Applicability of the Steady State Principle to the Autoxidation of Cuprous Chloride

HAKON NORD

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

The *steady state equation* for determination of oxygen in a solution through which an oxygen containing gasphase is blown, and in which oxygen is being consumed by a chemical reaction, is compared with the *differential equation* for the oxygen concentration. The error introduced by determination of the oxygen concentration by using the simpler equation is calculated, and is negligible.

It is customary in chemical kinetics to base the treatment of the overall rate problem for a sequence of reactions on the assumption that the system will quickly settle down to a state in which the rates of appearance and disappearance of molecular species, which do not occur in the stoichiometric reaction scheme, are equal. This method is only strictly valid for systems which are invariant in time, but the difference for other systems between treatments based on this principle and rigorous solutions of the system of simultaneous differential equations for all species in the given problem is very often far below the limits of experimental accuracy. The steady state principle is always applicable in cases where the intermediates are so shortlived that they only represent a negligible amount of the reaction system in comparison with the concentrations of the stoichiometric components. Sometimes it is, however, convenient to apply steady state treatment to systems where this condition is not strictly fulfilled, and in such cases it is desirable to have a method to test the reliability of the method.

A problem of this kind is found in the preceding paper¹. There it was found that the rate with which oxygen was used in a certain reaction was so high that the oxygen concentration in the reacting solution was essentially below saturation when a mixture of oxygen and nitrogen was blown through the reaction vessel. The oxygen concentration was in this case determined by the steady state principle, *i.e.*, by the equation

$$k_1 p_{O_2} - k_{-1} c_{O_2} - s = 0$$

(equation (I) in the preceding paper)

where everything except cO_2 was known. The problem should strictly have been solved by integration of the differential equation

$$\frac{dcO_2}{dt} = k_1 pO_2 - k_{-1} cO_2 - s$$

with appropriate boundary conditions. The objections against the use of the steady state principle in kinetics originate in the difference between these two equations, the apparent paradox introduced by equating to zero the rate of change of something which actually does change.

In the present problem the first term on the right hand side of the differential equation is a constant, and the next two terms are proportional to the oxygen concentration, s being a function of time. The problem is now to determine the difference between α determined by the equation

$$a - \alpha(b + y) = 0 \quad (I)$$

and by integration of the differential equation

$$\frac{d\alpha}{dt} = a - \alpha(b + y) \quad (II)$$

the boundary condition being that $\alpha = 0$ for $t = 0$.

The general solution of the differential equation is

$$\alpha = a \cdot e^{-\int_0^t (b+y) dt} \int_0^t e^{\int_0^\tau (b+y) d\tau} d\tau \quad (III)$$

This expression can be transformed in a convenient way by means of the following relations:

$$\begin{aligned} \int e^{F(x)} dx &= \int \frac{1}{f(x)} \cdot e^{F(x)} dF(x) = \frac{1}{f(x)} \cdot e^{F(x)} - \int \frac{d1/f(x)}{dF(x)} e^{F(x)} dF(x) = \\ &= \frac{1}{f(x)} e^{F(x)} - \int \frac{d1/f(x)}{dx} e^{F(x)} dx = \frac{1}{f(x)} e^{F(x)} + \int \frac{f'(x)}{f(x)^2} e^{F(x)} dx; \\ f(x) &\equiv F'(x) \end{aligned}$$

The boundary condition given above is satisfied when the integration constant

$$\frac{1}{f(0)}$$

is subtracted. Introduction into the general solution for the differential equation gives:

$$\begin{aligned} \alpha &= a \cdot e^{-\int_0^t (a+y) dt} \left\{ \frac{1}{b+y} e^{\int_0^t (a+y) dt} - \frac{1}{b+y_0} - \int_0^t \frac{y}{(b+y)^2} e^{\int_0^\tau (b+y) d\tau} d\tau \right\} \\ \alpha &= \frac{a}{b+y} - \frac{a}{b+y_0} e^{\int_0^t (a+y) dt} - a e^{-\int_0^t (a+y) dt} \int_0^t \frac{y'}{(b+y)^2} e^{\int_0^\tau (b+y) d\tau} d\tau \quad (IV) \end{aligned}$$

This expression is identical with the general solution above. The first term is identical with the solution of the steady state equation (I). The second term is the initial value of the steady state solution multiplied by an exponential factor. It is easy to investigate how quickly this term vanishes in a given problem. The third term is identical with (III) apart from the factor immediately after the big sign of integration. The contribution from this term is determined by calculation of this factor, and is negligible if

$$\frac{y'}{(b+y)^2} \ll 1.$$

In the preceding paper it was found that k_1 for the applied experimental conditions has the value

$$0.0483 \text{ equivalent/liter} \cdot \text{minute} \cdot \text{atmosphere}$$

In the state of saturation we have:

$$\text{or} \quad a = b \cdot \alpha$$

$$\begin{array}{l} \text{As now} \\ \text{we have} \end{array} \quad \frac{pO}{cO} \sim 800 \text{ atmospheres/mole}$$

$$k_{-1} = 60$$

y is the function, which by multiplication with cO_2 (α) gives s , so we have

$$y \cdot cO_2 = \frac{62.6 \cdot c \cdot h}{0.875 + h} \cdot pO_2 = \frac{50\,000 \cdot c \cdot h}{0.875 + h} \cdot cO_2$$

Introduction of $c = 0.01$ and $h = 0.1$ gives

$$y = 50$$

so the exponential factor has the value

$$e^{-110t}$$

which reaches the value 0.01 in less than three seconds.

Under the chosen experimental conditions we have:

$$y \sim 5\,000 \cdot c$$

or

$$y' \sim 5\,000 \cdot \frac{dc}{dt}$$

We were (preceding paper equation (VI)) able to express the variation of c in time by the empirical formula

$$-\frac{dt}{dc} = \frac{20.7}{pO_2} + \frac{1.62 \cdot 10^{-2}}{pO_2 \cdot c} + \frac{1.40 \cdot 10^{-2}}{pO_2 \cdot c \cdot h}$$

Introduction of the values for c and h above and $pO_2 = 0.2$ gives

$$-\frac{dt}{dc} \sim 100 + 30 + 300 = 430$$

or

$$-\frac{dc}{dt} \sim 0.002$$

This gives $y' = -5\,000 \cdot 0.002 = -10$

We therefore have

$$-\frac{y'}{(k_{-1} + y)^2} \sim \frac{10}{110^2} \sim 0.0008 \ll 1$$

Thus also the third term of (IV) is small and it is seen that the special application of the steady state principle in the preceding paper is fully justified.

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