

Free energy stored and retrieved [tln18]

Consider a classical ideal gas confined to a cylinder with walls in thermal equilibrium with a heat reservoir at temperature T .

Reversible cyclic process:

1. Push the piston in from position 1 to position 2 quasi-statically.
The work on the system is done reversibly.

$$\Delta W_{12} = \int_1^2 F dx = \int_1^2 dA = \int_1^2 (-SdT - pdV) \text{ with } dT = 0, dV < 0.$$

$$\Rightarrow \Delta W_{12} = A_2 - A_1 > 0.$$

The work done is equal to the excess Helmholtz potential (free energy).

2. Move the piston out from position 2 to position 1 quasi-statically.

$$\Delta W_{21} = \int_2^1 dA = \int_2^1 (-SdT - pdV) \text{ with } dT = 0, dV > 0.$$

$$\Rightarrow \Delta W_{21} = A_1 - A_2 = -\Delta W_{12} < 0.$$

All the energy stored (in the form free energy) is converted back into work done by the system.

Irreversible cyclic process:

1. Push the piston in from position 1 to position 2 rapidly.
The initial and final equilibrium states are the same as previously, but the process requires more work. The gas heats up, which produces a larger pressure than in the quasi-static process.

$$\Rightarrow \Delta W_{12} > A_2 - A_1 > 0.$$

Only part of the work done on the system is stored as free energy.

2. (a) Move the piston out from position 2 to position 1 quasi-statically.

$$\Rightarrow |\Delta W_{21}| = |A_1 - A_2| < |\Delta W_{12}|.$$

All the free energy is converted back into work but that amount is smaller than the work previously done on the system.

- (b) Move the piston out from position 2 to position 1 rapidly.

$$\Rightarrow |\Delta W_{21}| < |A_1 - A_2| < |\Delta W_{12}|.$$

Only part of the available free energy is converted back into work, where the full amount of free energy is only part of the work previously done on the system.