

On the geometric formulation of non-isothermal mass action chemical reaction networks

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- 1 Recall of network formulation of isothermal detailed-balanced mass action kinetics chemical reaction networks
- 2 Port-thermodynamic formulation in non-isothermal case

Dynamics of chemical reaction network having r reactions among m chemical species with concentrations $x \in \mathbb{R}_+^m$

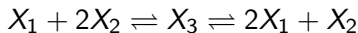
$$\dot{x} = Nv(x),$$

where N is $m \times r$ **stoichiometric matrix**, which can be factorized as

$$N = ZB$$

with Z the $m \times c$ **complex composition matrix** and B the **incidence matrix** of the graph of complexes.

For example, for



$$N = \begin{bmatrix} -1 & 2 \\ -2 & 1 \\ 1 & -1 \end{bmatrix}, \quad Z = \begin{bmatrix} 1 & 0 & 2 \\ 2 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \quad B = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix}$$

Mass action kinetics of j -th reaction, from a substrate complex \mathcal{S}_j to a product complex \mathcal{P}_j , is given as

$$v_j(x) = k_j^+ \prod_{i=1}^m x_i^{Z_{i\mathcal{S}_j}} - k_j^- \prod_{i=1}^m x_i^{Z_{i\mathcal{P}_j}},$$

where $Z_{i\rho}$ is the (i, ρ) -th element of the complex composition matrix Z , and k_j^+, k_j^- are the forward/backward reaction constants of the j -th reaction.

This can be rewritten as

$$v_j(x) = k_j^+ \exp(Z_{\mathcal{S}_j}^T \text{Ln}(x)) - k_j^- \exp(Z_{\mathcal{P}_j}^T \text{Ln}(x))$$

The network $\dot{x} = Nv(x)$ is called **detailed balanced** if there exists equilibrium x^* satisfying

$$v(x^*) = 0$$

that is,

$$k_j^+ \exp(Z_{\mathcal{S}_j}^T \text{Ln}(x^*)) = k_j^- \exp(Z_{\mathcal{P}_j}^T \text{Ln}(x^*)), \quad j = 1, \dots, r$$

Define **equilibrium constant** K_j^{eq} of the j -th reaction as

$$K_j^{eq} := \frac{k_j^+}{k_j^-}$$

Then

$$K_j^{eq} = \exp \left(Z_{\mathcal{P}_j}^T \text{Ln}(x^*) - Z_{\mathcal{S}_j}^T \text{Ln}(x^*) \right), \quad j = 1, \dots, r$$

This amounts to the vector equation

$$K^{eq} = \text{Exp} \left(B^T Z^T \text{Ln}(x^*) \right) = \text{Exp} \left(N^T \text{Ln}(x^*) \right),$$

where K^{eq} is the r -dimensional vector with j -th element K_j^{eq} .

Hence, there exists $x^* \in \mathbb{R}_+^m$, and thus the network is **detailed balanced**, if and only if (generalized **Wegscheider conditions**)

$$\text{Ln} \left(K^{eq} \right) \in \text{im } N^T$$

Then **all** equilibria x^{**} also satisfy $v(x^{**}) = 0$.

Define 'conductance' of j -th reaction as

$$\kappa_j(x^*) := k_j^+ \exp\left(Z_{S_j}^T \text{Ln}(x^*)\right) = k_j^- \exp\left(Z_{P_j}^T \text{Ln}(x^*)\right)$$

Then

$$v_j(x) = \kappa_j(x^*) \left[\exp\left(Z_{S_j}^T \text{Ln}\left(\frac{x}{x^*}\right)\right) - \exp\left(Z_{P_j}^T \text{Ln}\left(\frac{x}{x^*}\right)\right) \right]$$

Defining the $r \times r$ diagonal matrix of conductances as

$$\mathcal{K} := \text{diag}(\kappa_1(x^*), \dots, \kappa_r(x^*))$$

it follows that

$$v(x) = -\mathcal{K}B^T \text{Exp}\left(Z^T \text{Ln}\left(\frac{x}{x^*}\right)\right),$$

and thus the dynamics takes the form

$$\dot{x} = -ZB\mathcal{K}B^T \text{Exp}\left(Z^T \text{Ln}\left(\frac{x}{x^*}\right)\right)$$

$L := BKB^T$ defines **weighted Laplacian** matrix for graph of complexes.

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Define **chemical potential** vector μ and **reference** chemical potential vector μ^0 as

$$\mu(x) := RT \text{Ln} \left(\frac{x}{x^*} \right), \quad \mu^0 := -RT \text{Ln}(x^*)$$

with T the temperature and R universal gas constant.

Define **Gibbs' free energy** as

$$G(x) = RTx^T \text{Ln} \left(\frac{x}{x^*} \right) + RT(x^* - x)^T \mathbb{1}_m, \quad \frac{\partial G}{\partial x}(x) = \mu(x)$$

Then dynamics is also given as

$$\dot{x} = -ZL \text{Exp} \left(\frac{1}{RT} Z^T \frac{\partial G}{\partial x}(x) \right)$$

Can be put into **port-Hamiltonian** form.

Hence $\gamma(x) := Z^T \frac{\partial G}{\partial x}(x) = Z^T \mu(x)$ determines the dynamics.

The Gibbs' free energy G can be used as a Lyapunov function, using the fundamental result

$$\gamma^T L_{\text{Exp}} \gamma \geq 0 \text{ for all } \gamma, \quad \gamma^T L_{\text{Exp}} \gamma = 0 \text{ iff } B^T \gamma = 0$$

where $B^T \gamma$ is the vector of **affinities**.

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Consider the thermodynamic system:

extensive variables x_1, \dots, x_m, S, E

intensive variables μ_1, \dots, μ_m, T

Gibbs' relation

$$dE = TdS + \mu_1 dx_1 + \dots + \mu_m dx_m,$$

Geometric picture

Start with manifold $x \in Q$ of concentrations (or, mole numbers), and consider $(x, S, E) \in Q^e = Q \times \mathbb{R} \times \mathbb{R}$.

Denote by T^*Q^e the **cotangent bundle** T^*Q^e **without** its zero-section.

Coordinates (p, p_S, p_E) for the cotangent space will be **homogeneous coordinates** for the space of **intensive** variables

$$(\mu_1, \dots, \mu_m, T) = \left(\frac{p}{-p_E}, \frac{p_S}{-p_E} \right)$$

Contact manifold $\mathbb{P}(T^*Q)$ defines thermodynamic phase space of extensive and intensive variables.

Forward and backward reaction constants depend on temperature T .
By Arrhenius equations

$$k_j^+(T) = \bar{k}_j^+ \exp\left(-\frac{E_j^+}{RT}\right), \quad k_j^-(T) = \bar{k}_j^- \exp\left(-\frac{E_j^-}{RT}\right),$$

where E_j^+ , E_j^- are **activity energies**, and \bar{k}_j^+ , \bar{k}_j^- are the forward and backward rate constants.

Hence equilibrium constants K_j^{eq} are

$$K_j^{eq}(T) = \frac{k_j^+(T)}{k_j^-(T)} = \frac{\bar{k}_j^+}{\bar{k}_j^-} \exp\left(\frac{E_j^- - E_j^+}{RT}\right)$$

and equilibrium $x^*(T)$ (also depending on T) satisfies

$$\text{Ln } K^{eq}(T) = N^T \text{Ln } x^*(T)$$

Also conductances κ_j depend on T , as well as Laplacian $L = BKBT^T$.

Consider **entropy representation** $S = S(x, E)$, generating the homogeneous Lagrangian submanifold \mathcal{L} describing the **state properties** of the network:

$$\frac{\partial S}{\partial x}(x, E) = -\frac{\mu}{T}, \quad \frac{\partial S}{\partial E}(x, E) = \frac{1}{T}$$

Dynamics is given by Hamiltonian vector field with homogeneous Hamiltonian

$$K^a = -p^T Z \text{LExp} \frac{-Z^T}{R} \frac{\partial S}{\partial x}(x, E) - p_S \frac{\partial S}{\partial x T}(x, E) Z \text{LExp} \frac{-Z^T}{R} \frac{\partial S}{\partial x}(x, E)$$

This implies that for an isolated chemical reaction network

$$\frac{d}{dt} S = \frac{1}{T} \mu^T Z \text{LExp} \left(\frac{Z^T \mu}{RT} \right) =: \sigma \geq 0,$$

with equality if and only if $B^T Z^T \mu = N^T \mu = 0$, i.e., if and only if **affinities** are zero.

Hence equilibria of the system correspond to states of minimal (= zero) **entropy production** σ .

Use $-S$ as Lyapunov function: any initial vector $x(0)$ will converge to one of these equilibria.

Possible **control Hamiltonian** K^c for the non-isothermal case is

$$K^c = p_S \frac{\partial S}{\partial E}(x, E) + p_E,$$

corresponding to **heat flow** input, and a rate of entropy conjugate output

$$y_e = \frac{\partial S}{\partial E}(x, E)|_{\mathcal{L}} = \frac{1}{T}$$

Another possibility is

$$K^c = p_S \frac{\partial S}{\partial x_i}(x, E) + p_i,$$

corresponding to material in/outflow of the i -th chemical species, with rate of entropy conjugate output

$$y_e = \frac{\partial S}{\partial x_i}(x, E)|_{\mathcal{L}} = \frac{\mu_i}{T}$$

of the i -th chemical species divided by the temperature T .

- Compact and efficient isothermal network formulation extends to port-thermodynamic system formulation in non-isothermal case.
- Opportunities for control (e.g., CSTR !) to be investigated.