Using $U = \rho V$ and $S = sV$, we can write this as

$$\mathrm{d}\rho - T\,\mathrm{d}s = \big(Ts - \rho - P\big)\frac{\mathrm{d}V}{V} \ . \tag{3.1.55}$$

In equilibrium, the entropy density, energy density and pressure are intensive quantities that can be written as functions only of the temperature, $\rho(T)$, $s(T)$, $P(T)$, so that $\mathrm{d}\rho - T\mathrm{d}s \propto \mathrm{d}T$. The coefficients of the $\mathrm{d}T$ and $\mathrm{d}V$ terms must vanish separately because one is intensive (independent of volume) and the other is extensive (depends on the size of the system). For example, one could consider a volume change at constant temperature, $\mathrm{d}T = 0$, which implies that the coefficient of $\mathrm{d}V$ term must be zero. This relates the entropy density to the energy density and pressure

$$s = \frac{\rho + P}{T} \ . \tag{3.1.56}$$

Using (3.1.35) and (3.1.45), the total entropy density for a collection of different particle species is

$$s = \sum_i \frac{\rho_i + P_i}{T_i} \equiv \frac{2\pi^2}{45} g_{\star S}(T) T^3 \ , \tag{3.1.57}$$

where we have defined the *effective number of degrees of freedom in entropy*,

$$g_{\star S}(T) = g_{\star S}^{th}(T) + g_{\star S}^{dec}(T) \ . \tag{3.1.58}$$

Note that for species in thermal equilibrium $g_{\star S}^{th}(T) = g_\star^{th}(T)$. However, given that $s_i \propto T_i^3$, for decoupled species we get

$$g_{\star S}^{dec}(T) \ \equiv \ \sum_{i=b} g_i \left(\frac{T_i}{T}\right)^3 \ + \ \frac{7}{8}\sum_{i=f} g_i \left(\frac{T_i}{T}\right)^3 \ \neq \ g_\star^{dec}(T) \ . \tag{3.1.59}$$

Hence, $g_{\star S}$ is equal to $g_\star$ only when *all* the relativistic species are in equilibrium at the same temperature. In the real universe, this is the case until $t \approx 1$ sec.

In cosmology, the conservation of entropy is a more useful conservation law than the conservation of energy. In particular, entropy is conserved in equilibrium and hence $sa^3 = const.$

Proof.—Consider the time derivative of sa^3,

$$\begin{aligned} \frac{T}{a^3}\frac{d(sa^3)}{dt} &= \frac{T}{a^3}\frac{d}{dt}\left(\frac{\rho+P}{T}a^3\right) \\ &= \frac{d\rho}{dt} + 3\frac{\dot a}{a}(\rho + P) + \frac{dT}{dt}\left(\frac{dP}{dT} - \frac{\rho+P}{T}\right) \\ &= \frac{dT}{dt}\left(\frac{dP}{dT} - \frac{\rho+P}{T}\right) \ , \end{aligned} \tag{3.1.60}$$

where we have used the continuity equation (1.3.98) to go from the second to the third line. To show that (3.1.60) vanishes, we consider the definition of P

$$\frac{dP}{dT} = \frac{g}{2\pi^2}\int \mathrm{d}p\, \frac{df}{dT}\frac{p^4}{3E} \ . \tag{3.1.61}$$

Since $f(E/T)$, we use $df/dT = -(E/T)\, df/dE = -(E^2/Tp)\, df/dp$ to write (3.1.61) as

$$\frac{dP}{dT} = -\frac{1}{T} \times \frac{g}{6\pi^2}\int \mathrm{d}p\, Ep^3 \frac{df}{dp} \ . \tag{3.1.62}$$