Methods of computer thermodynamic analysis of chemical reactions in ecological systems

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Abstract. The technique for constructing a thermodynamic model of chemical transformations that occur in ecological systems, which can be used to study the course of ecology, is proposed. The information necessary for students studying environmental disciplines for the independent implementation of thermodynamic calculations is presented.

1. Introduction

The main principles for modeling in scientific research are given in chapter 3 of the manual [1].

The purpose of this article is to acquire skills in constructing thermodynamic models of chemical transformations of substances occurring in ecosystems.

As a rule, the task in mathematical modeling is in obtaining a reasonable prediction of the kinetics of the components of any ecological system [2].

2. Brief information on chemical transformations in ecological systems

According to the authors' definition [3], “the ecological system is a spatially defined set of living organisms of different species and their habitats, combined by material-energy and informational interactions”.

Energy losses for informational interactions are insignificant and do not upset the balance in ecosystems, but they ensure consistent behavior of subsystems (self-organization), as a result of which the degree of ordering of the system increases, i.e., entropy decreases (Mileshko L.P., Kotenko V.V., Nestyurina E.E.) [4].

The composition of biotic components includes three functional groups of organisms. The first group of organisms includes producers or autotrophic organisms, which are divided into photo- and chemoautotrophs [5].

Photoautotrophs (some bacteria and all green plants) use sunlight as a source of energy, and the inorganic substances such as carbon dioxide and water are the nutrient material for them. They synthesize carbohydrates, or sugars (CH₂O)n in the process of life in the light [5]:

\[
\text{CO}_2 + \text{H}_2\text{O} = (\text{CH}_2\text{O})_n + \text{O}_2
\]

Chemoautotrophs (nitrifying bacteria) use energy that is released during chemical reactions. They oxidize ammonia to nitrous, and then nitric acid [5]:
2NH₃ + 3O₂ = 2HNO₂ + 2H₂O + Q₁
2HNO₂ + O₂ = 2HNO₃ + Q₂

Bacteria consume the chemical energy released during these reactions to restore CO₂ to carbohydrates.

Plant green organisms play a major role in the formation of organic substances. Chemosynthetic bacteria are relatively small in this process.

The second group of organisms (consumers or heterotrophic organisms) decomposes organic substances [5].

These organisms use organic matter as a source of both energy and nutrient material. They are divided into phagotrophs and saprotrophs [5].

Phagotrophs (large animals - macroconsumers) eat plant or animal organisms directly for nutrition.

Saprotrophs feed on the organic matter of dead residues.

Reducers make up the third group of organisms, microscopic organisms, bacteria, fungi, and other microconsumers involved in the last stage of decomposition, which is called mineralization, to inorganic compounds (CO₂, H₂O, etc.) of organic substances. Thanks to reducers, substances return to the cycle, turning into forms that are accessible to producers.

The ecosystem functions due to the interaction of the flow of energy, community and the circulation of substances.

A part of the energy flow directed in one direction by autotrophs is converted into organic matter, but most of the energy passing through the ecological system leaves it in the form of thermal energy.

An ecological system cannot be hermetic because a living community could not endure such isolation.

3. The formation and decomposition of organic matter

Photosynthesis is a process of the formation of organic substances in the light, which consists in the accumulation of part of the solar energy through its conversion into potential energy of chemical bonds [5].

Photosynthesis is a necessary link between inanimate and living nature. According to the second law of thermodynamics, life on our planet would cease forever if there were no influx of energy from the Sun.

Cornelis Bernardus van Niel proposed the equation of photosynthesis [5]:

\[ \text{CO}_2 + 2\text{H}_2\text{A} \xrightleftharpoons{\text{Light}} (\text{CH}_2\text{O})_n + \text{H}_2\text{O} + 2\text{A} \]

where H₂A is water (H₂O) in the case of green plants and algae; hydrogen sulfide (H₂S) for purple sulfur bacteria; hydrogen or an oxidizable substance for other bacteria.

In the 30s of the last century, this idea was confirmed experimentally using the heavy oxygen isotope (18O) [5]:

\[ \text{CO}_2 + 2\text{H}_2^{18}\text{O} \xrightleftharpoons{\text{Light}} (\text{CH}_2\text{O})_n + \text{H}_2\text{O} + ^{18}\text{O}_2 \]

The equation of photosynthesis for green plants and algae began to be written in the following form [5, 6]:

\[ 6\text{CO}_2 + 6\text{H}_2\text{O} \xrightleftharpoons{\text{Light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

In aerobic respiration, a process inverse to normal photosynthesis, when C₆H₁₂O₆ decomposes again and H₂O and CO₂ are formed and the potential energy released in this substance is released [5]:

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + Q_1 \]
wherein: $Q_1 = Q_{pot} = 668 \text{ kJ} \times \text{mmol}^{-1}$

In anaerobic respiration, proceeding without the participation of gaseous oxygen, acetic acid, and not oxygen, can be, for example, an electron acceptor [5]:

$$C_6H_{12}O_6 + CH_3COOH \rightarrow 4CO_2 + 4CH_4 + Q_2$$

in this case, $Q_2 < Q_{pot}$, and methane, which is released, still has some energy reserve $q_1$ and can be used as fuel or spontaneously ignite and oxidize under natural conditions [5]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + q_1$$

In the case of fermentation - anaerobic respiration, during which the electron acceptor is an organic matter itself [5]:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + Q_3$$

In this case, $Q_3 < Q_{pot}$, and the resulting alcohol also has a certain amount of energy that can be used by other organisms [5]:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + q_2$$

4. Technique of computer thermodynamic modeling

In this work, for the thermodynamic assessment of the feasibility of chemical reactions, the usual criterion, the negative value of the Gibbs energy change, is accepted:

$$\Delta G_{298}^o = \Delta H_{298}^o - 298.15 \times \Delta S_{298}^o < 0,$$

where: $\Delta H_{298}^o$ is a change in standard enthalpy; $\Delta S_{298}^o$ is a change in standard entropy.

The value $|\Delta G_{298}^o|$ characterizes a measure of chemical affinity or reactivity of substances [7, p. 218, 220].

“The greater the absolute value $|\Delta G_{298}^o|$, the fuller the substances react among themselves” [7, p.218].

After computer calculations of the values of standard thermodynamic functions from all formally possible reactions, it is necessary to select reactions with a maximum value of $-\Delta G_{298}^o$, which have the lowest molecular weight.

Change in the thermodynamic characteristics of $Y(\Delta H_{f,298}^o \text{ и } S_{298}^o)$ calculated by the generalized equation [8]:

$$\Delta Y = \sum_{i=1}^{i} v'Y'_i - \sum_{i=1}^{i} vY_i$$

where $Y'_i$ is the molar value of the thermodynamic function of the substance related to the reaction products, and $Y_i$ is a corresponding value for the substance related to the reagents; $v'_i$, $v_i$ are stoichiometric coefficients of the products and reagents, respectively.

To reduce the time required to search for reference data, the values of the enthalpies of formation and entropies of the formation of substances were borrowed from [9–11] and are given in table 1.

The calculation of the values of changes in standard thermodynamic functions is carried out in MATLAB environment.
Table 1. Standard enthalpies of formation $\Delta H_{298}^\circ$ and entropy of formation $S_{298}^\circ$ of substance.

| Substance | Condition | $-\Delta H_{298}^\circ$ kJ/mmol | $S_{298}^\circ$ J/(mmol.K) |
|-----------|-----------|-------------------------------|--------------------------|
| C         | Mineral carbon | 0                            | 5.74                     |
| CaCO3     | solid      | 1207                          | 88                       |
| Ca(HCO3)2 | solid      | 2344                          | 155                      |
| CH3COOH   | liquid     | 484                           | 160                      |
| C2H5OH    | liquid     | 277.63                        | 160.7                    |
| C6H12OH6  | solid      | 1268                          | -908.9                   |
| CH4       | gas        | 75                            | 186                      |
| CO        | gas        | 110.52                        | 197.54                   |
| CO2       | gas        | 393.51                        | 213.68                   |
| $CO^{2-}$ | In hydrous solution | 676.64                  | -56.04                   |
| $CO^{3-}$ | In hydrous solution | 0                  | 20.869                   |
| $e^-$     | In hydrous solution | 0                  | 0.000                    |
| $H^+$     | In hydrous solution | 0                  | 0.000                    |
| $HCO_3^-$ | In hydrous solution | 691.28               | 92.57                    |
| HNO2      | liquid     | 119                           | 153                      |
| HNO3      | liquid     | 174                           | 156                      |
| H2O       | liquid     | 285.83                        | 70.08                    |
| H2S       | solution   | 40                            | 121                      |

| Substance | Condition | $-\Delta H_{298}^\circ$ kJ/mmol | $S_{298}^\circ$ J/(mmol.K) |
|-----------|-----------|-------------------------------|--------------------------|
| 1         | 2         | 3                             | 4                        |
| N2        | gas       | 0                            | 199.9                    |
| NH3       | gas       | 46                           | 192                      |
| N2O       | gas       | -82.0                         | 219.9                    |
| NO        | gas       | -90.25                        | 210.6                    |
| NO2       | gas       | -33.0                         | 240.2                    |
| N2O3      | gas       | -83.3                         | 307.0                    |
| N2O5      | Hexagonal | 42.7                          | 178.0                    |
| $NO_2^-$  | In hydrous solution | 104.6                 | 139.55                   |
| $NO_3^-$  | In hydrous solution | 207.4                 | 17.21                    |
| $O_2^-$   | gas       | 0                            | 205                      |
| $OH^-$    | In hydrous solution | 230.04                | -10.86                   |
| 1         | white, cube | 0                   | 10.275                   |
| $P(\overset{4}{P4})$ | In hydrous solution | 1271.5             | -221.43                  |
| $PO_4^{3-}$ | In hydrous solution | 1531.53           | 140.26                    |
| P2O5      | solid     | 0                            | 33                       |
| S         | solid     | 0                            | 33                       |
5. Guidelines for building a thermodynamic model
Make a list of chemical equations that occur in ecosystems. Calculate the values of thermodynamic functions in MATLAB medium [12] and compile a table with reactions arranged in decreasing order of magnitude $|\Delta G^\circ|$. For example, for the reaction $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + q_1$, choose the most favorable reaction from the thermodynamic point of view.

$$|\Delta G^\circ| = 879.5 \text{kJ mmol}^{-1}.$$

6. Conclusion
The technique for constructing a thermodynamic model of chemical transformations that occur in ecological systems, which can be used to study the course of ecology, is proposed.

The information necessary for students studying environmental disciplines useful for the independent implementation of thermodynamic calculations is presented.

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