Exercise 1 to section 4.9

Derive the reaction rate expression for a simple general synthesis of AB from A and B using the first-, second-, and third-degree polynomial approximation to the function $(4.470)_1$. Ideal (gas) mixture is supposed.

Try to answer before continuing reading.

It can be easily checked that in these case of three components (A, B, AB) formed from two (general) atoms (A, B) only one independent reaction is possible. The *first degree* polynomial approximation to its rate is:

$$J = k_{000} + k_{100}c_{\mathrm{A}} + k_{010}c_{\mathrm{B}} + k_{001}c_{\mathrm{AB}}. \tag{1}$$

Let us select as the independent reaction just the synthesis A + B = AB with the equilibrium constant (cf. (4.474))

$$K = \frac{a^o_{\mathrm{AB}}}{a^o_{\mathrm{A}}a^o_{\mathrm{B}}}. \tag{2}$$

Substituting from (2) to the equilibrium form of the first degree polynomial we get (c_S is the standard concentration, cf. (4.475))

$$0 = k_{000} + k_{100}c^o_{\mathrm{A}} + k_{010}c^o_{\mathrm{B}} + k_{001}Kc_S^{-1}c^o_{\mathrm{A}}c^o_{\mathrm{B}}. \tag{3}$$

Because (3) should be valid for any values of the equilibrium concentrations all the coefficients k_{ijk} should be zero. Consequently, the first degree approximating polynomial vanishes and cannot be used to formulate the rate equation.

The *second degree* polynomial approximation is:

$$\begin{aligned} J =& k_{000} + k_{100}c_{\mathrm{A}} + k_{010}c_{\mathrm{B}} + k_{001}c_{\mathrm{AB}} + k_{200}c^2_{\mathrm{A}} + k_{020}c^2_{\mathrm{B}} + k_{002}c^2_{\mathrm{AB}} + \\ & k_{110}c_{\mathrm{A}}c_{\mathrm{B}} + k_{101}c_{\mathrm{A}}c_{\mathrm{AB}} + k_{011}c_{\mathrm{B}}c_{\mathrm{AB}}. \end{aligned} \tag{4}$$

Substituting from (2) to its equilibrium form:

$$\begin{aligned} 0 =& k_{000} + k_{100}c^o_{\mathrm{A}} + k_{010}c^o_{\mathrm{B}} + k_{001}Kc_S^{-1}c^o_{\mathrm{A}}c^o_{\mathrm{B}} + \\ & k_{200}(c^o_{\mathrm{A}})^2 + k_{020}(c^o_{\mathrm{B}})^2 + k_{002}(Kc_S^{-1}c^o_{\mathrm{A}}c^o_{\mathrm{B}})^2 + \\ & k_{110}c^o_{\mathrm{A}}c^o_{\mathrm{B}} + k_{101}c^o_{\mathrm{A}}Kc_S^{-1}c^o_{\mathrm{A}}c^o_{\mathrm{B}} + k_{011}c^o_{\mathrm{B}}Kc_S^{-1}c^o_{\mathrm{A}}c^o_{\mathrm{B}}. \end{aligned} \tag{5}$$

After some rearrangement:

$$\begin{aligned} 0 =& k_{000} + k_{100}c^o_{\mathrm{A}} + (k_{001}Kc_S^{-1} + k_{110})c^o_{\mathrm{A}}c^o_{\mathrm{B}} + k_{200}(c^o_{\mathrm{A}})^2 + \\ & k_{020}(c^o_{\mathrm{B}})^2 + k_{010}c^o_{\mathrm{B}} + k_{002}(Kc_S^{-1})^2(c^o_{\mathrm{A}}c^o_{\mathrm{B}})^2 + \\ & k_{101}Kc_S^{-1}(c^o_{\mathrm{A}})^2c^o_{\mathrm{B}} + k_{011}Kc_S^{-1}c^o_{\mathrm{A}}(c^o_{\mathrm{B}})^2. \end{aligned} \tag{6}$$

This polynomial should vanish for all (arbitrary) values of the equilibrium concentrations. Consequently, all its coefficients should equal zero. This, in fact, means that all rate parameters (k_{ijl}) are zero except k_{110} (and k_{001}) and:

$$k_{001}Kc_S^{-1} + k_{110} = 0 \;\Rightarrow\; k_{001} = -K^{-1}c_S k_{110}. \tag{7}$$

The final form of the thermodynamic polynomial resulting from the second degree polynomial approximation thus is:

$$J = k_{110}(c_{\mathrm{A}}c_{\mathrm{B}} - K^{-1}c_S c_{\mathrm{AB}}) \tag{8}$$

which is very close to the traditional rate expression obtained in the framework of the mass-action kinetics. It can be modified to $J = k_{110}(c_{\mathrm{A}}c_{\mathrm{B}} - \bar{K}^{-1}c_{\mathrm{AB}})$ where $\bar{K}^{-1} = K^{-1}c_S$.

The *third degree* approximating polynomial adds following terms into eq. (4):

$$\begin{aligned}&k_{111}c_{\mathrm{A}}c_{\mathrm{B}}c_{\mathrm{AB}} + k_{300}c_{\mathrm{A}}^3 + k_{030}c_{\mathrm{B}}^3 + k_{003}c_{\mathrm{AB}}^3 + k_{210}c_{\mathrm{A}}^2c_{\mathrm{B}} + k_{201}c_{\mathrm{A}}^2c_{\mathrm{AB}} +\\ &k_{120}c_{\mathrm{A}}c_{\mathrm{B}}^2 + k_{102}c_{\mathrm{A}}c_{\mathrm{AB}}^2 + k_{021}c_{\mathrm{B}}^2c_{\mathrm{AB}} + k_{012}c_{\mathrm{B}}c_{\mathrm{AB}}^2.\end{aligned} \tag{9}$$

and after substitution from (2):

$$\begin{aligned}&k_{111}Kc_S^{-1}(c_{\mathrm{A}}^o c_{\mathrm{B}}^o)^2 + k_{300}(c_{\mathrm{A}}^o)^3 + k_{030}(c_{\mathrm{B}}^o)^3 + k_{003}(Kc_S^{-1})^3(c_{\mathrm{A}}^o c_{\mathrm{B}}^o)^3 +\\ &k_{210}(c_{\mathrm{A}}^o)^2c_{\mathrm{B}}^o + k_{201}Kc_S^{-1}(c_{\mathrm{A}}^o)^3c_{\mathrm{B}}^o + k_{120}c_{\mathrm{A}}^o(c_{\mathrm{B}}^o)^2 + k_{102}(Kc_S^{-1})^2(c_{\mathrm{A}}^o)^3(c_{\mathrm{B}}^o)^2 +\\ &k_{021}Kc_S^{-1}c_{\mathrm{A}}(c_{\mathrm{B}}^o)^3 + k_{012}(Kc_S^{-1})^2(c_{\mathrm{A}}^o)^2(c_{\mathrm{B}}^o)^3.\end{aligned}$$

The equilibrium form of the full third degree approximating polynomial is:

$$\begin{aligned}0 =\, &k_{000} + k_{100}c_{\mathrm{A}}^o + (k_{001}Kc_S^{-1} + k_{110})c_{\mathrm{A}}^o c_{\mathrm{B}}^o + k_{200}(c_{\mathrm{A}}^o)^2 + k_{020}(c_{\mathrm{B}}^o)^2 +\\ &k_{010}c_{\mathrm{B}}^o + (k_{002}(Kc_S^{-1})^2 + k_{111}Kc_S^{-1})(c_{\mathrm{A}}^o c_{\mathrm{B}}^o)^2 + (k_{101}Kc_S^{-1} + k_{210})(c_{\mathrm{A}}^o)^2c_{\mathrm{B}}^o +\\ &(k_{011}Kc_S^{-1} + k_{120})c_{\mathrm{A}}^o(c_{\mathrm{B}}^o)^2 + k_{300}(c_{\mathrm{A}}^o)^3 + k_{030}(c_{\mathrm{B}}^o)^3 + k_{003}(Kc_S^{-1})^3(c_{\mathrm{A}}^o c_{\mathrm{B}}^o)^3 +\\ &k_{201}Kc_S^{-1}(c_{\mathrm{A}}^o)^3c_{\mathrm{B}}^o + k_{102}(Kc_S^{-1})^2(c_{\mathrm{A}}^o)^3(c_{\mathrm{B}}^o)^2 + k_{021}Kc_S^{-1}c_{\mathrm{A}}(c_{\mathrm{B}}^o)^3 +\\ &k_{012}(Kc_S^{-1})^2(c_{\mathrm{A}}^o)^2(c_{\mathrm{B}}^o)^3.\end{aligned} \tag{10}$$

Again, all coefficients in (10) should vanish and this means that all coefficients in the original thermodynamic polynomial are zero except those in the summation parentheses in (10):

$$k_{111} = -k_{002}Kc_S^{-1},\; k_{210} = -k_{101}Kc_S^{-1},\; k_{011} = -k_{120}(Kc_S^{-1})^{-1} \tag{11}$$

and (7). The final rate equation then is:

$$\begin{aligned}J =\, &k_{110}(c_{\mathrm{A}}c_{\mathrm{B}} - K^{-1}c_S c_{\mathrm{AB}}) + k_{101}(c_{\mathrm{A}}c_{\mathrm{AB}} - Kc_S^{-1}c_{\mathrm{A}}^2c_{\mathrm{B}}) +\\ &k_{002}(c_{\mathrm{AB}}^2 - Kc_S^{-1}c_{\mathrm{A}}c_{\mathrm{B}}c_{\mathrm{AB}}) + k_{120}(c_{\mathrm{A}}c_{\mathrm{B}}^2 - K^{-1}c_S c_{\mathrm{B}}c_{\mathrm{AB}}).\end{aligned} \tag{12}$$

This form is a bit more complex then (8) resulting from the second degree approximation. We can rewrite (12) to form containing "explicitly and only" the traditional mass-action expression for the independent reaction:

$$J = (k_{110} - Kc_S^{-1}k_{101}c_{\mathrm{A}} - Kc_S^{-1}k_{002}c_{\mathrm{AB}} + k_{120}c_{\mathrm{B}})(c_{\mathrm{A}}c_{\mathrm{B}} - K^{-1}c_S c_{\mathrm{AB}}). \quad (13)$$

The expression in the first parentheses can be viewed as a concentration dependent rate coefficient k in an expression resembling (8):

$$J = k(c_{\mathrm{A}}c_{\mathrm{B}} - K^{-1}c_S c_{\mathrm{AB}}) \equiv k(c_{\mathrm{A}}c_{\mathrm{B}} - \bar{K}c_{\mathrm{AB}}).$$

Alternatively, we can interpret (12) as containing, besides the term corresponding to the independent reaction, terms of three additional (dependent) reactions affecting reaction rate:

A + AB = 2A + B,
2AB = A + B + AB,
A + 2B = B + AB.