

Conservation of the Properties of Equilibrium Chemical Composition Under Temperature and Pressure Variations

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Abstract

A new method is developed, allowing control of chemical equilibrium in such a way that a criterion depending on the chemical composition is constant with temperature and pressure variations. The application of the implicit function theorem and Kuhn-Tucker conditions allows calculating the sensitivity of chemical composition with respect to internal parameters. The equations are derived that allow calculation of the dependence between temperature and pressure under a fixed value of a linear or non-linear function of chemical composition. Numerical calculations are conducted that confirm the theoretical results.

1 Introduction

The dependence of chemical equilibrium composition of complex reacting systems (i.e., including tens and hundreds of components) on temperature and pressure is not explicit. Simple formulas are available only for simple cases: otherwise, numerical methods are required.

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The usual equilibrium problem statement for an isothermal and isobaric system is as follows [12]:

$$\mathbf{n}^{eq} = \arg \min_{\mathbf{n} \in D} G(\mathbf{n}, T, P). \quad (1)$$

$$G(\mathbf{n}, T, P) = \sum_{j=1}^N \mu_j(\mathbf{n}, T, P) n_j. \quad (2)$$

Here $\mathbf{n}$ is a chemical composition vector, $G(\cdot)$ is Gibbs free energy, $\mu_j(\cdot)$ is the chemical potential of the j -th component, T is temperature, P is pressure, and D is the admissible set of chemical compositions.

$$D = \{\mathbf{n} : \mathbf{A}\mathbf{n} = \mathbf{b}, \mathbf{n} \geq 0\}. \quad (3)$$

Here inequality $\mathbf{n} \geq 0$ means that all the components of $\mathbf{n}$ are non-negative. The matrix $\mathbf{A}$ with dimensions $(M \times N)$ is a molecular matrix with elements a_{ij} counting the number of i -th atoms in a molecule of the j -th component, and $\mathbf{b}$ is the elemental composition vector. Usually, $\dim \mathbf{b} = M < N = \dim \mathbf{n}$.

The optimization problems (1) and (3) are convex if we assume ideal phase approximations (and they are strictly convex if we consider ideal gas mixtures). In this case, the numerical solution of (1) and (3) is a relatively simple task that can be handled by many numerical packages. For ideal gases, chemical potential can be written as follows [5]:

$$\mu_j(\mathbf{n}, T, P) = \mu_j^0(T) + R_g T \ln \left[\frac{P n_j}{P_0 \sigma(\mathbf{n})} \right]. \quad (4)$$

Here $\mu_j^0(T)$ is the standard chemical potential of the j -th component, which can be calculated using thermochemical tables (for example, [11, 18]), $\sigma(\mathbf{n})$ is the sum of moles of gas-phase components, R_g is the universal gas constant (8.31446 J/mol/K), and standard pressure is 1 atm by convention.

Knowing temperature, pressure, chemical potentials, and elemental composition, one can calculate equilibrium composition by minimizing Gibbs free energy. Other conditions can be considered as an extension

of this problem [3].

The main issue is that chemical engineers usually do not know optimal temperature and pressure before using thermodynamic tools. More important is the inverse equilibrium problem: to determine temperature and pressure such that the equilibrium composition satisfies some requirements (high conversion, low yield of by-products, fixed ratio of several components, etc.). Some inverse problems were considered in previous works [7, 17].

The aim of the present study is to develop an algorithm allowing the solution of the inverse equilibrium problem in a specific statement. Let us consider some couple (T_1, P_1) resulting in an admissible equilibrium composition $\tilde{\mathbf{n}}$ according to the optimization problem (1). The question arises: are there other couples of temperature and pressure that would result in the same chemical composition or, at least, conserve some characteristics of this composition? This question leads to inverse optimization problems. Some intuition can be extracted from the Le Chatelier-Braun principle (moderation theorems [19]), but the general solution requires including Kuhn-Tucker conditions into the sensitivity analysis.

A similar approach was proposed in works by Fishtik et al. on chemical equilibrium sensitivity [8, 9]. The main results of these works were the expressions for the derivatives of equilibrium chemical composition with respect to temperature, pressure and initial composition. The approach included transformations of the stoichiometric matrix and the Hesse matrix. However, the analysis was based on the stoichiometric approach. The influence of different parameters was considered separately. In the present work, we use more generalized the sensitivity approach [17] and derive new thermodynamic relations.

A simple consideration shows that it is almost impossible to conserve the equilibrium composition with changing parameters. However, it is possible to conserve a wide range of linear combinations associated with equilibrium compositions. Moreover, there may be continuous curves in the $P - T$ plane on which these linear combinations are conserved, and there is a simple algorithm to calculate these curves. The paper is organized as follows: Sec. 2 considers a simple case allowing conservation of

equilibrium chemical composition; Sec. 3 considers conservation of linear combinations; Sec. 4 shows several numerical examples; Sec. 5 discusses the results; finally, Sec. 6 concludes the paper.

2 Conservation of equilibrium composition

Let us consider a simple system with the only dissociation reaction:



The chemical equilibrium follows a well-known mass-action law:

$$\frac{x_{\text{P}}^n}{x_{\text{R}}} = \exp\left(-\frac{\Delta G_r^0}{R_g T}\right). \quad (6)$$

Here x is a molar fraction and $\Delta G_r = n\mu_{\text{P}}^0 - \mu_{\text{R}}^0$ is the difference of standard chemical potentials between products and reagents. If the chemical composition holds constant, then the l.h.s. of (6) is also constant. The condition of the constant equilibrium composition is therefore the following:

$$\delta\left(\frac{\Delta G_r^0}{R_g T}\right) = \delta T \frac{\partial}{\partial T} \left(\frac{\Delta G_r^0}{R_g T}\right) + \delta P \frac{\partial}{\partial P} \left(\frac{\Delta G_r^0}{R_g T}\right) = 0. \quad (7)$$

Taking the derivatives and using thermodynamic relations, one can obtain:

$$-\delta T \frac{\Delta H_r^0}{R_g T^2} + \delta P \frac{\Delta V_r^0}{R_g T} = 0. \quad (8)$$

Here ΔH_r^0 is the difference of molar enthalpies (reaction thermal effect is $Q_r = -\Delta H_r^0$), and ΔV_r^0 is the difference of volumes occupied by reagents and products. The expression leads to the known formula (similar to the Clausius-Clapeyron equation [5]):

$$\frac{\delta \ln P}{\delta T} = -\frac{Q_r}{R_g T^2 \Delta N_r^0}. \quad (9)$$

Here ΔN_r^0 is the difference of moles of products and reagents (in our

case $\Delta N_r^0 = n - 1$). The formula shows that in order to maintain the chemical composition in a simple reacting system with the only reaction, one should increase pressure with temperature if the reaction is endothermic and decrease pressure if the reaction is exothermic. It is also important to have a reaction with a change of volume (number of moles), since otherwise the expression is singular (which makes sense: it is impossible to influence volume-conserving reaction equilibrium by pressure due to the Le Chatelier-Braun principle).

It is now possible to generalize the problem to many reactions occurring simultaneously: all the reactions should hold equilibrium constants unchanged under varying temperature and pressure, i.e., by (9), all reactions should have the same relation $Q_r/\Delta N_r^0$. Although the fulfillment of this condition may be achieved by coincidence, in general it is practically impossible to tune a reacting system (allowing hundreds of reactions) into the same value.

3 Conservation of a criterion depending on chemical composition

Let us consider a quantity characterizing the reacting system performance:

$$Y(\mathbf{n}) = \mathbf{c}^T \mathbf{n} = \sum_{j=1}^N c_j n_j. \quad (10)$$

Here coefficients c_j are some costs, for example, product value, by-products loss, harmful substances penalty, etc. The main difference from the previous section is that we do not require the system to hold the equilibrium chemical composition: it may vary preserving the value of $Y(\mathbf{n})$.

The algorithm for the calculation of temperature and pressure, which allows to achieve a given value of the criterion (10), will be published in our future works. Here we consider the case when a couple (T_1, P_1) was already found, such that the criterion Y achieved an admissible (not necessarily optimal) value. The next step is to study the neighborhood of the point

(T_1, P_1) to find other points (T, P) with equal performance.

The main idea of the paper is to apply the implicit function theorem in order to obtain formulas linking the equilibrium chemical composition with temperature and pressure. These formulas are not explicit, but the solution of the equilibrium problem (1) gives all necessary values to proceed with the calculations.

At first, Kuhn-Tucker conditions [15] for the problem (1) with linear constraints (3) can be presented as follows:

$$\mu_j(\mathbf{n}, T, P) + \sum_{i=1}^M \lambda_i a_{ij} = 0, \forall j, \quad (11)$$

$$\sum_{j=1}^N a_{ij} n_j - b_i = 0, \forall i. \quad (12)$$

Further, we consider the system (11), (12) as a vector function $\mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})$ with components f_k . The system (11), (12) can be presented as $\mathbf{F}(\mathbf{n}^{eq}, \boldsymbol{\lambda}^{eq}) = 0$. This vector function produces equilibrium chemical composition and Lagrange multipliers as its roots. To find the necessary derivatives, we should calculate the Jacobi matrix [13]:

$$\mathbf{J} = \begin{pmatrix} \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{n}} & \mathbf{A}^T \\ \mathbf{A} & \mathbf{0} \end{pmatrix}. \quad (13)$$

Here $\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{n}}$ is the matrix consisting of elements $\frac{\partial \mu_i}{\partial n_j}$, and $\mathbf{0}$ is the zero matrix of proper dimensions $(M \times M)$.

Now we consider the variation of $\mathbf{F}$ with respect to some parameter U :

$$\begin{aligned} \delta \mathbf{F} &= \delta U \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial U} + \delta U \sum_j^N \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial n_j} \frac{\partial n_j}{\partial U} + \delta U \sum_i^M \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial \lambda_i} \frac{\partial \lambda_i}{\partial U} = \\ &= \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial U} \delta U + \mathbf{J} \begin{pmatrix} \frac{\partial \mathbf{n}}{\partial U} \\ \frac{\partial \boldsymbol{\lambda}}{\partial U} \end{pmatrix} \delta U. \end{aligned} \quad (14)$$

In order to maintain the equilibrium conditions, we require that $\delta \mathbf{F} = 0$.

In the paper [8] the same approach was applied to the variation of reaction affinities. This method is also used in analysis of stationary states in chemical kinetics [4]. The equilibrium sensitivity coefficients are as follows:

$$\begin{pmatrix} \frac{\partial \mathbf{n}}{\partial U} \\ \frac{\partial \boldsymbol{\lambda}}{\partial U} \end{pmatrix} = -\mathbf{J}^{-1} \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial U}. \quad (15)$$

The expression (see also [17]) gives the implicit formulas to calculate the derivative of the equilibrium chemical composition with respect to some parameter U using the solution of the optimization problem (1). Indeed, the modern solvers allow calculating all the input data (the Jacobi matrix is a Hessian matrix of the Lagrange function) as auxiliary variables.

In the case when $U = T$, the derivative is the r.h.s. in (15), which is the following:

$$\frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial T} = \begin{pmatrix} -\mathbf{s}(\mathbf{n}, T, P) \\ \mathbf{0} \end{pmatrix} = - \begin{pmatrix} \mathbf{h}(T, P) - \boldsymbol{\mu}(\mathbf{n}, T, P) \\ \mathbf{0} \end{pmatrix}. \quad (16)$$

Here $\mathbf{s}$ is a vector of specific entropy values, and $\mathbf{h}$ is a vector of specific enthalpy values.

If $U = P$, then the formula simplifies:

$$\frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial P} = \begin{pmatrix} \mathbf{V}(T, P) \\ \mathbf{0} \end{pmatrix}. \quad (17)$$

Here $V(T, P) = \frac{R_g T}{P}$ is the specific molar volume of an ideal gas, and $\mathbf{V}$ is the vector consisting of repeating values of V .

Now let us introduce the cutting matrix $\mathbf{M}$:

$$\mathbf{M} = (\mathbf{E} \ \mathbf{0}). \quad (18)$$

Here $\mathbf{E}$ is the identity matrix of $N \times N$, and the zero matrix has dimensions $N \times M$. Using the matrix $\mathbf{M}$ we can write:

$$\frac{\partial \mathbf{n}}{\partial U} = -\mathbf{M} \mathbf{J}^{-1} \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial U}. \quad (19)$$

Therefore, we can calculate the derivative of the criterion Y :

$$\frac{\partial Y}{\partial U} = \mathbf{c}^T \frac{\partial \mathbf{n}}{\partial U} = -\mathbf{c}^T \mathbf{M} \mathbf{J}^{-1} \frac{\partial \mathbf{F}(\mathbf{n}, \boldsymbol{\lambda})}{\partial U}. \quad (20)$$

Now, we require the criterion Y not to change under varying temperature and pressure. The condition is the following:

$$\delta T \frac{\partial Y}{\partial T} + \delta P \frac{\partial Y}{\partial P} = 0. \quad (21)$$

The previous expressions give the relation between variations in the following form:

$$\frac{\delta P}{\delta T} = \frac{\mathbf{c}^T \mathbf{M} \mathbf{J}^{-1} \begin{pmatrix} \mathbf{s}(\mathbf{n}, T, P) \\ \mathbf{0} \end{pmatrix}}{\mathbf{c}^T \mathbf{M} \mathbf{J}^{-1} \begin{pmatrix} \mathbf{V}(T, P) \\ \mathbf{0} \end{pmatrix}}. \quad (22)$$

The equality (22) holds only for infinitely small increments, i.e., this is a first-order ordinary differential equation for a thermodynamic system with chemical reactions [20]. The values of Lagrange multipliers are not necessary for calculation (they do not appear in (13) due to the linear type of constraints (3)).

It should be noted that the expression (22) does not imply any chemical mechanism: the calculations require only a list of substances and their thermodynamic properties. The numerator is related to thermal processes (change of entropy weighted by special matrices), and the denominator is related to mechanical processes (changes of volume, also weighted), which is similar to (9).

There could be degenerated statements, for example, if coefficients c_j are non-zero only for non-reactive species, or the vector $\mathbf{c}^T$ is a row from the matrix $\mathbf{A}$, or if the system is apparently low-dimensional. These issues require specific study in all different cases. We assume that the reacting system has "good enough" properties so equation (22) is well-defined in the given range of parameters.

Given the expression (22), one can use a simple algorithm to find couples (T, P) maintaining the linear criterion value. Solving the optimization

problem in the point (T_1, P_1) , we obtain chemical potentials and specific entropy values and calculate the matrix $\mathbf{J}$ and the auxiliary vectors. Then we update temperature by a small amount (for example, 1 K) and use equation (22) to calculate the pressure update corresponding to the temperature change. Then we solve the optimization problem under parameters $(T_1 + \delta T_1, P_1 + \delta P_1)$ and repeat until some stopping condition becomes active (for example, maximum available temperature is reached). If the step is small enough, then the Euler method can be used; otherwise, iterative methods may be a better choice. It should be noted that every step of the method requires solving the optimization problem, so computational gain and losses should be considered carefully.

If the criterion is non-linear, then equation (22) can be generalized as follows:

$$\frac{\delta P}{\delta T} = \frac{\left(\frac{\partial Y}{\partial \mathbf{n}}\right)^T \mathbf{M} \mathbf{J}^{-1} \begin{pmatrix} \mathbf{s}(\mathbf{n}, T, P) \\ \mathbf{0} \end{pmatrix}}{\left(\frac{\partial Y}{\partial \mathbf{n}}\right)^T \mathbf{M} \mathbf{J}^{-1} \begin{pmatrix} \mathbf{V}(T, P) \\ \mathbf{0} \end{pmatrix}}. \quad (23)$$

Here $\frac{\partial Y}{\partial \mathbf{n}}$ is the gradient vector. In this case, however, the existence and stability of the solution depend on the properties of the criterion. Some of these properties reveal themselves in calculations (see next section).

With these formulas, we can study chemical processes in thermodynamic equilibrium on the $P - T$ plane.

4 Numerical examples

As in our previous paper [7], we considered a methane reforming process in arbitrary stoichiometry. Methane conversion processes are of particular interest due to hydrogen demands and production of synthetic liquid fuels from syngas [1, 16]. The problems concerned with optimal conditions of methane conversion include many parameters, including catalyst stability, flow control, and gas cleaning. We consider only the thermodynamic parameters that influence the conversion product composition; equilib-

rium analysis is always the first step of reactor design. Some macrokinetic features could be included in thermodynamic analysis through additional constraints (see, for example, [14]), but this matter is beyond the present work.

The initial mixture consists of $\{\text{CH}_4, \text{CO}_2, \text{H}_2\text{O}, \text{N}_2\}$ with 1 mole of each component. The aim products are $\{\text{CO}, \text{H}_2\}$. The molecular matrix is as follows:

	N_2	CH_4	H_2O	CO_2	CO	H_2
C	0	1	0	1	1	0
H	0	4	2	0	0	2
N	2	0	0	0	0	0
O	0	0	1	2	1	0

(24)

The elemental composition vector is $\mathbf{b}^T = (2, 6, 2, 3)$. We used thermodynamic data from [11]. The interior point method with slight modifications was used to solve the equilibrium problem (1) [12]. The explicit Euler method was used to solve the differential equations (22) and (23). The computational capacities of the High-Temperature Circuit Multi-Access Research Center (MESI SB RAS) were used in the study.

In all cases we consider $(T_1, P_1) = (1000 \text{ K}, 1 \text{ atm})$ as a reference state. All the calculations are conducted based on the characteristics of the equilibrium composition at these parameters, which is the following: $n_{\text{CH}_4} = 0.04, n_{\text{CO}_2} = 0.49, n_{\text{H}_2\text{O}} = 0.51, n_{\text{N}_2} = 1, n_{\text{CO}} = 1.47, n_{\text{H}_2} = 2.37$.

4.1 Constant hydrogen yield

The first criterion is $Y(\mathbf{n}) = n_{\text{H}_2}$: in some cases, hydrogen is the aim product of methane conversion, and its yield should be maintained at the fixed level [6]. Fig. 1 shows the calculated $P - T$ curve that holds hydrogen yield at the same level as at 1000 K and 1 atm. The curve rises, so it can be concluded that the average thermal effect of hydrogen formation is endothermic in the studied range. The numerical error (which is $\varepsilon = Y - Y_{T_1, P_1}$) increases when moving from the starting point due to the finite difference approximation, but the relative error is less than 1%

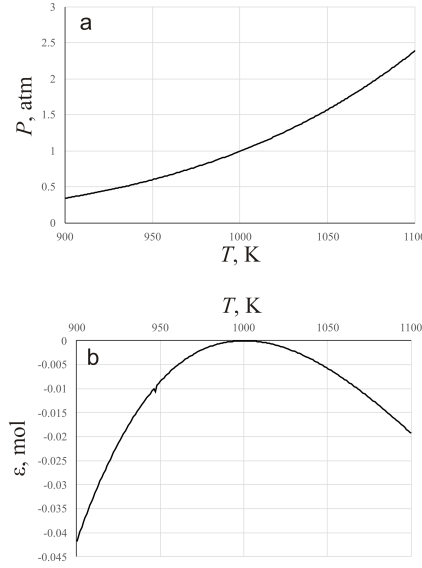


Figure 1. The dependence of pressure on temperature given fixed hydrogen yield (a) and the corresponding numerical error in hydrogen yield (b).

in the range of 200 K, which is precise enough for engineering analysis.

4.2 Constant heating value

Let us now consider the heating value of the reacting mixture. The combustible components are $\{\text{CH}_4, \text{CO}, \text{H}_2\}$, and their individual heating values are 802, 283 and 242 kJ/mol, correspondingly. Then we can construct a new criterion:

$$Y(\mathbf{n}) = \sum_{j=1}^N Q_j n_j = 802 \times 10^3 n_{\text{CH}_4} + 283 \times 10^3 n_{\text{CO}} + 242 \times 10^3 n_{\text{H}_2}. \quad (25)$$

This is a linear criterion that was considered above. At the conditions of 1000 K and 1 atm, the equilibrium mixture has the heating value of 1.02 MJ. Using the developed technique, we extend the range of conditions with this heating value. Fig. 2 shows the corresponding dependence between

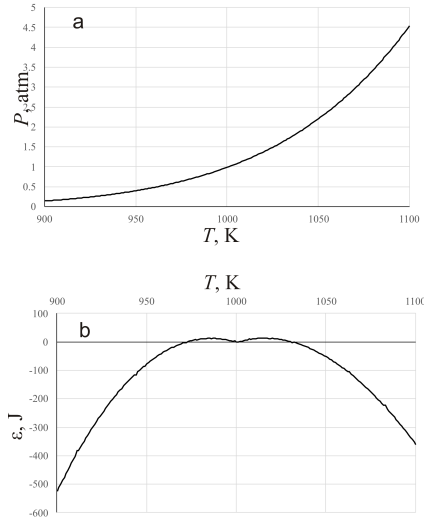


Figure 2. The dependence of pressure on temperature given fixed heating value (a) and the corresponding numerical error (b).

temperature and pressure. Again, the formation of combustible products is an endothermic process on average. Although the error in heating value reaches hundreds of J (mainly due to large factors in (25)), the relative error is again less than 1%.

4.3 Constant CO/H₂ ratio

If the syngas is used for liquid fuel synthesis, then the ratio CO/H₂ is the main characteristic of its composition [2] (at 1000 K and 1 atm it is 0.62, which is not optimal for any industrial process: the following calculation is just an example of the numerical method use). The criterion is then a non-linear function of the equilibrium chemical composition:

$$Y(\mathbf{n}) = \frac{n_{\text{CO}}}{n_{\text{H}_2}}. \quad (26)$$

In this case, we use equation (23) with $\partial Y / \partial n_{\text{CO}} = 1/n_{\text{H}_2}$ and $\partial Y / \partial n_{\text{H}_2} = -n_{\text{CO}}/n_{\text{H}_2}^2$. Fig. 3 shows the calculation results. The increase of temperature leads to a higher hydrogen yield, so in order to suppress its for-

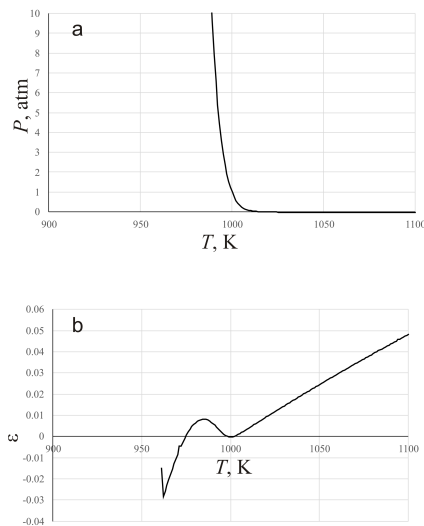


Figure 3. The dependence of pressure on temperature given fixed CO/H_2 ratio (a) and the corresponding numerical error (b).

mation, a pressure decrease is necessary. And vice versa, at lower temperatures, pressure sharply increases. At 976 K, the required pressure already surpasses 100 atm, and the further calculations make no sense due to the non-ideal gas mixture state. On the other side, at 1010 K, the pressure becomes lower than 0.1 atm. Therefore, implementing the constraints on operating pressure, one can obtain the temperature range allowing one to hold the constant CO/H_2 ratio.

The differential equations are non-linear even for a linear criterion, and therefore, one should not expect a drastic increase in numerical error. But the maximum error turns out much higher, reaching 7% at 1100 K. However, the pressure at this temperature is in the range of deep vacuum. Restricting the pressure interval between 0.1 and 100 atm, we obtain the maximum error slightly more than 1%.

5 Discussion

It can be seen that the $P - T$ curves are similar to phase diagrams, which follows from the mentioned analogy between (22), (23), and the Clapeyron-Clausius equation. The difference is in the arbitrary nature of a chosen criterion. Another possible interpretation is based on the Le Chatelier-Braun principle: in order to hold some composition-based quantity constant, one should compensate for the thermal effect (change of temperature) by mechanical (pressure) correction. This is another "unnoticed identity in chemical thermodynamics" [10].

It should be noted that we did not require ideality when deriving eqs. (22) and (23). However, the optimization problem would become more computationally complex for non-ideal mixtures. For multiphase equilibria, some Kuhn-Tucker conditions (11) may turn into inequalities. In this case, auxiliary variables can be introduced to restore equalities and obtain the formulas for derivatives.

A modification of criterion is surely possible. The addition of terms taking into account temperature and pressure may help avoiding extremal reaction conditions and expensive materials use. For multi-criteria analysis, additional constraints can be added in the matrix $\mathbf{A}$. These prospects require further investigation with more realistic reacting systems.

6 Conclusion

In this paper we proposed a numerical approach to calculate the $P - T$ curves corresponding to constant values of functions depending on the chemical composition of equilibrium reacting systems. The equations of these curves were derived and solved using the Euler method. It is shown that the curves are similar to phase transition diagrams and could be interpreted in a way of simultaneous thermal and mechanical control over the reacting systems. The methane conversion process was studied using the proposed numerical approach, and the numerical errors and the parameters' boundaries were discussed. The developed method could be useful in thermodynamic analysis of chemical reactors with respect to the choice of

operating ranges.

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