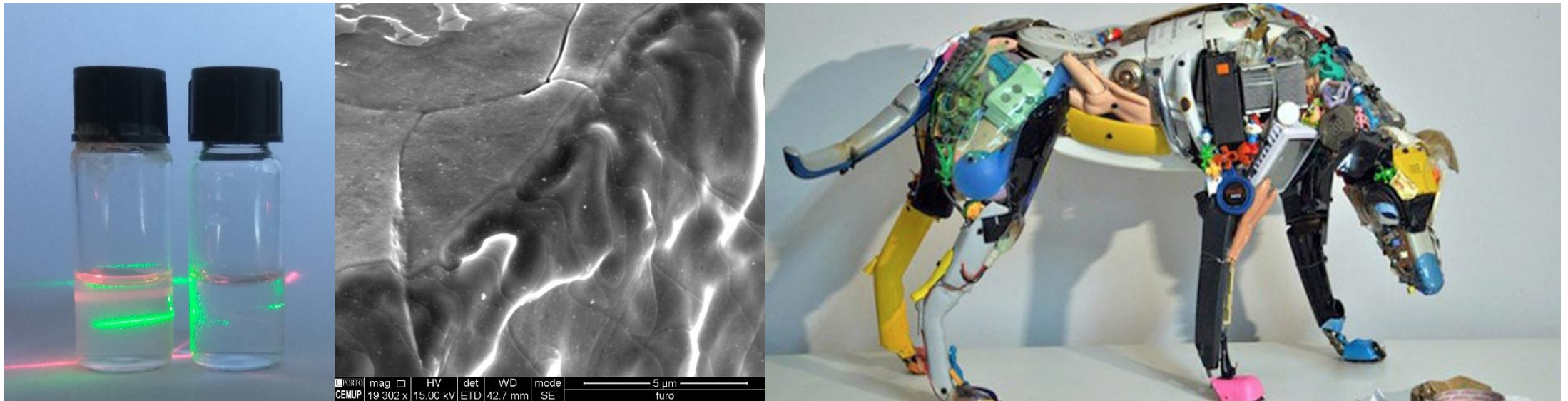


Physical Chemistry

... iremos explorar, refletir, aprender ?..

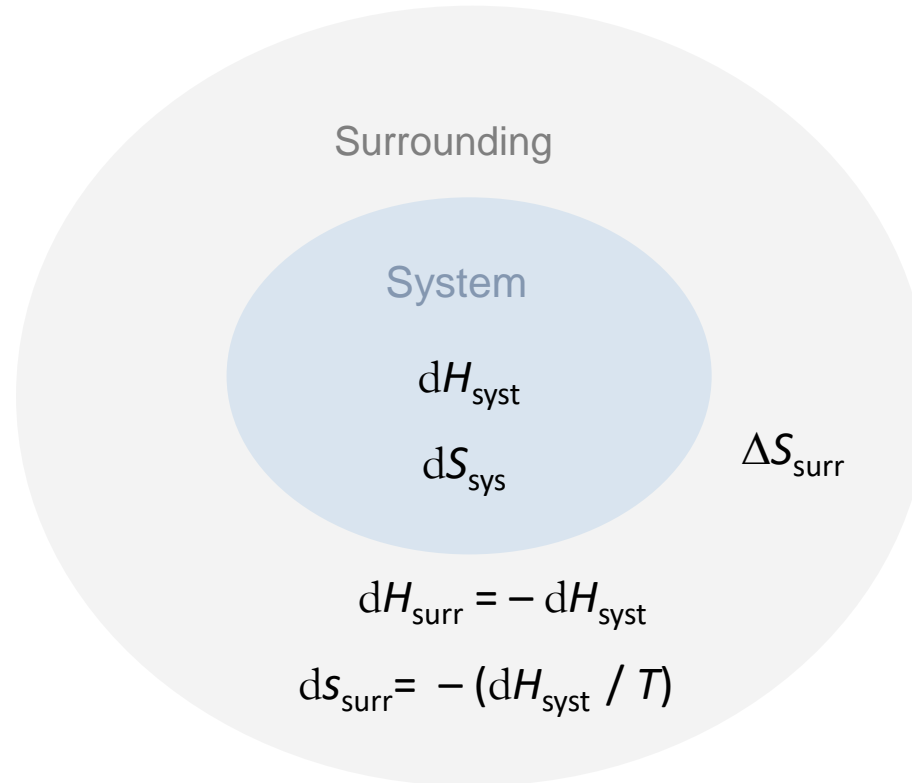
Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.



Keep the energy dispersal

$$dS \geq 0$$

Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.



Spontaneous process:

$$dS_{\text{univ}} = dS_{\text{sys}} + dS_{\text{surr}} > 0$$

Equilibrium:

$$dS_{\text{univ}} = 0$$

Constant pressure $ds_{\text{surr}} = -(dH_{\text{sys}} / T)$

Constant temperature $\Delta s_{\text{surr}} = -(\Delta H_{\text{sys}} / T)$

Example 3.1 Calculating the entropy change for the isothermal expansion of a perfect gas

Calculate the entropy change of a sample of perfect gas when it expands isothermally from a volume V_i to a volume V_f .

Answer Because the temperature is constant, eqn 3.2 becomes

$$\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

From eqn 2.11, we know that

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_f}{V_i}$$

It follows that

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

As an illustration of this formula, when the volume occupied by 1.00 mol of any perfect gas molecules is doubled at any constant temperature, $V_f/V_i = 2$ and

$$\Delta S = (1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 2 = +5.76 \text{ J K}^{-1}$$

Second Law of Thermodynamics

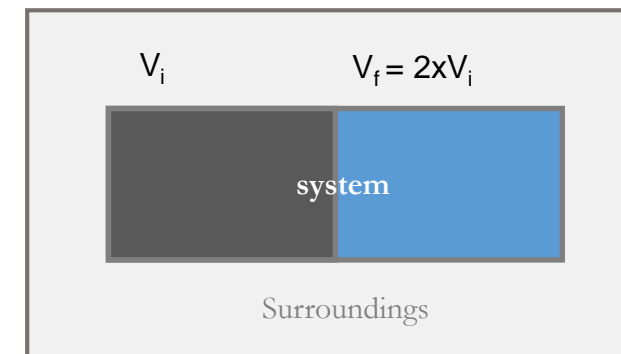
the amount of disorder in a thermodynamic system always increases.

$$dS \geq 0$$

Isothermal

$$\Delta U = q_{\text{rev}} + w_{\text{rev}} = 0$$

$$dS_{\text{univ}} = dS_{\text{sys}} + dS_{\text{surr}}$$



(a) Isothermally Expansion

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

System is always the same !

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} = -\frac{q_{\text{rev}}}{T} = -nR \ln \frac{V_f}{V_i}$$

Surroundings ..it depends !

$\Delta S_U = 0$, which is what we should expect for a reversible process

If the **isothermal expansion occurs freely** ($w = 0$) and irreversibly, then $q = 0$ (because $\Delta U = 0$). $\Delta S_{\text{sur}} = 0$!

$$\Delta S_{\text{tot}} = nR \ln \frac{V_f}{V_i}$$

In this case, $\Delta S_{\text{tot}} > 0$, as we expect for an irreversible process.

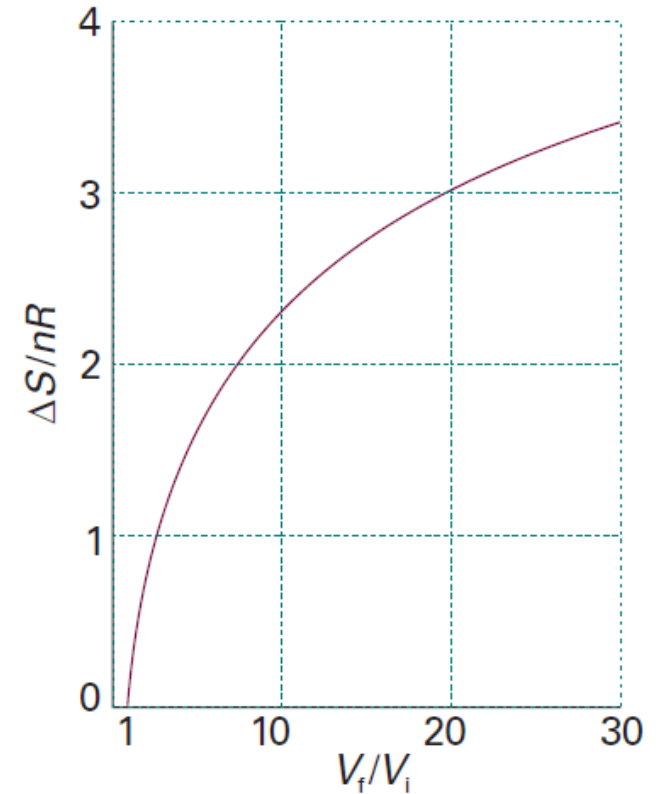


Fig. 3.12 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

The entropy as a state function

$$\oint \frac{dq_{\text{rev}}}{T} = 0$$

where the symbol \oint denotes integration around a closed path.

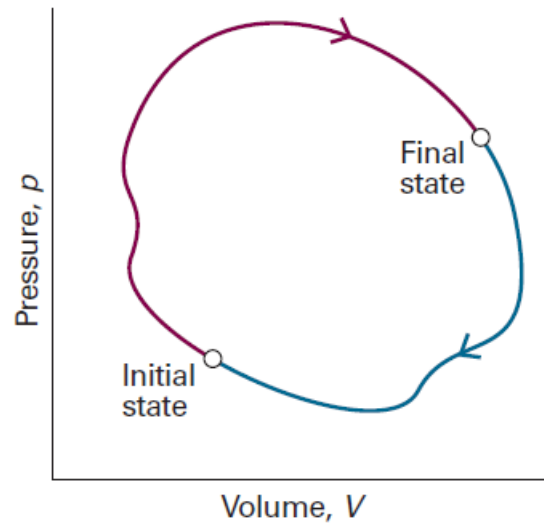


Fig. 3.5 In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.

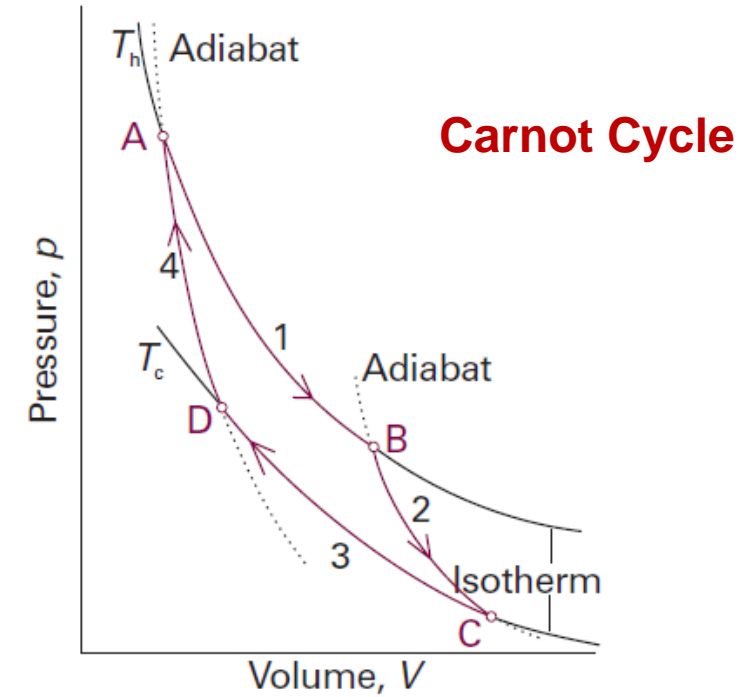
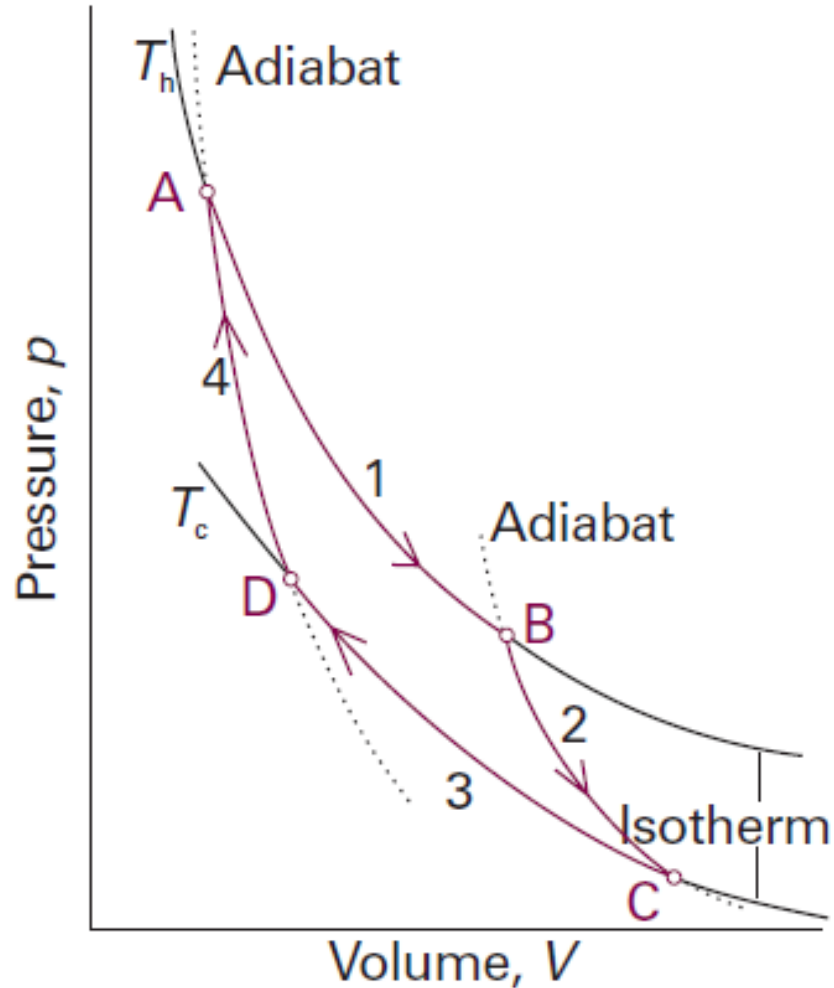


Fig. 3.6 The basic structure of a Carnot cycle. In Step 1, there is isothermal reversible expansion at the temperature T_h . Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c . In Step 3 there is an isothermal reversible compression at T_c , and that isothermal step is followed by an adiabatic reversible compression, which restores the system to its initial state.



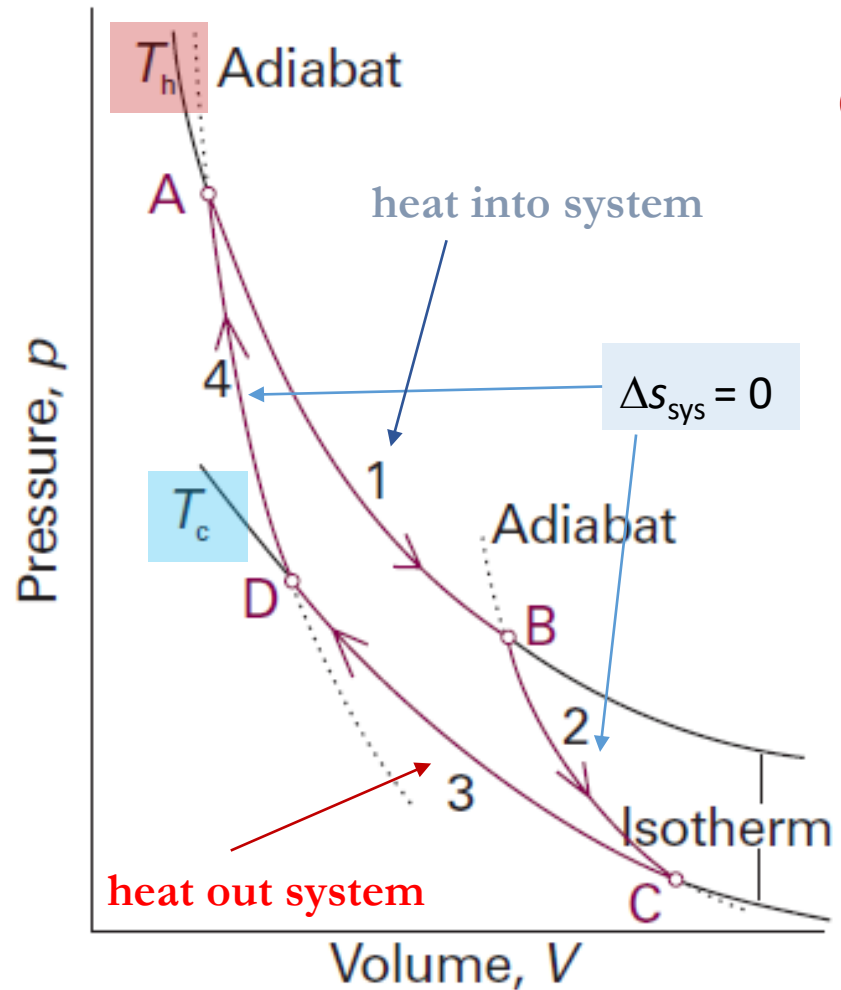
The entropy as a state function

Carnot Cycle

$$\oint \frac{dq_{\text{rev}}}{T} = 0$$

where the symbol \oint denotes integration around a closed path.

Fig. 3.6 The basic structure of a Carnot cycle. In Step 1, there is isothermal reversible expansion at the temperature T_h . Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c . In Step 3 there is an isothermal reversible compression at T_c , and that isothermal step is followed by an adiabatic reversible compression, which restores the system to its initial state.



Carnot Cycle

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

1. Reversible isothermal expansion from A to B at T_h ; the entropy change is q_h/T_h , where q_h is the energy supplied to the system as heat from the hot source.
2. Reversible adiabatic expansion from B to C. No energy leaves the system as heat, so the change in entropy is zero. In the course of this expansion, the temperature falls from T_h to T_c , the temperature of the cold sink.
3. Reversible isothermal compression from C to D at T_c . Energy is released as heat to the cold sink; the change in entropy of the system is q_c/T_c ; in this expression q_c is negative.
4. Reversible adiabatic compression from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from T_c to T_h .

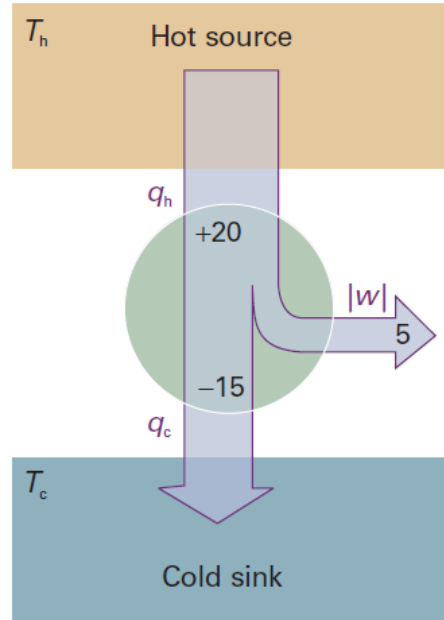
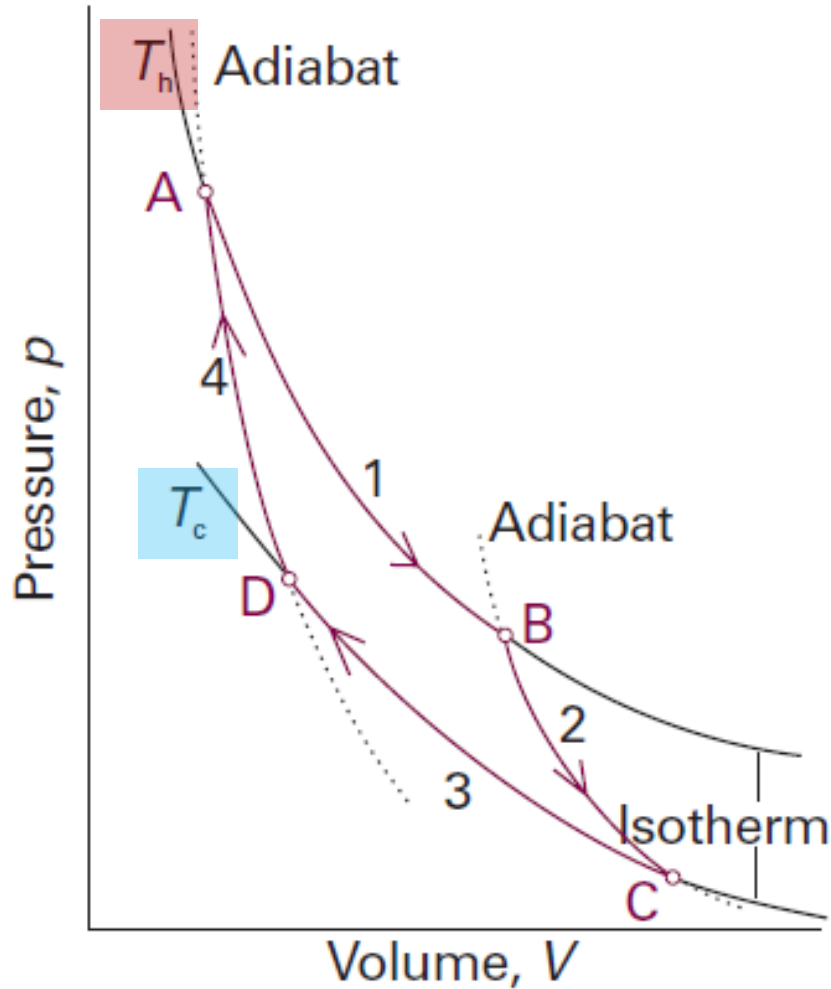


Fig. 3.7 Suppose an energy q_h (for example, 20 kJ) is supplied to the engine and q_c is lost from the engine (for example, $q_c = -15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_h + q_c$ (for example, 20 kJ + (-15 kJ) = 5 kJ). The efficiency is the work done divided by the energy supplied as heat from the hot source.

Carnot Cycle

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} \qquad \oint \frac{dq_{rev}}{T} = 0$$

$$\frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

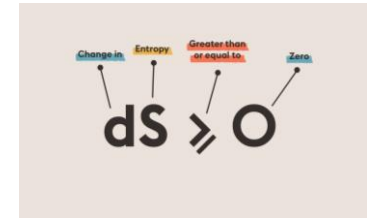
efficiency, ϵ (epsilon), of a heat engine

$$\epsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h}$$

$$\epsilon = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

(Remember that $q_c < 0$.)

$$\epsilon_{rev} = 1 - \frac{T_c}{T_h}$$



Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

Coefficient of performance, c

$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|}$$

$$\frac{1}{c} = \frac{|q_h| - |q_c|}{|q_c|} = -\frac{|q_h|}{|q_c|} - 1$$

$$c = \frac{T_c}{T_h - T_c}$$

For a refrigerator withdrawing heat from ice-cold water ($T_c = 273 \text{ K}$) in a typical environment ($T_h = 293 \text{ K}$), $c = 14$,

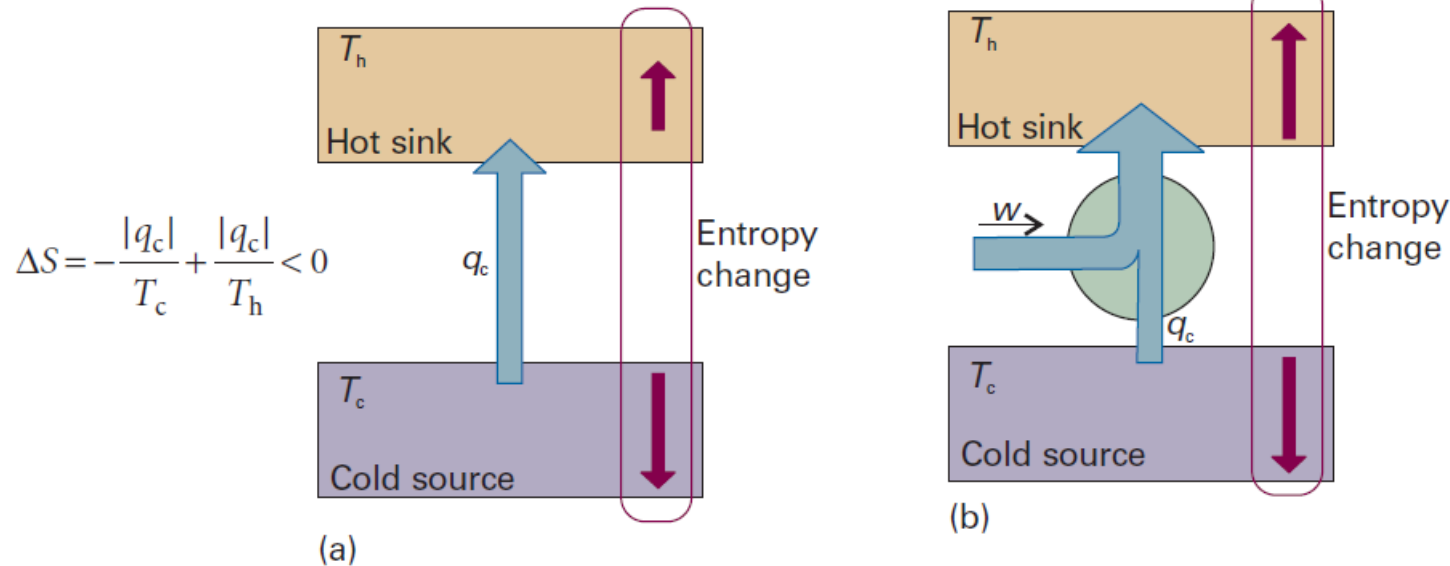
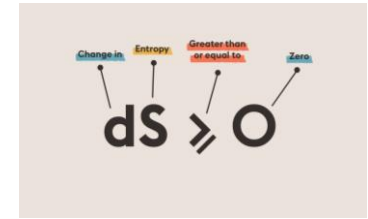


Fig. 3.10 (a) The flow of energy as heat from a cold source to a hot sink is not spontaneous. As shown here, the entropy increase of the hot sink is smaller than the entropy increase of the cold source, so there is a net decrease in entropy. (b) The process becomes feasible if work is provided to add to the energy stream. Then the increase in entropy of the hot sink can be made to cancel the entropy decrease of the hot source.



Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

Coefficient of performance, c

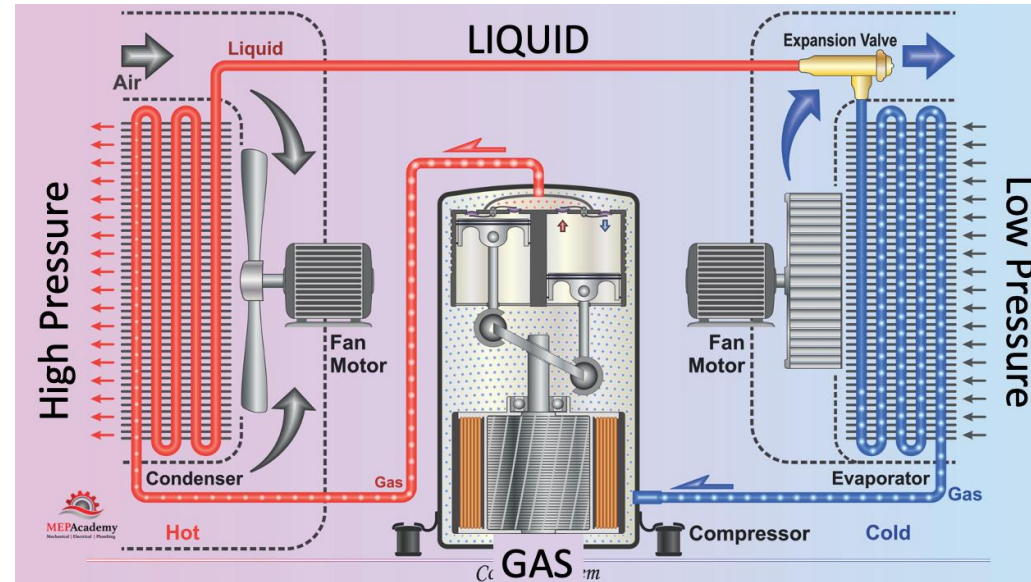
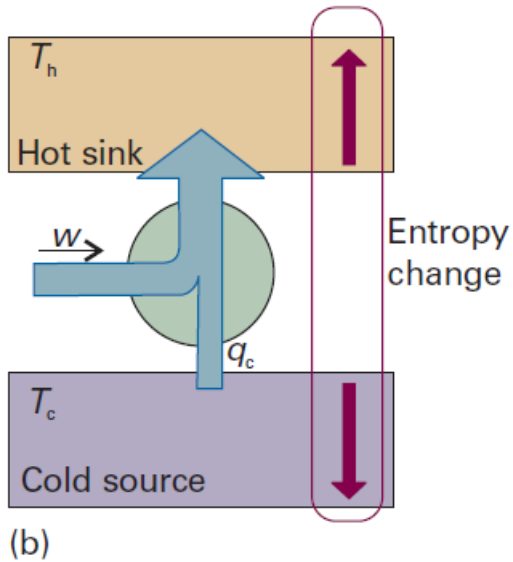
$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|}$$

$$\frac{1}{c} = \frac{|q_h| - |q_c|}{|q_c|} = -\frac{|q_h|}{|q_c|} - 1$$

$$c = \frac{T_c}{T_h - T_c}$$

e.g. refrigeration system ...

also the partial condensation of the gas is involved !



W - work

Spontaneous Physical and Chemical Processes !!?

$$dS \geq 0$$

Change in Entropy Greater than or equal to Zero

Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

