\Delta E}{R} - \frac{q}{RC} = -\frac{1}{RC}(q - C \cdot \Delta E) \tag{71}$$

$$\frac{\mathrm{d}q}{\mathrm{d}t} + \frac{1}{RC}(q - C \cdot \Delta E) = 0 \tag{72}$$

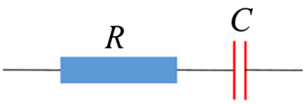


Fig. 10 The resistor formed by the electrolyte solution having the resistance R and the capacitor formed by the double layer of the electrode having the capacitance C in an electrochemical cell

Equation 72 is a *nonhomogeneous* linear first-order differential equation. Integration of Eq. 72 in the limits of 0 and q, and 0 and t gives:

$$\int_0^q \frac{\mathrm{d}q}{q - C \cdot \Delta E} = -\frac{1}{RC}\int_0^t \mathrm{d}t = -\frac{t}{RC} \tag{73}$$

At $t = 0$ follows $q = 0$ from the assumption that the electrode is initially at the potential of zero charge. To solve the integral on the left side, one needs to make the following substitution:

$$q' = q - C \cdot \Delta E \tag{74}$$

from which follows $q = q' + C \cdot \Delta E$ and $\mathrm{d}q = \mathrm{d}q'$.

$$\int_{q'_{t=0}}^{q'_t} \frac{\mathrm{d}q'}{q'} = -\frac{t}{RC} \tag{75}$$

(This is equal to solving the differential equation $\frac{\mathrm{d}q'}{\mathrm{d}t} + \frac{1}{RC}q' = 0$).

$$[\ln q']_{q'_{t=0}}^{q'_t} = -\frac{t}{RC} \tag{76}$$

Back-substitution $q' = q - C \cdot \Delta E$ and $\mathrm{d}q' = \mathrm{d}q$ and defining $q'_{t=0} = -C \cdot \Delta E$ (this equals to the condition $q_{t=0} = 0$) lead to:

$$\ln(q - C \cdot \Delta E) - \ln(-C \cdot \Delta E) = -\frac{t}{RC} \tag{77}$$

$$\ln\left(\frac{q - C \cdot \Delta E}{-C \cdot \Delta E}\right) = -\frac{t}{RC} \tag{78}$$

$$-\left(\frac{q - C \cdot \Delta E}{C \cdot \Delta E}\right) = \mathrm{e}^{-t/RC} \tag{79}$$

$$q - C \cdot \Delta E = -C \cdot \Delta E \cdot \mathrm{e}^{-t/RC} \tag{80}$$

$$q = -C \cdot \Delta E \cdot \mathrm{e}^{-t/RC} + C \cdot \Delta E \tag{81}$$

$$q = C \cdot \Delta E(1 - \mathrm{e}^{-t/RC}) \tag{82}$$

Since $I = \mathrm{d}q/\mathrm{d}t$ it follows from Eq. 82 that:

$$I = \frac{\mathrm{d}q}{\mathrm{d}t} = -\frac{1}{RC}(-C \cdot \Delta E) \cdot \mathrm{e}^{-t/RC} = \frac{\Delta E}{R} \cdot \mathrm{e}^{-t/RC} \tag{83}$$

Since the $\Delta E/R$ must be equal to the initial current I_0 at $t = 0$, Eq. 83 gives the current transient:

$$I = I_0 \cdot \mathrm{e}^{-t/RC} \tag{84}$$

describing the exponential decay of current following a potential step. RC is also called the time constant τ and one can write:

$$I = I_0 \cdot \mathrm{e}^{-t/\tau} \tag{85}$$

Table 1 Overview of the discussed cases of applications of a first-order differential equation $a_1 \frac{\mathrm{d}y}{\mathrm{d}x} + a_2 y = 0$

	Differential equation	a_1	a_2	y	x	Integrated equation
Bouguer–Lambert–Beer law	$-\frac{\mathrm{d}I(x)}{\mathrm{d}x} - \kappa c I(x) = 0$	-1	$-\kappa c$	I	x	$\ln \frac{I_0}{I} = \kappa c x_\mathrm{e}$
Time constant of a sensor	$a_1 \frac{\mathrm{d}z}{\mathrm{d}t} + a_2 z(t) = 0$ for the equation: $S = S_\mathrm{max} - z(t)$	a_1	a_2	z	t	$z(t) = z_0 \mathrm{e}^{-\frac{a_2}{a_1}t}$ yielding: $S = S_\mathrm{max}\left(1 - \mathrm{e}^{-\frac{t}{\tau}}\right)$ with $\frac{a_1}{a_2} = \tau$
Kinetics of chemical reaction	$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} + k c_\mathrm{A} = 0$	$+1$	$+k$	c_A	t	$c_{\mathrm{A}_t} = c_{\mathrm{A}_0} \mathrm{e}^{-kt}$
Radioactive decay	$\frac{\mathrm{d}N}{\mathrm{d}t} + \lambda N = 0$	1	λ	N	t	$N_\mathrm{f} = N_0 \mathrm{e}^{-\lambda t}$
Bloch equation (a)	$\frac{\mathrm{d}M_z}{\mathrm{d}t} + \frac{M_z - M_0}{T_1} = 0$	$+1$	$1/T_1$	$M_z - M_0$	t	$M_z = M_0\left(1 - 2\mathrm{e}^{-t/T_1}\right)$
Bloch equation (b)	$\frac{\mathrm{d}M_y}{\mathrm{d}t} + \frac{M_y}{T_2} = o$	$+1$	$1/T_2$	M_y	t	$M_y = M_0 \cdot \mathrm{e}^{-t/T_2}$
Resistor and capacitor in series	$\frac{\mathrm{d}q'}{\mathrm{d}t} + \frac{1}{RC} q' = 0$	1	$\frac{1}{RC}$	q' $q' = q - C \cdot \Delta E$	t	$[\ln q']_{q'_{t=0}}^{q'_t} = -\frac{t}{RC}$ $q = C \cdot \Delta E\left(1 - \mathrm{e}^{-t/RC}\right)$ $I = \frac{\Delta E}{R} \cdot \mathrm{e}^{-t/RC} = I_0 \cdot \mathrm{e}^{-t/RC}$

Another possibility to solve the *nonhomogeneous* linear first-order differential Eq. 72, consists in solving first the homogeneous equation

$$\frac{\mathrm{d}q_\mathrm{h}}{\mathrm{d}t} + \frac{1}{RC} q_\mathrm{h}(t) = 0 \tag{86}$$

yielding $q_\mathrm{h}(t)$ as usual in an exponential form. After that, a particular solution $q_\mathrm{p}(t)$ of the nonhomogeneous differential equation can be found applying the equation

$$q_\mathrm{p}(t) = u(t) \cdot q_\mathrm{h}(t) \tag{87}$$

and its first derivative

$$q'_\mathrm{p}(t) = u'(t) \cdot q_\mathrm{h}(t) + u(t) \cdot q'_\mathrm{h}(t) \tag{88}$$

Both expressions for $q_\mathrm{p}(t)$ and for its first derivative $q'_\mathrm{p}(t)$ are substituted in Eq. 72, which finally leads to the determination of $u(t)$ and thus to $q_\mathrm{p}(t)$. The complete solution of Eq. 72 is then the sum of the solution of the homogeneous differential equation $q_\mathrm{h}(t)$ and the particular solution $q_\mathrm{p}(t)$, i.e.

$$q(t) = q_\mathrm{h}(t) + q_\mathrm{p}(t). \tag{89}$$

Both mathematical approaches result in Eq. 85.

In many experiments, it is crucial to know the value of the *RC* time constant of the electrode/electrolyte system, because the charging current may be superimposed to faradaic currents that are investigated.

For a more detailed understanding of the used electrochemical terms, we suggest to consult an electrochemical dictionary [14].

Conclusions

Table 1 gives an overview of the discussed cases of application of first-order differential equations to chemistry.

It should be mentioned that there are many other processes in science, which are based on first-order differential equations, e.g. the so-called “exponential growth” of bacteria cultures, the barometric formula or Newton’s law of cooling.

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