Chapter 4

Macroscopic parameters and their measurement

Feng Zhe

4.1 Work and internal energy

$$W = \int_{V_i}^{V_f} \bar{p}(V)\, dV$$

$$\Delta \bar{E} = -W$$

$$\bar{E}_b - \bar{E}_a = -W_{ab} = -\int_a^b đW$$

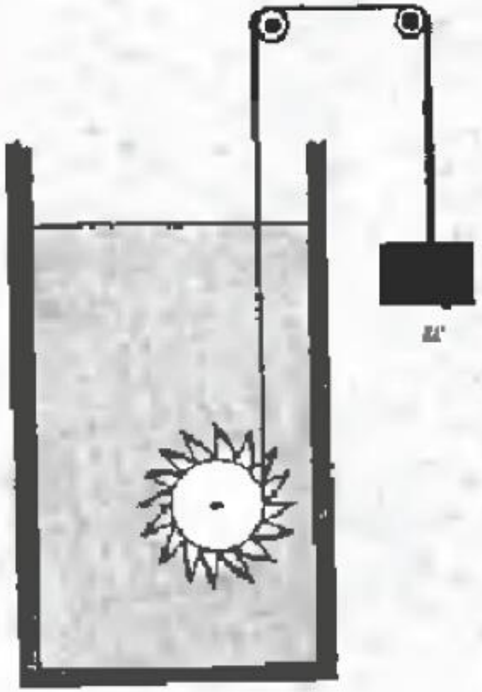


Fig. 2·7·5 A system consisting of a vessel containing a liquid and a paddle wheel. The falling weight can perform work on the system by rotating the paddle wheel.

4.1 Work and internal energy

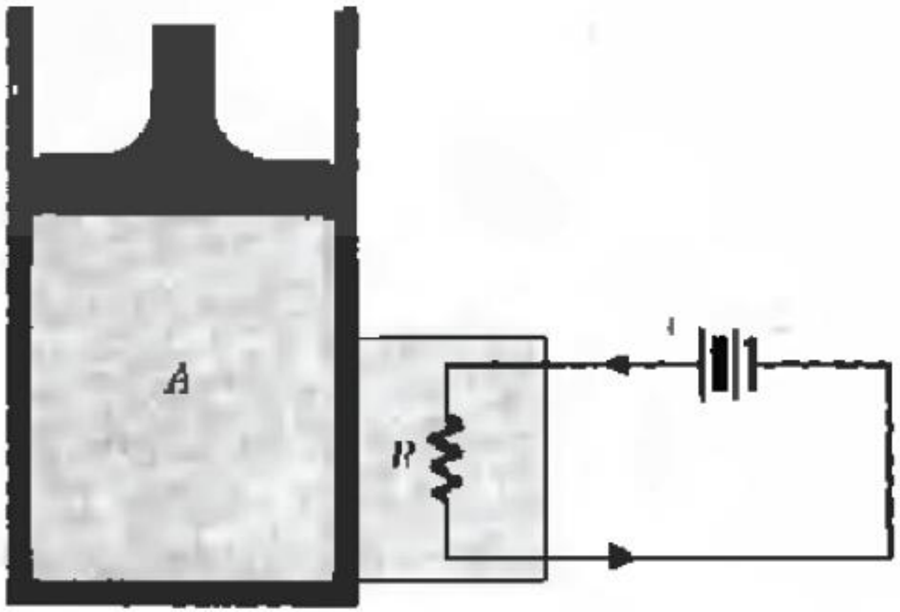


Fig. 4-1-2 A system consisting of a cylinder containing a gas. The volume V of the gas is determined by the position of the movable piston. The resistor R can be brought into thermal contact with this system.

$$\bar{E}_b = \bar{E}_a - W_{ac} + (\mathcal{W} - \Delta\bar{\epsilon})$$

$\Delta\bar{\epsilon}$: the change in mean energy of the resistor

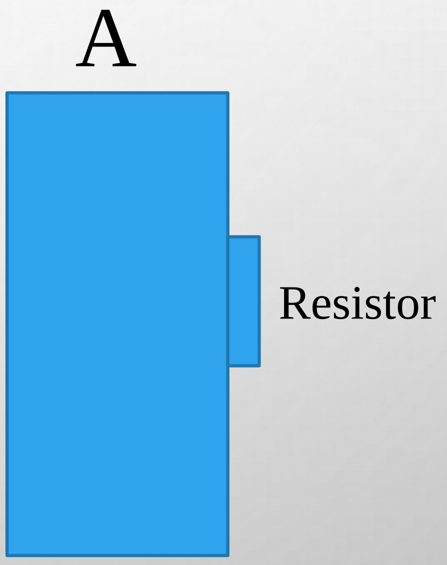
4.2 Heat

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

(1) Direct measurement in terms of work

$$\mathcal{W} = \Delta\bar{E} + \Delta\bar{\epsilon}$$

$$Q_{ab} = \Delta\bar{E}$$
$$Q_{ab} = \mathcal{W} - \Delta\bar{\epsilon}$$



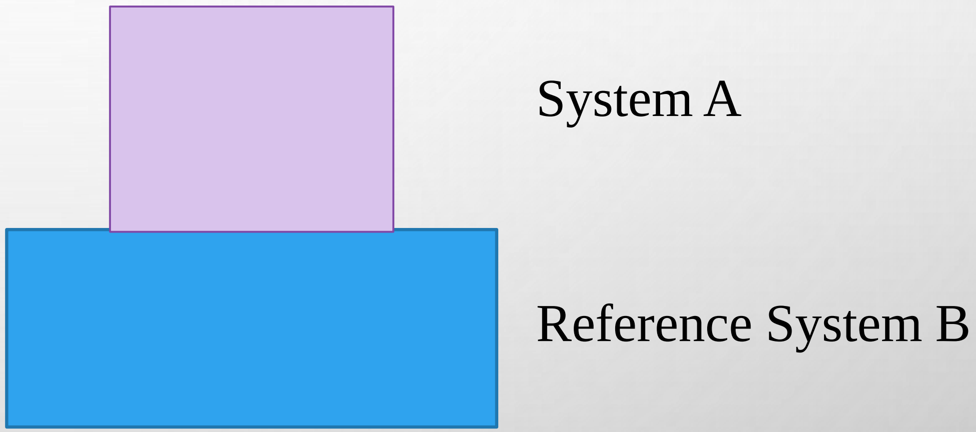
4.2 Heat

(2) Method of mixture

$$\Delta \bar{E}_A + \Delta \bar{E}_B = 0$$

$$Q_A + Q_B = 0$$

$$Q_A = -Q_B$$

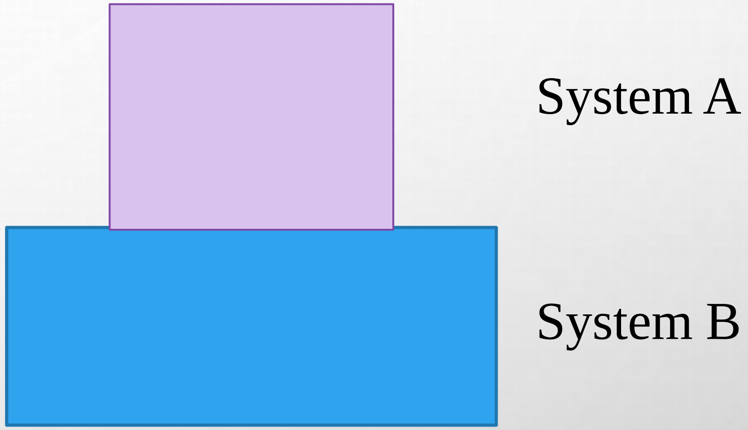


4.3 Heat capacity

$$C \equiv \frac{Q}{\Delta T}.$$

$$C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$



For a given amount of heat absorbed, $c_p > c_v$

4.4 Enthalpy

$$H \equiv U + PV.$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

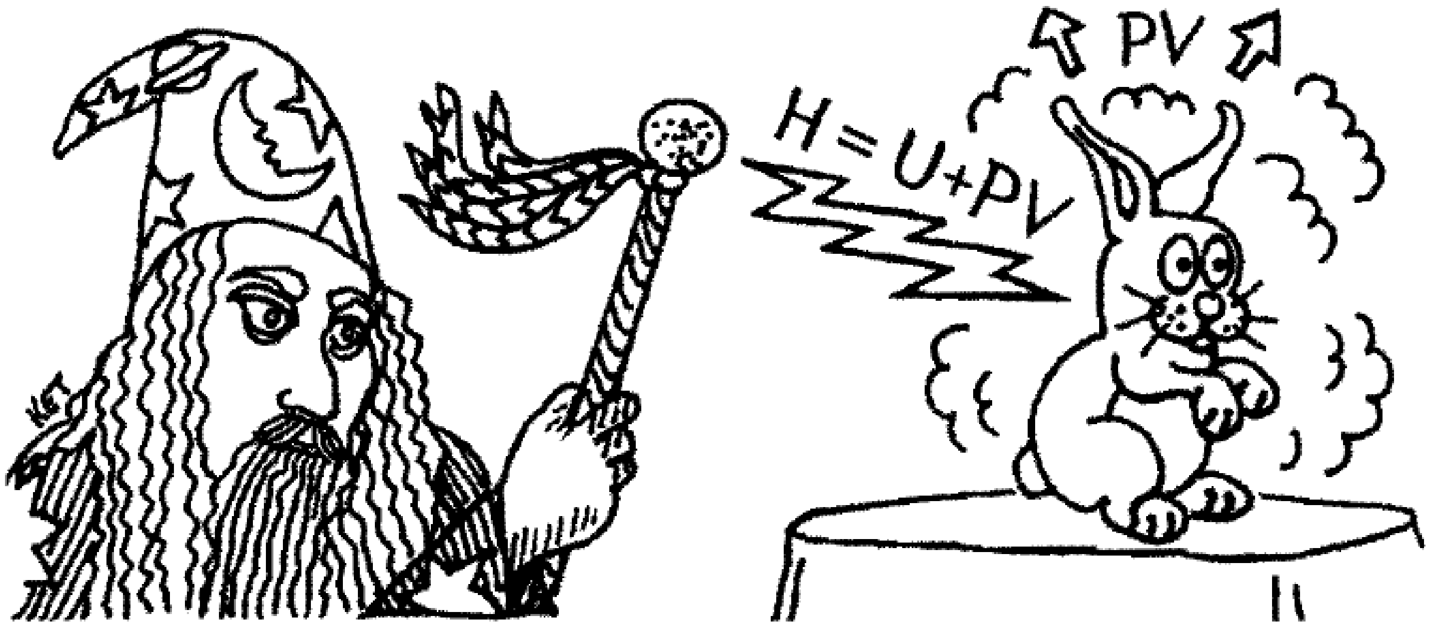


Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

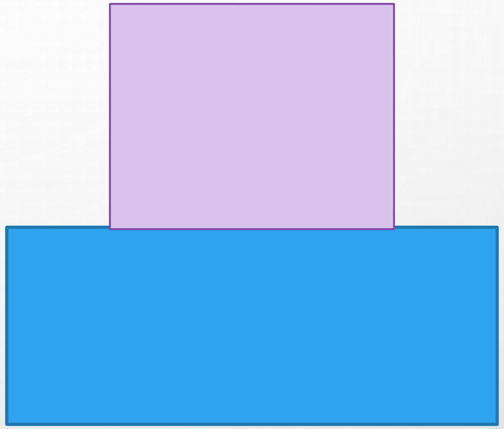
4.5 Entropy

$$dS = \frac{dQ}{T}$$ (reversible process)

$$S_b - S_a = \int_{\substack{a \\ (\mathrm{eq})}}^{b} \frac{dQ}{T}$$

$$S(T_b) - S(T_a) = \int_a^b \frac{dQ}{T} = \int_{T_a}^{T_b} \frac{C_V(T')\, dT'}{T'}$$

$$S(T_b) - S(T_a) = C_V \ln \frac{T_b}{T_a}$$



4.5 Entropy

$$\Delta S_A = S_A(T_f) - S_A(T_A) = \int_{T_A}^{T_f} \frac{m_A c_A' \, dT}{T} = m_A c_A' \ln \frac{T_f}{T_A}$$

$$\Delta S_A + \Delta S_B = m_A c_A' \ln \frac{T_f}{T_A} + m_B c_B' \ln \frac{T_f}{T_B}$$

$$\ln x \le x - 1 \qquad (= \text{sign for } x = 1)$$
$$-\ln x \ge -x + 1$$

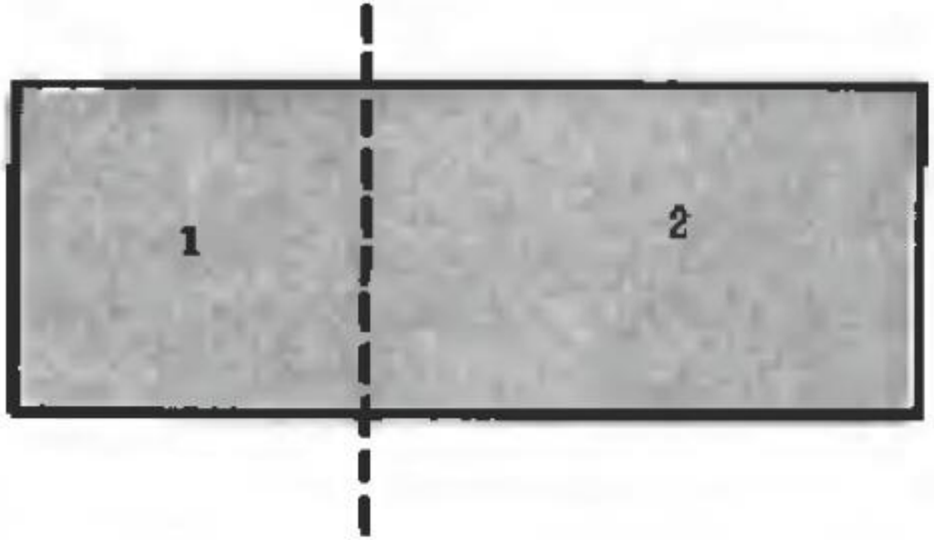
$$\ln y \ge 1 - \frac{1}{y} \qquad (= \text{sign for } y = 1)$$

$$\begin{aligned} \Delta S_A + \Delta S_B &\ge m_A c_A' \left(1 - \frac{T_A}{T_f}\right) + m_B c_B' \left(1 - \frac{T_B}{T_f}\right) \\ &= T_f^{-1}[m_A c_A'(T_f - T_A) + m_B c_B'(T_f - T_B)] \\ &= 0 \qquad \text{by (4·4·13)} \end{aligned}$$

Thus $\quad \Delta S_A + \Delta S_B \ge 0$

4.6 Extensive and intensive parameters

1. $y_1 + y_2 = y$: extensive
2. $y_1 = y_2 = y$: intensive



Extensive parameters: V, M, E, C, S, etc
Intensive parameters: ρ, P, T, etc

$$\frac{Extensive\ parameter\ 1}{Extensive\ parameter\ 2} = Intensive\ parameter$$

Thank you!!