Electronic Supplementary Information

Entropy in Multiple Equilibria, Theory and Applications
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ESI1. Derivation of equation (14)

\[ ZX_{rc-1} + X \rightleftharpoons ZX_{rc} \quad K_{rc} \quad (S1) \]

\[ K_{rc} = \frac{[ZX_{rc}]}{[ZX_{rc-1}][X]} \quad (S2) \]

\[ \prod_{j=1}^{rc} K_j = \frac{[ZX_1][ZX_2]}{[Z][ZX_1]} \cdots \frac{[ZX_{rc-1}][ZX_{rc}]}{[ZX_{rc-2}][ZX_{rc-1}]} \left( \frac{c^\theta}{c} \right)_{rc} \quad (S3) \]

From this we obtain for $rc=n$ the desired expression (14):

\[ Z + nX \rightleftharpoons ZX_n \quad K_{tot} \quad (S4) \]

\[ K_{tot} = \left[ \frac{ZX_n}{[Z]} \right] \left( \frac{c^\theta}{c} \right)^n = \prod_{rc=1}^{n} K_{rc} \quad (S5) \]

ESI2. Derivation of equation (15)

We evaluate the product, eqn (14):

\[ K_{tot}^{pd} = \prod_{rc=1}^{n} K_{rc}^{pd} \quad (S6) \]

It is convenient to introduce the following abbreviation:

\[ f(r) = \frac{r}{r+1} \frac{n-r}{n-r+1} \quad (S7) \]

This allows us to write:

\[ K_{r+1}^{pd} = K_r^{pd} f(r) \quad (S8) \]

Using this we can write the following sequence of equations, which finally lead to the desired result:

\[ K_{tot}^{pd} = K_1^{pd} \cdot K_2^{pd} \cdot K_3^{pd} \cdot \ldots \cdot K_{n-2}^{pd} \cdot K_{n-1}^{pd} \cdot K_n^{pd} \quad (S9) \]

\[ K_{tot}^{pd} = K_1^{pd} \cdot K_1^{pd}(1) \cdot K_2^{pd}(2) \cdot \ldots \cdot K_{n-3}^{pd}(n-3) \cdot K_{n-2}^{pd}(n-2) \cdot K_{n-1}^{pd}(n-1) \cdot K_n^{pd}(n-1) \]

\[ K_{tot}^{pd} = \ldots \]
\[ K_{\text{tot}}^{pd} = (K_{1}^{pd})^n \cdot \{ f(1) \cdot f(1)f(2) \cdot \ldots \cdot f(1)f(2)f(3) \ldots f(n-3)f(n-2)f(n-1) \} \]

\[ K_{\text{tot}}^{pd} = (K_{1}^{pd})^n \cdot \left\{ f(1) \cdot \frac{2}{r=1} f(r) \cdot \frac{3}{r=1} f(r) \cdot \ldots \cdot \frac{n-2}{r=1} f(r) \cdot \frac{n-1}{r=1} f(r) \right\} \]

\[ K_{\text{tot}}^{pd} = (K_{1}^{pd})^n \cdot \{ f(1)^{n-1}f(2)^{n-2} \ldots f(n-1) \} = (K_{1}^{pd})^n \prod_{r=1}^{n-1} f(r)^{n-r} \]

\[ K_{\text{tot}}^{pd} = \left( \frac{K_{1}^{pd}}{n} \right)^n \]

(S10)

ESI3. Experimental equilibrium constants \( K_f \) and \( K_g \) of dicarboxylic acids \( HOOC-(CH_2)_m-COOH \)

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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<td>10^{-4.21}</td>
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<td>10^{-4.41}</td>
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<tr>
<td>( K_g )</td>
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ESI4. Derivation of the equations (29) and (29a)

We start with the hypothesis that eqns (21,23) are equivalent to Langmuir’s isotherm equation and we test if this hypothesis is valid. For this we write:

\[
\frac{[X]A}{1 + [X]B} = \frac{[X]\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)}{1 + [X]\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)} = \frac{[X]\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)}{1 + [X]\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)}
\]

Using \( K_i = K_1K_2 \ldots K_i \) we write:

\[
\frac{[X]A}{1 + [X]B} = \frac{[X]\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)}{1 + [X]\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)}
\]

The following relation must hold if the hypothesis is correct:

\[
\frac{[X]A}{1 + [X]B} = \frac{[X]K_L}{1 + [X]K_L}
\]

We multiplying (S13) with \((1 + [X]B)(1 + [X]K_L)\):

\[
\]

Multiplying this with \([X]\) leads to:

\[
\]

We insert the expressions for A and B from (S12):

\[
K_L + [X]K_L\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right) = \left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right) + [X]K_L\left(\frac{1}{n}K_1 + [X]^2K_2 + \ldots + [X]^{n-1}K_{n} \right)
\]

(S16)
Equation (S16) can be rearranged in order to obtain (S17):

\[ K_L \left( 1 - \frac{1}{n} \right) \kappa_1 = [X]^2 \kappa_1 + [X]^n \kappa_n + [X]K_L \left( \frac{1}{n} - 1 \right) \kappa_1 + [X]^2 \kappa_2 + \ldots + [X]^{n-2} \left( \frac{n-1}{n} - 1 \right) \kappa_{n-1} \]  

(S17)

Ordering (S17) according to the power of \([X]\):

\[ K_L \left( 1 - \frac{1}{n} \right) \kappa_1 = [X] \left( 2 \kappa_1 + \kappa_1 \left( \frac{1}{n} - 1 \right) K_L \right) + [X]^2 \left( \kappa_3 + \frac{2}{n} - 1 \right) \kappa_2 K_L \ldots + [X]^{n-1} \left( \kappa_n + \left( \frac{n-1}{n} - 1 \right) K_L \right) \]  

(S18)

Equation (S18) hold for all physically accessible and reasonable concentration values of \([X]\). This is only possible if the right side of (S18) is equal to zero. From this we know that eqn (S18) holds for:

\[ K_L \left( 1 - \frac{1}{n} \right) \kappa_1 = 0 \]  

(S19)

This result means that we can write eqn (S20) which corresponds to the eqns (29) and (29A):

\[ \Theta = \frac{K_L [X]}{1 + K_L [X]} \quad \text{with} \quad K_L = \frac{1}{n} K_1 \]  

(S20)

ESI5. Comparison of the Langmuir isotherm with the sum of the concentrations of bound \(X\)

We graphically compare equations (21)-(23) with Langmuir’s eqn (29,29A) for \(n = 48\) equilibrium reactions and two different values for \(K_1\). It is no surprise that they match perfectly well because (29) is a consequence of (21)-(23).

Fig. S1 Comparison of the Langmuir isotherm eqn (29) (yellow solid) and with the sum of the concentrations of bound \(X\), eqns (21)-(23), (red, dots) as a function of the concentration of free \(X\), shown for 48 equilibria, hence, \(n=48\), and for two values of \(K_1\), namely 0.1 and 0.01. \([X]_{\text{tot}}\) is divided by 48 in order to scale it to the value range of the Langmuir function \(\Theta\). \(\delta\) indicated the difference between the numerical values of \(\Theta([X])\) and \([X]_{\text{tot}}([X])\).

ESI6. Derivation of equation (9)

In order to solve the eqns (33A) and (33B) we write them as differential equations with the initial condition (33C).

\[ \frac{dN_0}{dn} = -p_b N_0 \]  

(S21)

\[ \frac{dN_b}{dn} = p_{b-1} N_{b-1} - p_b N_b; \quad B \geq b \geq 1 \]  

(S22)
We solve eq S11, using eqn (18) for \( b = 0 \):

\[
\int \frac{dN_0}{N_0} = -\int p_0 dn \quad \text{with} \quad p_0 = \frac{B}{BN - n}
\]  

(S23A)

The result reads as follows:

\[
ln N_0 = -\int \frac{B}{BN - n} dn = B ln (BN - n) + ln C_0
\]  

(S23B)

\[
N_0 = C_0 (BN - n)^B
\]  

(S23C)

The integration constant \( C_0 \) follows from the initial condition (S33C).

The solution of eqn (S22) is found by first solving it for \( N_1 \) and then solving it for \( N_2 \).

The solution for the general case \( N_b \) is readily found from this.

\[
\frac{dN_1}{dn} + B - 1 \frac{N_1}{BN - n} = \frac{B}{BN - n} N_0
\]  

(S24)

We insert the result (S23C) for \( N_0 \):

\[
\frac{dN_1}{dn} + B - 1 \frac{N_1}{BN - n} = \frac{B}{BN - n} C_0 (BN - n)^B
\]  

(S24A)

It is convenient to write the solution of (S24A) as follows:

\[
N_1 = G(n)^{U(n)}
\]  

(S24B)

and then to determine \( U(n) \) and \( G(n) \):

\[
U(n) = -\int \frac{B - 1}{BN - n} dn = (B - 1) ln (BN - n) + C_{11}
\]  

(S24C)

\[
G(n) = \int \frac{B}{BN - n} C_0 (BN - n)^B e^{-(U(n))} dn
\]  

(S24D)

Rearrangement and simplification leads to (S24E) and then (S24F):

\[
G(n) = BC_0 \int (BN - n)^{B - 1} e^{-(B - 1) ln (BN - n) + C_{11}} dn
\]  

(S24E)

\[
G(n) = BC_0 \int e^{-C_{11} dn} = BC_0 (n + C_{10}) e^{-C_{11}}
\]  

(S24F)

Inserting (S24C) and (S24F) in (S24B) leads to

\[
N_1 = BC_0 (n + C_{10}) e^{-C_{11} e^{-(B - 1) ln (BN - n) + C_{11}}}
\]  

(S24G)

This equation simplifies to the solution (S15) we have been searching for:

\[
N_1 = BC_0 (n + C_{10}) (BN - n)^{(B - 1)}
\]  

(S25)

The solution (S16) for \( N_2 \) is readily found by the same procedure:

\[
N_2 = BC_0 (B - 1) \left( \frac{n^2}{2} + nC_{10} + C_{20} \right) (BN - n)^{(B - 2)}
\]  

(S16)

On the basis of the solution (S23C), (S25), and (S26) for \( N_0, N_1 \) and \( N_2 \) we find the general solution for \( N_b \) to read as follows:
\[ N_b(n,B,N) = \frac{B!C_0}{(B-b)!} (BN-n)^{(B-b)} \sum_{i=0}^{b} \frac{C_i^0 n^{b-1}}{(b-1)!} \]  

(S27)

Inserting the solution (S27) into (S22) we find that the initial condition (28C) is fulfilled if we use eqn (S28).

\[ C_0 = \frac{B}{(BN)^b}, \quad C_{00} = 1, \quad \text{and} \quad C_{b0} = 0 \text{ for } b > 0 \]  

(S28)

\[ \sum_{i=0}^{b} \frac{C_i^0 n^{b-1}}{(b-1)!} = \frac{n^b}{b!} \]  

(S28A)

Insertion of the results (S28) and (S28A), which are a consequence of the initial condition (28C), into eqn (S27) leads readily to the eqn (9) we have been searching for.
