This useful relation will be called the **thermodynamic identity.** The form with N variable will appear in (5.38). A simple transposition gives

$$dU = \tau d\sigma - p dV, \quad \text{or} \quad dU = TdS - p dV. \tag{34b}$$

If the actual process of change of state of the system is reversible, we can identify $\tau d\sigma$ as the heat added to the system and $-pdV$ as the work done on the system. The increase of energy is caused in part by mechanical work and in part by the transfer of heat. **Heat** is defined as the transfer of energy between two systems brought into thermal contact (Chapter 8).

HELMHOLTZ FREE ENERGY

The function

$$\boxed{F \equiv U - \tau\sigma} \tag{35}$$

is called the Helmholtz free energy. This function plays the part in thermal physics at constant temperature that the energy U plays in ordinary mechanical processes, which are always understood to be at constant entropy, because no internal changes of state are allowed. The free energy tells us how to balance the conflicting demands of a system for minimum energy and maximum entropy. The Helmholtz free energy will be a minimum for a system $\mathcal{S}$ in thermal contact with a reservoir $\mathcal{R}$, if the volume of the system is constant.

(1)   We first show that F is an extremum in equilibrium at constant τ and V. By definition, for infinitesimal reversible transfer from $\mathcal{R}$ to $\mathcal{S}$,

$$dF_{\mathcal{S}} = dU_{\mathcal{S}} - \tau d\sigma_{\mathcal{S}} \tag{36}$$

at constant temperature. But $1/\tau \equiv (\partial\sigma_{\mathcal{S}}/\partial U_{\mathcal{S}})_V$, so that $dU_{\mathcal{S}} = \tau d\sigma$ at constant volume. Therefore (36) becomes

$$dF_{\mathcal{S}} = 0 , \tag{37}$$

which is the condition for F to be an extremum with respect to all variations at constant volume and temperature. We like F because we can calculate it from the energy eigenvalues ε_s of the system (see p. 72).