Basic Thermodynamics

Handout 4

Entropy

$đQ_{\text{rev}}/T$ is an exact differential, so we define

$$\mathrm{d}S = đQ_{\text{rev}}/T,$$

where S is a function of state which we call **entropy**. In general, from Clausius' theorem,

$$\mathrm{d}S \geq \frac{đQ}{T},$$

which means that for a thermally isolated system ($đQ = 0$)

$$\mathrm{d}S \geq 0$$

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,

$$\boxed{\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V}.$$

This is also known as the **fundamental equation of thermodynamics**.

Note that:

$\mathrm{d}U = đW + đQ$	always true
$đW = -p\,\mathrm{d}V$	only true for reversible changes
$đQ = T\,\mathrm{d}S$	only true for reversible changes
$\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V$	always true

For irreversible changes:

$$đQ \leq T\,\mathrm{d}S, \qquad đW \geq -p\,\mathrm{d}V$$

A **Joule expansion** is an example of an irreversible process. In a Joule expansion, a gas expands irreversibly from a chamber A of volume V_{A} into an evacuated chamber B of volume V_{B}, so that he initial volume of the gas is $V_1 = V_{\text{A}}$ and the final volume $V_2 = V_{\text{A}} + V_{\text{B}}$. 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),

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