Basic Thermodynamics

Handout 2

Definitions

System = whatever part of the Universe we select.

Open systems can exchange particles with their surroundings. **Closed** systems cannot.

An **isolated** system is not influenced from outside its boundaries.

A **Thermodynamic process** is when a system undergoes a series of changes.

A **quasistatic** process is one carried out so slowly that the system passes throughout by a series of equilibrium states so is always in equilibrium. A process which is quasistatic and has no hysteresis is said to be **reversible**.

An **irreversible** process involves friction (i.e. dissipation).

Isothermal = at constant temperature.

Isentropic = at constant entropy.

Isovolumetric = at constant volume.

Isobaric = at constant pressure.

Adiathermal = without flow of heat. A system bounded by adiathermal walls is **thermally isolated**. Any work done on such a system produces an adiathermal change.

Diathermal walls allow flow of heat. Two systems separated by diathermal walls are said to be **in thermal contact**.

Adiabatic = adiathermal and reversible.

Put a system in thermal contact with some new surroundings. Heat flows and/or work is done. Eventually no further change takes place: the system is said to be in a state of **thermal equilibrium**.

Thermodynamic state: a system is in a "thermodynamic state" if macroscopic observable properties have fixed, definite values, independent of 'how you got there'. These properties are **variables of state** or **functions of state**. Examples are volume, pressure, temperature etc. In thermal equilibrium these variables of state have no time dependence.

Functions of state can be:
(a) **Extensive** (proportional to system size) e.g. energy, volume, magnetization, mass;
(b) **Intensive** (independent of system size) e.g. temperature, pressure, magnetic field, density.

Total work done on a system and total heat put into a system are **not** functions of state — you cannot say a system has a certain amount of heat, or a certain amount of work.

Equation of state = an equation which connects functions of state: for a gas this takes the form $f(p, V, T) = 0$. An example is the equation of state for an ideal gas: $pV = nRT$.

Second Law of Thermodynamics

Clausius' statement:

No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

Kelvin's statement:

No process is possible whose sole result is the complete conversion of heat into work.

Heat engines

A **Heat engine** is a cyclic process which converts heat into work. The efficiency of a heat engine is

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1},$$

where Q_1 = heat in, Q_2 = heat out, and W = work out.

The Carnot engine

Carnot engine An idealized heat engine which uses a perfect gas as the working substance and which operates between two temperatures T_1 and T_2 ($T_1 > T_2$). The engine operates the **Carnot cycle**, which comprises simple isothermal and adiabatic processes:

A $\rightarrow$ B: Isothermal expansion at T_1; heat Q_1 enters.
B $\rightarrow$ C: Adiabatic expansion.
C $\rightarrow$ D: Isothermal compression at T_2; heat Q_2 expelled.
D $\rightarrow$ A: Adiabatic compression back to original volume.

The amount of heat entering and leaving during the first and third steps are related by

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Carnot realised that the efficiency is maximised if all processes are reversible:

$$\eta_{\text{Carnot}} = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1},$$

where T_1 is the temperature of the hotter reservoir, and T_2 is the temperature of the colder reservoir.

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