We redefine $\alpha_2 = \alpha$, $\alpha_1 = 1 - \alpha$ and use α hereafter as the sole reaction variable. Then from Eqs. (3.27) and (3.28) we get:

$$Tds = de + pdv - (\mu_2 - \mu_1)d\alpha. \tag{3.29}$$

So far we have been looking at an isolated element of mass. But if we assume that this mass element is part of a continuous medium which is in a state of non-uniform stress, strain and motion, then the variables e and v must satisfy the energy and mass conservation equations, (3.4) and (3.5). Substituting these equations into Eq. (3.29) we get:

$$T(ds/dt)_{irrev.} = -vq(\partial u/\partial x) - (\mu_2 - \mu_1)d\alpha/dt \tag{3.30}$$

We assume no heat to be deposited from the outside, so the entropy change is entirely due to the internal irreversible process. It should be noted that the Lagrangian derivative used in Eqs. (3.4) and (3.5) is identical to the convective derivative implied in Eq. (3.30). If we look closely at Eq. (3.30), we can see the sources of irreversibility. These are a chemical affinity $(\mu_2 - \mu_1)$, (25), and a velocity gradient. These quantities are called "forces" in irreversible thermodynamics and are denoted by $X_i(i=1,2...)$. The phenomena caused by these forces, such as phase changes, are called "fluxes" and are described by $J_i(i=1,2...)$. Then Eq. (3.30) becomes:

$$T(ds/dT)_{irrev.} = \sum_{i=1}^{2} J_i X_i \tag{3.31}$$

where

$$X_1 = -\partial u/\partial x \tag{3.32}$$

$$X_2 = -(\mu_2 - \mu_1) \tag{3.33}$$

$$J_1 = qv \tag{3.34}$$

$$J_2 = d\alpha/dt. \tag{3.35}$$

There is some arbitrariness in the choice of terms for forces and fluxes. The above choice is taken from Hirschfelder et al. (26). Another possible combination is:

$$X_1 = -qv$$

$$X_2 = -(\mu_2 - \mu_1)$$

$$J_1 = \partial u/\partial x$$

$$J_2 = d\alpha/dt.$$

When the irreversible entropy change is expressed in terms of forces and fluxes, there are two basic assumptions made. The first is called the linear phenomenological law and the second the Onsager reciprocal relation:

1. Phenomenological law

$$J_i = \sum_{j=1}^{n} g_{ij} X_j \tag{3.36}$$

where g_{ij} are constant.

2. Onsager's reciprocal relation

$$g_{ij} = g_{ji}. \tag{3.37}$$

Then from Eqs. (3.32) through (3.35):

$$d\alpha/dt = g_{11}(\mu_2 - \mu_1) + g_{12}(\partial u/\partial x) \tag{3.38}$$

$$vq = g_{21}(\mu_2 - \mu_1) + g_{22}(\partial u/\partial x) \tag{3.39}$$

where $g_{12} = g_{21}$.