CHAPTER - V

NON-LINEAR THEORY AND SYMMETRIES OF HIGHER ORDER IN IRREVERSIBLE PROCESS

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5.1 INTRODUCTION

The Onsager's reciprocal relations (1931) in the linear theory of irreversible phenomena have a fundamental importance. In irreversible thermodynamics according to some pioneers it is recognished as a law of thermodynamics. In support of the view, the invariance of the Onsager's reciprocal relations under a group of linear transformations was also established (Meixner, 1943; Prigogine, 1946-'49).

But de Groot (1951) pointed out its unsuitability in some of the irreversible phenomena, for instance, those in which chemical processes are involved. The non-linear theory concerns with the symmetry relations of higher order. Dutta (1966), established the invariance of the symmetry relations of higher order under a general group of linear transformations of forces and fluxes and hence his claim for the non-linear theories to be a physical law was ensured.

Dutta (1966), in his development, started with the entropy generation, considering it to be a basic phenomenological law.

By using the simple well-known definition of thermodynamic generalised forces as the differences or gradients of some thermodynamic quantities, the generalisation of linear theory upto any higher order was obtained.

In Section-2.3 - 2.5, the essentially stochastic model, due to Dutta, mainly for the reversible processes is generalised, with a few assumptions, for the discussion of the irreversible processes too and the linear reciprocal relations resembling those celebrated linear relations due to Onsager (1931), were established. In this chapter, we like to start therefrom and to develop the corresponding non-linear theory by establishing some sort of symmetry relations of higher order.

5.2 DEVELOPMENT OF THE SYMMETRY RELATIONS OF HIGHER ORDER : UPTO THIRD ORDER.

If X, Y are the two fundamental entities say, energy and mass, then by Section-2.3 - 2.4, from (2.54)

$$\Delta X = a_{11} \Delta\alpha + a_{21} \Delta\beta ,$$

$$\Delta Y = a_{12} \Delta\alpha + a_{22} \Delta\beta ,$$

where,

$$a_{11} = \overline{X^2} - (\bar{X})^2$$

$$a_{12} = \iint (XY - \bar{X}\bar{Y})\ P(X,Y,t)\ dx\ dy$$

$$a_{21} = \iint (XY - \bar{X}\bar{Y})\ P(X,Y,t)\ dx\ dy$$

$$a_{22} = \overline{Y^2} - (\bar{Y})^2 \quad .$$

The subscripts used here are changed slightly from those used in Chapter-II. The last one at the extreme right end, denotes the corresponding additive basic entity (extensive variable). The next one to the left denotes the variable (intensive variable) with respect to which the differentiation is done; 1 and 2 respectively indicate, that the differentiation is done with respect to α and β .

e.g.,

$$a_{21} = \frac{\delta \bar{X}}{\delta \beta}$$

$$a_{12} = \frac{\delta \bar{Y}}{\delta \alpha} \quad .$$

It is proved in the Section-2.3 - 2.4,

$$a_{21} = a_{12} = \overline{XY} - \bar{X}\bar{Y} \quad ,$$

showing the linear symmetry relation.

Generalising, to the coefficients of higher order, with the same interpretation of the subscripts, mentioned in the previous paragraph, we can write

$$a_{112} = \frac{\delta a_{12}}{\delta \alpha} = \frac{\delta^2 \bar{Y}}{\delta \alpha^2}$$

$$= \frac{\delta}{\delta \alpha} (\overline{XY} - \bar{X}\,\bar{Y})$$

$$= \frac{\delta}{\delta \alpha} \left(\frac{\iint xy\, e^{\alpha x+\beta y}\, dx\, dy}{\Phi}\right) - \frac{\delta \bar{X}}{\delta \alpha} \cdot \bar{Y} - \bar{X} \cdot \frac{\delta \bar{Y}}{\delta \alpha}$$

$$= \frac{\Phi \iint x^2 y\, e^{\alpha x+\beta y}\, dxdy - \frac{\delta \Phi}{\delta \alpha} \iint xy\, e^{\alpha x+\beta y}\, dx\, dy}{\Phi^2}$$

$$- a_{11}\,\bar{Y} - a_{12}\,\bar{X}$$

$$= \overline{X^2 Y} - \overline{XY}\;\bar{X} - a_{11}\,\bar{Y} - a_{12}\,\bar{X}, \qquad \ldots(5.1)$$

where Φ is given by (2.52).

Now since

$$a_{12} = a_{21}, \qquad \frac{\delta a_{12}}{\delta \alpha} = \frac{\delta a_{21}}{\delta \alpha}$$

$$\therefore \qquad a_{112} = a_{121} \qquad . \qquad \ldots(5.2)$$

Again, assuming that the commutativity of the order of partial differentiation is satisfied for $\bar{X}(\alpha(t), \beta(t))$ and $\bar{Y}(\alpha(t), \beta(t))$, we can write

$$\frac{\delta^2 \bar{X}}{\delta\alpha\ \delta\beta} = \frac{\delta^2 \bar{X}}{\delta\beta\ \delta\alpha}$$

i.e.,
$$a_{121} = a_{211} \quad . \qquad \ldots(5.3)$$

Thus from (5.1), (5.2) and (5.3), we can write,

$$a_{112} = a_{121} = a_{211} = \overline{X^2Y} - \overline{XY}\,\bar{X} - a_{12}\,\bar{X} - a_{11}\,\bar{Y} \qquad \ldots(5.4)$$

Proceeding in the same way, we get,

$$a_{212} = \frac{\delta a_{12}}{\delta\beta}$$

$$= \frac{\delta}{\delta\beta}\,(\overline{XY} - \bar{X}\,\bar{Y})$$

$$= \overline{XY^2} - \overline{XY}\,\bar{Y} - a_{22}\,\bar{X} - a_{21}\,\bar{Y} \quad . \qquad \ldots(5.5)$$

Since

$$a_{12} = a_{21}$$

$$\frac{\delta a_{12}}{\delta\beta} = \frac{\delta a_{21}}{\delta\beta}$$

i.e.,
$$a_{212} = a_{221} \quad . \qquad \ldots(5.6)$$

Again assuming the commutativity of the order of partial derivatives,

$$\frac{\delta^2 \bar{Y}}{\delta\beta\ \delta\alpha} = \frac{\delta^2 \bar{Y}}{\delta\alpha\ \delta\beta} ,$$

i.e., $a_{212} = a_{122}$ . ...(5.7)

Thus, from (5.5), (5.6) and (5.7), we get,

$$a_{212} = a_{122} = a_{221} = \overline{XY^2} - \overline{XY}\ \bar{Y} - a_{22}\ \bar{X} - a_{21}\ \bar{Y} \quad ..(5.8)$$

Now by Taylor's theorem upto second order, we can wbite,

$$\Delta\bar{X} = \left(\frac{\delta\bar{X}}{\delta\alpha}\ \Delta\alpha + \frac{\delta\bar{X}}{\delta\beta}\ \Delta\beta\right) + \frac{1}{2!}\left\{\frac{\delta^2\bar{X}}{\delta\alpha^2}(\Delta\alpha)^2 + 2\frac{\delta^2\bar{X}}{\delta\alpha\ \delta\beta}\ \Delta\alpha\ \Delta\beta + \frac{\delta^2\bar{X}}{\delta\beta^2}(\Delta\beta)^2\right\}$$

...(5.9)

$$\Delta\bar{Y} = \left(\frac{\delta Y}{\delta\alpha}\ \Delta\alpha + \frac{\delta Y}{\delta\beta}\ \Delta\beta\right) + \frac{1}{2!}\left\{\frac{\delta^2\bar{Y}}{\delta\alpha^2}(\Delta\alpha)^2 + 2\frac{\delta^2 Y}{\delta\alpha\ \delta\beta}\ \Delta\alpha\ \Delta\beta + \frac{\delta^2\bar{Y}}{\delta\beta^2}(\Delta\beta)^2\right\}$$

...(5.10)

Writing in the notation, we have adopted,

$$\Delta \bar{X} = (a_{11}\Delta\alpha + a_{21}\Delta\beta) + \frac{1}{2!}(a_{111}(\Delta\alpha)^2 + 2a_{121}\Delta\alpha\,\Delta\beta + a_{221}(\Delta\beta)^2) \quad ...(5.11)$$

$$\Delta \bar{Y} = (a_{12}\Delta\alpha + a_{22}\Delta\beta) + \frac{1}{2!}(a_{112}(\Delta\alpha)^2 + 2a_{122}\Delta\alpha\,\Delta\beta + a_{222}(\Delta\beta)^2) \quad ...(5.12)$$

From (5.4), (5.8), we have

$$a_{121} = a_{112} \quad ...(5.13a)$$

and

$$a_{221} = a_{122} \quad , \quad ...(5.13b)$$

which establish the symmetry relations of second order.

Following the same method, and by Taylor's series considering upto third order,

$$\Delta \bar{X} = (a_{11}\Delta\alpha + a_{21}\Delta\beta) + \frac{1}{2!}(a_{111}\Delta\alpha^2 + 2a_{121}\Delta\alpha\,\Delta\beta + a_{221}\Delta\beta^2) + \frac{1}{3!}(a_{1111}\Delta\alpha^3 + 3a_{1121}\Delta\alpha^2\Delta\beta + 3a_{1221}\Delta\alpha\,\Delta\beta^2 + a_{2221}\Delta\beta^3) \quad ...(5.14)$$

$$\Delta \bar{Y} = (a_{12}\Delta\alpha + a_{22}\Delta\beta) + \frac{1}{2!}(a_{112}\Delta\alpha^2 + 2a_{122}\Delta\alpha\,\Delta\beta + a_{222}\Delta\beta^2) + \frac{1}{3!}(a_{1112}\Delta\alpha^3 + 3a_{1122}\Delta\alpha^2\Delta\beta + 3a_{1222}\Delta\alpha\,\Delta\beta^2 + a_{2222}\Delta\beta^3) \quad ...(5.15)$$

In order to establish the symmetry relations upto third order, we follow the procedure, given below :

Differentiating (5.4) and (5.8) with respect to α , we get respectively,

$$a_{1112} = a_{1121} = a_{1211} \qquad \ldots(5.16)$$

and

$$a_{1212} = a_{1122} = a_{1221} \,. \qquad \ldots(5.17)$$

Now, differentiating (5.8) with respect to β, we get,

$$a_{2212} = a_{2122} = a_{2221} \,. \qquad \ldots(5.18)$$

Again assuming the commutativity property of the partial derivatives, we have,

$$\frac{\delta^3 \bar{Y}}{\delta\alpha\ \delta\beta^2} = \frac{\delta^3 \bar{Y}}{\delta\beta^2\ \delta\alpha}$$

i.e.,

$$a_{1222} = a_{2212} \qquad \ldots(5.19)$$

From (5.18) and (5.19), it follows,

$$a_{2212} = a_{2122} = a_{2221} = a_{1222} \,. \qquad \ldots(5.20)$$

Thus the symmetry relations upto third order, is ensured from (5.16), (5.17) and (5.20), as we have therefrom,

$$\text{(i)} \quad a_{1121} = a_{1112} \qquad \ldots(5.21a)$$

$$\text{(ii)} \quad a_{1221} = a_{1122} \qquad \ldots(5.21b)$$

$$\text{(iii)} \quad a_{2221} = a_{1222} \qquad \ldots(5.21c)$$

5.3 THE SYMMETRY RELATIONS UPTO n^{th} ORDER AND A GENERAL RULE IN THIS CONNECTION.

Using the expansion in Taylor's series upto n^{th} order, we have,

$$\Delta \bar{X} = \left(\frac{\delta \bar{X}}{\delta \alpha} \Delta\alpha + \frac{\delta \bar{X}}{\delta \beta} \Delta\beta\right) + \ldots + \frac{1}{n!} \left(\frac{\delta^n \bar{X}}{\delta \alpha^n} \Delta\alpha^n\right.$$

$$+ {}^nC_1 \frac{\delta^n \bar{X}}{\delta \alpha^{n-1} \delta\beta} \Delta\alpha^{n-1} \Delta\beta + {}^nC_2 \frac{\delta^n \bar{X}}{\delta \alpha^{n-2} \delta\beta^2} \Delta\alpha^{n-2} \Delta\beta^2$$

$$\left. + \ldots + {}^nC_r \frac{\delta^n \bar{X}}{\delta \alpha^{n-r} \delta\beta^r} \Delta\alpha^{n-r} \Delta\beta^r + \ldots + \frac{\delta^n \bar{X}}{\delta \beta^n} \Delta\beta^n\right)$$

$$\ldots(5.22)$$

$$\Delta\overline{Y} = \left(\frac{\delta\overline{Y}}{\delta\alpha}\ \Delta\alpha + \frac{\delta\overline{Y}}{\delta\beta}\ \Delta\beta\right) + \cdots + \frac{1}{n!}\left(\frac{\delta^{n}\overline{Y}}{\delta\alpha^{n}}\ \Delta\alpha^{n}\right.$$

$$+ {}^{n}C_{1}\ \frac{\delta^{n}\overline{Y}}{\delta\alpha^{n-1}\ \delta\beta}\ \Delta\alpha^{n-1}\Delta\beta + {}^{n}C_{2}\ \frac{\delta^{n}\overline{Y}}{\delta\alpha^{n-2}\ \delta\beta^{2}}\ \Delta\alpha^{n-2}\ \Delta\beta^{2}$$

$$\left. + \cdots + {}^{n}C_{r}\ \frac{\delta^{n}\overline{Y}}{\delta\alpha^{n-r}\ \delta\beta^{r}}\ \Delta\alpha^{n-r}\ \Delta\beta^{r} + \cdots + \frac{\delta^{n}\overline{Y}}{\delta\beta^{n}}\ \Delta\beta^{n}\right) .$$

...(5.23)

Using the notation, used in Section-5.2, we get,

$$\Delta\overline{X} = (a_{11}\ \Delta\alpha + a_{21}\ \Delta\beta) + \cdots + \frac{1}{n!}\left(a_{\underbrace{1\cdots1}_{n+1}}\ \Delta\alpha^{n}\right.$$

$$+ {}^{n}C_{1}\ a_{\underbrace{1\cdots1}_{n-1}21}\ \Delta\alpha^{n-1}\ \Delta\beta + {}^{n}C_{2}\ a_{\underbrace{1\cdots1}_{n-2}221}\Delta\alpha^{n-2}\ \Delta\beta^{2}$$

$$+ \cdots + {}^{n}C_{r}\ a_{\underbrace{1\cdots1}_{n-r}\ \underbrace{2\cdots2}_{r}\ 1}\ \Delta\alpha^{n-r}\ \Delta\beta^{r} +$$

$$\left. \cdots + a_{\underbrace{2\cdots2}_{n}1}\ \Delta\beta^{n}\right) \qquad \ldots(5.24)$$

and

$$\Delta\bar{Y} = (a_{12}\ \Delta\alpha + a_{22}\ \Delta\beta) + \dots + \frac{1}{n!}\ (\ a_{\underbrace{1\cdots1}_{n}\,2}\ \Delta\alpha^{n}$$

$$+\ {}^{n}C_{1}\ a_{\underbrace{1\cdots1}_{n-1}\,22}\ \Delta\alpha^{n-1}\ \Delta\beta + {}^{n}C_{2}\ a_{\underbrace{1\cdots1}_{n-2}\ \underbrace{2\cdots2}_{3}}\ \Delta\alpha^{n-2}\,\Delta\beta^{2}$$

$$+ \cdots + {}^{n}C_{r}\ a_{\underbrace{1\cdots1}_{n-r}\ \underbrace{2\cdots2}_{r+1}}\ \Delta\alpha^{n-r}\ \ \Delta\beta^{r}$$

$$+ \cdots + \ a_{\underbrace{2\cdots2}_{n+1}}\ \ \Delta\beta^{n}\ ) \quad . \qquad \dots(5.25)$$

The number of occurrence of the digit 1 or 2 in the subscript is noted at the bottom of the corresponding subscript, e.g.,

$$\frac{\delta^{n}\,\bar{X}}{\delta\alpha^{n-r}\ \delta\beta^{r}} = a_{\underbrace{1\cdots1}_{n-r}\ \underbrace{2\cdots2}_{r}\ 1} \qquad \dots(5.26)$$

$$\frac{\delta^{n}\,\bar{Y}}{\delta\alpha^{n-1}\ \delta\beta} = a_{\underbrace{1\cdots1}_{n-1}\ 22} \qquad \dots(5.27)$$

To establish the symmetry relations of n^{th} order, we are to show,

$$a_{\underbrace{1\cdots1}_{n-r-1}\underbrace{2\cdots2}_{r+1}1} = a_{\underbrace{1\cdots1}_{n-r}\underbrace{2\cdots2}_{r+1}} , \quad \ldots(5.28)$$

for $r = 0,1,2, \ldots, (n-1)$.

(i) For $r = 0$.

Since $a_{21} = a_{12}$

$$\therefore \quad \frac{\delta^{n-1} a_{21}}{\delta \alpha^{n-1}} = \frac{\delta^{n-1} a_{12}}{\delta \alpha^{n-1}}$$

so that

$$a_{\underbrace{1\cdots1}_{n-1}21} = a_{\underbrace{1\cdots1}_{n}2} \quad \ldots(5.29)$$

(ii) For $r = 1$.

As $a_{221} = a_{122} = a_{212}$

then,

$$\frac{\delta^{n-2} a_{221}}{\delta \alpha^{n-2}} = \frac{\delta^{n-2} a_{122}}{\delta \alpha^{n-2}} = \frac{\delta^{n-2} a_{212}}{\delta \alpha^{n-2}}$$

so that,

$$a_{\underbrace{1\cdots1}_{n-2}221} = a_{\underbrace{1\cdots1}_{n-1}22} = a_{\underbrace{1\cdots1}_{n-2}212}$$

i.e.,

$$a_{\underbrace{1\cdots1}_{n-2}221} = a_{\underbrace{1\cdots1}_{n-1}22} . \qquad \ldots(5.30)$$

(iii) For $r = 2$.

We have $a_{212} = a_{221} = a_{122}$

so that,

$$\frac{\delta^{n-2} a_{212}}{\delta \alpha^{n-3} \delta\beta} = \frac{\delta^{n-2} a_{221}}{\delta \alpha^{n-3} \delta\beta} = \frac{\delta^{n-2} a_{122}}{\delta \alpha^{n-3} \delta\beta}$$

i.e.,

$$a_{\underbrace{1\cdots1}_{n-3}2212} = a_{\underbrace{1\cdots1}_{n-3}2221} = a_{\underbrace{1\cdots1}_{n-3}2122} \qquad \ldots(5.31)$$

Again,

$$\frac{\delta^{n} \bar{Y}}{\delta \alpha^{n-2} \delta\beta^{2}} = \frac{\delta^{n} \bar{Y}}{\delta \alpha^{n-3} \delta\beta\ \delta\alpha\ \delta\beta}$$

i.e.,

$$a_{\underbrace{1\cdots1}_{n-2}222} = a_{\underbrace{1\cdots1}_{n-3}2122} . \qquad \ldots(5.32)$$

Thus from (5.31) and (5.32), we get,

$$a_{\underbrace{1\cdots1}_{n-3}\,2212} = a_{\underbrace{1\cdots1}_{n-3}\,\underbrace{2\cdots2}_{3}\,1} = a_{\underbrace{1\cdots1}_{n-3}\,2122} = a_{\underbrace{1\cdots1}_{n-2}\,222}$$

$$\ldots(5.33)$$

Hence,

$$a_{\underbrace{1\cdots1}_{n-3}\,\underbrace{2\cdots2}_{3}\,1} = a_{\underbrace{1\cdots1}_{n-2}\,\underbrace{2\cdots2}_{3}} \qquad \ldots(5.34)$$

(iv) For $r = s$, $0 \quad s \quad n - 1$.

As $a_{21} = a_{12}$

$$\frac{\delta^{n-1} a_{21}}{\delta\alpha^{n-s-1}\,\delta\beta^{s}} = \frac{\delta^{n-1} a_{12}}{\delta\alpha^{n-s-1}\,\delta\beta^{s}}$$

i.e.,

$$a_{\underbrace{1\cdots1}_{n-s-1}\,\underbrace{2\cdots2}_{s+1}\,1} = a_{\underbrace{1\cdots1}_{n-s-1}\,\underbrace{2\cdots2}_{s}\,12} \,. \qquad \ldots(5.35)$$

Again by the commutativity of the order of the partial derivatives,

$$\frac{\delta^{n}\,\overline{Y}}{\delta\alpha^{n-s-1}\,\delta\beta^{s}\,\delta\alpha} = \frac{\delta^{n}\,\overline{Y}}{\delta\alpha^{n-s}\,\delta\beta^{s}}$$

i.e.,

$$a_{\underbrace{1\cdots1}_{n-s-1}\,\underbrace{2\cdots2}_{s}\,12} = a_{\underbrace{1\cdots1}_{n-s}\,\underbrace{2\cdots2}_{s+1}} \,. \qquad \ldots(5.36)$$

(5.35) and (5.36) together imply

$$a_{\underbrace{1\cdots1}_{n-s-1}\,\underbrace{2\cdots2}_{s+1}\,1} = a_{\underbrace{1\cdots1}_{n-s}\,\underbrace{2\cdots2}_{s+1}} \quad . \qquad \ldots(5.37)$$

Proceeding in the similar manner symmetry relation can be proved true for $r = (s + 1), \ldots , (n-1)$.

Thus the symmetry relations of n^{th} order, are established, i.e.,

$$a_{\underbrace{1\cdots1}_{n-r-1}\,\underbrace{2\cdots2}_{r+1}\,1} = a_{\underbrace{1\cdots1}_{n-r}\,\underbrace{2\cdots2}_{r+1}} \; ,$$

$$\text{for} \quad r = 0,1,2, \ldots , (n-1) \; .$$

Hence, the symmetry relations upto any order can be established by using the linear reciprocal relations and the commutativity of the order of partial derivatives.

The procedure followed in this chapter to establish the symmetry relations of higher order leads us to infer the following rule, with the same interpretation of the subscripts, already mentioned, associated with the coefficients of higher order.

The Rule :

All possible permutations of the subscripts associated with the coefficients of the same order, keep the values of the coefficients unchanged, provided the total number of respective subscripts remains invariant, e.g.,

$$a_{\underbrace{1\cdots1}_{n-r}\underbrace{2\cdots2}_{r+1}} = a_{\underbrace{1\cdots1}_{n-r-1}\underbrace{2\cdots2}_{r}12}$$

$$\text{for} \quad r = 0,1,2,\ldots,(n-1).$$

The above result is true corresponding to the symmetry relations of the n^{th} order.

CONCLUDING REMARKS

The results obtained in this chapter ensure that our approach based on the essentially stochastic model is not only worthy to establish important results of linear theory of the irreversible processes, but also useful for deriving symmetry relations of higher order in accordance with the non-linear theory of the same.