APPLICATIONS OF
CALCULUS IN CHEMISTRY

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Teaching undergraduate physical chemistry can be demanding on both the teacher and the students. The demand lies in balancing the science and mathematical tools required to explore and extend it. Often times the teacher is confronted with the burden of reviewing, if not reteaching, the essentials of calculus. This can be frustrating sometimes, to say the least.

On the part of the students, this requires them to replace their concepts of *x* and *y* variables with that of real physical variables. To some, this can come naturally; however, to most students an extra effort is required to the extent of giving some subjects an unnecessary reputation for difficulty.

It is our hope that a middle ground can be reached, which will minimize the mathematical handicap of most student taking physical sciences and engineering courses. One of the possible approaches is to use realistic science examples in teaching calculus. There are excellent calculus textbooks that use this approach. If the students are made aware of the power and the utility of their tools, perhaps they will appreciate it more and will learn to apply it more effectively. The following are some examples of applications of calculus in chemistry. This is far from exhaustive but, I hope this will motivate some teachers to teach calculus as a tool for solving a wide variety of mathematical and physical problems.

Chemical thermodynamics. One of the operational problems in thermodynamics is finding an alternative expression that will reduce the present expression in terms of measurable quantities. To attain this goal, manipulations of partial derivatives is required. The proper concepts of finite vs. infinitesimal changes, and exact vs. inexact differentials are also implied.

The following expressions represent the fundamental equations in thermodynamics in energy representation U, and the various thermodynamic potentials for a closed simple system.

$$dU = TdS - PdV \tag{6.1}$$

$$H = U + PV \tag{6.2}$$

$$A = U - TS \tag{6.3}$$

$$G = H - TS \tag{6.4}$$

Differentiating equations (6.2) to (6.4) and inserting (6.1) into each of them yields,

$$dH = TdS - VdP \tag{6.5}$$

$$dA = -SdT - PdV \tag{6.6}$$

$$dG = -SdT + VdP \tag{6.7}$$

Equations (6.5) to (6.7) are called the ***enthalpy*** H, ***Helmholtz Free Energy*** A, and the ***Gibbs Free Energy*** G. They are exact differentials and by employing Euler's reciprocity relation on each of them, one gets,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P, \text{ from } dH;$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \text{ from } dU;$$

$$\left(\frac{\partial S}{\partial V}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V, \text{ from } dA;$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \text{ from } dG.$$

In thermodynamics, they are commonly called ***Maxwell's relations*** (when applied to P, V, and T variables). Using these relations and the fact that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

for exact differentials, one can reduce most of the thermodynamic relations into expressions involving measurable quantities of P, T, and V. Consider the following sample problems:

6.1 EXAMPLE. How much does the internal energy of the van der Waals gas increase when the volume increases from V_1 to V_2 at constant pressure?

Method. The object here is to express the fundamental equation (6.1) in terms of measurable quantities. Differentiating the fundamental equation (6.1) with respect to V at constant T, gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T .$$

The first differential on the right hand side of the equation contains an entropy component (S) and is not directly measurable. Using one of Maxwell's relations, the differential can be replaced as

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Thus, we now have everything in terms of measurable quantities P, T, and V.

Solution. The van der Waals equation of state is

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2},$$

and, hence, $(\partial P/\partial T)_V = nR/(V - nb)$. Insertion of these two expressions into the internal energy equation above gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{nR}{V - nb}\right) - \left[\frac{nRT}{V - nb} - \frac{n^2a}{V^2}\right] = \frac{n^2a}{V^2} .$$

Finally, to find the internal energy change, we integrate the above result between the limits V_1 and V_2 to give

$$\Delta U = \int_{V_1}^{V_2} \frac{n^2 a}{V^2} dV = n^2 a \left(\frac{V_2 - V_1}{V_1 V_2} \right).$$

6.2 EXAMPLE. The density (gm./cm.^{3}) of a certain material (mol. mass = 63.54 g./mol) between 100 ^oC and 200 ^oC at constant pressure, can be expressed as

$$\rho = 4.186 - 1.62 \times 10^{-3} T - 4.56 \times 10^{-6} T^2$$

where T is the temperature in ^oC. Calculate the change in entropy of a mole of material per unit pressure at 150 ^oC.

Method. We are interested in the relationship between the entropy and pressure at fixed temperature. Here we can use one of Maxwell's relations to get the relationship between entropy and measurable quantities. Then by using the chain rule and the definition of density ($V = M/V$), we can relate the measurable quantity to our existing data, i.e., $\rho(T)$, as follows

$$\left(\frac{\partial S}{\partial P} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_P$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial V}{\partial \rho} \right)_P \left(\frac{\partial \rho}{\partial T} \right)_P$$

$$= -\frac{M}{\rho^2} \left(\frac{\partial \rho}{\partial T} \right)_P$$

Solution. Taking the derivative of density with respect to temperature and evaluating it at $T = 150$ ^oC gives,

$$\left(\frac{\partial \rho}{\partial T} \right)_P = -1.62 \times 10^{-3} - 2\,(4.56 \times 10^{-6})T$$

$$= -2.99 \times 10^{-3} \ g./cm.^3 \ {}^oC$$

Also at 150 ^oC the density is 3.84 $g./cm.^3$, hence

$$\left(\frac{\partial S}{\partial P}\right)_T = -1.29 \times 10^{-2} \text{ cm.}^3\text{/mol }^\circ C.$$

6.3 EXAMPLE. Find the three equations of state for the system with the fundamental equation

$$U = \left(\frac{v_0\theta}{R^2}\right)\frac{S^2}{NV},$$

then proceed to find $P = P(V,T)$.

Method. By differentiating the fundamental equation with respect to entropy S, volume V, and N, one can obtain the equations of state as pressure, temperature, and the chemical potential respectively

Solution.

$$\left(\frac{\partial U}{\partial S}\right)_{N,V} = T = 3\left(\frac{v_0\theta}{R^2}\right)\frac{S^2}{NV},$$

$$\left(\frac{\partial U}{\partial V}\right)_{N,S} = -P = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{NV^2},$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{N^2V}.$$

Solving for S in the first equation and substituting it into the second equation gives pressure as a function of V and T as

$$P = -\frac{1}{9}\frac{\sqrt{3}T\sqrt{\dfrac{TR^2NV}{v_0\theta}}}{V}.$$

Chemical kinetics. This division of physical chemistry deals with the change in a specific property of matter (i.e., concentration) with respect to time. Here the proper concepts of simple differential equations can be very useful. The bulk of the job is focused on the processing of these concentration vs. time information (obtained from experiment) to establish the rate law of the reaction.

The rate law is a differential equation, which must be integrated to obtain the concentration of species as a function of time. In the following discussion, we assume that the reaction is carried out at constant temperature T and volume and the reaction is irreversible.

6.4.1 DEFINITION. ***Zero-order reactions*** are those reactions having the differential rate equation of the form

$$\frac{d[A]}{dt} = -k \, .$$

Upon integration (using $[A] = [A]_o$ at $t = 0$), it gives

$$[A] = [A]_0 - k\,t$$

where $[A]_0$ is the initial concentration, k is the rate constant, and t represents the time. For this type of reaction, a plot of $[A]$ vs. t will give a straight line with a slope k and intercept $[A]_0$.

6.4.2 DEFINITION. ***First-order reactions*** are those reactions represented by $A \rightarrow$ Products, where the rate law is expressed as

$$\frac{d[A]}{dt} = - k[A]$$

with $[A]$ and t as variables.

This equation can be rearranged and integrated to get

$$\int_1^2 \frac{d[A]}{[A]} = -\int_1^2 kdt, \quad \text{or}$$

$$\ln \frac{[A]_2}{[A]_1} = -k(t_2 - t_1)\, .$$

If state 1 is taken to be the state of the reaction when $[A] = [A]_0$ and $t = 0$, then the last equation becomes

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

which rearranges to

$$[A] = [A]_0 e^{-kt}.$$

If a reaction is of first order, a plot of ln $[A]/[A]_0$ vs. t gives a straight line with a slope equal to k.

6.4.3 DEFINITION. For a ***second-order reaction*** $\nu = k\,[A]^2$, the differential rate equation is given by

$$\frac{d\,[A]}{dt} = -k[A]^2.$$

Rearranging and integrating the preceding equation, we obtain

$$\int_1^2 \frac{d[A]}{[A]^2} = -\int_1^2 kdt\,, \text{ or}$$

$$\frac{1}{[A]_2} - \frac{1}{[A]_1} = kt\ .$$

Plotting $1/[A]_2 - 1/[A]_1$ vs. t gives a straight line with a slope equal to k.

Temperature dependence of rate constants. The rate constants depend strongly on temperature and increase rapidly with increasing T. In 1889, Arrhenius proposed that the $k(T)$ data for many reactions can be fitted into the following expression

$$k = A\ \exp(\frac{Ea}{RT}),$$

where A and Ea are constants characteristic of the reaction. Taking logarithms, one obtains $\ln k = \ln A - Ea/RT$. Differentiating $\ln k$ with respect to T (temperature), one gets

$$\left(\frac{\partial \ln k}{\partial T}\right)_V = \frac{Ea}{RT^2}, \text{ and}$$

$$Ea = -R\frac{d\ln k}{d(1/T)}.$$

This implies that the activation energy Ea can be obtained from the slope of a plot of $\ln k$ against $1/T$.

The preceding examples illustrate the importance of calculus in the chemical science. The coverage is, however, limited but the point has been made that it is an indispensable tool for modern day chemist. It is my hope that calculus will not be taught as an end in itself but rather as a subject that is closely tied to the physical world, and I feel that it is misleading to teach it any other way.

> *The more progress physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation.*
>
> – Adolphe Quetelet, (1796–1874)

Appendix: graphical representation of equations. For every curve arising in chemistry, there is an equation, and, conversely, for every expression in x and y for which the roots are real, there is a corresponding curve. The curve gives at once the relation between variables and it is a great aid in clear thinking.

The quantitative study of the influence of one variable on another constitutes one of the common operation in science. The influence of pressure on the volume of a gas, or the temperature on the solubility of a salt, or of time on the course of the chemical reaction are all examples. The simplest way to represent the relation between such variables is to draw a picture. Certain conventions have to be adopted, however, which render the graphical representation extremely simple.

Straight lines. Lines represent equations of the first degree, i.e., algeb-raic equations containing no exponents other than 1. The most general form of the equations which give a straight line is

$$C_1 x + C_2 y + C_3 = 0,$$

where C_1, C_2, and C_3 are constants. This can be changed by transposing, and dividing through by C_2,

$$y = -\frac{C_1}{C_2}x - \frac{C_3}{C_2}.$$

This can be changed into simpler forms as

$$y = mx + b,$$

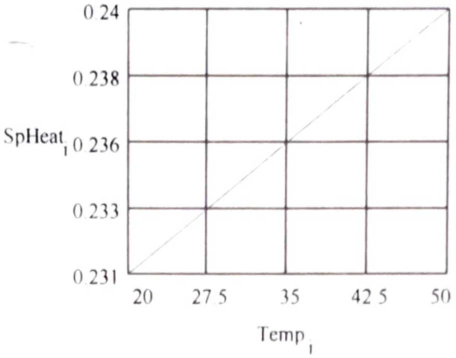
where m and b are constants ($m = -C_1/C_2$ and $b = -C_3/C_2$).

6.5 EXAMPLE. The specific heat of chloroform has the following values:

Temp (°C)	20.0	30.0	40.0	50.0
Sp.Heat	0.2311	0.2341	0.2371	0.2401

The data is plotted and the best straight line is drawn to points. Find the equation of the line that gives the specific heat of chloroform as a function of temperature (^{o}C)

Method. The slope m may be calculated by taking the two end points, however, to do that one must assume that the point fall on a straight line. The only way to check this is by plotting.



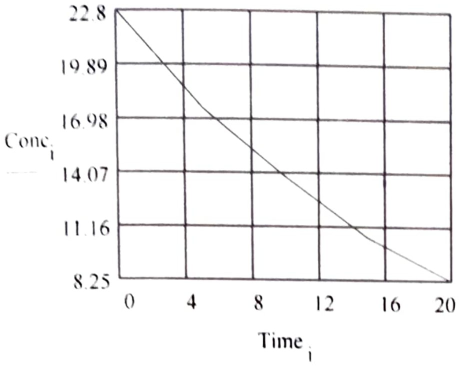
Answer. The slope = 3.0×10^{-4}, intercept = 0.2251, the relationship may be expressed as:

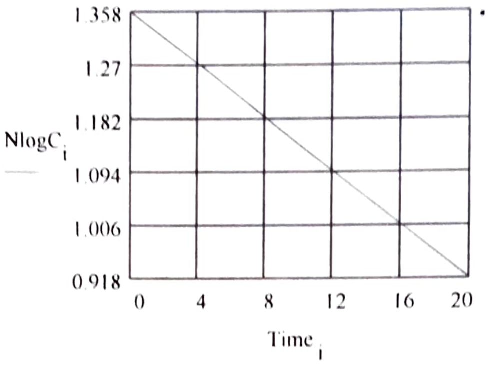
Specific Heat = 3.0×10^{-4} Temp (^{o}C) + 0.2251.

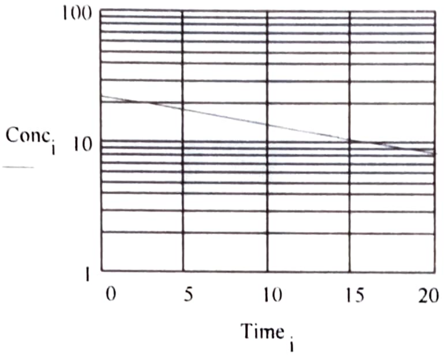
Exponential equations. Exponential or logarithmic equations are very common in physical and chemical phenomena. One of the best ways to know whether or not a given set of phenomena can be expressed by an exponential or logarithmic equation is to plot the logarithm of one property against another property. For example, the first of the three graphs below represent how the concentration (see the table below) of a particular substance changes with time.

Time (min)	0	5	10	15	20
Conc. (M)	22.8	17.6	13.8	10.5	8.25

Graphing is much easier in the third case because the graphing paper itself takes the place of the logarithm table. The second method, however, offers some flexibility. Functions of the type $y = kx^{a}$ give a straight line when plotted with logarithm along both axis. However, functions of the type $y = a^x$ give a straight line when plotted with logarithm along one axis.







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