

Is $d^2S/dt^2 \leq 0$ for simple reactions?

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1978 J. Phys. A: Math. Gen. 11 L227

(<http://iopscience.iop.org/0305-4470/11/9/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 18:59

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Is $\ddot{S} \leq 0$ for simple reactions?

G West

Department of Physics, Philipps-University, Mainzer Gasse 33, D-3550 Marburg, West Germany

Received 1 June 1978

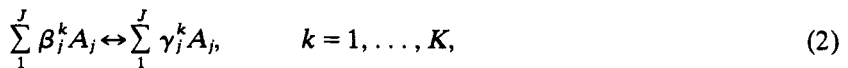
Abstract. For a special class of spatially homogeneous simple reaction systems we prove that the second time derivatives of the most essential thermodynamic potentials are indefinite.

For many kinetic models the inequality

$$\ddot{S} \leq 0 \tag{1}$$

is valid (see Simons 1976 and the literature cited there), but not generally as shown by Maass (1970) for the spatially inhomogeneous Boltzmann equation. In the following we shall prove (1) for a special class of simple reactions in spatially homogeneous systems.

The following representation of simple reactions is closely related to Aris (1965, 1967/8). Let the system be spatially homogeneous and consist of J species $\{A_j\}_1^J$ with molar densities $\{n_j\}_1^J$. Let the chemical reactions arise from the collision processes



with entire non-negative coefficients $\{\beta_j^k, \gamma_j^k\}$ giving the numbers of molecules of species A_j entering the k th collision and inverse collision, respectively. With the stoichiometric coefficients

$$r_j^k = -\beta_j^k + \gamma_j^k, \quad j = 1, \dots, J, \quad k = 1, \dots, K, \tag{3}$$

one gets the substance balances

$$\dot{n}_j = \sum_k r_j^k \xi_k$$

and

$$\dot{N}_j = \sum_k r_j^k \Xi_k, \tag{4}$$

respectively. The reaction rates for isochoric processes are

$$\xi_k = K_k \prod_{m=1}^J (n_m)^{\beta_m^k} - K'_k \prod_{m=1}^J (n_m)^{\gamma_m^k} \tag{5}$$

$$:= Q_k - Q'_k \tag{6}$$

with non-negative reaction velocities $\{K_k, K'_k\}$. (It is not assumed that the columns of the stoichiometric matrix (r_j^k) are linearly independent.) Generally, for non-isochoric processes too, the reaction equations are

$$\dot{\Xi}_k = V(Q_k - Q'_k) \quad (7)$$

where the time-dependence of volume V has to be considered for integration of the equations.

For the following processes

Process	Constant thermodynamic parameters	Potential	
Isothermal–isochoric	T, V	Free energy	$F(T, V, N_1, \dots, N_J)$
Isothermal–isobaric	T, p	Free enthalpy	$G(T, p, N_1, \dots, N_J)$
Adiabatic–isochoric	U, V	Entropy	$S(U, V, N_1, \dots, N_J)$
Adiabatic–isobaric	H, p	Entropy	$S(H, p, N_1, \dots, N_J)$

(8)

one gets the well known time derivatives

$$\left. \begin{array}{l} \dot{F}_{\text{isothermal–isochoric}} \\ \dot{G}_{\text{isothermal–isobaric}} \\ -T\dot{S}_{\text{adiabatic–isochoric}} \\ -T\dot{S}_{\text{adiabatic–isobaric}} \end{array} \right\} = \sum \mu_i \dot{N}_i := -VRT\chi. \quad (9a)$$

Considering the relations between the reaction velocities and the chemical potentials (mass-action law) we have

$$\chi = \sum (\ln Q_k - \ln Q'_k)(Q_k - Q'_k). \quad (9b)$$

Because of the strict monotony of the logarithm function the form χ is non-negative term by term and zero exactly in equilibrium states, i.e. if

$$\bigwedge_k Q_k = Q'_k \quad (10)$$

is valid ('detailed' balance). The equilibrium state is always located in the inner part of the region of the non-negative concentrations $\{n_j\}$, the boundary of which is defined by the vanishing of at least one concentration.

If one species, e.g. A_1 , appears in every collision process and every inverse collision process,

$$\bigwedge_k \{\beta_1^k \neq 0, \gamma_1^k \neq 0\}, \quad \bigvee_{k_0} \beta_1^{k_0} \neq \gamma_1^{k_0}, \quad (11)$$

all rates Q_k and Q'_k are zero on that part of the boundary of the region of $\{n_j\}$ where n_1 disappears, and χ vanishes there, too. As already stated, χ is zero in the equilibrium states that lie in the inner part of the region of concentrations too, and is positive in all other states. Because the first time derivatives ($-\dot{F}$, $-\dot{G}$, \dot{S}) listed in (8) also have these properties, the second time derivatives of these potentials must be indefinite under the stated conditions.

References

- Aris R 1965 *Archs Ration. Mech. Analysis* **19** 81–99
— 1967/68 *Archs Ration. Mech. Analysis* **27** 356–64
Maass W 1970 *J. Phys. A: Math. Gen.* **3** 331–4
Simons S 1976 *J. Phys. A: Math. Gen.* **9** 413–6