

Thermodynamic Criteria for a Non-Equilibrium State

A thermodynamic system is said to be in a non-equilibrium state when its macroscopic properties are such that an irreversible process can take place. The presence of a difference or gradient in a physical quantity provides the driving force for the process.

For example, if two parts of a system are at different temperatures,

$$T_1 > T_2$$

heat flows from the region at T_1 towards the region at T_2 . The temperature difference is therefore responsible for the heat flow.

Similarly, a difference in concentration produces diffusion, a velocity gradient produces momentum transfer and an electrical potential gradient produces the flow of electric charge.

Thus, the occurrence of an irreversible transport process is associated with two quantities: the **driving force** and the **flux**. The driving force produces the transport, while the flux represents the amount of the transported quantity passing through unit area per unit time.

For a simple transport process, the relation between flux and driving force can be written as

$$J = LX$$

where J is the flux, X is the driving force and L is the proportionality coefficient characteristic of the system.

For heat conduction, the driving force is the temperature gradient and the flux is the heat flux:

$$J_q = -K \frac{dT}{dx}$$

where K is the thermal conductivity. The negative sign indicates that heat flows towards decreasing temperature.

For diffusion, the concentration gradient acts as the driving force:

$$J_m = -D \frac{dc}{dx}$$

where D is the diffusion coefficient.

For momentum transfer, the velocity gradient is responsible for the transport:

$$J_M = -\mu \frac{du}{dx}$$

and for electrical conduction the potential gradient produces an electric flux.

These examples show that a system can be away from equilibrium because different regions of the system possess different values of an intensive property. The resulting gradient tends to disappear as the irreversible process proceeds.

For heat conduction, for instance, if initially

$$T_1 > T_2$$

heat is transferred until the temperature difference becomes zero:

$$T_1 = T_2$$

At this point there is no net heat transfer due to the temperature difference. The system has reached thermal equilibrium.

A chemical reaction provides another type of non-equilibrium process. For a reaction involving several components, the thermodynamic driving force is expressed in terms of the chemical potentials. The corresponding quantity is called the **affinity** of the reaction:

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

where ν_i is the stoichiometric coefficient of the i -th component and μ_i is its chemical potential.

The reaction rate acts as the flux corresponding to this driving force. At chemical equilibrium,

$$A = 0$$

and there is no net progress of the reaction.

Therefore, the thermodynamic criterion for a system to be away from equilibrium is the existence of a non-zero thermodynamic driving force. Depending on the process, this may appear as a temperature gradient, concentration gradient, potential gradient or chemical affinity.

The important transport processes can therefore be represented as

Temperature gradient $\rightarrow$ heat flow

Concentration gradient $\rightarrow$ mass transfer

Velocity gradient $\rightarrow$ momentum transfer

Potential gradient $\rightarrow$ electric current

Chemical affinity $\rightarrow$ chemical reaction