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AUTOMATED CALCULATION OF EQUILIBRIUM CONSTANT USING THE TOMKIN - SCHWARZMAN METHOD

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Abstract: *The quantitative characteristic of equilibrium in a chemical system is the thermodynamic quantity Equilibrium constant. There are various methods for calculating the equilibrium constant of a chemical reaction. One of them is the Tymkin-Schwartzman method.*

The present work presents an automated method for calculating the equilibrium constant of a chemical reaction by computer processing of reference data. The method of calculation is related to the establishment of interdisciplinary links between physicochemistry and information technology. The development could be used in the students' independent extracurricular work. It is an example of modern chemistry training through the use of modern computer skills.

Key words: *electronic application, tabular data, chemistry, equilibrium constant, Tymkin - Schwartzman.*

INTRODUCTION

Experience has shown that many chemical processes are reversible. With each reversible chemical reaction, it is possible to select the experimental conditions in such a way as to ensure the flow of the processes in both directions. It reaches a point where the speeds of the two processes equalize, after which the composition of the system does not change over time. A state of chemical equilibrium occurs. The main thermodynamic quantitative characteristic of the chemical equilibrium is the equilibrium constant. It provides information about the state of the reaction system. It can also determine the yield of chemical reaction products (2). Various methods have been developed in the literature - experimental and computational to determine its value (Atkins, P., & J.Paula, 2006). Depending on the particular reaction and the conditions under which it takes place, various equations known in thermodynamics are applied. Calculating the equilibrium constant of a chemical reaction without attempting to study equilibrium is one of the important practical applications of thermodynamics.

EXPOSITION

Tymkin-Schwartzman method for calculating the equilibrium constant of a chemical reaction

The computational methods for determining the equilibrium constant of a chemical reaction are related to the ability for calculating the change in thermodynamic function G^0 (Gibbs energy). In thermodynamics, an equation is derived that relates the change in Gibbs standard energy (ΔG^0) and the equilibrium constant (K_p) of any chemical reaction (Berry, R., S. D. Rice, J. Ross, 2000):

$$\ln K_p = -\frac{\Delta G_T^0}{RT}, \quad (1)$$

where ΔG_T^0 can be calculated according to the equations:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \quad (2)$$

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta c_p dT \quad (3)$$

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^{T} \Delta c_p \frac{dT}{T} \quad (4)$$

$$\Delta c_p = \Delta a + \Delta bT + \Delta aT^2 + \Delta c^{\mathrm{I}} T^{-2} \quad (5)$$

The values of ΔH_{298}^0, ΔS_{298}^0, a, b and c^{I} for the studied reaction components are extracted from an electronic reference (relational database) set on MS Excel Table 1 (Haralanova, T., & M. Petrova, 2010). Methods have been developed in which the above equations are taken into account, while simplifying the calculations. Of essential importance is the Tymkin-Schwartzman method. For the calculation of the equilibrium constant in this method the equation is used:

$$\ln K_p = -\frac{\Delta H_{298}^0}{RT} + \frac{\Delta S_{298}^0}{R} + \frac{1}{R}\left(\Delta aM_0 + \Delta bM_1 + \Delta cM_2 + \Delta c^{\mathrm{I}} M_{-2} + \Delta dM_3\right) \quad (6)$$

Table1. 1. Thermochemical table

№	substance	ΔH^0_f,298kj/mol	S^0_{298},J/(mol,K)	α	$10^3\beta$	$10^{-5}c'$
1	Ag	0	42,69	23,97	5,28	-0,25
2	Al	0	28,31	20,67	12,39	-
3	Au	0	47,45	23,68	5,19	-
…	…	…	…	…	…	…
25	H_2	0	130,6	27,28	3,26	0,502
…	…	…	…	…	…	…
34	N_2	0	191,5	27,87	4,27	-
…	…	…	…	…	…	…
125	NH_3	-46,2	192,5	29,8	25,48	-1,67

Constant values M0, M1, M2, M-2 and M3 in equation 6 are taken from an electronic directory (relational database) set again in MS Excel Table 2.

Table. 2. Constants in the Tymkin - Schwartzman equation

T	M_0	M_1*10^3	M_2*10^6	$M_{-2}*10^{-5}$	M_3*10^9
300	0,0000	0,0000	0,0000	0,0000	0,00000
400	0,0392	0,0130	0,0430	0,0384	0,00144
500	0,1133	0,0407	0,0140	0,0916	0,00553
600	0,1962	0,0759	0,0303	0,1423	0,01246
700	0,2794	0,1153	0,0498	0,1853	0,22570
800	0,3597	0,1574	0,0733	0,2213	0,03630
900	0,4361	0,2012	0,1004	0,2521	0,05411
…	…	…	…	…	…
2500	1,246	0,9696	1,0008	0,4363	1,29404

In our work, we demonstrate how students, using their knowledge of chemistry, physicochemistry, mathematics and information technology, as well as using the above method, can automate the calculation of the equilibrium constant at 500K of a chemical reaction:

$3H_2 + N_2 \leftrightarrow 2NH_3$

MS Excel software (Roman S., 2007) is used for this purpose. It is convenient for working with spreadsheets, and with its built-in functions and convenient interface makes mathematical calculations easy and pleasant. The elements involved in the chemical reaction and their coefficients are given as input. The values in the reference table 1 are automatically extracted for the indicated elements and the entry of each element is filled horizontally, which can be seen from Table 3.

By setting the appropriate mathematical formulas and using the built-in functions of the spreadsheets to extract the values of the constants M_0, M_1, M_2, M_{-2}, M_3, the results in the electronic application Table 3, where is the value of the equilibrium constant of the chemical reaction.

For an electronic application, it is essential to analyze and manage the accuracy with which the user wants the calculated results to be displayed. It is very important to keep track of the units of measurement of all the elements involved and, if necessary, to match them accordingly to Velheva, E., E. Lazarova, 1996) (Roman S., 2007).

The process of creating an electronic application is not easy; it requires a good knowledge of algorithmic techniques and information processing techniques. Tests for verifying the accuracy of the information displayed. But after its creation, the trainees see how it can be repeatedly applied to different chemical equations, just changing the input and outputting the results in seconds.

Therefore, we believe that the use of electronic applications motivates students to upgrade their knowledge of fundamental disciplines, such as higher mathematics and information technology, so that they can effectively use them in specialized disciplines.

If students can program in MS Excel, the electronic application can take on an even better look, because at the programming level, improvements can be made that cannot be achieved at the user interface level.

Table. 3. Setting and results of the reaction data processing

elements on the left side of the equation		set a factor in front of the element	$\Delta H^0_{f,298}$kj/mol	S^0_{298},J/(mol,K)	α	$10^3\beta$	$10^{-5}c'$
set item 1	H_2	3	0	130,6	27,3	3,26	0,502
set item 2	N_2	1	0	191,5	27,9	4,27	-
set item 3							
set item 4							
elements on the right side of the equation		**set a factor in front of the element**	**$\Delta H^0_{f,298}$kj/mol**	**S^0_{298},J/(mol,K)**	**α**	**$10^3\beta$**	**$10^{-5}c'$**
set item 1	NH_3	2	-46,19	192,5	29,8	25,48	-1,67
set item 2							
set item 3							
set item 4							
Results			**ΔH^o_{298}= -92380**		**Δα= -50,11**		
			ΔS^o_{298}= -198,3		**Δβ= 0,03691**		
			K_{p500}= 0,15		**Δc'= 1,834E+05**		

CONCLUSIONS

1. On the basis of data from thermochemical tables, the equilibrium constant of a specific chemical reaction was calculated using the Tömkin-Schwartzman method. This is an important practical application of thermodynamics.
2. When analyzing the value obtained for the equilibrium constant of the chemical reaction and the factors that affect the chemical equilibrium, the optimal conditions for the preparation of NH_3 can theoretically be selected.
3. The method described in the current work makes it possible to determine the equilibrium constant of any chemical reaction for which data are available in thermochemical tables.
4. The present development is an example of the effective entry of information technology into students' learning and extracurricular activities.
5. By solving the practical problem raised, personal initiatives of trainees in the use of ICT are stimulated, thus reaching new levels of knowledge.

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