Recurrence Relations for the Equilibrium Means of Distributions Arising in Chemical Reactions

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ABSTRACT: In this paper, we derive recurrence relations that describe how the equilibrium mean of the number of molecules of a reactant varies with each of the parameters defining the initial state for four basic reversible chemical reactions. In essence, the relations provide a rationale for updating the equilibrium mean following the addition (or removal) of a molecule of one of the types involved in the reaction, there being a relation for each type. With a new parameterization introduced for each reaction, the relations provide a convenient means of evaluating the means, variances and other important moments without any need to work out the underlying distributions. As an application, the relations are used to numerically assess approximate expressions for the means and variances.

The stochastic approach to chemical reaction kinetics (e.g., Darve et al. 1996, Staff 1967, Oppenheim et al. 1970, Thakur et al. 1978, and Formoso and Miguel 1979) treats the quantities of the reactants present at any time as random variables and offers a description of the course of the reaction concerned by finding the corresponding probability distributions. Interest is usually focussed on the equilibrium situation. However, the equilibrium distributions of the number of molecules of the reactants are difficult to handle algebraically and computationally. As an example, consider the equilibrium distribution for the number of molecules of reactant A in the reaction

\[ \frac{K}{K_1} A + B \rightleftharpoons C \]

as given by below (2.7a) below, where \( a, b, \gamma \) are the number of molecules of reactants A, B, C present at the start of the reaction, and \( K \) is the ratio of the forward to the backward reaction rates. In the simplest practical situation, the support of this distribution may well span all the integers in an interval like \([0, 10^5]\). The equilibrium means cannot be expressed solely in terms of the parameters, and computing it through the definition would entail working out the complete distribution, a massive exercise even for a single set of parameters. The approach adopted in the literature has been to seek normal and other approximations to these distributions and their moments. (See for example Dunstan and Reynolds, 1981 and Hall, 1983). This solves most of the practical situation. However, as will be shown here, the exact solution has more to offer.

In this paper, we look at the equilibrium distribution from a different angle, again referring to (2.7a) as an example. Instead of considering (2.7a) as a single distribution for a given fixed set of parameters, we look at it as a family of distributions indexed by the natural space of these parameters, noting that \( a, b, \gamma \) are non-negative integers. It will be shown that members of this family are tied by simple recurrence relations that are also reflected in their moments. Our main emphasis will be on the means and the variances. If these are known for a given member, they can be deduced for other members using the recurrence relations. This should be compared to the direct approach of computing the means and variances, where, for each...
member (i.e. for each set of parameters), the complete
distribution (2.7a) is worked out. In fact, for some
members of the family the means will be trivially known,
e.g. if $\beta = \gamma = 0$, then the mean equals $\alpha$. This, coupled with
the recurrence relations given in Theorem 2.1, can be used
to generate the mean for any member in the family.

In this paper, we shall be concerned with the four basic
reversible chemical reactions $A+B \rightarrow C, A+B \rightarrow C+D, 2A \rightarrow C+D$ and $2A \rightarrow C$ discussed by McQuarrie (1967) in his
survey paper on the stochastic approach to chemical
kinetics. For each of these reactions, we derive recurrence
relations that describe how the equilibrium mean varies with
each of the parameters defining the initial state when the
other parameters are kept constant. As a byproduct, we also
obtain expressions for the variances. The relations can be
interpreted, in the subject-matter context, as means of
updating the equilibrium mean following the addition or
removal of a molecule of one of the types involved in
the reaction. This is appealing because it gives rise to the
discovery of what might be considered basic chemical laws,
assuming the validity of the stochastic models. It would be
interesting if these laws can be justified, independently, by
a purely chemical argument. The relations can also be used
to derive approximate expressions for the means and
variances as will be shown in section 7. In addition, as
mentioned above, the relations provide a very effective
means of computing the means and variances and this
facility has been consolidated by introducing a new
parameterization for each reaction. This makes it feasible,
perhaps for the first time, to numerically assess the
approximate expressions for the equilibrium means and
variances over a large set of parameters, as will be done for
the reaction $A+B \rightarrow C$ in section 7. Finally, the relations
can be used to control the equilibrium mean to desired levels by
gauging the initial conditions. The stability of the
level might also be controlled by making use of the relations
obtained for the variances. This use of the relations is not
dealt with here.

The ideas involved in deriving the recurrence relations
for the four reactions are essentially the same. To avoid
repetition we give proofs only for reaction $A+B \rightarrow C$, dealt
with in section 2. In sections 3, 4 and 5 we give the
the corresponding relations for the other three reactions. Each
relation is verified using a simple example. In section 6 we
derive recurrence relations involving the factorial moments.
Finally, in section 7, as a demonstration of the usefulness of
the recurrence relations, we introduce and numerically assess
approximate expressions for the equilibrium mean and
variance for reaction (2.1).

The reaction $A + B \rightleftharpoons C$

Consider the reversible reaction

$$A + B \rightleftharpoons C$$

where $K_1$ and $K_2$ are the forward and backward reaction
rates. Assume initially we have $\alpha$ , $\beta$ and $\gamma$ molecules of
types $A$, $B$, and $C$ respectively. Let

$$K = K_1 / K_2$$

The number of molecules of types $A$, $B$, and $C$ at time $t$
will be denoted by $N_A(t)$, $N_B(t)$, and $N_C(t)$, respectively. The
conservation equations

$$\alpha - N_A(t) = \beta - N_B(t) = N_C(t) - \gamma$$

imply that the course of the reaction can be described by one
random variable. We choose $N_A$. The usual assumptions for
modeling the reaction as a stochastic process are as follows.
In any small interval of time $(t, t+h)$,

(i) the probability of a single AB association is

$$K_1 N_A(t) N_B(t) h + o(h)$$

(ii) the probability of a dissociation of a molecule of C is

$$K_2 N_C(t) h + o(h)$$

and

(iii) the probability of the occurrence of more than one event
is $o(h)$, where

$$\lim_{h \to 0} \frac{o(h)}{h} = 0$$

Let

$$p_r(t) = P(N_A(t) = r)$$

be the probability distribution of $N_A(t)$. Using the standard
procedure of representing $p_r(t+h)$ as a difference equation
in $p_r(t)$, it is easy to show that $p_r(t)$ satisfies the following
differential difference equation

$$\frac{dp_r(t)}{dt} = K_1 (\alpha + \gamma - r + 1) p_{r+1}(t) + K_2 (r+1)(\beta - \alpha + r + 1) p_r(t) - K_1 (\alpha + \gamma - r) - K_2 r (\beta - \alpha + r) p_r(t)$$

(2.5)
where \( r \) can take any integer value provided \( p_r(t) \) is defined as 0 for \( r \) outside the range \( \max(0, \alpha-\gamma) \leq r \leq \alpha+\gamma \). The equilibrium solution is obtained by putting the derivative in (2.5) equal to zero and solving for \( p_r = p_r(\infty) \). It can easily be verified that \( p_r \) satisfies the recurrence relation

\[
K(r+1)(\beta - \alpha + r + 1)p_{r+1} = (\alpha + \gamma - r)p_r
\]

as \( r \) approaches \( \infty \). This relation is true for all \( r \) by construction, it is true over the support of \( p_r(\gamma-1) \), namely, \( \max(0, \alpha-\gamma) \leq r \leq \alpha+\gamma-1 \). It is true for \( r = \gamma \) by direct substitution and noting that this value is outside the support of \( p_r(\gamma-1) \). Finally, it is trivially true for all other values of \( r \) as these are outside the supports of both \( p_r(\gamma-1) \) and \( p_r(\gamma) \).

In a similar way, we can also obtain the following relation from (2.9a)

\[
(\alpha + \gamma)p_r(\alpha - 1) = (\alpha + \gamma - r)p_r(\alpha)\frac{p_r(\gamma-1)}{p_r(\gamma)}
\]

(2.9b)

It can be shown that this relation is also true for all \( r \).

Now, summing (2.9a) over all \( r \) we get

\[
\frac{p_r(\gamma-1)}{p_r(\gamma)} = \frac{\alpha + \gamma}{\alpha + \gamma - \mu(\gamma)}
\]

(2.10)

Multiplying (2.9a) by \( r \) and summing over all \( r \) leads to the expression

\[
(\alpha + \gamma)(\gamma - 1) = (\alpha + \gamma - \mu(\gamma))\frac{\mu(\gamma) - \mu(\gamma-1)}{-\sigma^2(\gamma)}
\]

(2.11)

It follows from (2.10) and (2.11) that

\[
\sigma^2(\gamma) = (\alpha + \gamma - \mu(\gamma))[\mu(\gamma) - \mu(\gamma-1)]
\]

(2.12)

It follows similarly from (2.9b) that

\[
\sigma^2(\alpha) = (\alpha + \gamma - \mu(\alpha))[\mu(\alpha) - \mu(\alpha-1)]
\]

(2.12b)

where \( \sigma^2 \) and \( \mu \) are the variance and mean of \( N_c \). But as seen from (2.3) we have.
\[
\alpha - \beta + \mu_A = \alpha + \gamma - \mu_B = \mu_A = \mu, \quad \sigma^2 = \sigma_A^2 = \sigma_B^2 = \sigma_C^2.
\]

(2.13)

Hence, substituting in (2.12b) we get

\[
\sigma^2(\alpha) = \mu(\alpha)[\mu(\alpha - 1) - \mu(\alpha) + 1].
\]

(2.14)

Finally, interchanging \(\alpha\) and \(\beta\) and \(\mu(=\mu_B)\) and \(\mu_A\), we see from (2.14), by symmetry, that

\[
\sigma^2(\beta) = \sigma_B^2(\beta) = \mu_B(\beta)[\mu_B(\beta - 1) - \mu_B(\beta) + 1].
\]

(2.15)

Hence, substituting from (2.13) in (2.15), we get

\[
\sigma^2(\beta) = [\beta - \alpha + \mu(\beta)][\mu(\beta - 1) - \mu(\beta)].
\]

(2.16)

Substituting (2.12), (2.14) and (2.16), in turn, into (2.8) and simplifying the resulting expressions we arrive at the following theorem.

**Theorem 2.1.** The equilibrium mean \(\mu\) satisfies each of the following recurrence relations:

\[
K(\beta + \gamma) + 1 + K\mu(\alpha, \beta, \gamma - 1)]\mu(\alpha, \beta, \gamma)
= \alpha + \gamma + K(\alpha + \gamma)\mu(\alpha, \beta, \gamma - 1),
\]

(2.17)

\[
[1 + K\mu(\alpha, \beta - 1, \gamma)]\mu(\alpha, \beta, \gamma)
= \alpha + \gamma - K(\beta - \alpha)\mu(\alpha, \beta - 1, \gamma)
\]

(2.18)

\[
K(\beta - \alpha + 1 + \mu(\alpha - 1, \beta, \gamma) + 1)]\mu(\alpha, \beta, \gamma)
= \alpha + \gamma
\]

(2.19)

with initial values

\(\mu(0, \beta, 0) = 0\) and \(\mu(\alpha, 0, 0) = \alpha\)

(2.20)

Note that if the reaction starts with no molecules of types A and C, then the number of molecules of type A will remain zero irrespective of the number of molecules of type B. This explains the first initial value given in (2.20). The same logic is followed throughout in determining initial values.

The relations in Theorem 2.1 clearly describe how the equilibrium mean varies following the addition or removal of a molecule of one of the types involved in the reaction. They can be looked upon as basic chemical laws, assuming the validity of the model. One interesting application of the relations is in the evaluation of the means and variances.

The equilibrium mean can be evaluated using recurrence relation (2.17) and either of relations (2.18) or (2.19) with the appropriate starting values. Thus, for example, one can put \(\gamma = 0\) in (2.18) and set \(\beta = 1, 2, \ldots\) to express \(\mu(\alpha, \beta, 0)\) in terms of \(\mu(\alpha, 0, 0)\), making use of the second initial value in (2.20). One can now use (2.17) with \(\mu(\alpha, \beta, 0)\) as a starting value to evaluate \(\mu(\alpha, \beta, \gamma)\). It is possible, however, to evaluate \(\mu\) using a single recurrence relation. For this we introduce the parameters \(N\) and \(M\) defined by

\[
N = \alpha + \gamma, \quad M = \beta + \gamma
\]

(2.21)

This parametrization is the natural one in some applications. For example, in the study of the behaviour of ion-channels, reaction (2.1) corresponds to the so-called classical theory of drug action, where A is the molecule of the agonist drug, B is the free (closed) channel and C is the open channel (see, for example, Colquhoun & Hawkes, 1977, 1981). In that formulation \(M\) is the total number of molecules of the agonist drug and \(N\) is the total number of channels.

Noting the correspondences \((\alpha - 1, \beta, \gamma) \sim (N - 1, M)\), \((\alpha, \beta - 1, \gamma) \sim (N, M - 1)\), and \((\alpha, \beta, \gamma - 1) \sim (N - 1, M - 1)\), we can now rephrase and arrange Theorem 2.1 and the expressions for the variance in (2.17), (2.14) and (2.16) in the following theorem.

**Theorem 2.2.** (i) The equilibrium mean satisfies each of the relations:

\[
K(M - N + 1) + K \mu(N - 1, M) + 1]/\mu(N, M) = N,
\]

\(\mu(0, M) = 0\)

(2.22)

\[
[1 + K\mu(N, M - 1)]\mu(N, M) = N - K(M - N)\mu(N, M - 1),
\]

(2.23)

\[
[1 + K\mu(N - 1, M - 1)]\mu(N, M) = N - 1 + K\mu(N - 1, M - 1), \quad \mu(N, 0) = N,
\]

(2.24)

(ii) The corresponding expressions for the variance are:
RECURRENCE RELATIONS FOR THE EQUILIBRIUM MEANS

\[ \sigma^2(N, M) = \mu(N, M) \{ \mu(N - 1, M) - \mu(N, M) + 1 \} \]  
(2.25)

\[ \sigma^2(N, M) = [N - M + \mu(N, M)]/\mu(N, M - 1) - \mu(N, M) \]  
(2.26)

\[ \sigma^2(N, M) = [N - \mu(N, M)]/\mu(N, M) - \mu(N - 1, M - 1) \]  
(2.27)

It should be noted that any two of the relations (2.22), (2.23), and (2.24) lead to the third.

The use of Theorem 2.2 to evaluate \( \mu \) and \( \sigma^2 \) is best illustrated by an example.

Example: Let \( \alpha = 2 \), \( \beta = 3 \), \( \gamma = 1 \) and \( K = 1 \). Thus \( N = 3 \) and \( M = 4 \). Using (2.6) or (2.7a) it is easy to see that the equilibrium distribution is given as

\[
\begin{array}{c|cccc}
  r & 0 & 1 & 2 & 3 \\
  p_r & 24/73 & 36/73 & 12/73 & 1/73 \\
\end{array}
\]

Direct computation gives

\[ \mu = (3, 4) = 63/73 \] and \( \sigma^2 = \sigma'(3, 4) = 2820/5329 \).

From relation (2.22), the most feasible in the number of steps needed to obtain the mean in this case, we have:

\[ \mu(1, 4) = 1/5, \quad \mu(2, 4) = 10/21, \quad \text{and} \quad \mu(3, 4) = 63/73, \]

as required. Note the case with which these three means are generated without reference to the underlying distributions, as compared to the direct approach where we need first to work out those distributions. Now, from (2.24)

\[ \sigma^2(3, 4) = \mu(3, 4)[\mu(2, 4) - \mu(3, 4) + 1] = 2820/5329 \].

The variance can also be obtained from (2.7). Relations (2.22) and (2.23) lead to the same answers.

The reaction \( A + B = C + D \)

For the reaction

\[
\begin{align*}
  A + B & \rightleftharpoons C + D \\
  \kappa_1 & \rightleftharpoons \kappa_2
\end{align*}
\]

we assume initially we have \( \alpha, \beta, \gamma \) and \( \delta \) molecules of types \( A, B, C \) and \( D \) respectively. The equilibrium distribution of \( N \), satisfies the recurrence relation

\[ K(r + 1)(\beta + r - 1)p_{r+1} = (\alpha + \beta - r)(\alpha + \delta - r)p_r \],

with solution

\[ p_r = \frac{(\alpha + \gamma)! (\alpha + \delta)! (\beta + r)!}{K' r! (\alpha + \gamma + r - 1)! (\alpha + \delta + r - 1)! (\beta + r + 1)!} p_0 \]  
(3.3)

From (3.2) it follows that

\[ K\mu(\beta + \alpha + \mu) + K\sigma^2 = (\alpha + \gamma + \mu)(\alpha + \delta + \mu) + \sigma^2 \].

Note that when \( K = 1 \), we have

\[ \mu = \frac{(\alpha + \gamma)(\alpha + \delta)}{\alpha + \beta + \gamma + \delta} \].

(3.5)

Proceeding in exactly the same way as we did for reaction (2.1) it is easy to see that the expressions (2.12), (2.14) and (2.16) for \( \sigma^2 \) are still valid (but now \( \sigma^2 \) is a function of \( \alpha, \beta, \gamma \) and \( \delta \)). The variation of \( \sigma^2 \) with \( \delta \) is governed by the relation

\[ \sigma^2(\delta) = [\alpha + \delta - \mu(\delta)][\mu(\delta) - \mu(\delta - 1)] \]  
(3.6)

Eliminating \( \sigma^2 \) between each of these expressions and equation (3.4) we obtain the following theorem.

Theorem 3.1. Keeping the other parameters fixed, the mean varies with the argument according to the following relations

\[ [K(\beta - \alpha + 1) + 2\alpha + \gamma + \delta - 1 + (K - 1)\mu(\alpha - 1)]\mu(\alpha) = \]

\[ (\alpha + \gamma)(\alpha + \delta), \]  
(3.7)

\[ [\alpha + \beta + \gamma + \delta + (K - 1)\mu(\beta - 1)]\mu(\beta) = (\alpha + \gamma)(\alpha + \delta) \]

\[ - (K - 1)(\beta - \alpha)\mu(\beta - 1) \]  
(3.8)

\[ [K(\beta + \gamma) + \beta + \delta + (K - 1)(\gamma - 1)]\mu(\gamma - 1) = (\alpha + \gamma)(\alpha + \delta) \]

\[ + (K - 1)(\alpha + \gamma)\mu(\gamma - 1) \].

(3.9)
Thus $\mu = 28/15$ and $\sigma^2 = 116/225$. To economize on the number of steps needed to obtain $\mu$ we choose the relation involving $N$, the smallest of the 4 parameters. Direct computation leads to $\mu(1) = 2/3$, $\mu(2) = 40/31$, $\mu(3) = 28/15$, as it should. The other three relations lead to the same conclusion. The variance can now be obtained from (3.4).

The reaction \[2A \leftrightharpoons C + D\]

For the reaction

\[
\begin{align*}
&2A \leftrightarrow C + D, \\
&\mathcal{K}_r = 2A + C, \\
&\mathcal{K}_t = C + D.
\end{align*}
\]

the equilibrium distribution of $N_A$ satisfies the recurrence relation

\[
K(r + 1)(r + 2)p_{r+2} = (\alpha + 2\gamma - r)(\alpha + 2\delta - r)p_r.
\]

(4.2)

The equilibrium mean thus satisfies

\[
2K\mu(\mu - 1) + 2K\sigma^2 = (\alpha + 2\gamma - \mu)(\alpha + 2\delta - \mu) + \sigma^2.
\]

(4.3)

Manipulations similar to those employed in reaction (2.1) lead to the following expressions for $\sigma^2$:

\[
\sigma^2(\alpha) = \mu(\alpha)[\mu(\alpha - 1) - \mu(\alpha) + 1],
\]

(4.4)

\[
\sigma^2(\gamma) = [\alpha + 2\gamma - \mu(\gamma)][\mu(\gamma) - \mu(\gamma - 1)],
\]

(4.5)

\[
\sigma^2(\delta) = [\alpha + 2\delta - \mu(\delta)][\mu(\delta) - \mu(\delta - 1)].
\]

(4.6)

Eliminating $\sigma^2$ between each of these expressions and equation (4.3) we arrive at the following theorem.

Theorem 4.1. The equilibrium mean $\mu$ varies with each of $\alpha, \gamma, \delta$, keeping the other two fixed, according to the following relations:

\[
[2(\alpha + \gamma + \delta) + (2K - 1)\mu(\alpha - 1)]\mu(\alpha) = (\alpha + 2\gamma)(\alpha + 2\delta).
\]

(4.7)
Recurrence relations for the equilibrium means

\[
(\alpha + 2\delta + 2K(\alpha + 2\gamma - 1) + (2K - 1) \mu(\gamma - 1)) \mu(\gamma) = \\
(\alpha + 2\gamma)[\alpha + 2\delta + (2K - 1) \mu(\gamma - 1)],
\]

(4.8)

\[
[\alpha + 2\gamma + 2K(\alpha + 2\delta - 1) + (2K - 1) \mu(\delta - 1)] \mu(\delta) = \\
(\alpha + 2\delta)[\alpha + 2\gamma + (2K - 1) \mu(\delta - 1)].
\]

(4.9)

We introduce the new parameters defined by

\[
\alpha + 2\gamma = N, \quad \alpha + 2\delta = M.
\]

(4.10)

Note that \(\alpha + 2\gamma = 0\) implies that \(\alpha = 0\) and \(\gamma = 0\). Also \(\alpha + 2\gamma = 1\) implies that \(\alpha = 1\) and \(\gamma = 0\) and hence \(\mu = 1\). This explains the starting values that hold when expressing Theorem (4.1) in the following theorem.

**Theorem 4.2.** The equilibrium mean \(\mu\) varies with \(N\) and \(M\), according to the following relations

\[
\begin{align*}
\mu(N + 2K(M - 1) + (2K - 1) \mu(N - 2))/\mu(N) &= N/(M + (2K - 1) \mu(N - 2)), \quad \mu(0) = 0, \mu(1) = 1, \\
\mu(N + 2K(M - 1) + (2K - 1) \mu(M - 2))/\mu(M) &= N/(M + (2K - 1) \mu(M - 2)), \quad \mu(0) = 0, \mu(1) = 1.
\end{align*}
\]

(4.11)

**Example:** Take \(N = 4, \quad M = 6, \quad K = 1\). The equilibrium distribution is given by

<table>
<thead>
<tr>
<th>(p_i)</th>
<th>0</th>
<th>1/9</th>
<th>2/9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_i)</td>
<td>2</td>
<td>6/9</td>
<td>4</td>
</tr>
</tbody>
</table>

Hence \(\mu = 20/9\) and \(\sigma^2 = 104/81\). Using (4.11) we have \(\mu(0) = 0, \mu(2) = 3/2, \mu(4) = 20/9\). The other relations lead to the same answers. Had \(N\) been odd, one would have started with \(\mu(1) = 1\).

The reaction \(2A \rightarrow C\)

For the reaction

\[
2A \rightarrow C,
\]

(5.1)

we have

\[
K(r + 1)(r + 2)p_{r+2} = (\alpha + 2\gamma - r)p_r.
\]

(5.2)

It follows that

\[
K\mu(\mu - 1) + K\sigma^2 = \alpha + 2\gamma - \mu.
\]

(5.3)

Proceeding as for the previous reaction it can easily be shown that

\[
\sigma^2(\alpha) = \mu(\alpha)[\mu(\alpha - 1) - \mu(\alpha) - 1],
\]

(5.4)

\[
\sigma^2(\gamma) = [\alpha + 2\gamma - \mu(\gamma)][\mu(\gamma) - \mu(\gamma - 1)].
\]

(5.5)

Hence, we have Theorem 5.1.

\[
[1 + K\mu(\alpha - 1)]\mu(\alpha) = \alpha + 2\gamma
\]

(5.6)

\[
[K(\alpha + 2\gamma - 1) + K\mu(\gamma - 1)]\mu(\gamma) = (\alpha + 2\gamma)(1 + K\mu(\gamma - 1))
\]

(5.7)

We define the new parameter

\[
N = \alpha + 2\gamma.
\]

(5.8)

The following theorem is immediate from Theorem 5.1.

**Theorem 5.1.**

\[
[1 + K\mu(N - 1)]\mu(N) = N, \quad \mu(0) = 0,
\]

(5.9)

\[
[K(N - 1) + K\mu(N - 2)]\mu(N) = N[1 + K, \mu(N - 2)], \quad \mu(0) = 0, \quad \mu(1) = 1.
\]

(5.10)

**Example:** Let \(N = 5, \quad K = 1\). Then
Thus $\mu = 25/13$ and $\sigma^2 = 220/169$. Starting with $\mu(1) = 1$ in (5.10) we have $\mu(3) = 3/2$, $\mu(5) = 25/13$.

### Evaluating other moments

Factorial moments of the equilibrium distribution of $N_X$ can be evaluated recursively, once the value of the equilibrium mean is provided. The recurrence relations that make this possible are given, for each of the four reactions, in the following theorem.

**Theorem 6.1.** Let $m_n = 1$ and

\[
m_n = E[N_X(N_X-1) ... (N_X-n+1)], \quad n=1, 2, 3, ...
\]

The following relations hold for reaction (2.1), (2.2), (2.3) and (2.4), respectively, for each $n=0, 1, 2, ...$

\[
Km_n = (\alpha + \gamma - n)m_n - [K(\alpha + 1) + \gamma + n]m_{n+1}, \quad n=1, 2, ...
\]

(6.2)

\[
(K-1)m_n = (\alpha + \gamma - n)(\alpha + \delta - n)m_n - [K(\alpha + n + 1) - 2\alpha + \gamma + \delta - 2n + 1]m_{n+1}.
\]

(6.3)

\[
(2K-1)m_n - (\alpha + 2\gamma - n)(\alpha + 2\delta - n)m_n - [2(\alpha + \gamma + \delta) - 2n + 1]m_{n+1}, \quad n=1, 2, ...
\]

(6.4)

\[
Km_n = (\alpha + 2\gamma - n)m_n - m_{n+1}.
\]

(6.5)

**Proof:** We prove relation (6.2). The other relations can be proved similarly. From (2.5), it can easily be shown that

\[
(\alpha + \gamma) G(s) - [K(\alpha + 1) + s] \frac{dG}{ds} - Ks \frac{d^2G}{ds^2} = 0,
\]

(6.6)

where

\[
G(s) = E(S^{N_X})
\]

is the probability generating function of the equilibrium distribution of $N_X$. The result follows by differentiating (6.6) $n$ times, using the rule for the $n^{th}$ derivative of a product of two functions, namely,

\[
(FG)^{(n)} = \sum_{r=0}^{n} \binom{n}{r} F^{(r)} G^{(n-r)},
\]

and then putting $s = 1$.

### Assessment of Approximate Formulas for the Mean and Variance

The normal approximation derived by Dunstan and Reynolds (1981) gives approximate expressions for the mean and variance of the distribution in terms of the mode. A direct approximation of the mean, not much different from theirs, can also be justified. Note, for example, that replacing $\mu(N-1, M-1)$ by $\mu(N, M)$ in (2.24) should make little difference for fairly large values of $M$ and $N$. This amounts to approximating $\mu$ from (2.8) by simply putting $\sigma^2$ equal to zero. Thus, an approximate expression for the mean number of molecules of type $A$ in reaction (2.1) is given by the positive root of the equation

\[
K(\mu(N - N + \mu)) = N - \mu + \mu.
\]

(7.1)

where $M$ and $N$ are as defined in (2.21). It can also be shown, for the same reaction, that $\mu$ varies with $K$ according to the relation

\[
\frac{d\mu}{dK} = \frac{\sigma^2}{K}
\]

(7.2)

Differentiating (7.1) with respect to $K$ and simplifying leads to

\[
[K(\mu(N - N + \mu)) + K\mu + 1] \sigma^2 = K(\mu(N - N + \mu))
\]

(7.3)

Using (7.1) again we get

\[
\frac{1}{\sigma^2} = \frac{1}{\mu} + \frac{1}{N - \mu} + \frac{1}{M - N + \mu}.
\]

(7.4)

This is the same expression given by Dunstan and Reynolds except that the approximate mode is replaced by the approximate mean. The same expression was also derived by Babiker and Elsheikh (1992) assuming (7.1) and symmetry of the distribution. The other three reactions can be treated similarly.

It should be stated that, differentiating both sides of each of the relations (2.22), (2.23), and (2.24), and making use of (7.2) leads to the following relations:

\[
N_0 \sigma^2(N) = \mu(N)(\mu(N) - K\mu(N)\sigma^2(N - 1))
\]

(7.5)
\[ M \sigma^2(M) = [N - \mu(M)][N - \mu(M)] \]

\[ K(M - N + \mu(M))\sigma^2(M - 1) \]

\[ KMN\sigma^2(N - 1, M - 1) = [N - \mu(N - 1, M - 1)]^2 \]

\[ 1 + K\sigma^2(N - 1, M - 1) \]

These relations have been used for cross validation in the computational work reported below.

The approximations provided by (7.1) and (7.4) have been investigated for reaction (2.1) using the recurrence relations in Theorem 2.2 over a wide range of the values of the parameters. Specifically, values of \( M, N \leq 10^4 \), and \( 10^2 \leq K \leq 10^4 \) have been considered. (Values of \( K \geq 10^4 \) are not very interesting for the range of values of \( M \) and \( N \) considered in that they lead to small values of the mean or variance.) It turned out that there is remarkable agreement between the computed and approximate values for both the mean and variance for all values considered. The maximum difference is found to be less than 1 for both the mean and variance. Table 1 provides some of the cases considered.

### References


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