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## Heterogeneous Exchange of Precipitates

### VII. Fraction Exchange Calculation when the Composition of the System Changes During the Experiment\*

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(Received August 10, 1964)

#### 1. Introduction

The simple formula for fraction exchange

$$F = (\beta_0^L - \beta_t^L) / (\beta_0^L - \beta_\infty^L), \quad [1]$$

according to the formula on p. 8 in (1), is generally applicable if no change of the composition of the system occurred during the experiment ( $\beta^L$  represents the specific radioactivity of the liquid phase, the subscript letters the exchange time). If the composition of the system has changed, the simple formula [1] can produce erroneous results and essentially wrong conclusions if strictly applied (2). In order to obtain the real value for fraction exchange, some corrections have to be introduced, depending on the kind of the interfering process.

In this paper two cases are discussed for the systems with a labelled liquid phase:

1. the inactive solid phase dissolving during the experiment,
2. the solid phase was forming during the experiment from the substance previously labelled in the liquid phase.

#### 2. Fraction Exchange $F_1$

(The liquid phase being labelled, the concentration of exchangeable substance in the liquid phase increased during the experiment owing to the dissolution of the inactive solid phase).

The decrease of specific radioactivity of the liquid phase

$$\beta_0^L - \beta_t^L = (A_0/n_0^L) - (A_t/n_t^L),$$

representing the numerator in eq. [1], was produced by two independent processes: the heterogeneous exchange and the dissolution of the inactive solid phase ( $n^L$  standing for the number of gramatoms of exchangeable substance in the liquid phase and  $A$  for the radioactivity of the liquid phase per liter of the system). The experimentally obtained value

$$\beta_0^L - \beta_t^L = (\Delta\beta_m^L)_{0-t},$$

corresponding to the time interval  $0 - t$ , consists of two parts:

$$(\Delta\beta_m^L)_{0-t} = (\Delta\beta_{\text{exch}}^L)_{0-t} + (\Delta\beta_{\text{diss}}^L)_{0-t}, \quad [2]$$

the  $(\Delta\beta_{\text{exch}}^L)_{0-t}$  was due only to the heterogeneous exchange, and  $(\Delta\beta_{\text{diss}}^L)_{0-t}$  only to the dissolution of the inactive solid.

The value for  $(\Delta\beta_m^L)_{0-t}$  can be divided into parts

$$(\Delta\beta_m^L)_{0-t} = (\Delta\beta_m^L)_{0-1} + (\Delta\beta_m^L)_{1-2} + \dots + (\Delta\beta_m^L)_{(t-1)-t}, \quad [3]$$

if the corresponding values for  $A$  and for  $n^L$  were experimentally obtained at the time points  $0, 1, 2, \dots, (t-1), t$ . In order to calculate the  $(\Delta\beta_{\text{exch}}^L)$  value for each time interval  $(0-1, 1-2, \dots, (t-1)-t)$ , two extreme courses for the process should be assumed: a) the heterogeneous exchange occurred after the dissolution of the (inactive) solid phase had been completed; b) the dissolution of the (inactive) solid phase occurred after the heterogeneous exchange had been completed [the real course of the process took place between the extremes a) and b)]. Eq. [4] and eq. [5] show the calculation of  $(\Delta\beta_{\text{exch}}^L)$  value for the time interval  $1-2$  for both extreme courses, analogously applicable to any other time interval

$$[(\Delta\beta_{\text{exch}}^L)_{1-2}]_a = (A_1/n_2^L) - (A_2/n_2^L), \quad [4]$$

the other part of  $(\Delta\beta_m^L)_{1-2}$  being

$$[(\Delta\beta_{\text{diss}}^L)_{1-2}]_a = (A_1/n_1^L) - (A_1/n_2^L),$$

$$[(\Delta\beta_{\text{exch}}^L)_{1-2}]_b = (A_1/n_1^L) - (A_2/n_1^L), \quad [5]$$

the other part of  $(\Delta\beta_m^L)_{1-2}$  being

$$[(\Delta\beta_{\text{diss}}^L)_{1-2}]_b = (A_2/n_1^L) - (A_2/n_2^L).$$

The  $X$  value, corresponding to the numerator of eq. [1], is obtained by the sum of  $(\Delta\beta_{\text{exch}}^L)$  values for all the time intervals inside  $0-t$ , according to eq. [4] and [5]

$$X_a = (1/n_1^L) \cdot (A_0 - A_1) + (1/n_2^L) \cdot (A_1 - A_2) + \dots + (1/n_t^L) \cdot (A_{(t-1)} - A_t), \quad [6]$$

$$X_b = (1/n_0^L) \cdot (A_0 - A_1) + (1/n_1^L) \cdot (A_1 - A_2) + \dots + (1/n_{(t-1)}^L) \cdot (A_{(t-1)} - A_t). \quad [7]$$

\* Contribution number 114 from the Department of Physical Chemistry, Faculty of Sciences, University of Zagreb,

The denominator in eq. [1] represents the greatest possible decrease of specific radioactivity of the liquid phase from the moment of labelling till the uniform distribution of radioactive nuclides through the whole system,

$$\beta_{\infty}^L = A_0 / (n^L + n^S) \text{ for } t = \infty$$

( $n^S$  represents the number of gramatoms of exchangeable substance in the solid phase per liter of the system, ( $n^L + n^S$ ) is constant). If the last experiment was carried out at the time point  $r$ , the greatest possible decrease of specific radioactivity from that moment till the time  $t = \infty$  is expressed by

$$(A_r/n_r^L) - A_0 / (n^L + n^S).$$

The  $Y$  value, corresponding to the denominator in eq. [1], is represented by

$$Y_a = (1/n_1^L) \cdot (A_0 - A_1) + (1/n_2^L) \cdot (A_1 - A_2) + \dots + (1/n_r^L) \cdot (A_{(r-1)} - A_r) + (A_r/n_r^L) - A_0 / (n^L + n^S), \quad [8]$$

$$Y_b = (1/n_0^L) \cdot (A_0 - A_1) + (1/n_1^L) \cdot (A_1 - A_2) + \dots + (1/n_{(r-1)}^L) \cdot (A_{(r-1)} - A_r) + (A_r/n_r^L) - A_0 / (n^L + n^S). \quad [9]$$

The fraction exchange  $F_I$  for the extreme cases a) and b), limiting the region of the real value, is obtained by eq. [10] and eq. [11], if the correspondingly subscribed  $X$  and  $Y$  values from eq. [6], [7], [8], [9] are substituted

$$(F_I)_a = X_a / Y_a; \quad [10]$$

$$(F_I)_b = X_b / Y_b. \quad [11]$$

The counting rate of a definite volume of the liquid phase, corrected for the background, can generally be taken for  $A$  value. The error from radioactive decay has to be eliminated. It is convenient to divide the numerator and the denominator of eq. [10] and [11] by  $A_0$ , introducing the  $A/A_0$  values into the formula for  $(F_I)_a$  and  $(F_I)_b$ . It is often satisfying, if  $A$  and  $A_0$  for each  $A/A_0$  value have been determined immediately

one after the other (if the half-life of radioactive nuclide is short, the values for  $A$  and  $A_0$  have to be reduced to the same time point).

### 3. Fraction Exchange $F_{II}$

(The liquid phase being labelled, the concentration of the exchangeable substance in the liquid phase decreased owing to the formation of the solid phase during the experiment).

During the formation of the solid phase the specific radioactivities of the liquid and of the solid phase were equal. The formation of the solid introduced no change of the specific radioactivity of the liquid. The fraction exchange  $F_{II}$  can be calculated if eq. [1] is strictly applied, and eq. [12] is obtained after a rearrangement

$$F_{II} = [1 - (n_0^L/n_t^L) \cdot (A_t/A_0)] / [1 - n_0^L / (n^L + n^S)]. \quad [12]$$

The correct  $A_t/A_0$  determination, eliminating the error from radioactive decay, was described previously.

#### Summary

The calculation of fraction exchange is given for the case when the composition of the system changes during the heterogeneous exchange experiment.

In order to avoid essentially wrong conclusions, the change of specific activity of the liquid phase originating from heterogeneous exchange ought to be distinguished from the change originating from any other simultaneous process.

Two cases were considered: I. an inactive solid phase dissolving during the experiment, the liquid phase being previously labelled, and II. the solid phase formed during the experiment from exchangeable substance previously labelled in the liquid phase.

#### References

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