Statistical Approach to the Equilibrium Conditions in Connected Reaction Graphs

Igor Donskoy a,*

^a Melentiev Energy Systems Institute, 130 Lermontova st., Irkutsk, Russia, 664033 donskoy.chem@mail.ru

(Received April 1, 2025)

Abstract

The paper aims to find equilibrium conditions in connected reaction graphs (reaction networks) consisting of reaction complexes with some special properties. Such graphs often arise when studying complex chemical systems. Connectivity in this case implies the existence of linear stoichiometric relations, including all available complexes, which express material balance restrictions on the graph arcs. The methodology is based on chemical thermodynamics and statistical physics: connected graphs may be considered as an ensemble of chemical states, having their own meta-thermodynamic functions. It is shown that equilibrium composition can be calculated using the analogue of the partition sum. Some numerical examples are presented.

1 Introduction

The issues of chemical equilibrium on graphs of chemical transformations have been considered previously in a large number of works. For example, in the works [1–3] from the point of view of the fulfillment of the principle of

This work is licensed under a Creative Commons "Attribution 4.0 International" license.



^{*}Corresponding author.

detailed equilibrium, the conditions under which equilibrium can exist on the reaction graph were established. The extension of these results to heterogeneous and non-ideal systems is proposed in the works [4,5]. As shown in the monographs [6,7], qualitative features of the dynamic behavior of reacting systems can be obtained without solving differential equations or analyzing their stability, only by studying the graphs of chemical reactions. The analysis of reaction graphs based on Kirchhoff's laws (with a special type of potential function) was carried out in the works [8–10]. The stability of the behavior of systems with linear mechanisms was studied in [11–13].

Graphs of open chemical systems (interacting with chemostats) were analyzed in detail in [14], where analogues of Korzhinsky (semi-opened) potentials [15,16] are used for the outliers of their mass conservation equation ("mobile") components.

Equilibria on random graphs were studied in [17]. Tools for generating mechanisms of complex reactions using graph theory were developed in [18–20]. A joint consideration of chemical reactions and transport processes on graphs (the so-called thermodynamic graphs) was proposed by the authors of [21–23]; graph representation allows describing heterogeneous processes [24, 25]. Combinatorial analysis of the mechanisms of complex reactions to determine the connectivity threshold and extreme amounts of substances that can form during the reaction was carried out in several works [26–28], including checking of the consistency of the reaction mechanisms [29, 30].

The purpose of this work is to determine the equilibrium conditions for chemical systems of a special type, the graph of chemical transformations for which is connected and stoichiometrically consistent. Analysis of these conditions shows that such graphs can be represented as simple statistical systems for which the equilibrium is described by the Gibbs distribution.

2 Reaction graph statistics

Let us consider a connected reaction graph consisting of a set of reaction complexes (Fig. 1). Its feature is that the transitions between sets of sub-



Figure 1. Reaction graph scheme

stances (complexes) at the nodes occur stoichiometrically (i.e., the balance of atoms is maintained on any arc). When the reaction coordinate changes, the number of reagents and products changes strictly proportionally. We will assume that no more than two components participate in one chemical reaction [26, 27]. Then we can approximately consider each complex as a gross component of the reaction system.

Gibbs free energy in isothermal and isobaric reacting systems is a sum of its components contributions:

$$G = \sum_{j}^{components} \mu_j n_j. \tag{1}$$

Here μ_j is the chemical potential, and n_j is the molar quantity *j*-th component.

The minimum of the Gibbs energy in the form (1) does not necessarily correspond to the equilibrium for the reaction graph (for example, shown in Fig. 1), since the mutual transformations of substances occur in strict accordance with stoichiometry. Therefore, even if one of the components has a significantly lower chemical potential compared to the others, its equilibrium amount will be limited by the conditions of the transition from node to node; for example, it is impossible to form such a "low-energy" component from other components entering into the same reaction complex with it. Equilibrium conditions should take into account stoichiometry.

In this regard, we can divide Gibbs free energy into contributions of

reaction complexes (graph nodes):

$$G = \sum_{i}^{complexes} g_i.$$
 (2)

Here g_i is the *i*-th complex contribution: for example, $g_1 = \mu_A n_A + \mu_B n_B$. Given a special initial composition with a stoichiometric ratio of components in reaction complexes, we obtain $g_1 = n_A(\mu_A + \mu_B)$. In an ideal mixture, one can write:

$$g_1 = n_A \left[\mu_A^0 + \mu_B^0 + 2R_g T \ln\left(\frac{n_A}{\sigma}\right) \right]$$
(3)

Here σ is a sum of moles for all components. Further, we change variables from components to complexes:

$$g_1 = N_1 \left[\frac{\mu_A^0 + \mu_B^0}{2} + R_g T \ln \left(\frac{N_1}{N_0} \right) \right] = N_1 M_1 \tag{4}$$

The expression in square brackets can be considered as the apparent chemical potential of the reaction complex (correspondingly, the average standard chemical potential of the constituents is the apparent standard potential of the complex), and N_1 is the apparent quantity of this complex. Substituting eq. (6) into eq. (2), we obtain:

$$G = \sum_{i}^{complexes} N_i M_i = \sum_{i}^{complexes} N_i \left[M_i^0 + R_g T \ln\left(\frac{N_i}{N_0}\right) \right]$$
(5)

Stoichiometric restriction gives a linear equation:

$$\sum_{i}^{complexes} N_i = N_0. \tag{6}$$

Now let us find equilibrium composition using the Lagrange multipliers method [32]. The Lagrange function is as follows:

$$L = \sum_{i} N_i M_i + \lambda \left(\sum_{i} N_i - N_0 \right).$$
(7)

Partial derivatives of L can be found immediately:

$$\frac{\partial L}{\partial N_k} = M_k + \lambda = 0. \tag{8}$$

It follows that all apparent chemical potentials of the complexes in equilibrium are equal. Such an equilibrium condition could be immediately obtained from the transitivity of equilibrium (so-called "zero law of thermodynamics" [33]) for a connected set of complexes (see Fig. 1). If chemical equilibrium assumes that the sum of the chemical potentials of the products and reactants is equal (i.e., the difference in Gibbs energy is zero), then the sums of the chemical potentials in each node in the connected graph must be equal.

Note that equation (9) requires a number of conditions to be met, the main one being the stoichiometric transition between all pairs of complexes. This condition allows us to move immediately to the single condition (8) instead of considering the material balance for each chemical element (which would lead to several uncertain coefficients λ_j).

Solving eq. (9) with respect to N_k , we obtain:

$$\frac{N_k}{N_0} = \exp\left(-\frac{M_k^0 + \lambda}{R_g T}\right).$$
(9)

Then using eq. (8) we can find λ :

$$\exp\left(\frac{\lambda}{R_g T}\right) = \sum_{i}^{complexes} \exp\left(-\frac{M_i^0}{R_g T}\right).$$
(10)

The exponent in the l.h.s. of eq. (11) is an analogue of the partition sum, a normalization factor containing all available chemical states in the reacting mixture. Marking it with Q, we can rewrite eq. (10) in the following way:

$$\frac{N_k}{N_0} = \frac{1}{Q} \exp\left(-\frac{M_k^0}{R_g T}\right). \tag{11}$$

The distribution (12) highlights some important properties of the equilibrium in reacting systems. Evidently, the equilibrium fraction of a complex depends on its apparent standard chemical potential: the more the potential, the less the equilibrium fraction (although it does not reach zero in ideal mixtures due to logarithmic singularity at the boundary [34]).

The Lagrange multiplier λ is an analogue (up to the sign) of the statistical free energy for this distribution [35]:

$$\lambda = R_q T \ln Q = -A_G. \tag{12}$$

Here A_G is the free meta-energy of the graph, which determines the equilibrium of connected reaction complexes.

The requirement of graph connectivity is thus necessary for a complete accounting of the chemical states in the sum (11): the presence of several isolated "islands" would lead to a splitting of the equilibrium condition for the subsystems, each of which can be considered as independent (at least in the first approximation) of the state of the others. Connectivity for a system of reversible reactions allows one to use the weakened principle of detailed reversibility [3], and hence its statistical consequences.

Thus, a chemical system in the form of a connected graph (like the one shown in Fig. 1) behaves as a statistical-mechanical system associated with a thermostat: distribution (12) is nothing other than the Gibbs distribution in such a system. The energy states correspond to different reaction complexes, and the condition of material balance leads to the appearance of an additional parameter corresponding to the "effective temperature" of the distribution, which has the meaning of the equilibrium chemical potential.

3 Model example

Let us consider a simple reacting system consisting of three mutual isomers [32]:

$$A \Longleftrightarrow B \Longleftrightarrow C. \tag{13}$$

The equilibrium condition for this system is as follows:

$$\mu_A = \mu_B = \mu_C. \tag{14}$$

The stoichiometry condition is:

$$n_A + n_B + n_C = N. \tag{15}$$

Then, using the ideal mixture approximation, we can express fractions of B and C:

$$n_B = n_A \exp\left(\frac{\mu_A^0 - \mu_B^0}{RT}\right),\tag{16}$$

$$n_C = n_B \exp\left(\frac{\mu_B^0 - \mu_C^0}{RT}\right) = n_A \exp\left(\frac{\mu_A^0 - \mu_C^0}{RT}\right) \tag{17}$$

Then eq. (16) allows us to solve the problem:

$$n_A = \frac{\exp\left(-\frac{\mu_A^0}{RT}\right)}{\exp\left(-\frac{\mu_A^0}{RT}\right) + \exp\left(-\frac{\mu_B^0}{RT}\right) + \exp\left(-\frac{\mu_C^0}{RT}\right)}$$
(18)

The denominator in eq. (17) is the normalization factor given by eq. (11). It should be noted that although components A and C do not have mutual transitions, the system (14) forms a connected graph, so the theory is applicable.

It should be also noted that the estimation of equilibrium concentration using formula similar to eq. (18) was proposed in early works on the calculation of chemical equilibria [31].

4 Numerical example

Let us consider a connected graph of six nodes with arbitrarily specified values of chemical potentials for the complexes (Table 1). The equilibrium composition was found using the Gibbs energy minimization method (the numerical method is described in [32, 34]). At a pressure of 1 atm and a temperature of 300 K, the value of λ calculated using formula (11) is 1.018×10^4 J/mol; a comparison of the optimization results shows that the numerical values of the chemical potentials of all complexes in equilibrium are close to this value with good accuracy. As expected, a larger proportion

Complex	M^0	N^{eq}	M^{eq}
A_1	10^{3}	1.1298×10^{-2}	-1.0183×10^4
A_2	-10^{2}	1.7560×10^{-2}	-1.0182×10^4
A_3	10^{2}	1.6207×10^{-2}	-1.0182×10^{4}
A_4	10^4	3.0612×10^{-4}	-1.0183×10^{4}
A_5	-10^4	9.2944×10^{-1}	-1.0183×10^{4}
A_6	$ -10^3$	2.5190×10^{-2}	-1.0182×10^4

Table 1. Results of equilibrium calculation for six-node graph



Figure 2. Water shift reaction graph

of the complexes in the equilibrium state are those with a lower value of the standard chemical potential.

5 Water shift reaction

Let us now consider a typical reaction of syngas conversion [36]. The initial composition of the reactive mixture is 1 mole of CO, 1 mole of H_2O , and 10 moles of N_2 (inert diluent). Possible reaction products are CO_2 and H_2 . Depending on syngas use, one needs to have different CO/H_2 ratios. We consider the reaction graph presented in Fig. 2. Stoichiometric restriction holds, so the theory can be applied, although the reaction graph is the simplest possible, as it consists of two nodes.

Let us fix temperature and pressure at 800 K and 1 atm. The equilibrium composition for these conditions is presented in Table 2. Chemical potentials of reagents and products are equal (about -7.28×10^5 J/mol), and the graph free energy gives is nearly a half of its value ($\lambda = 3.47 \times 10^5$ J/mol). Equilibrium values calculated from eq. (11) are 0.33 and 0.67 moles, which is close to the solution obtained by minimization of Gibbs free energy.

Substance	μ^0 , J/mol	n^{eq}	μ^{eq}
CO	-2.77×10^5	0.327	-3.01×10^5
H_2O	-4.03×10^5	0.327	-4.27×10^5
H_2	-1.13×10^5	0.673	-1.32×10^5
CO_2	-5.77×10^{5}	0.673	$-5.96 imes 10^5$
N_2	-1.62×10^{5}	10	-1.63×10^{5}

Table 2. Results of equilibrium calculation for water shift reaction at800 K



Figure 3. Water shift equilibrium at different temperatures: solid line and squares $-H_2$; dashed line and circles -CO.

The observed agreement is not a coincidence. Fig. 3 shows the dependence of CO and H_2 fraction in the reactive mixture on temperature. Lines show results of equilibrium calculations by the Gibbs free energy minimization method, and markers show estimation by the proposed method. Good agreement between the two methods is observed.

Although simple, the new method has several disadvantages. Among numerical problems, there arise big exponents: typical standard chemical potentials (as can be seen from Table 2) have the order of 10^5 , so calculating the partition sum leads to summing large numbers. In such cases, methods may be applicable that were developed in statistical physics, such as the biggest term approximation [37], etc. The main problem, however, is a special form of the stoichiometry condition, which is not common.

It is interesting to develop similar methods for non-ideal systems and systems with more complicated stoichiometry. It can be shown that for separable systems (i.e., systems having several linear balance equations without intersecting variables), independent λ_i (subgraph free energies) parameters exist, corresponding to particular subsystems. Searching for new properties of reaction graphs may lead to more efficient methods of equilibrium calculations.

6 Conclusions

In the present work, a statistical mechanics approach is applied to the analysis of connected reaction graphs with special stoichiometric properties. It is shown that the equilibrium state in the reacting systems described by these kinds of graphs is governed by the chemical potentials of reaction complexes. The graph free energy approach can be applied to equilibrium calculations. The approach is illustrated by several numerical examples.

Acknowledgment: The research was carried out under State Assignment Project (no. FWEU-2021-0005) of the Fundamental Research Program of Russian Federation 2021-2030. Equipment of Multi-Access Centre "High-Temperature Circuit" was used in calculations

References

- R. Aris, Mathematical aspects of chemical reaction, Ind. Eng. Chem. 61 (1969) 17–29.
- [2] J. Schnakenberg, Network theory of microscopic and macroscopic behavior of master equation systems, *Rev. Mod. Phys.* 48 (1976) 571– 585.
- [3] M. Feinberg, The necessary and sufficient conditions for chemical equilibrium, Chem. Eng. Sci. 44 (1989) 1819–1827.
- [4] E. A. Smolenskii, A. N. Ryzhov, I. V. Chuvaeva, I. K. Maslova, A. L. Lapidus, Necessary and sufficient conditions for detailed balancing in mass action systems of arbitrary complexity, *Russ. Chem. Bull.* 67 (2018) 966–971.
- [5] A. M. Miangolarra, M. Castellana, On non-ideal chemical-reaction networks and phase separation, J. Stat. Phys. 190 (2023) #23.

- [6] A. I. Vol'pert, S. I. Hudjaev, Analysis in Classes of Discontinuous Functions and Equations of Mathematical Physics, Springer, 1985.
- [7] M. Feinberg, Foundations of Chemical Reaction Network Theory, Springer, 2019.
- [8] L. Peusner, D. C. Mikulecky, B. Bunow, S. R. Caplan, A network thermodynamic approach to Hill and King–Altman reaction–diffusion kinetics, J. Chem. Phys. 83 (1985) 5559–5566.
- [9] A. J. van der Schaft, S. Rao, B. Jayawadhana, On the mathematical structure of balanced chemical reaction networks governed by mass action kinetics, SIAM J. Appl. Math. 73 (2013) 953–973.
- [10] A. J. van der Schaft, S. Rao, B. Jayawadhana, On the network thermodynamics of mass action chemical reaction networks, *IFAC Proc. Vol.* 46 (2013) 24–49.
- [11] V. I., Bykov, A. N. Gorban, Quasi-thermodynamics of reactions without binary interactions, *Zhurnal fizicheskoj khimii (Rus.)* 57 (1983) 2942–2948.
- [12] E. D. Sontag, Structure and stability of certain chemical networks and applications to the kinetic proofreading model of T-cell receptor signal transduction, *IEEE Trans. Autom. Control* 46 (2001) 1028–1047.
- [13] A. N. Gorban, O. Radulescu, A. Y. Zinovyev, Asymptotology of chemical reaction networks, *Chem. Eng. Sci.* 65 (2010) 2310–2324.
- [14] R. Rao, M. Esposito, Nonequilibrium thermodynamics of chemical reaction networks: Wisdom from stochastic thermodynamics, *Phys. Rev. X* 6 (2016) #041064.
- [15] D. S. Korzhinsky, Theoretical Principles of Analysis of Mineral Parageneses, Nauka, 1973. (in Russian)
- [16] T. L. Hill, Statistical Mechanics: Principles and Selected Applications, Dover, New York, 1956.
- [17] G. Cimini, T. Squartini, F. Saracco, D. Garlaschelli, A. Gabrielli, G. Caldarelli, The statistical physics of real-world networks, *Nat. Rev. Phys.* 1 (2019) 58–71.
- [18] J. T. Margraf, K. Reuter, Systematic enumeration of elementary reaction steps in surface catalysis, ACS Omega 4 (2019) 3370–3379.

- [19] Q. Zhao, B. M. Savoie, Simultaneously improving reaction coverage and computational cost in automated reaction prediction tasks, *Nat. Comput. Sci.* 1 (2021) 479–490.
- [20] M. Wen, E. W. C. Spotte-Smith, S. M. Blau, M. J. McDermott, A. S. Krishnapriyan, K. A. Persson, Chemical reaction networks and opportunities for machine learning, *Nat. Comput. Sci.* 3 (2023) 12–24.
- [21] G. Oster, A. Perelson, A. Katchalsky, Network thermodynamics, Nature 234 (1971) 393–399.
- [22] A. S. Perelson, Network thermodynamics, *Biophys. J.* 15 (1975) 667– 685.
- [23] D. C. Mikulecky, Network thermodynamics and complexity: a transition to relational systems theory, *Comput. Chem.* 25 (2001) 369–391.
- [24] I. V. Fryazinov, An algorithm for the solution of difference problems by graphs, *Comput. Math. Math. Phys.* **10** (1970) 268–273.
- [25] I. G. Donskoy, V. A. Shamansky, A. N. Kozlov, D. A. Svishchev, Coal gasification process simulations using combined kineticthermodynamic models in one-dimensional approximation, *Combust. Theory Modell.* **21** (2017) 529–559.
- [26] M. A. Kozlova, V. A. Shamansky, Application of graphs for the analysis of the mechanism of chemical kinetics, *Inf. Math. Tech. Sci. Manag.* 28 (2022) 108–118.
- [27] M. A. Kozlova, V. A. Shamansky, Searching for an extreme component content in a reacting system using graph of chemical reactions, *Vestnik Kibernetiki* 22 (2023) 21–28.
- [28] A. N. Gorban, D. Constales, G. S. Yablonsky, Transient concentration extremum and conservatively perturbed equilibrium, *Chem. Eng. Sci.* 231 (2021) #116295.
- [29] A. N. Gorban', E. M. Mirkes, A. N. Bocharov, V. I. Bykov, Thermodynamic consistency of kinetic data, *Combust. Explos. Shock Waves* 25 (1989) 593–600.
- [30] J. Toth, A. L. Nagy, I. G. Zsely, Structural analysis of combustion mechanisms, J. Math. Chem. 53 (2015) 86–110.
- [31] W. B. White, S. M. Johnson, G. B. Dantzig, Chemical equilibrium in complex mixtures, J. Chem. Phys. 28 (1958) 751–755.

- [32] A. N. Gorban, B. M. Kaganovich, S. P. Filippov, A. V. Keiko, V. A. Shamansky, I. A. Shirkalin, *Thermodynamic Equilibria and Extrema. Analysis of Attainability Regions and Partial Equilibria*, Springer, New York, 2006.
- [33] M. Grmela, Thermodynamics and rate thermodynamics, J. Stat. Phys. 191 (2024) #75.
- [34] I. A. Shirkalin, Solution of convex programming problem with wide range of the values of variables, SEI preprint, 1997. (in Russian)
- [35] L. D. Landau, E. M. Lifshitz, *Statistical Physics: V. 5*, Elsevier, 2013.
- [36] W. H. Chen, C. W. Tsai, Y. L. Lin, R. Y. Chein, C. T. Yu, Reaction phenomena of high-temperature water gas shift reaction in a membrane reactor, *Fuel* **199** (2017) 358–371.
- [37] T. L. Hill, An Introduction to Statistical Thermodynamics, Addison-Wesley, Reading, 1960.