Heat Capacity

• The amount of heat required to raise a certain mass of a material by a certain temperature is called heat capacity.
  • Heat capacity can be measured at constant pressure ($C_p$):
    \[ C_p = \left( \frac{\partial E}{\partial T} \right)_p \]
  • Heat capacity at constant Volume ($C_v$):
    \[ C_v = \left( \frac{\partial E}{\partial T} \right)_v \]

• Example: Water with a high heat capacity of 75 J/(mol·K) (15 °C, 101.325 kPa) heats up slowly as compared to air (with a heat capacity, $C_p = 29.07$ J/K/mole) ⇒ this implies that oceans will heat up slowly as compared to the atmosphere.
• As $T$ is close to 0 K, the heat capacity tends to zero. Near 0 K very little heat is required to raise the temperature of a sample.

Perpetual machine of the first kind

• Without any input energy, can this machine rotate automatically and do work for others forever?

No! It violates the first law of thermodynamics. Energy can not be created!
First law of Thermodynamics

• What first law of thermodynamics tells us are
  • Total energy is conserved.
  • the possible / permitted states of the thermodynamical system
  • Heat and work can be transformed from each other.

• What first law of thermodynamics doesn’t tell us is
  • the direction of the process

Reversible and irreversible processes

• Reversible

• Irreversible
The second law of thermodynamics

• It states it is impossible to build a cyclic machine that converts heat (random molecular motion) into work (ordered motion) with 100% efficiency. (Kelvin’s statement)

• The system always tends to lose ordering if there is no any work or heat from outside.

• Entropy ($S$) is such a thermodynamic parameter to evaluate the ordering of a system. Small entropy indicates a high ordering.

The second law of thermodynamics

• Heat does not ‘flow’ from a colder body to a hotter body, without an concomitant change outside of the two bodies. (Clausius’s statement)

• Because the ‘flow of heat’ from a colder body to a hotter body is NOT a spontaneous process.

\[ \Delta S < 0 \]

• Surrounding needs to do work for this heat transfer, which will result in the change of surrounding.
Perpetual machine of the second kind

• Perpetual machine of the second kind is able to absorb all the heat caused by the friction between it and ground, and then totally convert the absorbed heat into kinetic energy. In that way, it can keep moving on forever. Will it come true?

No! Although it obeys the first law of thermodynamics, but the energy conversion from heat into kinetic energy cannot reach 100%. It will slow down and finally stop.

Open, closed and isolated systems

• Open system
  Both matter and energy exchange between system and surrounding

• Closed system
  Only energy exchange between system and surrounding

• Isolated system
  Neither matter nor energy exchange between system and surrounding
Entropy change

- For spontaneous processes in an isolated system:
  \[ \Delta S \geq 0 \]
- \( \Delta S \): entropy change of the system
- reversible (isentropic) process: \( \Delta S = 0 \) (ideal)
- irreversible process: \( \Delta S > 0 \)

Heat engine

- A device that converts heat energy to work

\[ W = Q_{\text{hot}} - Q_{\text{cold}} \]
The efficiency of a heat engine

- The efficiency of a heat engine is the amount of work output divided by the amount of heat input.

\[ \eta_{\text{heat engine}} = \frac{W_{\text{output}}}{q_{\text{input}}} \]

- This efficiency depends only on the ratio of the temperature of the sink to the temperature of the source. The maximum efficiency achievable is given by the formula below.

\[ \eta_{\text{heat engine}}^{\text{max}} = 1 - \left( \frac{T_{\text{sink}}}{T_{\text{source}}} \right) \]

The Carnot Cycle