Definition: Reversible process. A process is reversible if carried out in such a way that the system is always infinitesimally close to the equilibrium condition. For example, if the entropy is a function of the volume, any change of volume must be carried out so slowly that the entropy at any volume V is closely equal to the equilibrium entropy $\sigma(V)$. Thus, the entropy is well defined at every stage of a reversible process, and by reversing the direction of the change the system will be returned to its initial condition. In reversible processes, the condition of the system is well defined at all times, in contrast to irreversible processes, where usually we will not know what is going on during the process. We cannot apply the mathematical methods of thermal physics to systems whose condition is undefined.

A volume change that leaves the system in the same quantum state is an example of an isentropic reversible process. If the system always remains in the same state the entropy change will be zero between any two stages of the process, because the number of states in an ensemble (p. 31) of similar systems does not change. Any process in which the entropy change vanishes is an isentropic reversible process. But reversible processes are not limited to isentropic processes, and we shall have a special interest also in isothermal reversible processes.

PRESSURE

Consider a system in the quantum state s of energy ε_s. We assume ε_s to be a function of the volume of the system. The volume is decreased slowly from V to $V - \Delta V$ by application of an external force. Let the volume change take place sufficiently slowly that the system remains in the same quantum state s throughout the compression. The "same" state may be characterized by its quantum numbers (Figure 3.5) or by the number of zeros in the wavefunction.

The energy of the state s after the reversible volume change is

$$\varepsilon_s(V - \Delta V) = \varepsilon_s(V) - (d\varepsilon_s/dV)\Delta V + \cdots . \tag{21}$$

Consider a pressure p_s applied normal to all faces of a cube. The mechanical work done on the system by the pressure in a contraction (Figure 3.6) of the cube volume from V to $V - \Delta V$ appears as the change of energy of the system:

$$U(V - \Delta V) - U(V) = \Delta U = -(d\varepsilon_s/dV)\Delta V. \tag{22}$$