

Transformation of Generalized Fluxes and Forces

The entropy production of an irreversible process can be expressed as a sum of products of thermodynamic fluxes and their corresponding generalized forces. The choice of fluxes and forces is not unique. Different sets of fluxes and forces may be used to describe the same physical process, provided that the entropy production remains unchanged.

For a set of irreversible processes, the rate of entropy production may be written as

$$\sigma = \sum_i J_i X_i$$

where J_i is the generalized flux and X_i is its corresponding generalized thermodynamic force.

Chemical Reaction as an Example

For a chemical reaction, the reaction rate is the flux. With the affinity convention used here,

$$A = \sum_i \nu_i \mu_i$$

the entropy production due to the reaction is

$$\sigma = -\frac{Av}{T}$$

Therefore, the generalized flux and generalized force can be chosen as

$$J = v$$

and

$$X = -\frac{A}{T}$$

so that

$$\boxed{\sigma = JX}$$

The negative sign in $X = -A/T$ is a consequence of the affinity convention

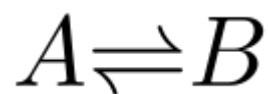
$$A = \sum_i \nu_i \mu_i$$

. If affinity is defined with the opposite sign, the generalized

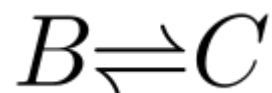
force is correspondingly written as A/T .

Consecutive Reactions

Consider two consecutive reactions

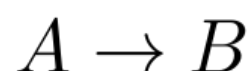


and



Let their reaction rates be v_1 and v_2 , respectively.

For reaction 1, using



the stoichiometric coefficients are

$$\nu_A = -1, \quad \nu_B = +1$$

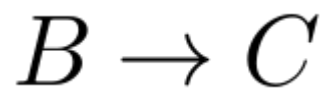
Therefore, with $A = \sum_i \nu_i \mu_i$, its affinity is

$$A_1 = -\mu_A + \mu_B$$

or

$$A_1 = \mu_B - \mu_A$$

For reaction 2,



and therefore

$$\nu_B = -1, \quad \nu_C = +1$$

Hence,

$$A_2 = -\mu_B + \mu_C$$

or

$$A_2 = \mu_C - \mu_B$$

Entropy Production for the Original Set of Reactions

For reaction 1,

$$\sigma_1 = -\frac{A_1 v_1}{T}$$

For reaction 2,

$$\sigma_2 = -\frac{A_2 v_2}{T}$$

Therefore, the total entropy production is

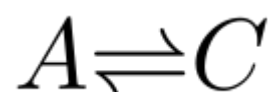
$$\sigma = -\frac{1}{T}(A_1 v_1 + A_2 v_2)$$

or

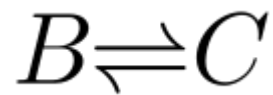
$$T\sigma = -(A_1 v_1 + A_2 v_2)$$

Transformation to Another Set of Reactions

The same overall chemical changes can be represented by another set of reactions. Consider

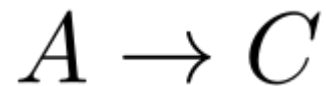


and



Let the corresponding reaction rates be v'_1 and v'_2 .

For the first new reaction,



the affinity is

$$A'_1 = \mu_C - \mu_A$$

Using

$$A_1 = \mu_B - \mu_A$$

and

$$A_2 = \mu_C - \mu_B$$

we obtain

$$A_1 + A_2 = (\mu_B - \mu_A) + (\mu_C - \mu_B)$$

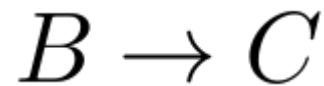
The μ_B terms cancel:

$$A_1 + A_2 = \mu_C - \mu_A$$

Therefore,

$$A'_1 = A_1 + A_2$$

For the second new reaction,



which is actually the same chemical transformation as the original second reaction. Hence,

$$A'_2 = A_2$$

Transformation of Fluxes

For the original consecutive reactions, the changes in the amounts of the species are

$$\frac{dn_A}{dt} = -v_1$$

and

$$\frac{dn_C}{dt} = v_2$$

For species B , reaction 1 produces B , whereas reaction 2 consumes B . Therefore,

$$\frac{dn_B}{dt} = v_1 - v_2$$

For the new reaction scheme, the first reaction $A \rightarrow C$ has rate v'_1 , while the second reaction $B \rightarrow C$ has rate v'_2 .

Thus,

$$\frac{dn_A}{dt} = -v'_1$$

Comparison with

$$\frac{dn_A}{dt} = -v_1$$

gives

$$\boxed{v'_1 = v_1}$$

For species B , the new scheme gives

$$\frac{dn_B}{dt} = -v'_2$$

while the original scheme gives

$$\frac{dn_B}{dt} = v_1 - v_2$$

Therefore,

$$-v'_2 = v_1 - v_2$$

and hence

$$v'_2 = v_2 - v_1$$

Thus, the fluxes are transformed when a different set of independent reactions is chosen.

Invariance of Entropy Production

The new representation must describe the same physical process. Therefore, the entropy production must have the same value.

For the original representation,

$$T\sigma = -(A_1 v_1 + A_2 v_2)$$

For the transformed representation,

$$T\sigma = -(A'_1 v'_1 + A'_2 v'_2)$$

Substituting

$$A'_1 = A_1 + A_2$$

$$A'_2 = A_2$$

$$v'_1 = v_1$$

and

$$v'_2 = v_2 - v_1$$

gives

$$T\sigma = -[(A_1 + A_2)v_1 + A_2(v_2 - v_1)]$$

Expanding the expression,

$$T\sigma = -[A_1v_1 + A_2v_1 + A_2v_2 - A_2v_1]$$

The two terms containing A_2v_1 cancel:

$$T\sigma = -(A_1v_1 + A_2v_2)$$

Therefore,

$$T\sigma_{\text{new}} = T\sigma_{\text{old}}$$

and hence

$$\sigma_{\text{new}} = \sigma_{\text{old}}$$

General Transformation

The example shows that the generalized forces and fluxes can be transformed from one set to another without changing the physical entropy production.

If the original forces and fluxes are X_i and J_i , and the transformed quantities are

X'_i and J'_i , then the fundamental requirement is

$$\sum_i J_i X_i = \sum_i J'_i X'_i$$

This condition is called the **invariance of entropy production**.

Thus, generalized forces may be expressed as suitable linear combinations of the original forces, while the generalized fluxes are transformed correspondingly so that their scalar product, and hence the entropy production, remains unchanged.

The transformation of forces and fluxes is important because the choice of independent irreversible processes is not unique. Different descriptions can therefore be used for the same physical system, provided that the entropy production remains invariant.