Nuclear Chemistry of Tellurium: Chemical Effects of Isomeric Transition*

RUSSELL R. WILLIAMS, JR.
University of Notre Dame, Notre Dame, Indiana
(Received February 4, 1948)

The chemical consequences of isomeric transitions in the nuclei Te^{127}, Te^{129}, and Te^{131} have been investigated in aqueous solutions of varying composition. The nuclear reaction gives rise to chemical reduction or oxidation, and a mechanism has been proposed to account for the observed effects. Evidence has been advanced which indicates that the maximum efficiency of the chemical separation of the nuclear isomers can be taken as a measure of the degree of internal conversion.
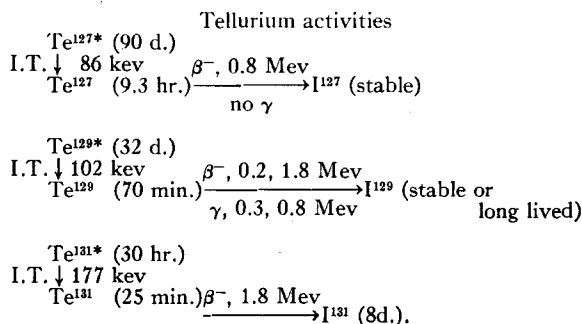
INTRODUCTION

CHANGE in chemical state as a result of isomeric transition has been demonstrated with several isotopes.[1-3] With tellurium, it has been shown that the nuclear decay is accompanied by a reduction of the tellurium atom from 6+ to 4+. It is the purpose of this investigation to examine this chemical phenomenon quantitatively and to relate it to the characteristics of the nuclear process.

The mechanism by which such a chemical change results from isomeric transition was first suggested by Segrè, Halford, and Seaborg[2] and soon supported by further experimental work.[4] These investigators point out that the recoil from isomeric transition gammas is far from sufficient to break ordinary chemical bonds. However, these weak gammas are often highly internally converted, i.e., the decay energy is carried off by an extra-nuclear electron of the K or L shells. In filling the hole thus created, great disturbances may result in the valence shells with subsequent loss of peripheral electrons.[5] It is therefore postulated that chemical change can occur only when the gamma is internally converted, and that these two phenomena should be quantitatively related.

ACTIVE SPECIES

Three isotopes of tellurium undergo isomeric transition as follows:[6]

Tellurium activities

Te^{127*} (90 d.)
I.T. $\downarrow$ 86 kev β^-, 0.8 Mev
Te^{127} (9.3 hr.) $\xrightarrow[\text{no } \gamma]{}$ I^{127} (stable)

Te^{129*} (32 d.)
I.T. $\downarrow$ 102 kev β^-, 0.2, 1.8 Mev
Te^{129} (70 min.) $\xrightarrow[\gamma, \ 0.3, \ 0.8 \text{ Mev}]{}$ I^{129} (stable or long lived)

Te^{131*} (30 hr.)
I.T. $\downarrow$ 177 kev
Te^{131} (25 min.)β^-, 1.8 Mev $\xrightarrow{}$ I^{131} (8d.).

Note: Isomeric transition (I.T.) is the loss of energy by a nucleus without change in atomic or mass number. It may take place by emission of one or more quanta of gamma-radiation, or by interaction with an extra-nuclear electron (internal conversion).

The extent of internal conversion of the isomeric transitions in Te^{127*} and Te^{129*} has been presumed to be nearly 100 percent, since no unconverted gamma-rays have been observed in either case.[7] Samples of Te^{127*} and Te^{129*} were isolated from fission product mixtures furnished by the Tracer Supply Section of Clinton Laboratories. Maximum yields of 32d Te^{129*} are obtained from bombarded uranium metal which has decayed for a period of two weeks to several months. The 90-day Te^{127*} must be obtained from metal decayed at least eighteen months to insure only slight contamination by 32-day

[1] D. DeVault and W. F. Libby, J. Am. Chem. Soc. **63**, 3216 (1941).
[2] E. Segrè, R. S. Halford, and G. T. Seaborg, Phys. Rev. **55**, 321 (1939).
[3] G. T. Seaborg, J. J. Livingood, and J. W. Kennedy, Phys. Rev. **57**, 363 (1940).
[4] G. T. Seaborg, G. Friedlander, and J. W. Kennedy, J. Am. Chem. Soc. **62**, 1309 (1940).
[5] E. P. Cooper, Phys. Rev. **61**, 1 (1942).
[6] Plutonium Project Fission Product Survey, J. Am. Chem. Soc. **68**, 2411 (1946).
[7] A. C. Helmholz, Phys. Rev. **60**, 415 (1941).

Te[129]*. Carrier-free samples of these two activities were prepared by carrying the tellurium activity on selenium metal. The selenium carrier can be be removed later by volatilization of selenium bromide.

30-hr. Te[131]* was prepared by neutron bombardment of tellurium metal. 32-day Te[129]* is also obtained, making the study of the isotope of interest difficult. Absorption and decay curves indicate that Te[131] has a somewhat harder beta than Te[129], but the actual range could not be estimated.

CHEMICAL PREPARATIONS AND SEPARATIONS

Tellurium metal dissolves in nitric and hydrochloric acids principally as tellurous acid. If the nitric acid is removed by evaporation with HCl, the tellurium will be completely tellurous.

The present experiments have demonstrated

FIG. 1. Daughter separation of Te[129] in 3M NaOH.

□   Growth of tellurate fraction.
■ —·—   Decay of tellurite fraction by subtraction of growth from maximum.
○   Decay of tellurite fraction.
● — — —   Decay of 70-min. daughter.

that carrier-free tellurium tracer is not readily oxidized to tellurate, but macro amounts are easily treated by the method described by Seaborg, Livingood, and Kennedy.[3] This consists in the oxidation of solid silver tellurite by bromine. A solution of telluric acid is formed from which the solid silver bromide and excess bromine may be removed.

Reduction of macro amounts of telluric acid to tellurous acid is rapid in the presence of boiling hydrobromic acid. Further reduction to tellurium metal can be accomplished in hot hydrochloric acid solutions by gassing with sulfur dioxide. This agent reduces tellurous acid rapidly, but telluric acid only slowly, and was used by previous investigators[3] to separate the two valence states. In this work, the separation was made by the precipitation of tellurium sulfide in cold hydrochloric acid. Hydrogen sulfide is even less reactive than sulfur dioxide towards the oxidized state, Te[6+].

Gaseous tellurium hexafluoride was prepared by direct action of fluorine gas on tellurium metal at room temperature.[8] The compound is by far the most volatile of all the tellurium fluorides, having a vapor pressure of 29.4-mm Hg. at −79°C.[9] This property was used to effect purification by distillation and to aid in the isomer separations which will be described later.

EXPERIMENTAL RESULTS

Te[129], Daughter Reduction

The 32-day, 70-minute isomer pair was the subject of the most detailed study because of its availability. The procedure for most of the experiments was as follows:

Tellurium tracer with carrier was oxidized to tellurate. This solution, with various concentrations of acid and base, was allowed to stand at least five hours, in order that new 70-minute daughter atoms might be formed under the desired conditions. After this growth period, tellurite carrier was added, and the previously described separation of valence states made.

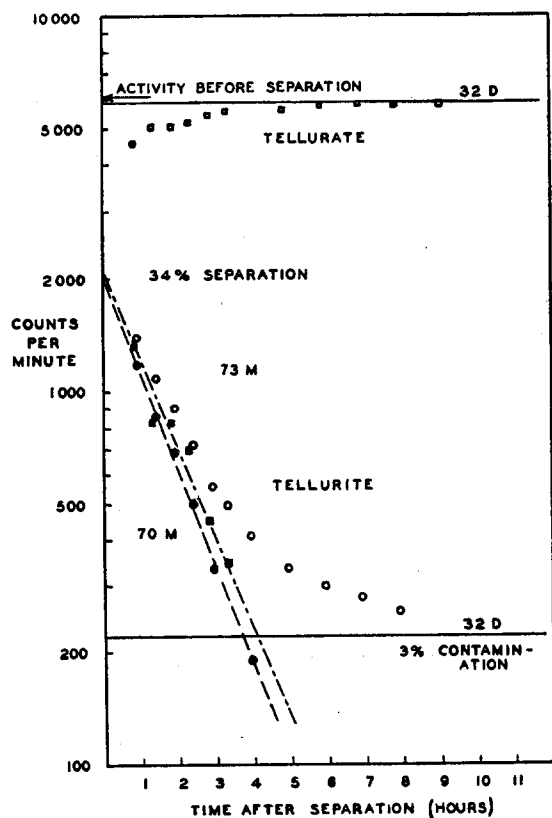As previously reported,[3] a considerable amount

[8] D. M. Yost and J. H. Simon, *Inorganic Synthesis* (McGraw-Hill Book Company, Inc., New York, 1939), Volume I, Prep. No. 44.
[9] D. M. Yost and W. H. Claussen, J. Am. Chem. Soc. **55**, 885 (1933).

of the 70-minute daughter activity is associated with the 4+ valence state, while the parent atoms remain 6+. Experimentally, this is revealed by a growth of beta-activity in the tellurate fraction, and a 70-minute decay of beta-activity in the tellurite fraction (see Fig. 1). Either growth or decay may be taken as a measure of the separation achieved. Some slight contamination by a 32-day parent is usually noted in the decaying tellurite fraction which may be attributed to incomplete separation.

Calculations based on the growth of the tellurite fraction are the most reliable since they involve counting only one sample. The activity extrapolated to separation time is compared with the activity at maximum growth. The decay of the parent is so slow that it is not usually necessary to correct this figure to separation time. However, if the separation is inefficient, the small amount of growth makes this approach inaccurate.

Calculations based on the decay of the tellurite fraction necessitate counting two samples, with the attendant difficulties of mounting and absorption variations. The 70-minute beta-activity, extrapolated to separation time, is compared with the beta-activity of a sample taken before the valence separation was made or with the beta-activity of the tellurate fraction at maximum growth. Both methods of measurement are illustrated in Fig. 1.

If tellurium activity is a mixture of 32-day and 90-day isotopes, the latter may be removed from consideration by the use of a 300 mg/cm² aluminum absorber.

The fraction of 70-minute tellurium activity reduced from tellurate to tellurite ("daughter reduction") was found to vary considerably with the acidity or basicity of the solution in which growth took place. The values obtained are summarized in column 1 of Table I. Buffer solutions were used to maintain the desired pH in nearly neutral solutions, and there is no reason to doubt the validity of the point at the pH value 8.8. This buffer is the only one which employed considerable concentrations of chloride ion, and the apparent inconsistency may be attributable to its reducing properties.

No variation in the yields was observed which could be attributed to presence or absence of

TABLE I. Daughter separation in Te¹²⁹.

Growth conditions	Column 1 daughter reduction (%)	Column 2 daughter oxidation (%)	Column 3 chemical oxidation of tellurium ion (%)
6M HCl	57±2		
6M HClO₄	53±2		
2M HCl	57±4	0	
0.1M HCl	56±2		
Buffer pH 3.4	54±2	<2	
Buffer pH 5.0	49±4	5±1	
Buffer pH 5.9	50±2		
Buffer pH 6.6	45±5		
Buffer pH 6.8	39±3	14±1	
Buffer pH 8.7	39±2		
Buffer pH 8.8*	48±2	6±1	
Buffer pH 9.6	40±2		
0.1 M NaOH	41±2	11±1	
0.5M NaOH	40±2	11±1	
1.2M NaOH	37±1	14±1	<3
3M NaOH	33±2	13±1	~4
6M NaOH	25±2	14±1	~15
9M NaOH	32±2		
12M NaOH	36±2	0	~30
16M NaOH	35±2		

* Only buffer containing chloride ion. See text.

tellurous carrier during the growth period or to variation of the temperature from 25 to 75°C.

Any oxidation of tellurous ion to telluric ion during the course of these experiments would lower the observed yields of tellurite daughter activity. The lowered yields in alkaline solutions especially must be shown to be independent of this ordinary chemical oxidation. Information on this point can be obtained from tellurium tracer experiments starting in the tellurite form. The experiments described in the following section were undertaken for a different purpose, but answer this question as well.

Te¹²⁹, Daughter Oxidation

The oxidation of tellurium daughter atoms as a result of isomeric transition has not been previously reported. It was observed in these experiments by placing tellurous tracer (with or without tellurous carrier) in alkaline solutions or the growth period previously described. At the end of this period, tellurate carrier was added and the usual separation of the oxidation states by sulfide precipitation made. The beta-activity of the tellurate fraction showed a 70-minute decay period, and the tellurite fraction a corresponding growth (see Fig. 2). The yield of this "daughter oxidation" was computed in exactly

the same manner as that used with the previously described experiments. Values obtained in solutions of different acidity and basicity are indicated in column 2 of Table I. Buffer solutions were again used for pH values of around 7. Note again the apparent inconsistency of the point at pH value 8.8.

Oxidation of tellurite ion not connected with the nuclear process can be observed after both fractions from the above experiments have returned to a 32-day half-life (see Fig. 2). This type of oxidation was observed in increasing degrees at hydroxide ion concentrations greater than one molar. At these concentrations appreciable amounts of the 70-minute tellurous activity formed in the "daughter reduction" experiments were re-oxidized to the telluric state, thus falsely lowering the yields. The estimated extent of oxidation in strongly basic solution was used to correct the observed values to the
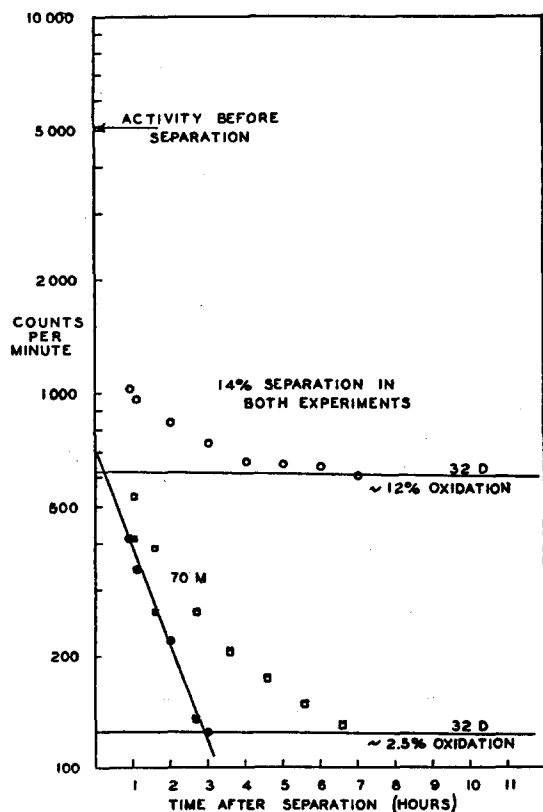

FIG. 2. Decay of tellurate fraction after daughter oxidation of Te^{129}.

○ Grown in 6M NaOH.
● Decay of 70-min. daughter.
□ Grown in 1M NaOH.
■ Decay of 70-min. daughter.

probable true "daughter reduction" values. The observed values of daughter reduction and oxidation in solutions of varying acidity and basicity are plotted in Fig. 3. The broken line for "daughter reduction" in basic solutions represents the estimated true values obtained by a consideration of the amount of ordinary chemical oxidation of the daughter tellurite in these solutions.

Te^{129}, Daughter Separations with Gaseous Tellurium Hexaflouride

In order to examine the phenomenon in a non-aqueous system, daughter separation experiments were performed starting with Te^{129} activity and carrier as tellurium hexafluoride gas. It is reasonable to assume that no other stable tellurium compound would be sufficiently volatile to have an appreciable vapor pressure at solid carbon dioxide temperatures. After a five-hour growth period at room temperature, separation of the active tellurium hexafluoride from any decomposition or reaction products due to the isomeric transition was accomplished by passing the gas through a trap cooled in a solid carbon dioxide-Cellosolve slurry. The undecomposed gas was then condensed in a two-cubic-centimeter bulb and sealed off. The growth of beta-activity in this bulb was followed at a low counter geometry to minimize any effects due to deposition of activity on the walls.

Pressures of tellurium hexfluoride were five to ten millimeters of mercury during the growth period. In some experiments there were also present about 100 millimeters pressure of some other gas. This should make it very likely that the fragments or activated molecules resulting from isomeric transition will suffer their first collision with some molecule other than tellurium hexfluoride, thus lowering the possibility of back reactions. The degree of daughter separation was computed from the growth of beta-activity in the undecomposed compound. Table II summarizes the conditions and results of these experiments. The observed values are undoubtedly, indistinguishable within the precision of the measurements.

Te^{127}, Daughter Separations

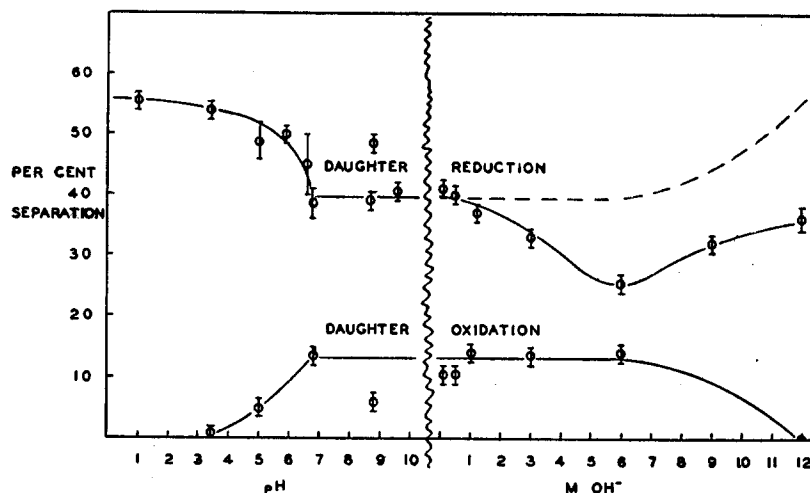A few experiments, similar in every respect to those in aqueous systems with Te^{129}, were con-

FIG. 3. Daughter separation in Te[129].

ducted using the 90-day, 9.3-hour isomer pair. Both "daughter reduction" and "daughter oxidation" were investigated, and the results reported in Table III.

Te[131], Daughter Separations

A few experiments were performed to determine the extent of "daughter reduction" with the 30-hour, 25-minute isomer pair. These were made difficult by the presence of other activities and should be regarded as only semiquantitative. Three experiments indicate a "daughter reduction" yield of 34 ± 4 percent in 1M HCl.

DISCUSSION

Daughter Separation in Aqueous Systems

The numerous experiments carried out with Te[129] in solutions of different acidity and basicity show some interesting relations. From Fig. 3 it is apparent that the yield of both "daughter oxidation" and "daughter reduction" changes abruptly at pH values near 6. In more acid solutions oxidation due to nuclear transformation is absent, and the reduction reaction has a yield of about 55 percent. In basic solutions the oxidation reaction shows a yield of about 15 percent and the reduction has dropped to about 40 percent. The situation in solutions above 6M in sodium hydroxide is again like that in acid solutions.

The two reactions are of course studied in separate experiments, but they apparently have some mechanistic relation, since the sum of their

yields remains essentially constant. Conditions under which the reduction process is partially ineffective are those under which the oxidation process becomes possible. Leaving out of consideration, for the moment, the 45 percent of nuclear decays which apparently have no chemical effect, the additivity of oxidation and reduction yields suggests a common reaction intermediate in the following sense: Starting with either tellurate or tellurite activity, the process of isomeric transition results in a common activated ion (probably highly oxidized). It is also postulated that the subsequent reactions of the intermediate state are independent of its ancestry, depending only on environment. (See diagram below.)

The constitution of the intermediate is difficult to predict. The opinion that it is highly ionized comes from the knowledge that con-

Proposed Mechanism

R. R. WILLIAMS, JR.

TABLE II. Daughter separation of Te^{129} with TeF_6 gas.

mm TeF_6	Conditions mm 2nd gas	% separation
12.5	—	45
5.5	—	55
9.5	—	45
4.5	105 (O_2)	47
5.0	85 (O_2)	49
5.0	150 (H_2)	51

TABLE III. Daughter separations of Te^{127} in aqueous systems.

Growth conditions	% daughter reduction	% daughter oxidation
1M HCl	85±2	0
1M NaOH	51±3	25±5

version in an isomeric transition usually results in the loss of more than one extra-nuclear electron.

Configurations can be visualized whose reactions would be dependent upon the constitution of the solution in the manner observed, or the "intermediate" might be two configurations always formed in the same proportions. The reactions of one of these might be independent of conditions, and the reactions of the other dependent on the acidity or basicity of the solution.

The fate of those isomeric transitions which do not seem to result in chemical change is indicated by a consideration of the conversion coefficient of this decay. In the next section evidence will be advanced to show that the conversion is probably 55 percent rather than 100 percent, as previously estimated.[7] If the revised value is accepted, it becomes clear that 45 percent of the isomeric transitions are incapable of producing any chemical change (see Introduction).

Note that the values of "daughter reduction" and "daughter oxidation" obtained with Te^{127*} conform to the remarks made above for the more detailed case of Te^{129*}. Similar observations could not be made on Te^{131*}.

The Conversion Coefficients of the Tellurium Isomeric Transitions

Helmholz[7] could find no unconverted gamma-rays in the Te^{129*} spectrum. A copper absorption curve taken during the couse of this work failed similarly, but these negative results might be due to interference of the weak gamma (0.3 Mev) of the 70-minute daughter. These observations seem to indicate that the conversion of Te^{129*} is nearly 100 percent. Since the process of conversion is thought to be at least a necessary condition for chemical change, the 100 percent separation reported by Seaborg, Livingood, and

Kennedy[3] did not seem unreasonable. These findings made it difficult to understand the 55 percent maximum separation obtained in this work, especially since experiments were also performed which duplicated the technique of Seaborg et al. as closely as possible, and these also gave 55 percent separation. It should be pointed out, however, that the 100 percent figure was obtained from experiments in which all three isomer pairs were considered. This involved the subtraction of several components in the decay curves, a method not used in this work because of its inaccuracy.

It was considered possible that the 55 percent separations observed with Te^{129*} did not measure up to the conversion due to some back reaction of activated ions which gave the initial valence state. This might be due, in aqueous solutions, to the "cage effect," which would make recombination of fragments quite possible. The experiments with gaseous tellurium hexafluoride were undertaken to observe daughter separation in a system where this possibility could be minimized. In a gaseous system, any molecular fragments formed by the isomeric transition are not likely to collide with each other before having an opportunity to react in other ways. Collision of a fragment or activated molecule with other tellurium hexafluoride molecules could also conceivably lead to a reaction which would return the daughter activity to the original chemical state. Large excesses of oxygen or hydrogen in the gaseous mixture made these molecules the most likely collision partner for activated or fragmentary tellurium hexafluoride molecules. The daughter separation values obtained in these gas phase experiments (see Table II) seemed to be constant and not significantly different from those obtained in the aqueous experiments. This indicates that the full value of the conversion is being realized in the separation experiments, and that the isomeric transition may be considerably less than 100 percent converted.

Consideration of the daughter separation experiments with Te¹²⁷* shows still more convincing evidence that the chemical method of isomer separation is highly efficient. Maximum separation in this case was 85 percent. The possible conversion of 100 percent sets the lower limit for the efficiency of the chemical reactions at 85 percent. Returning to the case of Te¹²⁹*, and making the very reasonable assumption that the reactions are exactly the same, we see that the conversion cannot be higher than 65 percent. The daughter separation of 34 percent obtained with Te¹³¹* predicts a conversion in this isomeric transition no greater than 40 percent. The lower limit of conversion in all cases is assumed to be the maximum separation value achieved.

On the Order-Disorder Transition in Solids. Part I

Yosio Mutō

Maebashi Medical College, Maebashi, Japan

(Received February 5, 1948)

Although the phenomena of order-disorder transition and the phenomena of condensation have a marked difference, there is a great similarity in their statistical mechanical treatment. Considering a hypothetical gas in which the molecules can occupy only lattice points of a crystal, and treating the "wrong" molecules as the gas molecules and the "right" molecules as the empty points, the partition function of a binary mixture is easily computed by applying Mayer's method. It is then pointed out that the ordered state is the analog of a condensing system.

SEVERAL years ago the author applied with slight modification Mayer's excellent method which he used in studying phase transition phenomena,[1] and studied the properties of regular solutions.[2] A formula that is more exact than Rushbrooke's was obtained.

The theory of imperfect gas with two components was also applied by the present author to the study of order-disorder phenomena in alloys.[3] The paper issued at that time contained some mistakes although the final result, the expression of the critical temperature as a series, is correct, agreeing with that found by Chang.

In the present paper the method was thoroughly modified and the analogy of condensation and the appearance of order is discussed.

THE PARTITION FUNCTION

As is always done, we assume that we can separate the configurational part from the entire partition function. The two equivalent sub-lattices are named α and β. In the completely ordered state, A molecules are at α and B's at β. We use the following notarions:

$[A]$: number of A molecules,
$[B]$: number of B molecules,
$[A_\alpha]$: number of A molecules at α,
$[B_\alpha]$: number of B molecules at α,
$[A_\beta]$: number of A molecules at β,
$[B_\beta]$: number of B molecules at β,
$N=2n$: number of total lattice points,
n : number of α and β lattice points each,
X : number of pairs of adjacent wrong atoms (nearest neighbors),
E_0 : potential energy at the completely ordered state (with no wrong molecule),
v_{AA}, v_{AB}, v_{BB} : potential energy of pairs of nearest neighbors,
z : number of nearest $\alpha(\beta)$ lattice points surrounding a $\beta(\alpha)$ lattice point,

$$w = 2v_{AB} - v_{AA} - v_{BB},$$

ϕ_A, ϕ_B : the part of partition function per molecule independent of configuration.

[1] J. E. Mayer, *Statistical Mechanics* (1940). This book is cited as "S.M."
[2] Y. Mutō, Journal of Physico-Mathematical Society of Japan (in Japanese) **17**, 86 (1943).
[3] See reference 2, p. 445.