
ANALYSIS OF CHEMICAL REACTION SYSTEMS BY MEANS OF NETWORK THERMODYNAMICS

José HORNO^a and Carlos F. GONZÁLEZ-FERNÁNDEZ^b

^a *Department of Applied Physics,
University College of Jaén, E-23071 Jaén, Spain and*

^b *Department of Applied Physics,
University of Granada, E-18071 Granada, Spain*

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The simple network thermodynamics approach is applied to chemical reaction systems, whereby chemical reactions can be studied avoiding complex mathematical treatment. Steady state reaction rates are obtained for two chemical reaction systems, viz. the decomposition of ozone and the reaction of hydrogen with bromine. The rate equations so obtained agree with those derived from the chemical kinetics concept.

This paper deals with the application of the network thermodynamics method to chemical reaction systems. By the network thermodynamics formalism developed by Peusner¹ and Oster and coworkers^{2,3}, non-equilibrium thermodynamics can be treated within the framework of dynamical system theory, thereby combining dynamic and topological analysis into a single effective tool. In this approach, any system or process is first handled as a black box with flows and forces as the inputs and outputs (a port). This black box is then reticulated step by step according to the data obtainable experimentally and the kind of information one wishes to gain. The reticulated system is represented by a bond-graph or a linear graph. In this manner, the system topology, which cannot be derived by methods conventionally employed for the analysis of chemical and biological systems, is obtained. As the dynamical equations, linear or nonlinear, can be generated algorithmically from the network graph, the well-elaborated methods of circuit analysis can be then employed to obtain the dynamical characteristics directly from the graph. The network approach is particularly well suited to the phenomenological description of the highly complex biological systems⁴ and for the study of structures involving simpler processes, which otherwise require solution of complex differential equations^{5,6}.

Despite its assets, the network approach has not received the attention it deserves. Few attempts have been made to apply it to chemical reaction systems, where it can be fruitfully utilized^{7,8}. The aim of this paper was to demonstrate the utility of this approach in deriving information useful to the chemist. For this, network models

were set up for two typical chemical reaction systems, and expressions were obtained for their steady state reaction rates. It is shown that the rate equations match those obtained by chemical kinetics methods.

Network Modelling of Chemical Reaction Systems

In the case of a chemical reaction system, the conjugated flows and forces are the rates of change in the number of moles of each chemical species involved, J_i , and the chemical potentials, μ_i , respectively. Assuming that the number of moles of the i -th component in a mixture is a unique function of its chemical potential, the flow J_i of the i -th species can be expressed as

$$J_i = dn_i/dt = (dn_i/d\mu_i)(d\mu_i/dt) = \gamma_i(d\mu_i/dt). \quad (1)$$

Its analogy with the current-voltage relation for an electrical capacitor implies that in this case, the capacitance γ_i is

$$\gamma_i = dn_i/d\mu_i. \quad (2)$$

Assuming the validity of the relation

$$\mu_i = \mu_i^0 + RT \ln x_i, \quad (3)$$

where x_i is the mole fraction of the i -th species and μ_i^0 is the reference chemical potential, Eq. (2) transforms into

$$\gamma_i = n_i/RT, \quad (4)$$

where R is the gas constant and T the absolute temperature.

The capacitance γ_i represents the pure storage aspect in a chemical process. However, another kind of chemical transaction, viz. energy dissipation, is also involved in any chemical reaction system. In network thermodynamics, dissipative effects are modelled by a resistor R_r .

The flow of a chemical reaction J_r is

$$J_r = 1/\vartheta_i(dn_i/dt), \quad (5)$$

where ϑ_i is the stoichiometric coefficient of the i -th species. A comparison of Eqs (1) and (5) shows that the flow of the i -th chemical capacitor transformed into a reaction flow weighted by stoichiometry. Network representation of the reaction stoichiometry requires the use of a transformer (Fig. 1a). An ideal two-port transformer is characterized by relations

$$e_2 = r e_1 \quad (6)$$

$$i_2 = i_1/r, \quad (7)$$

where $r = m_2/m_1$ is a constant called the turns ratio. In our case the scaling factor r is ϑ_1 . Thus, in the network representation a reactant and a product will be depicted as shown in Figs 1b and 1c, respectively.

While the μ_i 's and J_i 's are the externally measurable port parameters, the reaction rate is an internal variable driven by an internal conjugated force, the affinity A_r , which is

$$A_r = - \sum_i \vartheta_i \mu_i . \quad (8)$$

When the reaction approaches its equilibrium, chemical kinetics shows that

$$J_r = L_{rr} A_r , \quad (9)$$

where the phenomenological coefficient L_{rr} is given by

$$L_{rr} = v/RT , \quad (10)$$

v being the reaction rate at equilibrium. Comparing Eq. (9) to Ohm's law we see that the coefficient L_{rr} plays the same role in a chemical process as the conductivity in a resistor. Thus, the magnitude of R_r can be expressed as

$$R_r = 1/L_{rr} = RT/v . \quad (11)$$

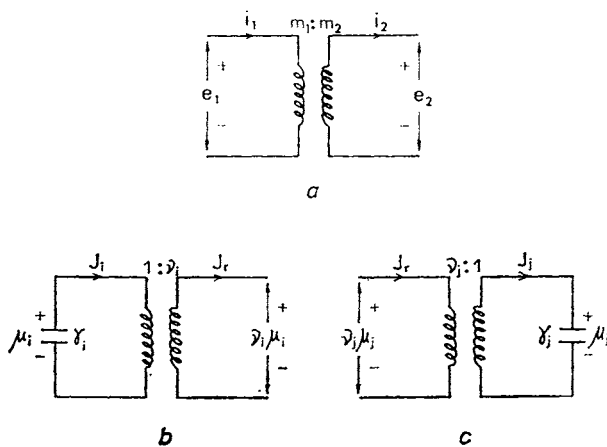


FIG. 1

Network representation of reaction stoichiometry

These ideal elements, R_r and γ_i , are sufficient to construct representations of the majority of chemical reaction systems. To illustrate how a network model is set up, let us consider several simple cases of chemical reactions.

The simplest is the case of a chemical reaction which involves **one substrate A** and one reaction product **B** and is first order in both directions:



(k_1 and k_{-1} are the rate coefficients of conversion of A and B, respectively). As the reaction proceeds, the chemical potential of A decreases and that of B increases, and when the equilibrium is reached, the two chemical potentials are equal to each other. Taking into account the fact that a chemical reaction is a dissipative process, the situation can be represented by a network (Fig. 2) where capacitor B is charged by capacitor A through a resistive element. At equilibrium, the potentials at capacitor A and capacitor B are equal in magnitude.

Applying Kirchoff's voltage law to the network shown in Fig. 2, we can write

$$J_r = (\mu_A - \mu_B)/R_r = A_r/R_r. \quad (12)$$

Comparing Eq. (9) with Eq. (12) we obtain

$$R_r = 1/L_{rr} = RT/k_1[A] = RT/k_{-1}[B], \quad (13)$$

where $[A]$ and $[B]$ are the equilibrium concentrations of A and B, respectively.

The situation is more complex for the chemical reaction

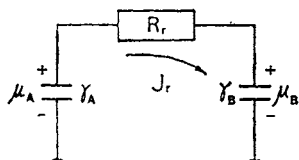
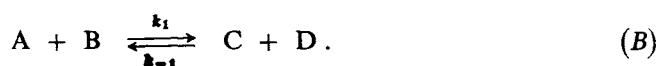


FIG. 2
Network representation of the reaction
 $A \rightleftharpoons B$

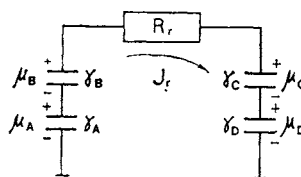


FIG. 3
Network representation of the reaction
 $A + B \rightleftharpoons C + D$

Based on the definitions (5) and (8), the reaction rate and affinity are obtained as

$$J_r = -J_A = -J_B = J_C = J_D \quad (14)$$

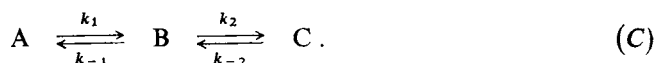
and

$$A_r = (\mu_A + \mu_B) - (\mu_C + \mu_D). \quad (15)$$

In view of its dissipative nature and with regard to Eqs (14) and (15), the network model for reaction (B) will be as shown in Fig. 3. In fact, Eqs (14) and (15) represent properties of a connection in series of the electrical elements. In this case, the resistive element value is

$$R_r = RT/k_1 [A] [B] = RT/k_{-1} [C] [D]. \quad (16)$$

Last, let us consider the consecutive reaction



Each step in this reaction will be represented by the circuit in Fig. 2, and each will have its own resistance, capacitances, reaction rates and affinities. The common element B indicates that the two circuits can be interconnected to form a network model for the consecutive reaction (C) (Fig. 4). Now the resistive elements are given by

$$R_1 = RT/k_1 [A] = RT/k_{-1} [B] \quad (17)$$

and

$$R_2 = RT/k_2 [B] = RT/k_{-2} [C]. \quad (18)$$

Network Analysis of Actual Chemical Reaction Systems

The dynamical equations generated from the network representations can be employed to obtain chemical kinetic information. Two well-known cases of chemical reaction systems are treated in the following text.

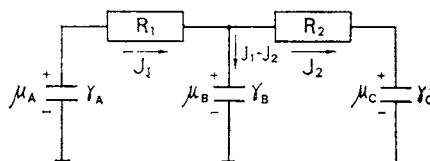
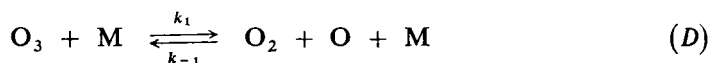


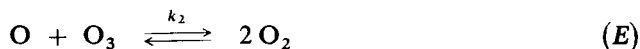
FIG. 4
Network representation of the consecutive reaction $A \rightleftharpoons B \rightleftharpoons C$

The first is the decomposition of ozone. Following the Benson–Axworthy theory⁹, the reaction mechanism can be written in two steps:

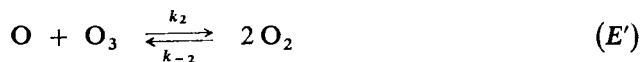
Step 1:



Step 2:



For setting up the network analogue, step 2 will be also regarded as a reversible reaction,



although ultimately, in the final equation for the steady state reaction rate, the rate coefficient k_{-2} will be put equal to zero to obtain the expression for the situation where step 2 is irreversible.

The mechanism is a generalization of the reaction (B); the network representations of reaction steps (D) and (E') are shown in Fig. 5. As has been pointed out, the two circuits can be interconnected through a common element. In this case, the common potential of capacitor O enables the chemical kinetic system (D), (E') to be represented as shown in Fig. 6. From this circuit it is clear that

$$J_1 = (\mu_{\text{O}_3} - \mu_{\text{O}_2} - \mu_{\text{O}})/R_1 \quad (19)$$

$$J_2 = (\mu_{\text{O}} + \mu_{\text{O}_3} - 2\mu_{\text{O}_2})/R_2. \quad (20)$$

At the steady state where $J_1 = J_2 = J_{\text{ss}}$, the network in Fig. 6 gives

$$J_{\text{ss}} = (2\mu_{\text{O}_3} - 3\mu_{\text{O}_2})/(R_1 + R_2). \quad (21)$$

Using the definition of the chemical potential (Eq. (3)), Eq. (21) can be written in the form

$$J_{\text{ss}} = \frac{2\mu_{\text{O}_3}^{\text{O}} - 3\mu_{\text{O}_2}^{\text{O}} + RT \ln ([\text{O}_3]^2/[\text{O}_2]^3)}{R_1 + R_2}. \quad (22)$$

According to classical thermodynamics, the reference affinity A_r^{O} is

$$A_r^{\text{O}} = - \sum_i \vartheta_i \mu_i^{\text{O}} = RT \ln K_{\text{eq}}, \quad (23)$$

where K_{eq} is the equilibrium constant of the reaction. Thus, in our case we can write

$$2\mu_{\text{O}_3}^0 - 3\mu_{\text{O}_2}^0 = RT \ln K_{\text{eq}} = RT \ln (k_1 k_2 / k_{-1} k_{-2}). \quad (24)$$

Eq. (22) can be rewritten as

$$J_{\text{ss}} = \frac{RT}{R_1 + R_2} \ln \left\{ \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} k_{-2} [\text{O}_2]^3} \right\}. \quad (25)$$

Expanding the logarithm in the neighbourhood of equilibrium and neglecting the second and higher order terms we obtain

$$J_{\text{ss}} = \frac{RT(k_1 k_2 [\text{O}_3]^2 - k_{-1} k_{-2} [\text{O}_2]^3)}{(R_1 + R_2) k_{-1} k_{-2} [\text{O}_2]^3}. \quad (26)$$

The resistive elements R_1 and R_2 can be evaluated in the same way as above in the analysis of reaction (A), viz. in terms of the rate coefficients and concentrations (cf. Eqs (12), (13)). Thus,

$$R_1 = RT/k_1 [\text{O}_3] [\text{M}] = RT/k_{-1} [\text{O}_2] [\text{O}] [\text{M}] \quad (27)$$

$$R_2 = RT/k_2 [\text{O}] [\text{O}_3] = RT/k_{-2} [\text{O}_2]^2. \quad (28)$$

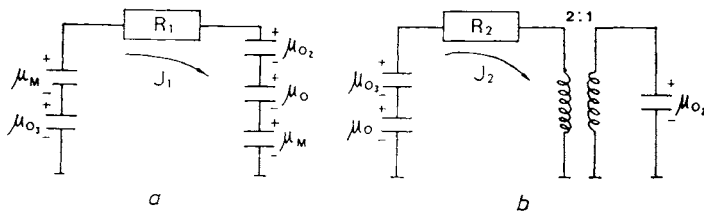


FIG. 5

Network representations of reaction steps a (D) and b (E')

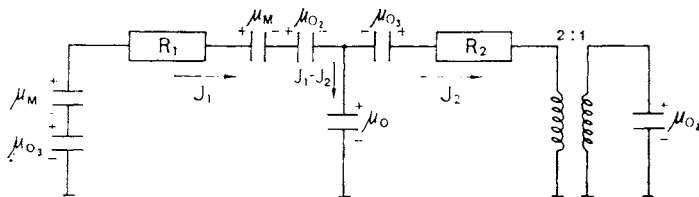


FIG. 6

Network model of the decomposition of ozone according to the Benson-Axworthy mechanism

Substituting for R_1 and R_2 in Eq. (26) we can write for the steady state reaction rate

$$J_{ss} = \frac{[M] (k_1 k_2 [O_3]^2 - k_{-1} k_{-2} [O_2]^3)}{k_{-1} [O_2] [M] + k_2 [O_3]} \quad (29)$$

If step 2 is irreversible ($(E') \rightarrow (E)$), then $k_{-2} = 0$ and Eq. (29) reduces to

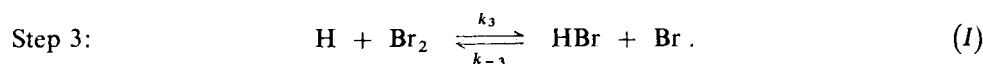
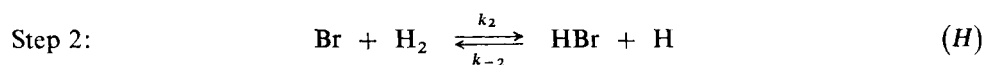
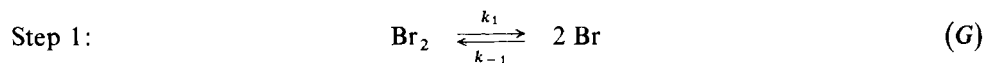
$$J_{ss} = \frac{k_1 k_2 [O_3]^2 [M]}{k_{-1} [O_2] [M] + k_2 [O_3]} \quad (30)$$

This equation agrees with that obtained by chemical kinetics treatment¹⁰.

Finally, let us consider the reaction



The mechanism of the reaction, proposed by Christiansen, Herzfeld and Polanyi¹⁰, involves the following steps:



Again, although actually irreversible, step 3 is written as reversible for the sake of construction of the network model, which is shown in Fig. 7; ultimately, the rate coefficient k_{-3} will be put equal to zero.

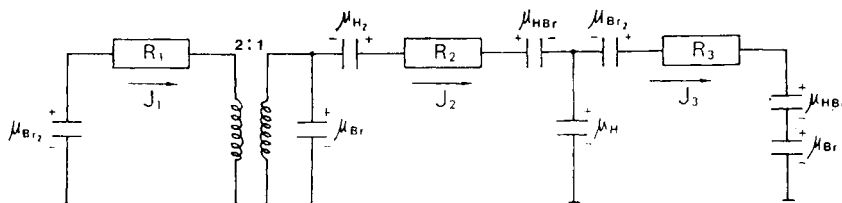


FIG. 7

Network representation of the chemical reaction system (F)

From the circuit shown in Fig. 7, it is clear that the flow through the capacitor representing Br and H becomes zero at the steady state ($J_{ss} = J_1 = J_2 = J_3$) and the steady rate can be written as

$$J_{ss} = \frac{2\mu_{Br_2} - 2\mu_{Br} + \mu_{H_2} - 2\mu_{HBr}}{R_1 + R_2 + R_3}. \quad (31)$$

Following the procedure outlined in the preceding case (cf. Eqs (22)–(26)), Eq. (31) can be transformed into

$$J_{ss} = \frac{RT(k_1k_2k_3[Br_2]^2[H_2] - k_{-1}k_{-2}k_{-3}[Br]^2[HBr]^2)}{(R_1 + R_2 + R_3)k_{-1}k_{-2}k_{-3}[Br]^2[HBr]}. \quad (32)$$

Now, the resistive elements can be written as

$$R_1 = RT/k_1[Br_2] = RT/k_{-1}[Br]^2 \quad (33)$$

$$R_2 = RT/k_2[Br][H_2] = RT/k_{-2}[HBr][H] \quad (34)$$

$$R_3 = RT/k_3[H][Br_2] = RT/k_{-3}[HBr][Br]. \quad (35)$$

Replacing the $(R_1 + R_2 + R_3)$ term in Eq. (32) we obtain

$$J_{ss} = \frac{k_2(k_1/k_{-1})^{1/2}[H_2][Br_2]^{1/2} \left(1 - \frac{k_{-2}k_{-3}[HBr]^2}{k_2k_3[H_2][Br_2]}\right)}{1 + (k_{-2}[HBr]/k_3[Br_2])(1 + k_3[H]/k_1)}. \quad (36)$$

At equilibrium the rates of the two opposing reactions are equal, and thus

$$k_3[H][Br_2] = k_{-3}[HBr][Br] \quad (37)$$

$$k_1[Br_2] = k_{-1}[Br]^2 \quad (38)$$

from which

$$k_3[H]/k_1 = k_{-3}[HBr]/k_{-1}[Br]. \quad (39)$$

The right-hand term, and hence also the left-hand term, is zero if the reaction (I) is irreversible ($k_{-3} = 0$), whereupon Eq. (36) reduces to

$$J_{ss} = \frac{k_2(k_1/k_{-1})^{1/2}[H_2][Br_2]^{1/2}}{1 + (k_{-2}[HBr]/k_3[Br_2])}. \quad (40)$$

The rate equation (40) also agrees with that obtained by kinetic treatment¹⁰.

In conclusion, the network thermodynamic method can be employed for a simple study of chemical reaction systems. For the two examples shown, the steady state rate equations could be derived avoiding complex mathematical treatment. An additional asset of this approach, apparent particularly in the case of extensive chemical reaction systems, consists in the possibility of computerizing the treatment using circuit simulation programs.

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