

Chapter 3

The second Law of Thermodynamics

3.1 Introduction

The first law: $\Delta U = q - W$

: Work and heat determine the change in U.



Introduction of a state function, **entropy, S**, for
the **quantification of the degree of irreversibility** of a process

3.2 Spontaneous or natural processes

A system (1) remains in the state or (2) tends to move toward equil'm.



eg., the mixing of two gases, the equalization of temperature

In thermodynamics, the determination of the equilibrium state is an important issue.

3.2 Spontaneous or natural processes

And the reaction proceeds in a certain direction until it reaches equilibrium.

The capacity of the system for further spontaneous change decreases.



3.3 Entropy and the Quantification of Irreversibility



When the weight-heat reservoir system undergoes a **spontaneous process** which causes the absorption of heat q at the constant temperature T , the entropy produced by the system, ΔS , is given by

$$\Delta S = \frac{q}{T} \quad (\text{eq.3.1})$$

3.3 Entropy and the Quantification of Irreversibility

Lewis and Randall* considered the following three processes:

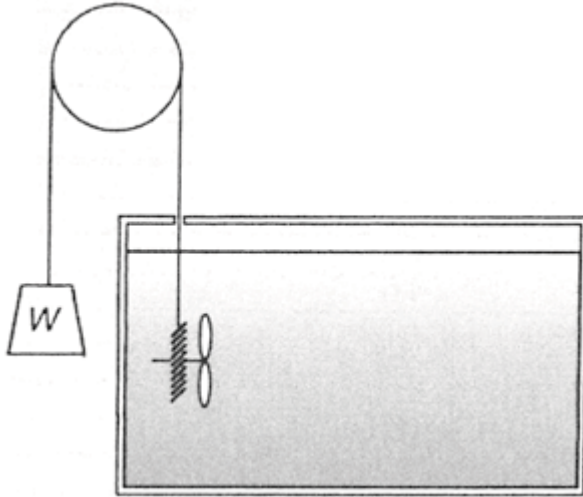
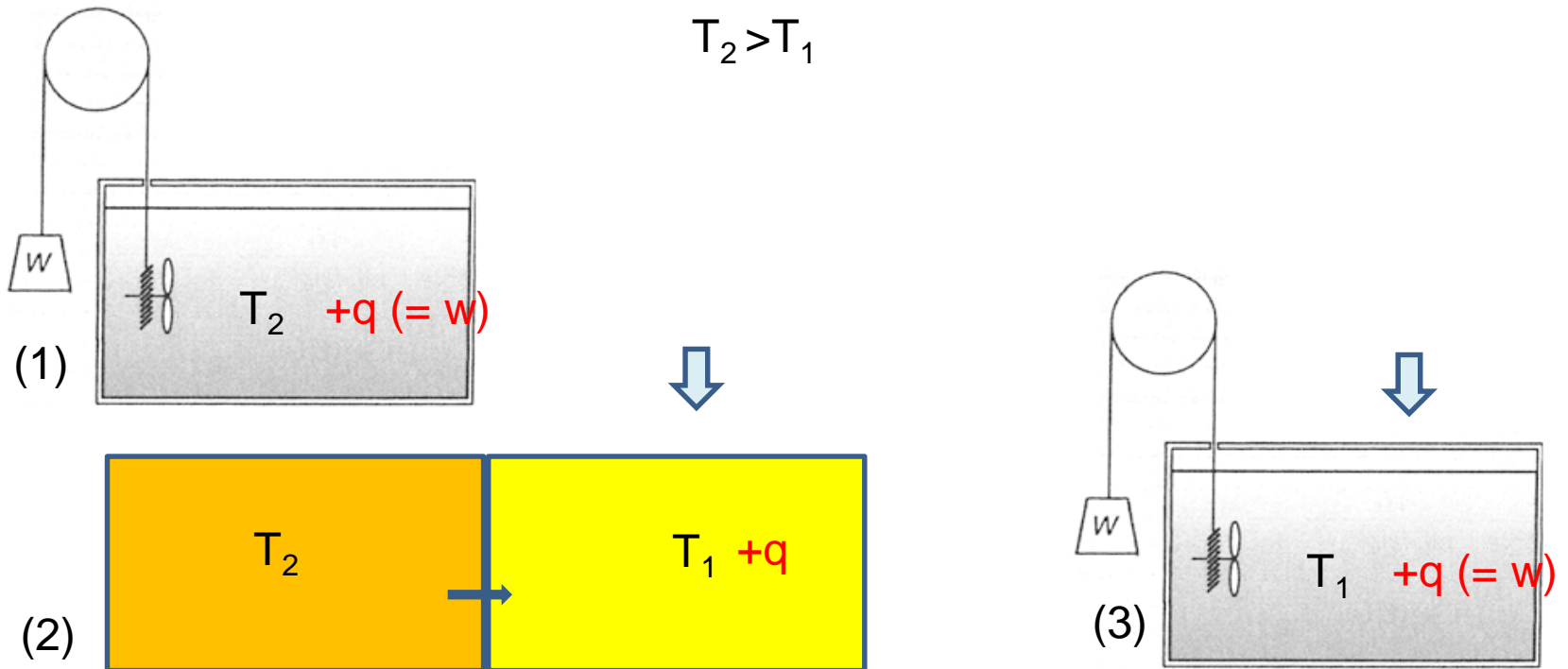


Figure 3.1 A weight pulley-heat reservoir arrangement in which the work done by the falling weight is degraded to heat, which appears in the heat reservoir

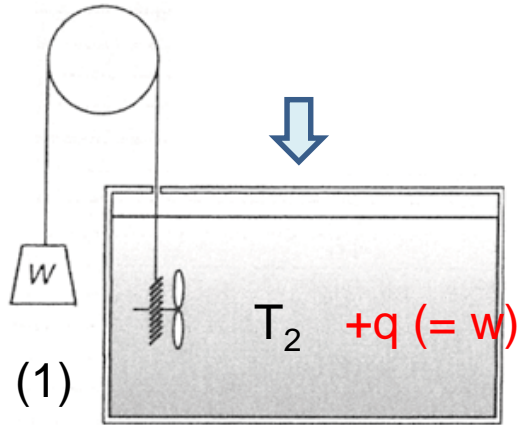
1. The heat reservoir in the weight-heat reservoir system is at the temperature T_2 . The weight is allowed to fall, performing work, w , and the heat produced, q , enters the heat reservoir.
2. The heat reservoir at the temperature T_2 is placed in thermal contact with a heat reservoir at a lower temperature T_1 , and the same heat q is allowed to flow from the reservoir at T_2 to the reservoir at T_1 .
3. The heat reservoir in the weight-heat reservoir system is at the temperature T_1 . The weight is allowed to fall, performing work, w , and the heat produced, q enters the reservoir.

3.3 Entropy and the Quantification of Irreversibility

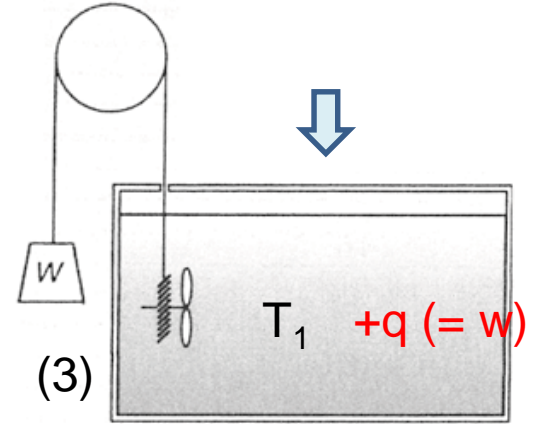


Which one is more irreversible?

3.3 Entropy and the Quantification of Irreversibility



$$T_2 > T_1$$



3.4 Reversible Processes

The magnitude of irreversibility depends on a process.

Then, there should be a way for the process to be conducted with min. Irreversibility.



3.4 Reversible Processes

If there is a reversible process from the state A to the state B,



If the direction of minute external force is reversed, the direction of the process reverses.

3.5 An Illustration of Irreversible and Reversible Processes

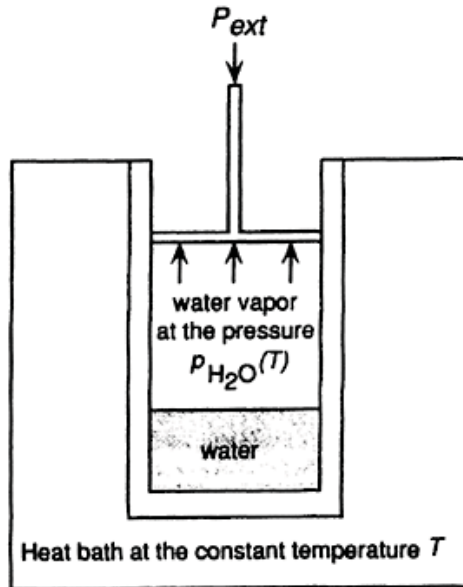


Figure 3.2 A thermo stalled piston and cylinder containing water and water vapor.

Equilibrium



When $P = P_{ext} - \Delta P$

- (1) P_{ext} is suddenly decrease by ΔP
- (2) evaporation of water ($=V$), causing temp. gradient between piston and reservoir. (endothermic rxn)
- (3) heat flow from reservoir to get back to the equilibrium

3.5 An Illustration of Irreversible and Reversible Processes

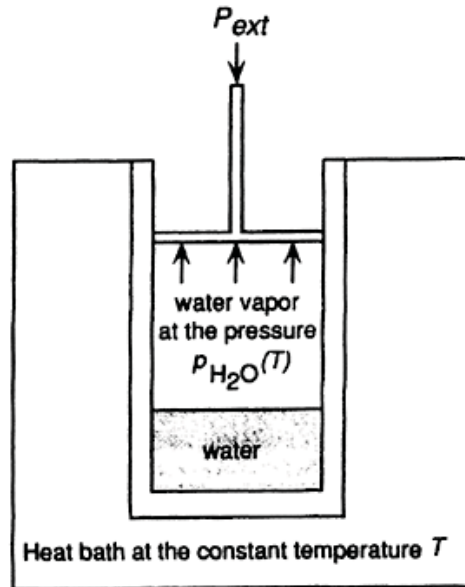


Figure 3.2 A thermo stalled piston and cylinder containing water and water vapor.

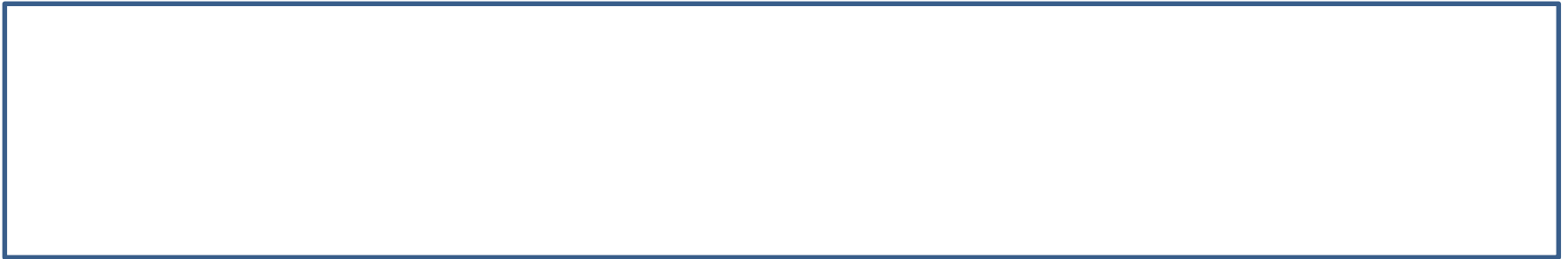
When $P = P_{ext} + \Delta P$

The process can be conducted reversibly, maintaining equilibrium.

Reversibility is approached when the evap. or condensation are carried out infinitesimally.

3.6 Entropy and Reversible Heat

Consider only the evaporation process.



ΔU is independent of whether the process is carried out reversible or not.

From the 1st law

If it is reversible, max. amount of heat, q_{rev} , enters the cylinder from the heat reservoir. $q_{\text{rev}} = \Delta U + w_{\text{max}}$

If irreversible, $q = \Delta U + w$. $q < q_{\text{rev}}$

3.6 Entropy and Reversible Heat

The difference between the works obtained in the reversible & irreversible Process, ($w_{\text{max}} - w$), is the mechanical energy degraded to the thermal Energy (heat) in the cylinder as a result of irreversible process.

Disturbance in water molecules- molecular interaction-push-pull, kinetic energy

(i) The rev. evaporation $\Delta S_{\text{heat reservoir}} = - \frac{q_{\text{rev}}}{T}$

3.6 Entropy and Reversible Heat

(ii) the evaporation is carried out irreversibly

$$\Delta S_{\text{heat reservoir}} = -\frac{q}{T} \quad q < q_{\text{rev}}$$

Total heat appearing in the cylinder = q from the reservoir + heat produced by degradation of work due to the irr. nature of process

$$\Delta S_{\text{water + vapor}} = \frac{q}{T} + \Delta S_{\text{irr}} \quad (\text{eq.3.2})$$

(iii) If reversible condensation occurs, W_{\min} (work done on the system has a min. value) $q_{\text{rev}} = W_{\min}$ (heat leaving the cylinder)



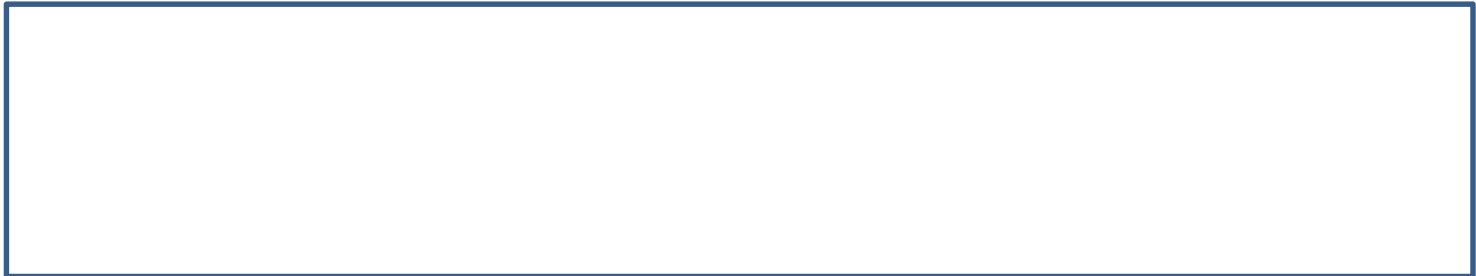
$$\Delta S_{\text{total}} = 0$$

(iv) for an irreversible condensation, $w = (P_{\text{ext}} + \Delta P)V$ and $V\Delta P$ is degraded to heat in irre. process

$$\Delta S_{\text{water + vapor}} = -\frac{q}{T} + \frac{q - q_{\text{rev}}}{T}$$



$$\Delta S_{\text{heat reservoir}} = \frac{q}{T}$$



$$\Delta S_{\text{water + vapor}} = -\frac{q}{T} + \Delta S_{\text{irr}} \quad (\text{eq.3.3})$$

The left sides of (eq.3.2) & (eq.3.3) are constant. $\Delta S_{\text{water + vapor}} = \frac{q_{\text{rev}}}{T}$

ΔS_{sys} between the initial and final states- indep. of whether the process is conducted reversibly or irreversibly.

Thus, S is a state function!

$$\Delta S = S_B - S_A = \frac{q}{T} + \Delta S_{\text{irr}} \quad (\text{eq.3.4a})$$

$$= \frac{q_{\text{rev}}}{T} \quad (\text{eq.3.4b})$$

Eq (3.4b) indicates that, as the change in entropy can be determined only by measurement of heat flow at the temperature T , then entropy changes can be measured only for reversible processes, in which case the measured heat flow is q_{rev} and $\Delta S_{\text{irr}}=0$.