1 Macroscopic Parameters and their measurement

1.1 Work & internal energy

From the first law of thermodynamics we always talk about

$$Q = \Delta \bar{E} + W$$

Given a system, work is easy measure i.e. we integrate

$$W = -\int p \mathrm{d}V$$

Measure of internal energy

• Thermal isolation case: Q = 0

$$\Delta \bar{E} = \bar{E}_b - \bar{E}_b = -W_{ab} = \int_a^b dW$$

e.g. a thermally isolated piston goes from state a to b.

1.2 Heat

The heat absorbed by a system going from macrostate a to b is simply

$$Q_{ab} = (\bar{E}_b - \bar{E}_a) + W_{ab}$$

Example A superconducting circuit A is connected to the circuit B with a resistor. Adding $20\,\mu\text{W}$ of heat to the system: we actually are doing work on a resistor.

Method of Mixers (Comparison Method)

Bring system A into contact with system B that has a known relation between its internal energy and some parameters (T).

$$Q_A = \Delta \bar{E}_B = -Q_B$$

e.g. system A is submerged in water B and we can measure the change in internal energy of water quite easily.

1.3 Entropy

We define entropy S

$$dS = \frac{dQ}{T}$$

and Absolute entropy from the 3rd law

$$T \to 0$$
, $S \to S_0$

Example: Tin

Two structures of a solid:

- 1. White tin—a metal \rightarrow stable > 298 K
- 2. Grey tin—semiconductor \rightarrow stable < 298 K

Thus it requires some amount of heat Q to transform from grey to white tin.

• Case 1: a mole of white tin from $T=0\to T_0$ with specific heat $C^{(w)}(T)$

$$S^{(w)}(T_0) = S^{(w)}(T=0) + \int_0^{T_0} \frac{C^{(w)}(T)}{T} dT$$

• Case 2: Grey tin from 0 K \rightarrow T_0 and then it transforms to white tin quasi-statically. It absorbs heat Q and the entropy change is

$$S^{(w)}(T_0) = S^{(g)}(T=0) + \int_0^{T_0} \frac{C^{(g)}(T)}{T} dT + \frac{Q}{T_0}$$

where

$$S^{(g)}(T=0) = S^{(w)}(T=0) = S_0$$



Figure 1.1: Mole of Tin (DALL-E 3)