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Chemical Equilibrium, Free Energy, and Entropy of Mixing

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Abstract: In this paper we describe an approach for teaching the relation between chemical equilibrium and free energy that is, according to our experience, very efficient and enlightening. This approach has a strong visual appeal and can be used at different levels, from simple presentation of the results as graphs of free energy versus reaction mixture composition, up to full derivation of formulas to find the equations of the curves.

Introduction

Teaching chemical equilibrium as a comprehensible fundamental concept is a challenging task. While the students usually understand quite well the reasons for the chemical equilibrium based on reaction kinetics considerations, the relationship between equilibrium and thermodynamic quantities, particularly the entropy of mixing, is often poorly understood, largely due to the difficulty of understanding the connection between mathematical expressions and the physical phenomena.

A considerable improvement in clarity has been attained in this matter by textbooks in the last few decades [1]. A curve of Gibbs free energy versus reaction progress (at constant temperature and pressure), showing a minimum that corresponds to equilibrium, is now commonplace, and students can easily understand why the reaction progress brings the system to the equilibrium (minimum G) point, regardless of the side from which it is started. *Why this curve has a minimum*, however, is still not easy to understand for most students, and *how to plot the curve* that would demonstrate the desired aspects is still a hard task for many lecturers. Different approaches have been proposed in articles on this matter: Cohen and Whitmer [2] give a demonstration largely based on chemical potential of reactants and products; MacDonald [3] shows clearly the importance of entropy of mixing in these processes; Shultz [4] also emphasizes the role of entropy discussing a specific reaction.

In this paper we propose an approach that requires a minimum of concepts. We found that if we choose a simple system, as the one described ahead, there is no real need to use the quantity defined as "extent of reaction," or "reaction progress"; the more intuitive *concentration* (mole fraction, to keep the mathematical transformations to a minimum) can be used instead. The concepts of entropy, entropy of mixing, and Gibbs free energy are also required; particularly important is a previous knowledge of the connection between Gibbs free energy and spontaneity of transformations.

The Proposed Approach

Chemical transformations can involve a variable number of substances, both as reagents and as products, and a variable molar proportion among the substances. Derivations based on general chemical equations usually demand a high level of abstraction, not easily attainable to the average junior student; definition of quantities such as the *extent of reaction* (see note [7]) are also required, resulting in a dispersion of the students' minds and opening the doors for mistaken interpretations (the student can, for instance, start to think that the *extent of reaction* is the fundamental quantity that explains the existence of equilibrium).

On the other hand, when we consider a simple system with strongly limited variations, we can go fast and straight to the heart of the problem, and a satisfactory first comprehension (that should later be complemented by considering more general approaches) can be easily attained.

A simple general chemical transformation will be considered here:

$$\begin{array}{ccccccc} \mathrm{A} & + & \mathrm{B} & \rightleftharpoons & \mathrm{C} & + & \mathrm{D} \\ 1\text{-}x & & 1\text{-}x & & x & & x \end{array}$$

To simplify the calculations, we will say that

(a) all compounds are ideal liquids ($\Delta H_{\text{mixing}} = 0$), and they are all miscible with each other;
(b) all mixtures to be considered contain no other substance besides A, B, C, and D;
(c) all mixtures contain a total amount of 2 mol; and
(d) The Gibbs free energy of (A + B) is higher than (or equal to) the free energy of (C + D), or $\left(G_{\mathrm{C}}^{0} + G_{\mathrm{D}}^{0}\right) - \left(G_{\mathrm{A}}^{0} + G_{\mathrm{B}}^{0}\right) \le 0$.

If we start from A (1 mol) and B (1 mol), *all* possible mixtures will have the composition summarized in Table 1.

The value of x can vary from 0 to 1, including the extremes. Clearly, the corresponding mole fractions (X_{A}, X_{B}, etc.) are obtained by dividing the corresponding amount (mol) by 2 (which is the total amount).

We will say that the free energy of the mixture of reactants (A + B) ($x = 0$) is G_1, and the free energy of the mixture of products (C + D) ($x = 1$) is G_2 [5]. The question we intend to answer is "*What is the free energy of the other possible compositions?*"

A simple way to achieve this objective occurs if we imagine that we can prepare mixtures of A, B, C, and D without any reaction taking place in the meanwhile. As this is an

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Table 1. Composition of the Reaction Mixture

Substance	Amount (mol)	Mole fraction
A	$1 - x$	$(1 - x)/2$
B	$1 - x$	$(1 - x)/2$
C	x	$x/2$
D	x	$x/2$

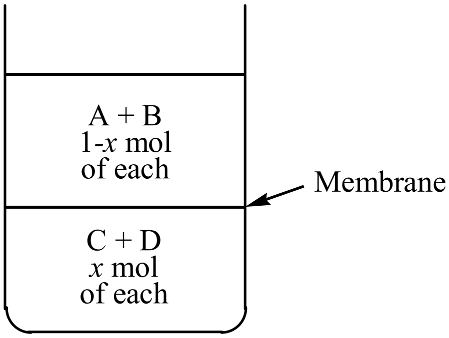


Figure 1. Mixture vessel with the membrane in place.

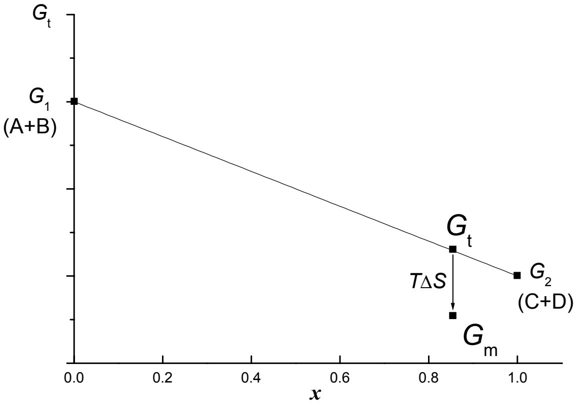


Figure 2. Energy of the several possible combinations of (A + B) with (C + D), **before mixing** (with the membrane still in place).

exclusively mental operation, it is easy to imagine that mixtures can be prepared in so short a time that no significant chemical transformation can occur during the process.

Under these premises, we prepare now in a vessel an equimolar mixture of A and B and, in another vessel, an equimolar mixture of C and D. Then we take an amount of the first mixture containing $(1 - x)$ mol of A (and, thus, containing also $(1 - x)$ mol of B), and an amount of the second mixture containing x mol of C (and, thus, containing also x mol of D).We put these two solutions in the same vessel, which is provided with a membrane that keeps the two solutions **SEPARATED** from each other (see Figure 1). What is the free energy of this system? Of course, it will be the sum of the free energies of each solution,

$$G_t = (1-x)G_1 + xG_2 \quad or \quad G_t = (G_2 - G_1)x + G_1 \qquad (1)$$

In a graph, this equation corresponds to the straight line between G_1 and G_2, as in Figure 2.

What will happen now if we remove the membrane of one of these combinations? As the substances are all miscible (assumed as a hypothesis), a complete homogenization will occur.

The spontaneity of the homogenization process already shows that the resulting mixture has a free energy value (G_m) that is *lower* than the corresponding G_t value (observe the points in Figure 2). As there is no enthalpy of mixing ($\Delta H_{mixing} = 0$, as assumed), the difference in free energy is due exclusively to the entropy of mixing (A + B) with (C + D) (a rather elaborated notation [6] for the entropy of mixing was used here for the sake of clarity, particularly in the following section).

$$G_m = G_t - T\Delta S^{A+B+C+D}_{(A+B)\leftrightarrow(C+D)} \qquad (2)$$

The entropy of mixing, then, is the reason why the graph of Gibbs free energy versus x is *not* a straight line like in Figure 2, but a *curve* with a minimum as discussed in the Conclusion section. We should remind the reader that this is valid only for ideal liquids or gases, otherwise the curve would include a more or less important contribution from ΔH_{mixing}.

At this point students should have understood the main points, and in a course for beginners it could be more advisable to jump from here to the section "Conclusions," because the next section involves too many mathematical operations to demonstrate quantitative aspects that are not essential for a first comprehension of the subject.

The Equation of the Curve

We could derive expressions to give G_m as a function of X_A, X_B, X_C, or X_D; all these mole fractions, however, can be easily calculated if we know the value of x (see Table 1) [7]; we can, therefore, find G_m as a function of x. After combining eqs 1 and 2, we have still to find $\Delta S^{A+B+C+D}_{(A+B)\leftrightarrow(C+D)}$ as a function of x.

The entropy of mixing for ideal liquids (or gases), which can be found in most physical chemistry texts, is

$$\Delta S_{mixing} = -nR \sum_i X_i \ln X_i$$

where n is the total amount of substances (in mol) and X_i is the mole fraction of component i.

Now we will consider the following points:

(a) A and B were already mixed together, the corresponding entropy being [8] (we remind the reader that there are always $1 - x$ mol of each component)

$$\Delta S^{A+B}_{A\leftrightarrow B} = -2R(1-x)\ln\frac{1}{2}$$

(b) C and D were also already mixed together (x mol of each), the corresponding entropy being

$$\Delta S^{C+D}_{C\leftrightarrow D} = -2Rx\ln\frac{1}{2}$$

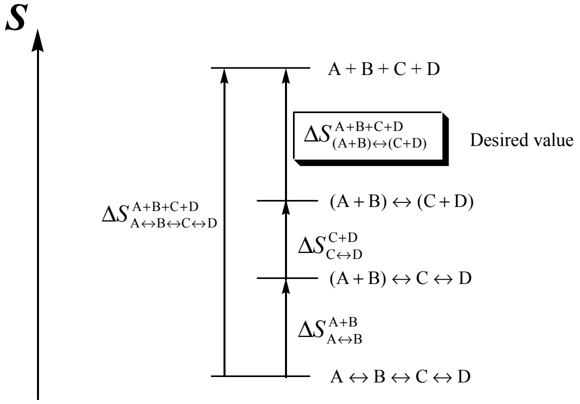


Figure 3. Relationship among values of entropy of mixing considered in the text.

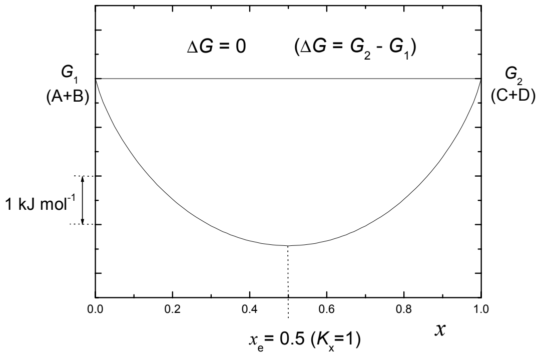


Figure 4. Curve of free energy for $\Delta G = 0$ (at 25 °C).

(c) The entropy of the whole mixture, starting from pure components ($1 - x$ mol of A, $1 - x$ mol of B, x mol of C, and x mol of D) is [9]

$$\Delta S^{\text{A+B+C+D}}_{\text{A}\leftrightarrow\text{B}\leftrightarrow\text{C}\leftrightarrow\text{D}} = -2R[(1-x)\ln(1-x) + x\ln x]$$
$$\underbrace{-2R(1-x)\ln\frac{1}{2}}_{\Delta S^{\text{A+B}}_{\text{A}\leftrightarrow\text{B}}} \underbrace{-2Rx\ln\frac{1}{2}}_{\Delta S^{\text{C+D}}_{\text{C}\leftrightarrow\text{D}}}$$

These three values are interrelated in the way depicted in Figure 3, from which we can find the desired value of the entropy:

$$\Delta S^{\text{A+B+C+D}}_{\text{(A+B)}\leftrightarrow\text{(C+D)}} = -2R\left[(1-x)\ln(1-x) + x\ln x\right] \quad (3)$$

Now, combining eqs 1 through 3:

$$G_m = (1-x)G_1 + xG_2 + 2RT\left[(1-x)\ln(1-x) + x\ln x\right] \quad (4)$$
$$0 < x < 1 \; [10]$$

This is the desired equation of the curve and can also be written as

$$G_m = x\Delta G + G_1 + 2RT\left[(1-x)\ln(1-x) + x\ln x\right] \quad (4a)$$
$$(\Delta G = G_2 - G_1);\; (0 < x < 1)\; [10]$$

If the curve has a minimum, in this minimum the value of the first derivative of the function is zero. The first derivative is

$$\frac{dG_m}{dx} = \Delta G + RT\left[\ln x^2 - \ln(1-x)^2\right]$$

In the minimum, x has the equilibrium value x_e:

$$0 = \Delta G + RT\left[\ln x_\text{e}^2 - \ln(1-x_\text{e})^2\right]$$

and then

$$\frac{x_\text{e}^2}{(1-x_\text{e})^2} = \text{e}^{\frac{-\Delta G}{RT}}$$

where the left expression can be regarded as a representation of the equilibrium constant K_x, because

$$K_x = \frac{X_\text{C}X_\text{D}}{X_\text{A}X_\text{B}} = \frac{\frac{x_\text{e}}{2}\cdot\frac{x_\text{e}}{2}}{\frac{1-x_\text{e}}{2}\cdot\frac{1-x_\text{e}}{2}}$$

(X_A, X_B, X_C, and X_D are, here, the mole fractions of the substances in the equilibrium state).

Conclusions

The equation of the curve of Gibbs free energy versus x for this system is very simple:

$$G_m = x\Delta G + G_1 + 2RT\left[(1-x)\ln(1-x) + x\ln x\right] \quad (4a)$$
$$(\Delta G = G_2 - G_1);\; (0 < x < 1)\; [10]$$

This can be easily introduced in any suitable computer program for plotting graphs with the desired values of ΔG and T. The lecturer can then use these curves to show how the *free energy difference* affects equilibrium.

Observing eq 4a the student can realize that the *shape* of the curve depends exclusively on the value of ΔG and on the expression $2RT\left[(1-x)\ln(1-x) + x\ln x\right]$, this expression being independent of energy values; G_1, whose value can be only arbitrarily assigned, can just move the curve up or downward, without shape modifications (it would be the same as if we just moved the vertical scale). This means that we can plot curves, for the sake of observing its shape, for any reaction with known ΔG (remembering all restrictions), regardless the impossibility to know the values of G_1 (and G_2); we can assign any arbitrary value to G_1 because the *shape* of the curve would be the same anyway.

Comparing eq 4a with its equivalent, eq 2, the student can also realize that the curve representing G_m can be interpreted as the addition (point by point) of two curves: a straight line given by the free energy of the extreme cases (G_t, or $x\Delta G + G_1$) and a curve given by the entropy of mixing ($-T\Delta S^{\text{A+B+C+D}}_{\text{(A+B)}\leftrightarrow\text{(C+D)}}$, or $2RT\left[(1-x)\ln(1-x) + x\ln x\right]$; cf. also eq 3). This curve has the shape depicted in Figure 4, and its depth is independent of the energy values; for this reason, when $|\Delta G|$ is large, we have a steep straight line and the

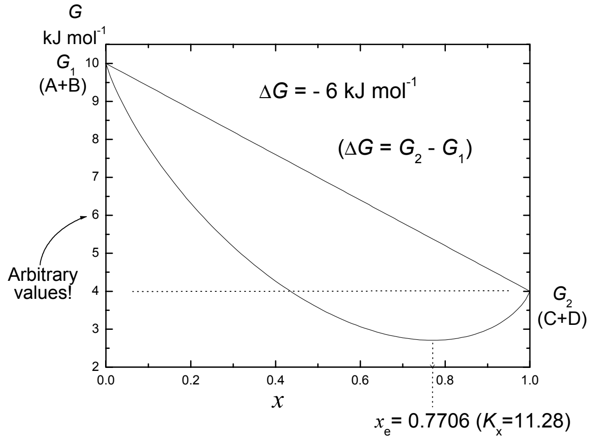


Figure 5. Curve of free energy for $\Delta G = -6$ kJ mol^{-1} (at 25 °C). The shape of the curve is strongly affected by the value of ΔG. In Figures 5, 6, and 7 are the curves for $\Delta G = 0$, $\Delta G = -20$ kJ mol^{-1} and $\Delta G = -40$ kJ mol^{-1}.

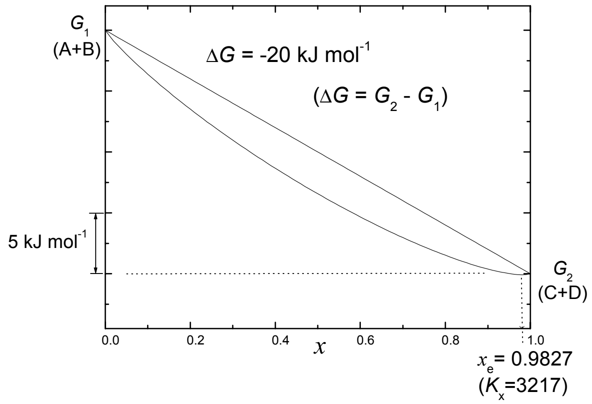


Figure 6. Curve of free energy for $\Delta G = -20$ kJ mol^{-1} (at 25 °C).

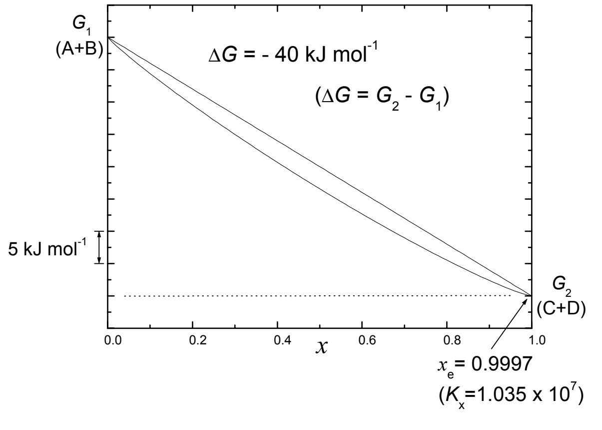


Figure 7. Curve of free energy for $\Delta G = -40$ kJ mol^{-1} (at 25 °C).

curve due to the entropy of mixing put on the same scale looks much less deep; the addition results in a shallow curve, as can be seen comparing Figures 4–7.

Figure 5 is the graph of eq 4 (or eq 4a) for values of G_1 and G_2 taken arbitrarily as $G_1 = 10$ kJ mol^{-1} and $G_2 = 4$ kJ mol^{-1} at 25 °C (298 K). The straight line G_1G_2 was included as a visual reference.

Comparing Figures 4 to 7, it is easy to see that, when the free energy difference is high ($|\Delta G| > 40$ kJ mol^{-1}, for instance), it is difficult to notice the occurrence of an equilibrium: the concentrations of the reactants are too low at equilibrium and, thus, are hard to detect. The appearance is that the reaction has proceeded to the end, transforming all reactants into products.

In Figure 4 we see that when ΔG = 0 (rather uncommon for chemical reactions but it can occur, for instance, when A is a chiral organic iodide, C its enantiomer, and B and D are I$^-$), the equilibrium point is in the center, with equal amounts of reactants and products.

Finally, this approach offers the student an opportunity to realize the importance of entropy as a determinative factor for the occurrence of chemical equilibrium, itself one of the most fundamental concepts in chemistry.

References and Notes

1. For instance, see Atkins, P. W. *Physical Chemistry,* 6th ed.; Oxford University Press: Oxford, 1998; Kotz, J. C.; Treichel Jr., P. *Chemistry & Chemical Reactivity,* 3rd ed.; Saunders College Publishing: Fort Worth, 1987.
2. Cohen, R. W.; Whitmer, J. C. *J. Chem. Educ.* **1981,** *58,* 21–24.
3. MacDonald, J. J. *J. Chem. Educ.* **1990,** *67,* 380–382.
4. Shultz, M. J. *J. Chem. Educ.* **1999,** *76,* 1391–1393.
5. Values G_1 and G_2 are the sum of free energies of the corresponding substances considering the entropy of mixing: $G_1 = G_A^0 + G_B^0 - T\Delta S_{A+B}$ and $G_2 = G_C^0 + G_D^0 - T\Delta S_{C+D}$ (at constant temperature and pressure). In the considered extreme cases, however, we would be mixing one mol of each compound (A + B *or* C + D), and $\Delta S_{A+B} = \Delta S_{C+D}$; hence, $G_2 - G_1 = \Delta G^0$ (the ΔG^0 value for the reaction, or the difference of free energy between reactants and products).
6. The solutions mentioned in this text were prepared in steps (first mixing A with B, then C with D, etc.), each step having its own value of entropy of mixing. It is, therefore, necessary to distinguish between entropy values belonging to different steps. The notation explained below intends to provide an indexing system that would enable the reader to identify to which step each value of entropy belongs: the symbol ΔS_M^N represents the entropy of mixing for a system in the initial state M and in the final state N; the double headed arrow $Y \leftrightarrow Z$ indicates that Y and Z are separated, while the sum signal Y+Z means that Y and Z are mixed together.
7. For this particular system, considering all restrictions, x has, in fact, the same value as the *extent of reaction* as defined, for instance, by MacDonald (see ref. 3):

$$x = \xi = \frac{n_M - n_M^0}{\nu_M}$$

n_M^0 : initial amount of component M;

n_M : amount of component M after some reaction has taken place;

ν_M : stoichiometric coefficient of M in the particle equation for the reaction (negative for a reactant, positive for a product); ν_M is a pure number, ξ is expressed in moles.

8. Summary of operations:

$$\Delta S_{\mathrm{A}\leftrightarrow\mathrm{B}}^{\mathrm{A+B}} = -\underbrace{2(1-x)}_{\mathrm{mol}}R\left(\frac{1-x}{2(1-x)}\ln\frac{1-x}{2(1-x)}+\frac{1-x}{2(1-x)}\ln\frac{1-x}{2(1-x)}\right)$$

$$\Delta S_{\mathrm{A}\leftrightarrow B}^{\mathrm{A+B}} = -2R(1-x)\left(\frac{1}{2}\ln\frac{1}{2}+\frac{1}{2}\ln\frac{1}{2}\right)$$

9. Summary of operations:

$$\Delta S_{\mathrm{A}\leftrightarrow\mathrm{B}\leftrightarrow\mathrm{C}\leftrightarrow\mathrm{D}}^{\mathrm{A+B+C+D}}$$

$$= -2R\left[\underbrace{\frac{(1-x)}{2}\ln\frac{(1-x)}{2}}_{\mathrm{A}}+\underbrace{\frac{(1-x)}{2}\ln\frac{(1-x)}{2}}_{\mathrm{B}}+\underbrace{\frac{x}{2}\ln\frac{x}{2}}_{\mathrm{C}}+\underbrace{\frac{x}{2}\ln\frac{x}{2}}_{\mathrm{D}}\right]$$

$$= -2R\left[(1-x)\ln\frac{(1-x)}{2}+x\ln\frac{x}{2}\right]$$

$$= -2R\left[(1-x)\ln(1-x)+(1-x)\ln\frac{1}{2}+x\ln x+x\ln\frac{1}{2}\right]$$

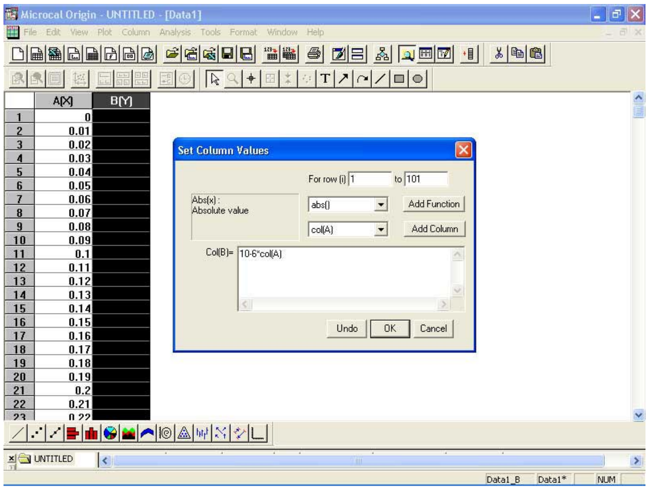
$$= -2R\left[(1-x)\ln(1-x)+x\ln x\right]-2R\left[(1-x)\ln\frac{1}{2}+x\ln\frac{1}{2}\right]$$

Equation 4 or 4a can easily be introduced in a computer program for plotting graphs (see ahead), but they cannot be used to calculate G_{m} for the extreme points ($x = 0$ and $x = 1$), because ln 0 would appear in both cases. We know, however, that $T\Delta S_{(\mathrm{A+B})\leftrightarrow(\mathrm{C+D})}^{\mathrm{A+B+C+D}} = 0$, in these cases, therefore,

$$\text{for}\quad x=0,\ G_{\mathrm{m}}=G_1$$

$$\text{for}\quad x=1,\ G_{\mathrm{m}}=G_2$$

10. The graphs on this paper were plotted using the computer program Microcal Origin 6.0, by Microcal Software Inc. (http://www.microcal.com/). An example is as follows for the graph shown in Figure 5 (observe in Figure 8 and Figure 9 the appearance of the monitor screen during the operations of setting column values). First, we set column A (x axis) values (of the data table), for row number (i) 1 to 101, as (i – 1)/100; this will give 101 points for the curve, evenly distributed in the horizontal direction. Then, we set column B values (y-axis values for the straight line), also for row number (i) 1 to 101 as G_1+(G_2 – G_1)*col(A) or, in this specific case, 10–6*col(A). Finally, we set column C (y-axis values for the curve) as –col(A)*6 + 10 + 2 *0.00831*298*((1–col(A))*ln(1–col(A))+col(A) *ln(col(A))). If this is set for row number (i) 1 to 101, the program will calculate the values, but will give an error for the first and last rows. These values should then be typed in the proper boxes (they are the same as the column B values for these extreme cases). After that, we have only to set the program to plot the graph with column A values in the x axis and both column B and column C values in the y axis.



For row (i) 1 to 101

Abs(x) :
Absolute value

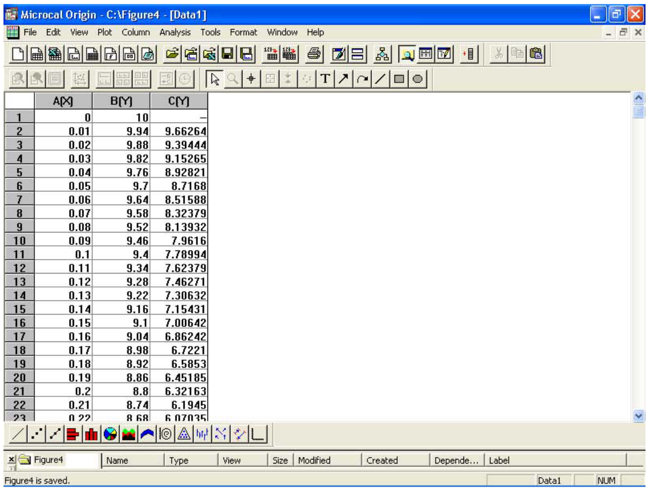
abs()

col(A)

Col(B)= 10-6*col(A)

	A[X]	B[Y]
1	0	
2	0.01	
3	0.02	
4	0.03	
5	0.04	
6	0.05	
7	0.06	
8	0.07	
9	0.08	
10	0.09	
11	0.1	
12	0.11	
13	0.12	
14	0.13	
15	0.14	
16	0.15	
17	0.16	
18	0.17	
19	0.18	
20	0.19	
21	0.2	
22	0.21	
23	0.22	

Figure 8. Appearance of the computer monitor screen while setting column B values.



	A[X]	B[Y]	C[Y]
1	0	10	–
2	0.01	9.94	9.66264
3	0.02	9.88	9.39444
4	0.03	9.82	9.15265
5	0.04	9.76	8.92821
6	0.05	9.7	8.7168
7	0.06	9.64	8.51588
8	0.07	9.58	8.32379
9	0.08	9.52	8.13932
10	0.09	9.46	7.9616
11	0.1	9.4	7.78994
12	0.11	9.34	7.62379
13	0.12	9.28	7.46271
14	0.13	9.22	7.30632
15	0.14	9.16	7.15431
16	0.15	9.1	7.00642
17	0.16	9.04	6.86242
18	0.17	8.98	6.7221
19	0.18	8.92	6.5853
20	0.19	8.86	6.45185
21	0.2	8.8	6.32163
22	0.21	8.74	6.1945
23	0.22	8.68	6.07035

Figure4 is saved.

Figure 9. Appearance of the computer monitor screen after all the column values have been set, but the first row of column C has not yet been corrected.

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