

Three Waves of Chemical Dynamics

A.N. Gorban^{1*}, G.S. Yablonsky²

¹Department of Mathematics, University of Leicester, Leicester, LE1 7RH, UK

² Parks College of Engineering, Aviation and Technology
Saint Louis University, Saint Louis, MO63103, USA

Abstract. Three epochs in development of chemical dynamics are presented. We try to understand the modern research programs in the light of classical works.

The first Nobel Prize in Chemistry was awarded in 1901 to Jacobus H. van't Hoff “in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions”. This award celebrated the end of the first epoch in chemical dynamics, discovery of the main laws. This epoch began in 1864 when Waage and Guldberg published their first paper about Mass Action Law [42]. Van't Hoff rediscovered this law independently in 1877. In 1984 the first book about chemical dynamics was published, van't Hoff's “*Études de Dynamique chimique* [40]”, in which he proposed the ‘natural’ classification of simple reactions according to the number of molecules that are simultaneously participate in the reaction. Despite his announcement, “I have not accepted a concept of mass action law as a theoretical foundation”, van't Hoff did the next step to the development of the same law. He also studied the relations between kinetics and thermodynamics and found the temperature dependence of equilibrium constant (the van't Hoff equation). In particular, he proved the “principle of mobile equilibrium”: the equilibrium in a system tends to shift in such a direction as to oppose the temperature change which is imposed upon the system. This principle was later on generalized by Le Chatelier. The temperature dependence of the reaction rate constants was analyzed further by Arrhenius (Nobel prize in chemistry in 1903). The famous Arrhenius equation is a particular case of the van't Hoff equation. Chemical dynamics was developed in line with thermodynamics. In particular, chemical equilibrium was recognised as a dynamic process, i.e. the balance between the forward and backward reactions. Their rates must be equal at the chemical equilibrium. During this period, Gibbs created modern chemical thermodynamics [14]. The kinetic law of a single reaction and its relation to thermodynamics were studied in full. Chemical dynamics was prepared to the next epoch, that is to the analysis of complex reaction networks.

The scientific context of the first decades of chemical dynamics was also very important. Maxwell [28] and Boltzmann [5] developed physical kinetics of gases. They used analogue of the Mass Action Law for collisions and discover the principle of detailed balance: at the equilibrium, each elementary process should be equilibrated by the reverse process. Maxwell used the principle of sufficient reason to justify detailed balance. For the same purpose Boltzmann employed reversibility of collision (for more detail

*Corresponding author. E-mail: ag153@le.ac.uk

see [16]). Detailed balance was used by Boltzmann to prove the H -theorem (entropy growth) in kinetics. Lorentz raised an objection against this theory [30]. He stated that the collision of polyatomic molecules are irreversible and therefore the principle of detailed balance is wrong. Boltzmann immediately invented a weaker condition, the principle of cyclic balance (it is known also as semidetailed balance or complex balance) [6] which is sufficient for the proof of H -theorem. Much later, Stueckelberg proved that the cyclic balance condition should hold for all systems with Markov micro-description [38] (he used the S -matrix representation of collisions, for more detail see [20]). Finally, in 1981, it was demonstrated that Lorentz was wrong and detailed balance holds for collisions of polyatomic molecules [8]. In 1902, equilibrium statistical mechanics was developed by Gibbs and mechanical backgrounds of thermodynamics became clear [15].

In 1901, Wegscheider studied reaction networks which consist of several elementary reactions [43]. He discovered that the equilibrium of such a network may not be an equilibrium of each reaction from the network if we define their rate constants independently (“Wegscheider’s paradox”). He found the conditions on the reaction rate constants which are necessary and sufficient for coincidence of the equilibrium of the network with the joint equilibrium of their elementary reactions (Wegscheider’s conditions of detailed balance). For example, in a simple linear cycle these conditions state that clockwise and anticlockwise products of reaction rate constants coincide. (The modern explanation could be found in many textbooks [44].) Of course, if we define the rate of each backward reaction thermodynamically, through the thermodynamic equilibrium constant and the reaction rate of the forward reaction, then Wegscheider’s conditions are satisfied automatically and Wegscheider’s paradox vanishes: the elementary reactions “do not know” about other reactions, they all “just know” the same thermodynamic properties of the reagents. Wegscheider’s conditions were used by Onsager [32] in his work about reciprocal relations awarded by Nobel Prize in Chemistry in 1968. The Onsager relations are, in their essence, the detailed balance conditions linearized near thermodynamic equilibrium.

Wegscheider’s work was a first milestone in analysis of chemical reaction networks. The great achievement here was the theory of chain reactions and of the critical effects in chain reactions [22, 37]. In 1956, Nobel Prize in Chemistry was awarded to Semenov and Hinshelwood “for their researches into the mechanism of chemical reactions”. The great problem approached by the theory of chain reaction may be formulated as follows: *how the structure of reaction network affects its dynamics?* Of course, it is solved only partially and remains the source of challenges for several generations of researchers. It appears that the work with this problem requires methods for model reduction [9]. Besides the obvious reason (it is easier to analyse systems of smaller dimension) there is a very important issue: in the whole system the critical effects are hidden. To see the critical effect, we have to simplify the model and to separate variables into fast and slow ones. The bifurcations in the fast subsystem correspond to observable critical phenomena like inflammation, ignition or, inverse, to quenching. This trick allowed Semenov and Hinshelwood to study critical effects in chain reactions. Several methods for model reduction were developed. Most famous of them are: quasi-steady states, quasi-equilibrium states and limiting steps and subsystems. Later on they were integrated into several more general technologies: methods of invariant manifolds [18, 19] and computation singular perturbations [29]. The mathematical backgrounds of all these methods are the theory of singular perturbations [35] and the theory of invariant manifolds of dynamical systems. Non-trivial dynamics of chemical systems attracted much attention and various oscillations, bifurcations and non-linear waves were found. Among them the famous example gives the Belousov-Zhabotinskii oscillatory reaction [45].

In 1965, the scientific program of new synthesis and rational analysis of chemical reaction networks was proposed by Aris [3, 4]. His enthusiasm, creativity and research reputation attracted many scientists and a series of research project was performed [12, 13, 23, 25, 33, 36]. The Aris program was driven by the needs of chemical engineering [2]. Nevertheless, the fundamental results of this program spread wider and are now important to various areas of science. Horn, Jackson and Feinberg rediscovered Boltzmann’s cyclic balance in the context of chemical kinetics [12, 23] (they call it the “complex balance” condition). This complex balance condition is sufficient for positivity of entropy production (it is the exact analogue

of the 1887 version of Boltzmann's H -theorem [6]). It guarantees decrease of the Helmholtz free energy of closed systems under isothermal isochoric conditions and of the Gibbs free energy (the free enthalpy) under isothermal isobaric conditions. It appears that this condition is important not only in chemical engineering [39] but also in algebraic geometry and related areas, in particular, in the theory of toric dynamical systems [10]. There are numerous links between chemical dynamics and modern algebraic geometry. Classification of the limits of systems with detailed balance when some of reactions become irreversible [21] practically coincides with the recently proved classification of binomial manifolds [11]. The methods of tropical geometry are efficient for model reduction in large reaction networks [31].

It is worth to mention other types of global Lyapunov functions which exist for some reaction mechanisms. For example, if we consider the reaction networks with elementary reactions of the form $mA_i \rightarrow \dots$ (with various coefficients m and right hand sides of the reaction equations, but with a positive linear conservation law like conservation of mass) then the l_1 -distance between all kinetic curves decreases in time [17]. For systems with arbitrary monotone kinetics the Lyapunov functions are constructed from reaction rate functions [1].

The question about connection between the structure of reaction network and its dynamics, remains one of the central problem of chemical dynamics. In parallel with answering this question we need to answer the question what is a kinetic law of complex chemical reaction. If we separate times and select fast and slow subsystems then this second question could be understood as an elimination problem: what are equations of slow dynamics after elimination of fast variables? This problem stimulated development of a new chapter of computer algebra [7]. For several classes of catalytic reactions this exclusion was performed and the steady-state kinetic law of the single overall reaction was presented as the single polynomial regarding the reaction rate. Such a polynomial may have several roots which correspond to different steady-states. At the same time its free term has a rigorous thermodynamic form and validates thermodynamic correctness of this presentation [26].

Various methods of graph theory were employed for analysis of chemical reaction networks. The general theory of equations on graphs was developed [41]. Now, several areas of applied and pure mathematics are used in chemical dynamics and are developed further due to this applications. "The beginning of this era was marked by the concerted effort of a few to raise the mathematical consciousness of the profession to think fundamentally about processes" [34]. After these 50 years of efforts we have to look back, to review the past and to ask about the future: what should we expect soon? New technologies will generate new questions. The quantum world will become closer to industry. Biological engineering will be as usual as is chemical engineering. The artificial intelligence and rapid computation will change the practice of mathematical modelling.

Three eras (or waves) of chemical dynamics can be revealed in the flux of research and publications. These waves may be associated with leaders: the first is the van't Hoff wave, the second may be called the Semenov-Hinshelwood wave and the third is definitely the Aris wave. The 'waves' may be distinguished based on the main focuses of the scientific leaders:

- Van't Hoff was searching for the general law of chemical reaction related to specific chemical properties. The term "chemical dynamics" belongs to van't Hoff.
- The Semenov-Hinshelwood focus was an explanation of critical phenomena observed in many chemical systems, in particular in flames. A concept "chain reactions" elaborated by these researchers influenced many sciences, especially nuclear physics and engineering.
- Aris' activity was concentrated on the detailed systematization of mathematical ideas and approaches.

Of course, the whole building was impossible without efforts of hundreds of other researchers. Few of them are mentioned in our brief review, more are cited in the papers of the issue.

This issue is opened by the reprint of the classical paper of A.I. Volpert, where he introduced the differential equations on graphs. The work of Gorban and Kolokoltsov analyzed appearance of Mass Action Law with complex balance conditions and their generalizations in the Michaelis-Menten-Stueckelberg limit of general Markov processes. Joshi and Shiu studied minimal reaction networks with multiple steady states. In the paper by Bykov and Tsybenova the classical nonlinear models of catalytic reaction

were augmented by the additional variable, i.e. temperature, and the extended models were systematically studied. Müller and Hofbauer applied the formalism of chemical reaction networks to kinetics of genetic recombination and analyze existence, uniqueness, and global stability of an equilibrium in such networks. Grigoriev, Samal, Vakulenko and Weber developed algebraic algorithms for analysis and reduction of larger metabolic reaction networks and studied several biochemical networks. Constales, Yablonsky and Marin analyzed kinetics of pulse-response experiments in the Temporal Analysis of Products (TAP) setup and demonstrated that in these special conditions the activity profile of a prepared catalytic system depends only on the total amount of admitted substance. Gorban demonstrated how to use a special geometric procedure, forward-invariant peeling, to produce forward-invariant subset from a given set in concentration space space and to prove persistence of a chemical dynamic system.

References

- [1] M.A. Al-Radhawi, D. Angeli. *Robust Lyapunov functions for complex reaction networks: An uncertain system framework*. In Decision and Control (CDC), 2014 IEEE 53rd Annual Conference, IEEE, 2014, 3101–3106.
- [2] R. Aris. *Introduction to the Analysis of Chemical Reactors*, Prentice Hall, Englewood Cliffs, NJ, 1965.
- [3] R. Aris. *Prolegomena to the rational analysis of systems of chemical reactions*. Arch. Ration. Mech. Anal., 19 (2) (1965), 81–99.
- [4] R. Aris. *Prolegomena to the rational analysis of systems of chemical reactions II. Some addenda*. Arch. Ration. Mech. Anal., 27 (5) (1968), 356–364.
- [5] L. Boltzmann, *Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen*, Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, 66 (1872), 275–370.
- [6] L. Boltzmann. *Neuer Beweis zweier Sätze über das Wärmegleichgewicht unter mehratomigen Gasmolekülen*. Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, 95 (2) (1887), 153–164.
- [7] V.I. Bykov, A.M. Kytmanov, M.Z. Lazman. *Elimination methods in polynomial computer algebra*. Mathematics and its Applications, V. 448. Springer, 1998.
- [8] C. Cercignani, M. Lampis. *On the H-theorem for polyatomic gases*. J. Stat. Phys., 26 (4) (1981) 795–801.
- [9] J.A. Christiansen. *The elucidation of reaction mechanisms by the method of intermediates in quasi-stationary concentrations*. Adv. Catal. , 5 (1953), 311–353.
- [10] G. Craciun, A. Dickenstein, A. Shiu, B. Sturmfels. *Toric dynamical systems*. J. Symb. Comput., 44 (11) (2009), 1551–1565.
- [11] D. Grigoriev, P.D. Milman. *Nash resolution for binomial varieties as Euclidean division. A priori termination bound, polynomial complexity in essential dimension 2*. Advances in Mathematics, 231 (6) (2012), 3389–3428.
- [12] M. Feinberg. *Complex balancing in general kinetic systems*. Arch. Ration. Mech. Anal., 49 (1972), 187–194.
- [13] Feinberg, M. *Chemical reaction network structure and the stability of complex isothermal reactors: I. The deficiency zero and deficiency one theorems*. Chem. Eng. Sci., 42 (10) (1987), 2229–2268.
- [14] J.W. Gibbs. *On the equilibrium of heterogeneous substances*. Trans. Conn. Acad. Art. Sci., 3 (1876-1878), 108–248, 343–524.
- [15] J.W. Gibbs. *Elementary Principles in Statistical Mechanics, developed with especial reference to the rational foundation of thermodynamics*. Yale Bicentennial Publications. Scribner and Sons, NY, 1902. [Dover Publications Inc.; Reprint edition, 2015.]
- [16] A.N. Gorban. *Detailed balance in micro- and macrokinetics and micro-distinguishability of macro-processes*. Results in Physics 4 (2014), 142–147.
- [17] A.N. Gorban, V.I. Bykov, G.S. Yablonskii. *Thermodynamic function analogue for reactions proceeding without interaction of various substances*. Chem. Eng. Sci., 41 (11) (1986), 2739–2745.
- [18] A.N. Gorban, I. Karlin. *Invariant Manifolds for Physical and Chemical Kinetics (Lecture Notes in Physics)*. Springer, 2005.
- [19] A.N. Gorban, I. Karlin. *Hilbert’s 6th Problem: exact and approximate hydrodynamic manifolds for kinetic equations*. Bulletin of the American Mathematical Society, 51(2) (2014), 186–246.
- [20] A.N. Gorban, M. Shahzad. *The Michaelis–Menten–Stueckelberg Theorem*. Entropy, 13 (2011) 966–1019. Corrected postprint: arXiv:1008.3296.
- [21] A.N. Gorban, G.S. Yablonskii. *Extended detailed balance for systems with irreversible reactions*. Chem. Eng. Sci., 66 (2011) 5388–5399. arXiv:1101.5280 [cond-mat.stat-mech].
- [22] C.N. Hinshelwood. *The Kinetics of Chemical Change*. The Clarendon press, Oxford, 1940.
- [23] F. Horn, R. Jackson. *General mass action kinetics*. Arch. Ration. Mech. Anal., 47 (1972), 81–116.
- [24] V.N. Kolokoltsov. *Nonlinear Markov processes and kinetic equations*. Cambridge Tracks in Mathematics 182, Cambridge Univ. Press, 2010.
- [25] F.J. Krambeck. *The mathematical structure of chemical kinetics in homogeneous single-phase systems*. Arch. Ration. Mech. Anal., 38 (5) (1970), 317–347.
- [26] M. Lazman, G. Yablonsky. *Overall Reaction Rate Equation of Single Route Catalytic Reaction*, Advances in Chemical Engineering, 34 (2008), 47–102.

- [27] G.N. Lewis. *A new principle of equilibrium*. Proceedings of the National Academy of Sciences, 11 (1925), 179–183.
- [28] J.C. Maxwell. *On the dynamical theory of gases*. Philosophical Transactions of the Royal Society of London, 157 (1867), 49–88.
- [29] S.H. Lam, D.A. Goussis. *The CSP method for simplifying kinetics*. International Journal of Chemical Kinetics, 26 (4) (1994), 461–486.
- [30] H.-A. Lorentz. *Über das Gleichgewicht der lebendigen Kraft unter Gasmolekülen*. Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, 95 (2) (1887), 115–152.
- [31] V. Noel, D. Grigoriev, S. Vakulenko, O. Radulescu. *Tropicalization and tropical equilibration of chemical reactions*. Tropical and Idempotent Mathematics and Applications, Contemporary Mathematics, 616 (2014), 261–277.
- [32] L. Onsager. *Reciprocal relations in irreversible processes. I*, Phys. Rev., 37 (1931), 405–426.
- [33] G.F. Oster, A.S. Perelson. *Chemical reaction dynamics*. Arch. Ration. Mech. Anal., 55 (3) (1974), 230–274.
- [34] D. Ramkrishna, N.R. Amundson. *Mathematics in Chemical Engineering: A 50 Year Introspection*. AIChE Journal, 50 (1) (2004), 7–23.
- [35] L.A. Segel, M. Slemrod. *The quasi-steady-state assumption: A case study in perturbation*. SIAM Rev., 31 (1989), 446–477.
- [36] P.H. Sellers. *Algebraic complexes applied to chemistry*. PNAS U.S.A., 55 (4) (1966), 693–698.
- [37] N.N. Semenov. *Chemical kinetics and chain reactions*. The Clarendon press, Oxford, 1935.
- [38] E.C.G. Stueckelberg. *Théorème H et unitarité de S*. Helv. Phys. Acta, 25 (1952), 577–580.
- [39] G. Szederkényi, K.M. Hangos. *Finding complex balanced and detailed balanced realizations of chemical reaction networks*. J. Math. Chem., 49, (6) (2011), 1163–1179.
- [40] J. H. van't Hoff. *Studies in Chemical Dynamics*. F. Muller & Co, Amsterdam, 1896. [A revised edition of Hoff's "Études de dynamique chimique". Revised and enlarged by E. Cohen, translated by T. Ewan.]
- [41] A.I. Volpert, S.I. Khudyaev. *Analysis in classes of discontinuous functions and equations of mathematical physics*. Nijoff, Dordrecht, The Netherlands, 1985.
- [42] P. Waage, C. M. Guldberg. *Studies concerning affinity*. Forhandlinger: Videnskabs - Selskabet i Christinia (Norwegian Academy of Science and Letters), (1864), 35–45. [English translation: J. Chem. Educ., 1986, 63 (12), 1044–1047.]
- [43] R. Wegscheider. *Über simultane Gleichgewichte und die Beziehungen zwischen Thermodynamik und Reaktionskinetik homogener Systeme*. Monatshefte für Chemie / Chemical Monthly, 32 (8) (1901), 849–906.
- [44] G.S. Yablonskii, V.I. Bykov, A.N. Gorban, V.I. Elokhin. *Kinetic Models of Catalytic Reactions*. Elsevier, Amsterdam, The Netherlands, 1991.
- [45] A.N. Zaikin, A.M. Zhabotinsky. *Concentration wave propagation in two-dimensional liquid-phase self-oscillating system*. Nature, 225 (1970), 535–537.