As more and better data on shock-induced transition become available, it will become important to develop some of the above models to describe the kinetics of phase transformation in shock waves. At present it is barely established that rate effects in shock-induced transformation exist, and we seek no more than a qualitative description of the effects of kinetics on the wave structure and some rough numbers for the magnitude of the reaction rate involved in the observed processes.

To this end we select a quite different approach, which is in some sense better founded, though formally limited to small deviations from equilibrium, in irreversible thermodynamics. In this approach there exist none of the conditions imposed in the above models, and it suggests a simple relaxation law for the transformation.

$$d\alpha/dt = (\alpha^{eq} - \alpha)/\tau \qquad (3.26)$$

where

 $\alpha^{eq}$  = equilibrium value of  $\alpha$ , or a completely relaxed value

 $\tau$  = relaxation time.

The derivation of the above relation from irreversible thermodynamics follows.

When a solid-solid transition occurs reversibly (or in equilibrium) by adiabatic compression, the entropy of a given system is constant and the process is called isentropic. If the transition is not reversible, the entropy will increase. However, ordinary thermodynamics does not give the precise amount

53

of increase; rather, it tells only the direction of increase:

## ds ≥0 irreversible

Basically, the idea of irreversible thermodynamics is to replace the inequality by an equality so that we can determine the increase of entropy caused by irreversible processes.

To establish the desired equality we assume that, although the total system is not in equilibrium, there exists within a small mass element a state of local equilibrium for which the total entropy change per unit mass, ds, is expressed by the Gibb's relation (24).

$$Tds = de + pdv - \sum_{i=1}^{n} \mu_i d\alpha_i \qquad (3.27)$$

where

 $\mu_i$  = partial specific Gibb's function

 $\alpha_i$  = mass fraction of the i-th component.

This means, for the case of a single-component phase transition, that when two phases are not in equilibrium with one another, we interpret them as if they are two different components with different specific Gibb's functions and each is in local equilibrium satisfying Eq. (3.27).

There is an additional constraint on Eq. (3.27) for a single-component system from total mass conservation. Since the total mass is constant:

$$d\alpha_1 + d\alpha_2 = 0.$$
 (3.28)

54