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Graphical Representation of Redistribution Equilibria

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Computer calculated and computer plotted graphs are presented showing the distribution of all products in a redistribution equilibrium as a function of the over-all composition of the mixture for a wide range of equilibrium constants. These curves permit a rapid estimation of the equilibrium concentration of redistribution products for any over-all composition of the system when the equilibrium constants are given.

Introduction

In recent years a great number of papers has appeared discussing studies of redistribution equilibria in inorganic and organometallic systems.[1-5] A concise mathematical description of such equilibria is realized in terms of sets of equilibrium constants. While this may be satisfactory to those actively working in this field, in most instances however, the mere listing of constants of the above type will not readily help visualize the complicated over-all distribution of the various species present at equilibrium. It was, therefore, of interest to provide graphs—calculated and plotted by computer—which give a representation of the equilibrium concentration of all species participating in a redistribution equilibrium as a function of the over-all composition for a wide range of values of the equilibrium constants. The algebraic calculation of such equilibrium concentrations for particular over-all compositions from equilibrium constants without the use of the available computer programs[6] is rather tedious and time consuming.[7] The graphs presented here, therefore, are intended to provide a basis for estimating equilibrium concentrations in systems having reached redistribution equilibrium for a given set of values of equilibrium constants and an over-all composition parameter. In many instances such approximate equilibrium concentrations is all that one is interested in when assessing the yields of products generated by redistribution reactions.

Results and Discussion

Equilibrium Constants. If we consider a single kind of central atom or moiety, Q, exhibiting a functionality of ν (ν is the number of exchangeable sites on Q) on which two kinds of substituents may be exchanged, and denote these substituents T and Z, there are $(\nu+1)$ possible reaction products of the formula $QT_{\nu-i}Z_i$, where $i=0, 1, 2, 3 \ldots\ldots \nu$. The system thus contains the molecules QT_ν, $QT_{\nu-1}Z$, $QT_{\nu-2}Z_2 \ldots QT_2Z_{\nu-2}$, $QTZ_{\nu-1}$ and QZ_ν, in which only Q–Z and Q–T bonds were redistributed. For the sake of simplicity, these molecules will be represented by the respective symbols z_0, z_1, z_2, ... $z_{\nu-2}$, $z_{\nu-1}$, and z_ν.

The equilibria resulting from the exchange of Z and T on Q may be treated in terms of the following set of general equations corresponding to $i=1, 2, 3, \ldots\ldots (\nu-1)$.

$$2[z_i] \rightleftharpoons [z_{i-1}]+[z_{i+1}] \qquad (1)$$

Accordingly, redistribution equilibria of the type described by equation (1) are characterized by $(\nu-1)$ equilibrium constants of the following form,

$$K_i = [z_{i-1}][z_{i+1}]/[z_i]^2 \qquad (2)$$

with i having an integer value ranging from 1 to $(\nu-1)$. Any other reaction equation or equilibrium constant in such systems may be derived from equs. (1) or (2), respectively.

In addition to equilibrium constants K_i, an over-all composition parameter is required to fix an additional variable in such systems. This parameter, R, may be defined as shown below.

$$R \equiv [Z]/[Q] = [z_1]+2[z_2]+3[z_3]+\ldots+\nu[z_\nu] \qquad (3)$$

Furthermore, as a matter of definition, the sum of the mole fractions of all species present is unity.

$$[z_0]+[z_1]+[z_2]+\ldots+[z_\nu] = 1 \qquad (4)$$

Equations (2) - (4) generally are sufficient to completely describe a system at redistribution equilibrium. Experience has shown[1-5] that the experimentally determined equilibrium constants in all cases are truly constant over a wide range of over-all compositions in a given system. Therefore, it is more than adequate to deal with the concentrations of the participating species rather than the activities.

Equilibria on Difunctional Central Moieties. For the case where the functionality of the central atom or moiety $\nu=2$, there are $\nu+1=3$ possible reaction products: QT_2, QTZ, and QZ_2. The general equili-

(1) «Redistribution Reactions in Chemistry», *Ann. N. Y. Acad. Sci.*, *159*, Art. 1, pp. 1-334 (1969).
(2) K. Moedritzer, *Adv. Organometal. Chem.*, *6*, 171 (1968).
(3) K. Moedritzer, *Organometal. Chem. Rev.*, *1*, 179 (1966).
(4) J. R. Van Wazer and K. Moedritzer, *Angew. Chem.*, *78*, 401 (1966), *Angew. Chem. Internat. Ed.*, *5*, 341 (1966).
(5) K. Moedritzer, *Organometallic Reactions*, Vol. 2, in press.
(6) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, 36, 303 (1964).
(7) D. W. Matula and J. R. Van Wazer, *J. Phys. Chem.*, *46*, 3123 (1967).

brium of equation (1), therefore, results in the equation below.

$$2QTZ \rightleftharpoons QT_2 + QZ_2 \qquad (5)$$

Since $i \leqslant (\nu - 1) = 1$, there is only one equilibrium constant required which is derived from equation (2) with i being 1. This constants is expressed below.

$$K_1^{(\nu=2)} = [QT_2][QZ_2]/[QTZ]^2 \qquad (6)$$

The curves displayed in Figure 1 show the distribution of the three species present at equilibrium, QT_2, QTZ, and QZ_2, as a function of the composition parameter $R \equiv [Z]/[Q]$ for a wide range of values of the equilibrium constant $K_1^{(\nu=2)}$ as defined by equation (6). These curves were calculated using a Control Data 6400 Computer with programs described proviously[6] and were machine plotted by a Calcomp 763 plotter.

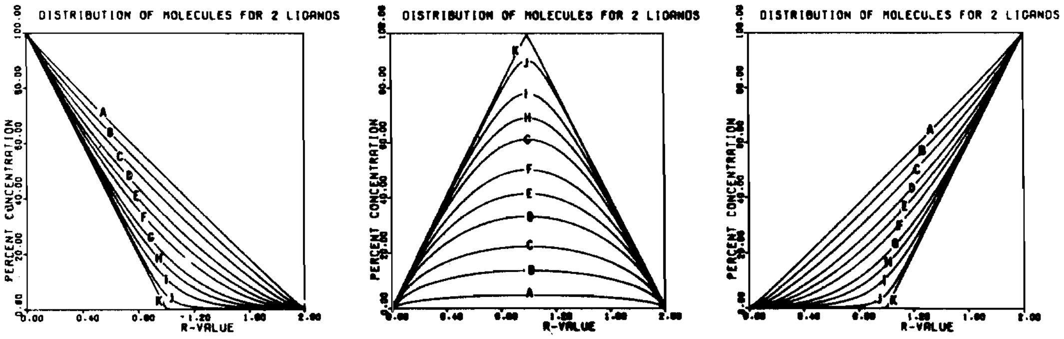

Figure 1. Equilibrium concentrations (in mole percent) in the system QT_2 *vs* QZ_2 for various values of $K_1^{(\nu=2)}$ [eq. (6)] as a function of the composition parameter $R \equiv [Z]/[Q]$. The left hand graph corresponds to the species QT_2, the center graph to QZT and the right hand graph to QZ_2. The letters refer to the following values of the equilibrium constant $K_1^{(\nu=2)}$: A, 100; B, 10; C, 3; D, 1; E, 0.5; F, 0.25 (ideal randomness); G, 0.1; H, 0.05; I, 0.02; J, 0.003; and K, 1×10^{-5}.

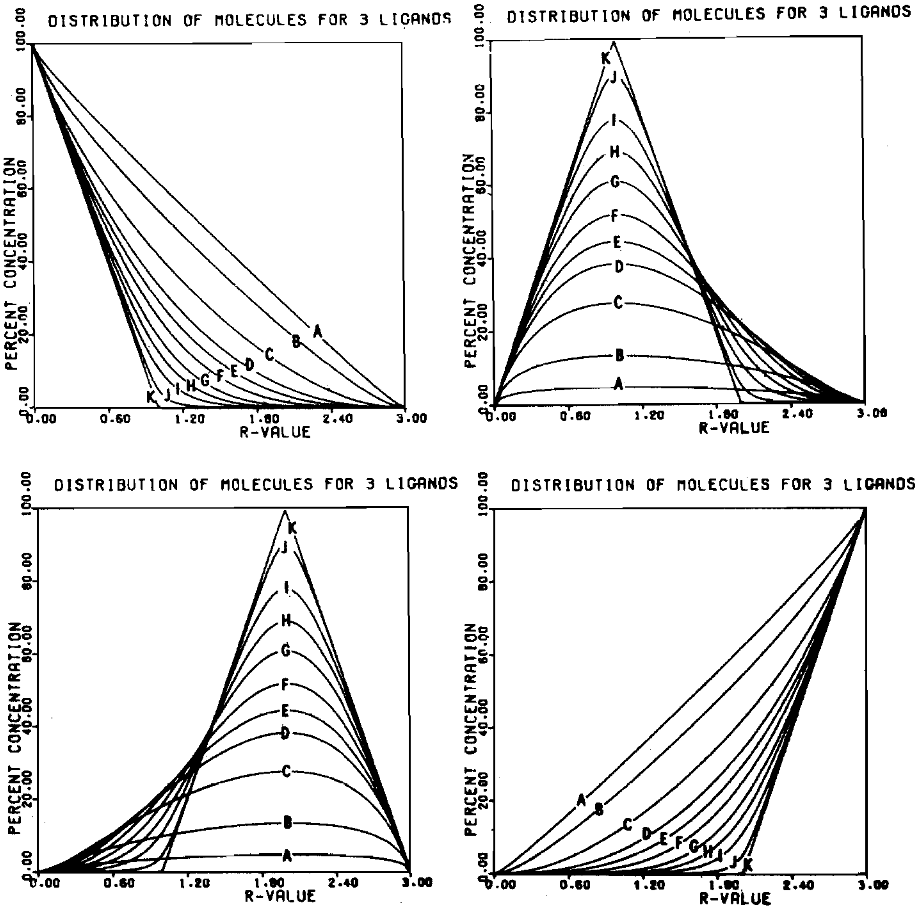

Figure 2. Equilibrium concentrations (in mole percent) in the system QT_3 *vs* QZ_3 for various values of $K_1^{(\nu=3)}$ and $K_2^{(\nu=3)}$ [eqs. (9) and (10)] as a function of the composition parameter $R \equiv [Z]/[Q]$. The top left hand graph corresponds to the species QT_3, the top right hand graph to QT_2Z, the bottom left hand graph to QTZ_2 and the bottom right hand graph to QZ_3. The letters refer to the following values of the equilibrium constants $K_1^{(\nu=3)}/K_2^{(\nu=3)}$: A, 10; B, 3; C, 1; D, 0.5; E, 0.333 (ideal randomness); F, 0.2; G, 0.1; H, 0.05; I, 0.02 J, 0.003; and K, 1×10^{-5}.

The three equations for the algebraic calculation of the equilibrium concentrations of all species are equations (3) and (4), both for $\nu=2$, and equation (6). It is seen that for very large values of $K_1^{(\nu=2)}$, *i.e.*, a case similar to the curves A in Figure 1, the equilibrium concentration of QTZ at any R value approaches zero, whereas QT_2 and QZ_2 become linear functions of R. In terms of the reaction of equation (5) this means that the equilibrium lies completely to the right. In the other extreme case, *i.e.*, when $K_1^{(\nu=2)}$ is very small, a case which is similar to the curves K in Figure 1, QTZ increases linearly from $R=0$ to $R=1$, at which point the equilibrium concentration approaches 100%, and from $R=1$ to $R=2$ it decreases linearly with increasing R. In this latter case the equilibrium of equation (5) lies completely to the left. The curves B though J represent situations which are intermediate between the two described above. The curves labeled F represent the ideal random distribution case.

Examples for systems where the difunctional central moiety Q is $(CH_3)_2Si$ and T and Z are a series of pairs of exchanging substitutents, resulting in a wide range of values of equilibrium constants, were summarized recently.[8]

Equilibria on Trifunctional Central Moieties. For the functionality of the central atom or moiety being $\nu=3$ there are $\nu+1=4$ possible reaction products: QT_3, QT_2Z, QTZ_2, and QZ_3. The general equilibrium reaction of equation (1) thus results in two equilibrium reactions since i in equation (1) may have the values 1 or 2. These are shown below.

$$2QT_2Z \rightleftharpoons QT_3 + QTZ_2 \quad (7)$$

$$2QTZ_2 \rightleftharpoons QZ_3 + QT_2Z \quad (8)$$

These equations result in the two equilibrium constants $K_1^{(\nu=3)}$ and $K_2^{(\nu=3)}$, shown below, which

$$K_1^{(\nu=3)} = [QT_3][QTZ_2]/[QT_2Z]^2 \quad (9)$$

$$K_2^{(\nu=3)} = [QZ_3][QT_2Z]/[QTZ_2]^2 \quad (10)$$

together with equations (3) and (4), with $\nu=3$, mathematically describe all equilibria in this type of system.

Again, a display of the distribution of the four species present in this system at equilibrium, QT_3, QT_2Z, QTZ_2, and QT_3, is shown in Figure 2 as a function of the composition parameter $R=[Z]/[Q]$ for a wide range of values of the equilibrium constants $K_1^{(\nu=3)}$ and $K_2^{(\nu=3)}$. The curves shown were calculated for the case where $K_1^{(\nu=3)}=K_2^{(\nu=3)}$. In many instances, however, $K_1^{(\nu=3)} \neq K_2^{(\nu=3)}$, although generally it has been found that the two equilibrium constants in a given system do not differ from each other considerably. In the latter cases only slightly modified curves are obtained since the equilibrium concentration of a given species to some extent is also a function of the other equilibrium constant. As a first approximation, however, the curves shown adequately represent a situation where the two equilibrium constants differ by less than about an order of magnitude.

(8) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 7, 2105 (1968).

Similar to the previous case, there are two extreme situations. The curves labeled A represent very large values of the equilibrium constants of equations (9) and (10) forming the products on the right side of equations (7) and (8). The curves labeled K represent very small values of the above two constants favoring at equilibrium the formation of the products on the left side of equations (7) and (8). The curves B through J represent intermediate situation with E describing the ideal random case of distribution.

Equilibria on Tetrafunctional Central Moieties. The general reaction of equation (1) results in 3 equilibrium reactions (i = 1, 2, or 3) and in five possible reaction products: QT_4, QT_3Z, QT_2Z_2, QTZ_3, and QZ_4.

$$2QT_3Z \rightleftharpoons QT_4 + QT_2Z_2 \quad (11)$$

$$2QT_2Z_2 \rightleftharpoons QT_3Z + QTZ_3 \quad (12)$$

$$2QTZ_3 \rightleftharpoons QT_2Z_2 + QZ_4 \quad (13)$$

The above equilibrium reactions result in the three equilibrium constants shown below which together with equations (3) and (4), with $\nu=4$, mathematically describe the present system.

$$K_1^{(\nu=4)} = [QT_4][QT_2Z_2]/[QT_3Z]^2 \quad (14)$$

$$K_2^{(\nu=4)} = [QT_3Z][QTZ_3]/[QT_2Z_2]^2 \quad (15)$$

$$K_3^{(\nu=4)} = [QT_2Z_2][QZ_4]/[QTZ_3]^2 \quad (16)$$

Again, the distribution of the five species present at equilibrium plotted as a function of the composition parameter $R \equiv [Z]/[Q]$ is shown in Figure 3 for a wide range of values of the equilibrium constants $K_1^{(\nu=4)}$, $K_2^{(\nu=4)}$, and $K_3^{(\nu=4)}$. Also this set of curves is based on the assumption that $K_1^{(\nu=4)}=K_2^{(\nu=4)}=K_3^{(\nu=4)}$. This assumption is not always realized; however, in most of the cases reported the three equilibrium constants of a given system do not differ from each other markedly. Only slight perturbations of the equilibrium curves will occur when $K_1^{(\nu=4)}$, $K_2^{(\nu=4)}$ and $K_3^{(\nu=4)}$ differ from each other by less than about an order of magnitude. Also in these cases curves A and K represent the extreme situations and similar reasoning may be applied as in the previously discussed systems.

Highest Obtainable Concentration of Mixed Species. For synthetic purposes it is often desirable to know the highest theoretically possible yield of a mixed species $QT_{\nu-i}Z_i$ that may be realized when it is prepared from the components QT_ν and QZ_ν according to the equation given below [i = 1, 2 . . . (ν–1)].

$$(\nu-i)QT_\nu + iQZ_\nu \longrightarrow \nu QT_{\nu-i}Z_i \quad (17)$$

Disregarding losses in the course of isolation and assuming that the rate of re-equilibration is small under the conditions of the separation, this yield will depend on the equilibrium constant K_i [i = 1, 2 . . . (ν–1)] of the form of eq. (2). In addition, it is quite obvious from the graphs in Figs. 1, 2 and 3 that the highest attainable equilibrium concentration of a species $QT_{\nu-i}Z_i$ is always found at the over-all composition that corresponds to the composition of the desired compound, *i.e.*, the concentration of the compound $QT_{\nu-i}Z_i$, regardless of the value of the appropriate equilibrium constant, will always maximize at an over-all composition characterized by $R \equiv [Z]/[Q] = i$. Therefore, if one wishes to prepare the compound $QT_{\nu-i}Z_i$ in the highest possible yield by the redistribution process, all that is required is an equilibrated mixture of the over-all composition $R \equiv [Z]/[Q] = i$. For this composition at equilibrium the concentration of the species $QT_{\nu-i}Z_i$ is at a maximum and its absolute concentration is a function of the corresponding equilibrium constants K_i.

For a system where the functionality of the central moiety Q is $\nu = 2$, eq. (17) simplifies to the equation given below.

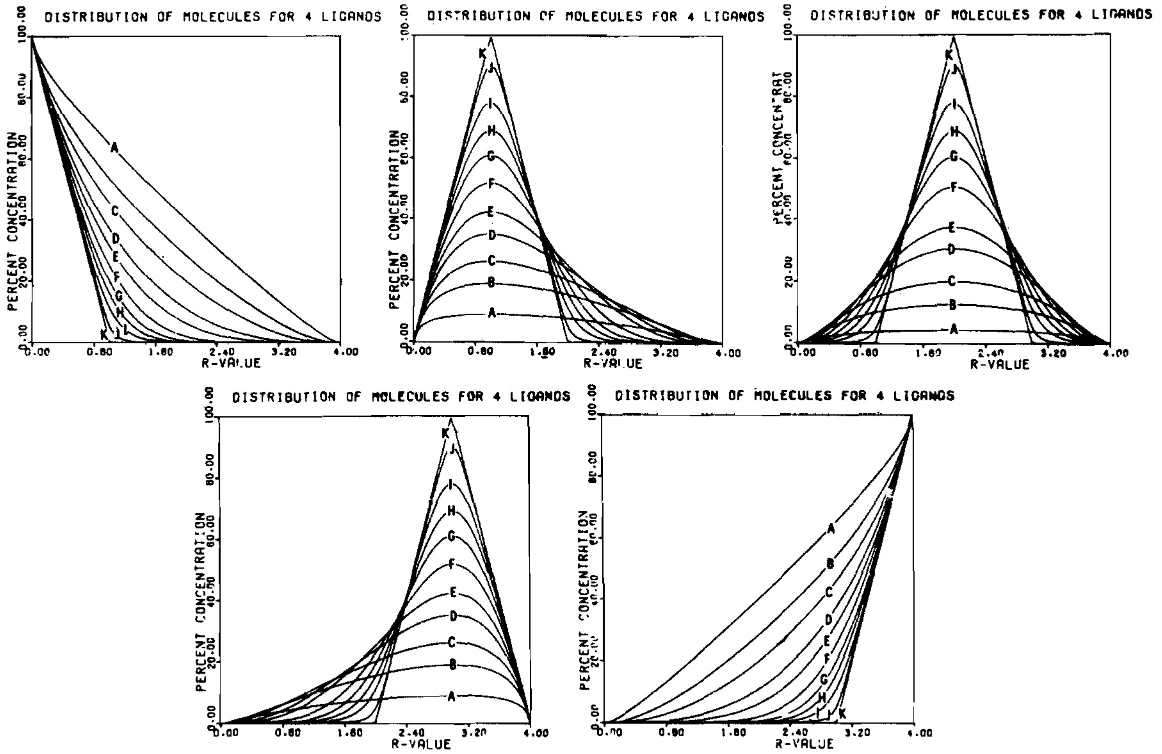

Figure 3. Equilibrium concentrations (in mole percent) in systems QT_4 *vs* QZ_4 for various values of $K_1^{(\nu=4)}$, $K_2^{(\nu=4)}$ and $K_3^{(\nu=4)}$ [eqs. (14), (15) and (16)] as a function of the composition parameter $R \equiv [Z]/[Q]$. The top right hand graph corresponds to the species QT_4, the top center graph to QT_3Z, the top left hand graph to QT_2Z_2, the bottom left hand graph to QTZ_3 and the bottom right hand graph to QZ_4. The letters refer to the following values of the equilibrium constants $K_1^{(\nu=4)} = K_2^{(\nu=4)} = K_3^{(\nu=4)}$: A, 3; B, 1.5; C, 1; D, 0.6; E, $K_1^{(\nu=4)} = K_3^{(\nu=4)} = 0.375$, $K_2^{(\nu=4)} = 0.444$ (ideal randomness); F, 0.2; G, 0.1; H, 0.05; I, 0.02; J, 0.003; and K, 1×10^{-5}.

$$QT_2 + QZ_2 \longrightarrow 2QTZ \qquad (18)$$

The highest obtainable yield of the compound QTZ when prepared according to eq. (18), provided that equilibrium is attained, solely is a function of the equilibrium constant $K_1^{(\nu=2)}$ of eq. (6). This highest attainable equilibrium concentration of the species QTZ at the over-all composition $R \equiv [Z]/[Q] = 1$. is shown in Fig. 4 (curve A) as a function of the value of the equilibrium constant $K_1^{(\nu=2)}$.

A similar curve is shown as curve B in Fig. 4 for the central moiety Q being $\nu = 3$. Equation (17) then results in 2 equations (i = 1 and 2) for the two redistribution products QT_2Z and QTZ_2.

$$2QT_3 + QZ_3 \longrightarrow 3QT_2Z \qquad (19)$$

$$QT_3 + 2QZ_3 \longrightarrow 3QTZ_2 \qquad (20)$$

Curve B applies to either one of the products of eqs.

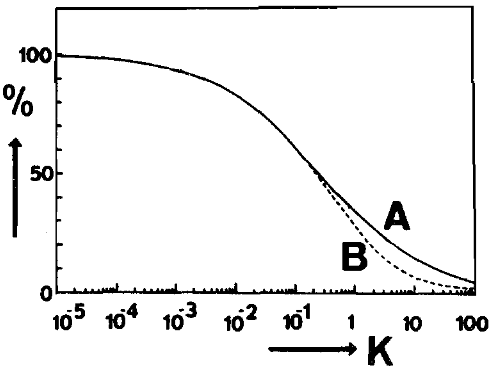

Figure 4. Highest attainable equilibrium concentration of a mixed species $QT_{\nu-i}Z_i$ in an equilibrated system as a function of the equilibrium constant. Curve A: Equilibrium concentration of QTZ in mole percent in the system QT_2 *vs* QZ_2 at $R \equiv [Z]/[Q] = 1$ as a function of the value of $K_1^{(\nu=2)}$ [eq. (6)]. Curve B: Equilibrium concentration (in mole percent) of QT_2Z or QTZ_2 in the system QT_3 *vs* QZ_3 at $R \equiv [Z]/[Q] = 1$ or 2, respectively, as a function of the value of the equilibrium constants $K_1^{(\nu=3)}$ [eq. (9)] or $K_2^{(\nu=3)}$ [eq. (10)], respectively, assuming $K_1^{(\nu=3)} = K_2^{(\nu=3)}$.

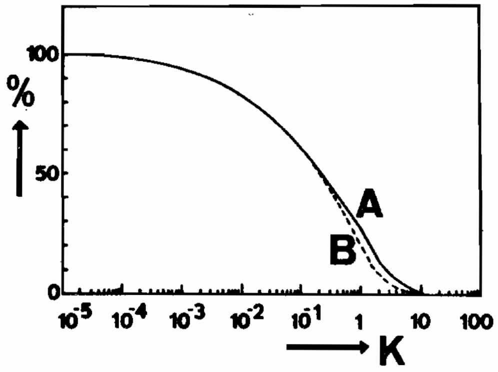

Figure 5. Highest attainable equilibrium concentration of a mixed species $QT_{4-i}Z_i$ in the system QT_4 *vs* QZ_4 as a function of the equilibrium constants. Curve A: Equilibrium concentration (in mole percent) of QT_3Z or QTZ_3 at $R \equiv [Z]/[Q] = 1$ or 3, respectively, as a function of the value of the equilibrium constant $K_1^{(\nu=4)}$ [eq. (14)] or $K_3^{(\nu=4)}$ [eq. (16)], respectively, assuming $K_1^{(\nu=4)} = K_2^{(\nu=4)} = K_3^{(\nu=4)}$. Curve B: Equilibrium concentration of QT_2Z_2 at the over-all composition $R \equiv [Z]/[Q] = 2$ as a function of the value of $K_2^{(\nu=4)}$ [eq. (15)], assuming $K_1^{(\nu=4)} = K_2^{(\nu=4)} = K_3^{(\nu=4)}$.

(19) and (20) the concentrations of which are determined by $K_1^{(\nu=3)}$ and $K_2^{(\nu=3)}$ of eqs. (9) and (10).

For the central moiety Q having a functionality $\nu = 4$, eq. (17) results in the 3 equations given below ($i = 1$, 2 and 3) which describe the formation of the 3 redistribution products QT_3Z, QT_2Z_2 and QTZ_3

$$3QT_4 + QZ_4 \longrightarrow 4QT_3Z \quad (21)$$

$$2QT_4 + 2QZ_4 \longrightarrow 4QT_2Z_2 \quad (22)$$

$$QT_4 + 3QZ_4 \longrightarrow 4QTZ_3 \quad (23)$$

In Fig. 5 the corresponding curves are shown which are based on $K_1^{(\nu=4)}$, $K_2^{(\nu=4)}$ and $K_3^{(\nu=4)}$ of eq. (14-16).

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