
Basic Thermodynamics

Handout 3

Entropy

$\bar{d}Q_{\text{rev}}/T$ is an exact differential, so

$$dS = \bar{d}Q_{\text{rev}}/T,$$

where S is a function of state which we call **entropy**.

In general, from Clausius' theorem,

$$dS \geq \frac{\bar{d}Q}{T},$$

which means that for a thermally isolated system ($\bar{d}Q = 0$)

$$dS \geq 0$$

and so entropy either increases (irreversible processes) or stays the same (reversible processes).

Application to the Universe:

First Law: The energy of the Universe is a constant.

Second Law: The entropy of the Universe can only increase.

The entropy form of the First Law:

For a p - V system,

$$\boxed{dU = T dS - p dV}.$$

Note that:

$dU = \bar{d}W + \bar{d}Q$	always true
$\bar{d}W = -p dV$	only true for reversible changes
$\bar{d}Q = T dS$	only true for reversible changes
$dU = T dS - p dV$	always true

For irreversible changes:

$$\bar{d}Q \leq T dS, \quad \bar{d}W \geq -p dV$$

A **Joule expansion** is an example of an irreversible process. In a Joule expansion, a gas expands irreversibly from a volume V_1 into a volume V_2 (initially a vacuum), so that the total volume of the gas after expansion is $V_1 + V_2$. The system is thermally isolated and no external work is done on the gas, so $\Delta U = 0$.

The entropy change in a Joule expansion is (for 1 mole),

$$\Delta S_{\text{gas}} = R \ln \left(\frac{V_1 + V_2}{V_1} \right).$$