Furthermore, from Eqs. (3.36) and (3.37) we get:

$$T(ds/dt)_{irrev.} = g_{11}X_1^2 + (g_{12}+g_{21})X_1X_2 + g_{22}X_2^2.$$

The second law of thermodynamics requires that the left-hand side is always positive or zero, so we must have the following relations for the constants g_{ij}:

$$g_{11} \geq 0, \quad g_{22} \geq 0$$

$$2\sqrt{g_{11}g_{22}} \geq |g_{12} + g_{21}|.$$

But this is all we get from thermodynamics; it will not give us the magnitudes of the coefficients, because they are characteristic numbers which depend upon materials. A complete understanding of the reaction mechanisms would provide a foundation for calculating the g_{ij}. For the present we assume the reaction rate to be independent of shear stress and set $g_{12} = 0$. g_{11} and g_{22} are chosen from available data and for computational convenience, respectively. Then Eqs. (3.38) and (3.39) reduce to:

$$d\alpha/dt = g_{11}(\mu_2-\mu_1) \tag{3.40}$$

$$q = g_{22}(1/v)(\partial u/\partial x). \tag{3.41}$$

Since we know the chemical affinity $(\mu_2-\mu_1)$ is zero at the equilibrium state, we can find the equilibrium value α^{eq} of α as a function of two independent thermodynamic parameters. For example:

$$\alpha^{eq} = \alpha^{eq}(v, T).$$

Then for a small deviation from equilibrium, we can expand the affinity in a Taylor's series:

$$\mu_2 - \mu_1 = (\mu_2 - \mu_1)^{eq} + \left(\frac{\partial(\mu_2 - \mu_1)^{eq}}{\partial\alpha}\right)_{v,T} (\alpha - \alpha^{eq}) \ \ldots \ .$$

Neglecting the higher-order terms:

$$\mu_2 - \mu_1 = \left(\frac{\partial(\mu_2 - \mu_1)^{eq}}{\partial\alpha}\right)_{v,T} (\alpha - \alpha^{eq}). \tag{3.42}$$

Equations (3.40) and (3.42) give:

$$d\alpha/dt = (\alpha - \alpha^{eq})/\tau \tag{3.43}$$

Where τ is a new constant to be determined from comparisons of calculations with experiments.

Eq. (3.41) shows that q has the character of a viscous force, as stated earlier. It is necessarily proportional to the first power of the strain rate because of the use of the linear phenomenological law. This first-power dependence is retained in the computations, but since its primary purpose is to smooth the shock transition it will be artificially modified after the manner described by Richtmyer and von Neumann (27): The coefficient g_{22} is made proportional to the cell thickness used in the computation. Then

$$q = C_L(\Delta x/v) \ |\partial u/\partial x| \tag{3.44}$$

where C_L = constant.