COMPLETE MONOTONICITY OF ENTROPY PRODUCTION IN CHEMICAL REACTION

Milan ŠOLC

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6

Received November 28th, 1979

The successive time derivatives of relative entropy and entropy production for a system with a reversible first-order reaction alternate in sign. It is proved that the relative entropy for reactions with an equilibrium constant smaller than or equal to one is completely monotonic in the whole definition interval, and for reactions with an equilibrium constant larger than one this function is completely monotonic at the beginning of the reaction and near to equilibrium.

In 1966, McKean arrived at the supposition that successive time derivatives of entropy alternate in sign[1]. This hypothesis was verified by numerical calculations for some mechanical systems and dissociation in the gas phase[2] (other literature is given in ref.[2]).

The aim of the present work was to test McKean's hypothesis on the reaction entropy of a reversible first-order reaction A $\rightleftharpoons$ B. In this case the entropy is known as an explicit function of time and the problem can be solved analytically.

Reaction Entropy

The following equation for the entropy, $S(t)$, produced by a reaction A $\rightleftharpoons$ B under thermal equilibrium conditions (reaction entropy) can be derived from the postulates of thermodynamics of irreversible processes[3]:

$$S(t) - S_e = -\boldsymbol{R}[n_A(t) \ln (n_A(t)/n_A^e) + n_B(t) \ln (n_B(t)/n_B^e)] , \tag{1}$$

where S_e denotes the entropy in equilibrium, $n_X(t)$ the concentrations of components X = A, B at time t, n_X^e their concentrations in equilibrium, and $\boldsymbol{R}$ the gas constant. The concentrations $n_X(t)$ can be determined as functions of time by integrating equations of the mass action law and using the initial condition $n_A(0) = n_0$, $n_B(0) = 0$:

$$n_A(t) = [n_0/(1 + K)] [1 + K.\exp(-\alpha t)] , \tag{2a}$$

$$n_B(t) = [n_0K/(1 + K)] [1 - \exp(-\alpha t)] , \tag{2b}$$

where $\alpha = k_1 + k_2$, k_1 is the rate constant of reaction A → B, k_2 for reaction B → A, and $K = k_1/k_2$ is the equilibrium constant. By substituting (*2a, b*) into (*1*) we obtain the time dependence of the reaction entropy in the explicit form:

$$S(t) - S_e = -[Rn_0/(1 + K)]\,[(1 + K\,.\exp(-\alpha t))\ln(1 + K\,.\exp(-\alpha t)) + $$
$$+ K(1 - \exp(-\alpha t))\ln(1 - \exp(-\alpha t))]\,. \tag{3}$$

Properties of Derivatives of Relative Entropy

A function $f(t)$ is according to the definition[4,5] completely monotonic in the interval $a < t < b$, if it has here derivatives of all orders and

$$(-1)^n \, d^n f(t)/dt^n \geqq 0\,. \tag{4}$$

We shall introduce a new function, the relative entropy, which is, in the stochastic interpretation, analogous to Schlögl's K function[6]:

$$H(t) = -(S(t) - S_e)/R = \sum_{X=A,B} n_X(t) \ln(n_X(t)/n_X^e)\,, \tag{5}$$

and we shall examine if it fulfils the condition (*4*).

For $K \leqq 1$, the logarithmic terms in Eq. (*3*) can be expanded in series and substituted into (*5*) to obtain

$$H(t) = [n_0/(1 + K)] \sum_{j=1}^{\infty} \exp[-(j + 1)\alpha t]\,[K + (-K)^{j+1}]/j(j + 1)\,. \tag{6}$$

By differentiating this series successively we obtain

$$d^n H(t)/dt^n = (-1)^n\,[n_0/(1 + K)]\,\alpha^n\,.$$
$$.\sum_{j=1}^{\infty} \exp[-(j + 1)\alpha t]\,[K + (-K)^{j+1}]\,(j + 1)^{n-1}/j\,. \tag{7}$$

This series is uniformly convergent in the interval $0 < h \leqq t < \infty$ and its termwise differentiating is justified in this interval. Since all terms to be summed in Eq. (*7*) are positive for $K < 1$ (non-negative for $K = 1$), we have

$$(-1)^n \, d^n H(t)/dt^n \geqq 0\,, \tag{8}$$

i.e., $H(t)$ is completely monotonic for $K \leqq 1$, $0 < h \leqq t < \infty$.

The function $H(t)$ can be written in the form

$$H(t) = [n_0/(1 + K)]\,[H_1(t) + H_2(t)]\,, \tag{9}$$

where

$$H_1(t) = [1 + K\,.\,\exp(-\alpha t)]\ln[1 + K\,.\,\exp(-\alpha t)] - K\,.\,\exp(-\alpha t) > 0\,, \tag{10a}$$

$$H_2(t) = K[1 - \exp(-\alpha t)]\ln[1 - \exp(-\alpha t)] + K\,.\,\exp(-\alpha t) > 0\,. \tag{10b}$$

That both these quantities are positive follows from the inequality $z \ln z > z - 1$, $z > 0$, $z \neq 1$. The function $H_2(t) = K \sum_{j=1}^{\infty} [1/j(j + 1)] \exp[-(j + 1)\alpha t]$ is completely monotonic in the interval $0 < h \leqq t < \infty$. Differentiation of the function $H_1(t)$ leads to the result

$$\mathrm{d}^n H_1(t)/\mathrm{d}t^n = (-1)^n \alpha^n \{K\,.\,\exp(-\alpha t)\ln[1 + K\,.\,\exp(-\alpha t)] + K^2 \exp(-2\alpha t)\, P_n(K\,.\,\exp(-\alpha t))/[1 + K\,.\,\exp(-\alpha t)]^{n-1}\}\,, \tag{11}$$

where $P_n(x)$ is a polynomial of degree $n - 2$ in $x = K.\exp(-\alpha t)$:

$$P_1(x) = 0\,, \quad P_n(x) = \sum_{i=0}^{n-2} a_i^{(n)} x^i\,, \quad n \geqq 2\,, \tag{12}$$

and the coefficients are given by the recurrent formula

$$a_i^{(n+1)} = \binom{n-1}{i} + (i + 2)\,a_i^{(n)} - (n - i - 2)\,a_{i-1}^{(n)}\,, \quad 0 \leqq i \leqq n - 1\,. \tag{13}$$

The polynomials $P_1(x)$ through $P_9(x)$ are listed below:

$$P_1(x) = 0\,, \quad P_2(x) = 1\,, \quad P_3(x) = 3 + 2x\,,$$

$$P_4(x) = 7 + 8x + 3x^2\,, \quad P_5(x) = 15 + 20x + 15x^2 + 4x^3\,,$$

$$P_6(x) = 31 + 34x + 46x^2 + 24x^3 + 5x^4\,,$$

$$P_7(x) = 63 + 14x + 126x^2 + 84x^3 + 35x^4 + 6x^5\,,$$

$$P_8(x) = 127 - 204x + 477x^2 + 188x^3 + 141x^4 + 48x^5 + 7x^6\,,$$

$$P_9(x) = 255 - 1240x + 2745x^2 - 456x^3 + 505x^4 + 216x^5 + 63x^6 + 8x^7\,.$$

These polynomials are positive in the interval $0 \leqq x < \infty$ and the time derivatives of $H_1(t)$ alternate in sign. From this and from the complete monotonicity of $H_2(t)$

it follows that the odd derivatives ($n = 1, 3, 5, 7, 9$) of $H(t)$ are negative and the even ones ($n = 2, 4, 6, 8$) are positive for any $K > 0$ and $0 < t < \infty$.

The absolute term of $P_n(x)$ is positive for $n \geqq 1$ and according to Eq. (*13*) equal to $2^{n-1} - 1$, hence for sufficiently large t values ($x \to 0$) we have

$$d^n H_1(t)/dt^n \approx (-1)^n \alpha^n 2^{n-1} K^2 \exp(-2\alpha t), \quad t \to \infty, \qquad (14)$$

$$d^n H_2(t)/dt^n \approx (-1)^n \alpha^n 2^{n-1} K \exp(-2\alpha t), \quad t \to \infty, \qquad (15)$$

and in the proximity of equilibrium we have

$$d^n H(t)/dt^n \approx (-1)^n n_0 \alpha^n 2^{n-1} K \exp(-2\alpha t), \quad t \to \infty. \qquad (16)$$

This is in accord with Pritchard's hypothesis[2] about the limiting behaviour of the entropy ($\ln |d^n S(t)/dt^n|$ is in the limit for large t values a linear function of t).

We define a new variable

$$u = 1 - \exp(-\alpha t). \qquad (17)$$

In the interval $0 < t < \infty$ we have $0 < u < 1$ and $du/dt = \alpha \exp(-\alpha t)$ is a completely monotonic function. On introducing u into $H_1(t)$ and $H_2(t)$ we obtain

$$H_1(t) + H_2(t) = g(u) = (1 + K - Ku) \ln (1 + K - Ku) + Ku \, . \ln u > 0, \qquad (18)$$

$$dg(u)/du = -K \ln (1 + K - Ku) + K \ln u < 0, \qquad (19)$$

$$d^n g(u)/du^n = (-1)^n (n-2)! \, K[1/u^{n-1} + $$
$$+ (-1)^n K^{n-1}/(1 + K - Ku)^{n-1}], \quad n \geqq 2. \qquad (20)$$

For even n, the expression in square brackets in Eq. (*20*) is positive in the interval $0 < u < 1$, for odd n it is positive if $(1 + K - Ku)/Ku > 1$, *i.e.*, for $K > 1$ in the interval $0 < u < (1 + K)/2K$ and hence for $0 < t < (1/\alpha) \ln [2K/(K - 1)]$, which corresponds to $n_A(t) > n_0/2$. It follows from the rule about differentiation of composite functions that the composite function $\varphi(\psi(t))$ is completely monotonic if φ is completely monotonic and ψ is a positive function with a completely monotonic derivative[5]. The function $H_1(t) + H_2(t) = g(u(t))$ fulfils these requirements for $K > 1$ in the interval $0 < t < (1/\alpha) . \ln [2K/(K - 1)]$.

The entropy production due to chemical reaction in a time unit, $dS(t)/dt = -dH(t)/dt$, is completely monotonic if the relative entropy $H(t)$ is completely monotonic. It has been shown that the function $H(t)$ has the property (*8*) for $K \leqq 1$

in the interval $0 < h \leqq t < \infty$ and for $K > 1$ in the interval $0 < t < (1/\alpha)$. ln $[2K/(K-1)]$ (*i.e.*, for $n_A(t) > n_0/2$) and in the limit $t \to \infty$ (close to equilibrium). In the general case for $K > 0$, at least the first nine successive derivatives of $H(t)$ alternate in sign in the interval $0 < t < \infty$ and the derivatives $d^nS(t)/dt^n$ ($n = 1, 2, \ldots, 8$) have no extremum. This generalizes numerical results obtained by Pritchard[7].

REFERENCES

1. McKean H. P.: Arch. Ratl. Mech. Anal. *21*, 343 (1966).
2. Pritchard H. O., Labib N. I., McElwain D. L. S.: Can. J. Chem. *52*, 2618 (1974).
3. Ishida K.: J. Phys. Chem. *70*, 3806 (1966).
4. Wider D. V.: *The Laplace Transform*, Chapter IV. Princeton Univ. Press, Princeton 1946.
5. Feller W.: *An Introduction to Probability Theory and Its Applications*, Vol. II, Chapter XIII. Wiley, New York 1971.
6. Schlögl F.: Z. Phys. *191*, 81 (1966).
7. Pritchard H. O.: Can. J. Chem. *53*, 1756 (1975).

Translated by K. Micka.