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# Thermodynamic analysis of environmental problems of energy

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**Abstract.** The paper discusses the problems of the ecological analysis of physicochemical processes in power units and the impact of energy systems on the nature in large territorial regions. The model of extreme intermediate states developed at the Energy Systems Institute based on the principles of classical equilibrium thermodynamics was chosen to devise specific computational methods. The results of the conducted studies are presented and directions for further work are outlined.

## 1 Introduction

Development of methods for the ecological analysis of the energy and other sectors of the national economy is stimulated both by the urgency of the problem of man-induced nature pollution and by the rapidly expanding possibilities for its fulfillment, which is determined by the improvement of computer engineering and information technologies. The model of extreme intermediate states (MEIS) was applied at the Energy Systems Institute for realization of the emerging possibilities [1]. This model is constructed based on simple and universal principles of classical mechanics and equilibrium thermodynamics: conservation, equilibrium and extremality. The model of extreme intermediate states is presented in the language of the mathematical programming which is a modern theory of equilibrium extreme states. Unlike the traditional thermodynamic models designed exclusively for searching for the final equilibrium point, it allows us to consider the entire region of thermodynamic attainability from the given initial state of the modeled system and to find the points corresponding to the extreme values of the quantities of interest to the researcher in this region. This gives an idea of the possible results of processes occurring in the system without determining the trajectories of their achievement. The accuracy of the created MEIS modifications significantly improved by the inclusion of kinetic constraints on individual stages of the studied processes. Circuit variants of the model of extreme intermediate states were designed to represent the objects of analysis in the one-dimensional, always potential, space of variables [1–4]. Graphs in the form of circuits can represent either real schemes of transport networks (electrical, pipeline), or conventional schemes of a wide variety of displacements (for example, rail and road transport). Application of the circuit MEISs allowed us to take advantages of the thermodynamic space of variables with monotonic characteristic functions, and the potential, one-dimensional space of variables. The next step in improving equilibrium thermodynamic modeling

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consisted in development of a method for constructing trajectories which is applicable to the analysis of both reversible and irreversible processes [3, 4]. The initial idea was to stop using the general equation of the process and to switch to the step-by-step increase in the optimal results of computations. It was decided to take the steps in space and time so small that the assumptions on the motion stationarity and the reducibility of the solved intrastep problem to the problem of the equilibrium search for an extreme state proved to be permissible.

The equilibrium thermodynamic analysis of the efficiency of energy technologies and systems which was conducted on the basis of the created MEIS modifications revealed to a great extent both the fruitfulness and the problems of further development of its ecological component. The issues of the optimal use of the gained experience are considered below.

## 2 The results and directions for the further development of thermodynamic analysis

The applied MEIS modifications which allow the analysis of fuel combustion and processing and formation of harmful substances in the atmospheric air found the most extensive application. In the case of fixed temperature $T$, pressure $P$ and initial composition of the reagents, this modification has the form:

find
$$\mathrm{extr}\left[F(\mathbf{x}) = \sum_{j \in J^{\mathrm{ext}}} c_j x_j\right] = F(\mathbf{x}^{\mathrm{ext}}) \quad (1)$$

subject to
$$\mathbf{Ax} = \mathbf{b}, \quad (2)$$

$$D_{\mathrm{t}}(\mathbf{y}) = \left\{ \mathbf{x} : \begin{vmatrix} \mathbf{x} \le \mathbf{y}, & (3) \\ \varphi_r(x_r) \le \psi_r, r \in R^{\mathrm{lim}}, & (4) \end{vmatrix} \right\}$$

$$G(\mathbf{x}) = \sum_j G_j(\mathbf{x}) x_j, \quad (5)$$

$$\mathbf{x} \ge 0, \quad (6)$$

where $\mathbf{x} = (x_1, \ldots, x_n)^T$ – vector of system composition (mole quantities of components); $\mathbf{y}$ – vector of initial composition, $\mathbf{y} \subset \mathbf{x}$; $\mathbf{x}^{\mathrm{ext}}$ – composition of mixture at the point of partial or full equilibrium that corresponds to the extreme value of the objective function $F(\mathbf{x})$; $J^{\mathrm{ext}}$ – set of indices of the components whose extreme concentration of the mixture should be determined; $c_j$ – coefficient ranking usefulness, harmfulness or any other property of the $j$-th component of $\mathbf{x}$; $\mathbf{A} - (m \times n)$ – matrix of element content in the system components; $\mathbf{b}$ – vector of element mole quantities; $D_{\mathrm{t}}(\mathbf{y})$ – region (set) of thermodynamic attainability from the initial state; $\varphi_r$ and $\psi_r$ – limiting kinetic function of the $r$-th component of $\mathbf{x}$ and its limiting value, respectively; $R^{\mathrm{lim}}$ – set of indices of constraints on the macroscopic kinetics; $G$ – Gibbs free energy of the system. In ecological problems the objective function $F(\mathbf{x})$ implies a sought concentration of harmful products of the studied process. Equation (2) is the material balance. Expression (3) is the condition that the Gibbs energy does not increase. Sign $\le$ inside the brackets is understood in a physical (thermodynamic) sense: $\mathbf{x}_2 \le \mathbf{x}_1$, if it is possible to switch from $\mathbf{x}_1$ to $\mathbf{x}_2$ by the path, along which $G(\mathbf{x})$ does not increase monotonically. The thermodynamic description of the kinetic constraint (4) applied to solve specific problems was the most complicated problem in constructing model (1)–(6). An example of such a problem is the analysis of harmful substance formation (for example, nitrogen oxides) in the flame combustion of brown coal. The traditional kinetic model can be constructed based on the information about the whole mechanism of the total process of every stage (pyrolysis, combustion of volatiles and combustion of coke), and the values of the kinetic coefficients. Application of MEIS includes only description of the limiting stages allowing such difficulties to be overcome.

The possibilities for improving the analysis of fuel combustion and processing were revealed in three main directions: 1) increase of the theoretical component share in estimating the limiting concentrations of harmful emissions, and, correspondingly, reduction of the required volume of full-scale experiments, 2) increase of the versatility of performed studies and transition from searching for the content of individual pollutants in the mixture of final reagents to searching for their complete composition; 3) determination of both the concentrations and the attainment trajectories of their limiting values. The last direction concerns improvement of the methods for control of technological processes and creation of opportunities to influence the environmental compatibility of these processes [3, 4].

In the thermodynamic analysis of atmospheric pollution, one of the successes was the substantiation of the possibility for such an analysis. After all, the opinion that thermodynamics cannot be applied to the atmospheric chemistry in principle is widely spread. It follows from the notion of the extremely low rate of chemical reactions at a relatively low air temperature and the unattainability of the point of final equilibrium. Simplicity of finding the points of both final and partial equilibria with the help of MEIS removed all difficulties associated with the slowly running atmospheric processes. This agrees well with the available experimental data of numerous results of calculations of the limiting concentrations of various atmospheric pollutants and change of these concentrations as a function of air temperature, pressure, and humidity.

The revealed influence of high-capacity wind power plants (500 and 1000 MW) on the physicochemical atmospheric processes turned out to be an interesting result [4]. The analysis was carried out with the help of the conventional circuit model for air flow distribution in the area of the wind power plant location. The performed calculations showed that the sudden fluctuations in atmospheric pressure caused by the wind turbine operation can lead to a sharp change in the ratio between the amounts of water vapor and condensate. In turn, the increase in the latter leads to an increase in the surface of the droplets, on which solutions of harmful substances are formed. As a result, the "harmful" precipitation becomes more probable.

The results achieved in the analysis of fuel combustion and processing and air pollution suggested to the authors the statement of a fundamentally new task of creating a conventional thermodynamic-hydrodynamic circuit model for propagation and transformation of energy and industrial emissions in the airspace of a large territorial region. The pollutant flows do not affect the distribution of air flows in the circuit, since they have an immeasurably smaller mass than the flows of the carrier "fluid" (air). At the same time, the material balances for these flows should be observed at the nodes of interface of the branches of the air "network", and the nodes of inflows and outflows of "dirt". In addition, it is necessary to determine changes in the composition of pollutants as a result of chemical reactions on the circuit branches. Under the accepted assumptions, the model of flow distribution takes the form:

find $$\min\left(\sum_{i=1}^{n} z_i x_{\mathrm{a}i}^{\beta+1} + \sum_{i=1}^{n} P_i^{\mathrm{W}} x_{\mathrm{a}i}\right) \tag{8}$$

subject to $$\mathbf{A}\mathbf{x}_{\mathrm{a}} = \mathbf{Q}, \tag{9}$$

$$\sum_{jk} x_{\mathrm{d}ki} = 0, \quad \sum_{\ell k} x_{\mathrm{d}ki} = 0, \tag{10}$$

$$\mathbf{x}_{\mathbf{d}i}^{\mathbf{end}} = f(\mathbf{x}_{\mathbf{d}i}^{\mathbf{beg}}), \tag{11}$$

where $\mathbf{x_a}$ – air flow vector on the branches; $\mathbf{P}^{\mathrm{W}}$ – pressure "loss" vector at wind turbines; $z_i$ – resistance of the $i$-th branch; $\mathbf{A} = [a_{ij}] - (m-1) \times n$ – matrix of connections of independent nodes and branches; $\mathbf{Q}$ – vector of external inflows and outflows; $j$ and $\ell$ – indices of nodes of air and dirt inflows and outflows, respectively; $\mathbf{x}_{\mathbf{d}k}$ – vector of flows of the $k$-th pollutant on the branches interfacing at the $j$-th node; $\mathbf{x}_{\mathbf{d}i}^{\mathbf{end}}$ and $\mathbf{x}_{\mathbf{d}i}^{\mathbf{beg}}$ – vectors of pollutant flows at the end and beginning points of the $i$-th branch, respectively. Transition from $\mathbf{x}_{\mathbf{d}i}^{\mathbf{beg}}$ to $\mathbf{x}_{\mathbf{d}i}^{\mathbf{end}}$ is the result of chemical reactions occurring on the branch. Tendency of the objective function to the minimum point is explained by the circuit passivity. The function $f(\mathbf{x}_{\mathbf{d}i}^{\mathbf{beg}})$ is determined using MEIS similar to model (1)–(6). In the analysis of the features of this function the pollutant inputs from the environment and the outflows into it are taken into account along with chemical reactions, In addition to pollution sources, this conventional scheme may include indirect pollutants: wind and hydraulic power stations which affect the air pressure and humidity and, consequently, the processes of harmful substance formation in it.

Development of the modifications of model (8)–(11) which could find wide practical application is surely associated with extremely great difficulties. However, the accumulated experience of equilibrium thermodynamic modeling allows us to hope for a successful solution of the emerging problems.

## 3 Conclusion

1. In the ecological analysis of energy development the role of equilibrium thermodynamic modeling should substantially increase, since the use of simple and universal natural regularities in it is perfectly combined with the use of modern computer engineering and information technologies.
2. In the application of thermodynamics the model of extreme intermediate states proved to be very effective. However, in further environmental studies its modifications will be equally important, representing the modeled systems and processes in both multi- and one-dimensional circuit spaces of variables.
3. In addition to estimating the efficiency of individual facilities and power plants, more attention should be paid to estimating the environmental efficiency of energy systems and energy sector as a whole.

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