



Chemistry and the material world

123.102

Unit 4, Lecture 5
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Revision

- ◆ First law of thermodynamics.
- ◆ Second law of thermodynamics.
- ◆ Third law of thermodynamics.
- ◆ Heat engines
- ◆ Efficiency
- ◆ Carnot cycle



The first law of thermodynamics

defines the conservation of energy:

$$U = q + w \quad (\text{internal energy } U, \text{ heat } q, \text{ work } w)$$

A thermodynamical system can store energy, this energy is conserved. The two forms of energy that influence this internal energy are heat, either transferred to the system from a source at higher temperature or lost to a sink at lower temperature and work, which can increase the internal energy if work is done on the system by its surroundings, or decrease the internal energy if the system does work to its surroundings.



The first law of thermodynamics

defines the conservation of energy:

$$U = q + w \quad (\text{internal energy } U, \text{ heat } q, \text{ work } w)$$

One form of work that is usually done by or to the system in chemical reactions is *pressure-volume-work*, pV . In order to look at the heat-content of a chemical reaction, we calculate:

$$\begin{aligned} H &= U + pV \\ &= q \end{aligned}$$

The enthalpy is the heat of the reaction at constant pressure.

The first law of thermodynamics

Consequences:

Energy cannot be produced or destroyed. A perpetual-motion machine (ie a machine that has a higher output of energy than it consumes) is impossible.

Makes theoretical physics viable. Solving equations would not be possible if we couldn't be sure that the energy on both sides of the equation wasn't the same.



The second law of thermodynamics

defines irreversibility:

Heat only flows spontaneously from a warmer body to a colder body.

Heat cannot be completely converted into work.

A process can only occur if it increases the total entropy of the universe.



The second law of thermodynamics

Consequences:

Since all useful forms of energy will eventually be converted into heat, the entropy of the universe rises until a final state of maximum entropy is reached.

This is called the heat death of the universe. (Timescale $> 10^{100}$ years)



The third law of thermodynamics

defines an absolute zero:

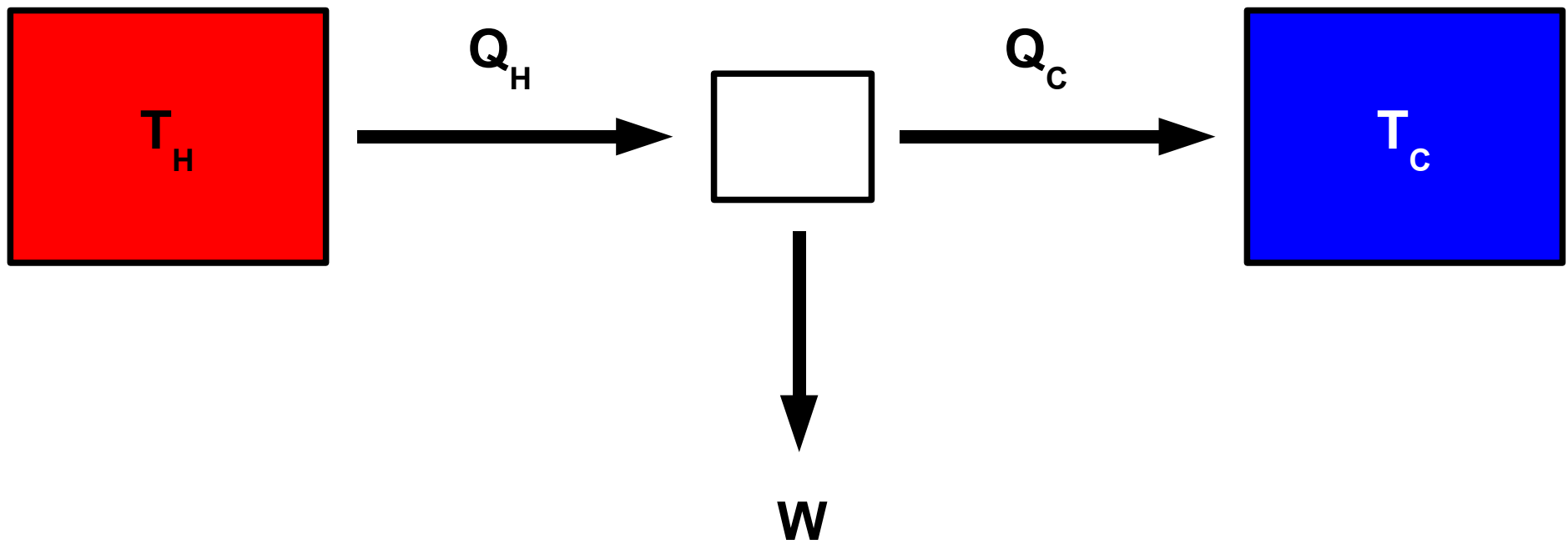
When a system is cooled to lower and lower temperatures and 0 K is approached, all processes come to a halt and the entropy of the system goes to a minimal value.

The entropy of a pure perfect crystal is zero at zero Kelvin.

It is impossible to cool a system to absolute zero Kelvin in a finite series of steps.

Heat engines

A heat engine transfers heat from a hot reservoir to a cold reservoir and converts some of that heat energy to mechanical work.



A heat engine can be reversed to use energy in order to transfer heat from a cold reservoir to a hot reservoir. In this case the engine is called a heat pump.



Entropy and turning heat into work:

We know that entropy is a state function, ie ΔS does not depend on the path. This only applies to the *system*, the total entropy of the system *and its surroundings* does depend on the path taken.



Entropy and turning heat into work:

For example:

The heat flow from a hot body to a cold body. If we remove heat q from a warm body its entropy decreases by an amount of $-q/T_H$ and if we transfer the same heat to the cold body, we increase its entropy by q/T_C .

So, the total entropy change $\Delta S = q((1/T_C) - (1/T_H))$ and is always positive because $T_H > T_C$.



Entropy and turning heat into work:

Because the temperature of the cold reservoir T_C is lower than the temperature of the hot reservoir T_H , we can still achieve a total increase in entropy if we transfer a heat q' into the cold system which is smaller than the heat we removed from the warm system q .

$$\Delta S = (q'/T_C) - (q/T_H)$$



Entropy and turning heat into work:

We see that

$$\Delta S = (q'/T_C) - (q/T_H)$$

will be positive if

$$(q'/T_C) > (q/T_H)$$

which means

$$q' > q (T_C/T_H)$$



Entropy and turning heat into work:

From

$$q' > q (T_C/T_H)$$

we can conclude that the maximum work we can extract is:

$$w_{\max} = q - q_{\min} = q (1 - (T_C/T_H))$$



Entropy and turning heat into work:

$$w_{\max} = q - q_{\min} = q \left(1 - (T_C/T_H) \right)$$

So, the ratio of work actually done and maximum possible work is called the efficiency ε :

$$\varepsilon = w_{\max} / q = 1 - (T_C/T_H) \quad (\text{what happens at: } T_C = 0?)$$

We see that the maximum efficiency only depends on the temperature difference between T_C and T_H .



Thermodynamic cycle

When a system is taken from an initial state through a series of intermediate states and then returns to its initial state we speak of a thermodynamic cycle.

Usually these cycles are theoretical models for existing engines: Otto cycle / Otto engine, Carnot cycle / Carnot engine



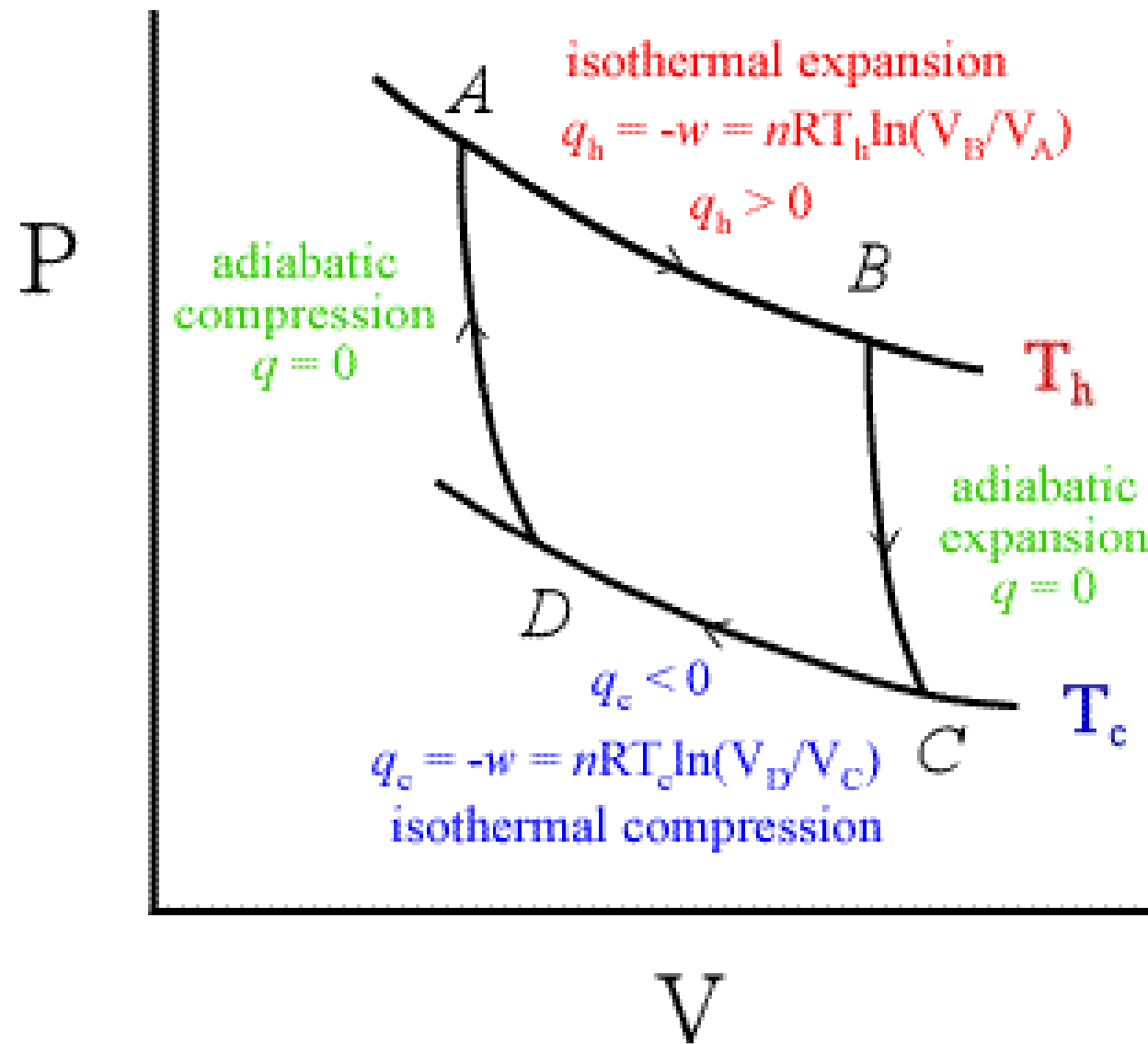
Carnot cycle

The Carnot cycle works in four steps:

1. Isothermal expansion of the gas at the temperature T_H .
2. Adiabatic expansion of the gas.
3. Isothermal compression of the gas at the temperature T_C .
4. Adiabatic compression of the gas.



Carnot cycle





Carnot cycle

The carnot cycle works in four steps:

1. Isothermal expansion of the gas at the temperature T_H .

In this first step the expanding gas could move a piston to do work on the surroundings. The expansion of the gas is driven by the absorption of heat from the hot reservoir.



Carnot cycle

The Carnot cycle works in four steps:

2. Adiabatic expansion of the gas.

In the second step the gas continues to expand (without heat flowing to or from the system) and thereby cools from the temperature of the hot reservoir down to the temperature of the cold reservoir.



Carnot cycle

The carnot cycle works in four steps:

3. Isothermal compression of the gas at the temperature T_C .

In the third step the surrounding does work on the gas compressing it and causing heat to flow out of the gas into the cold reservoir.



Carnot cycle

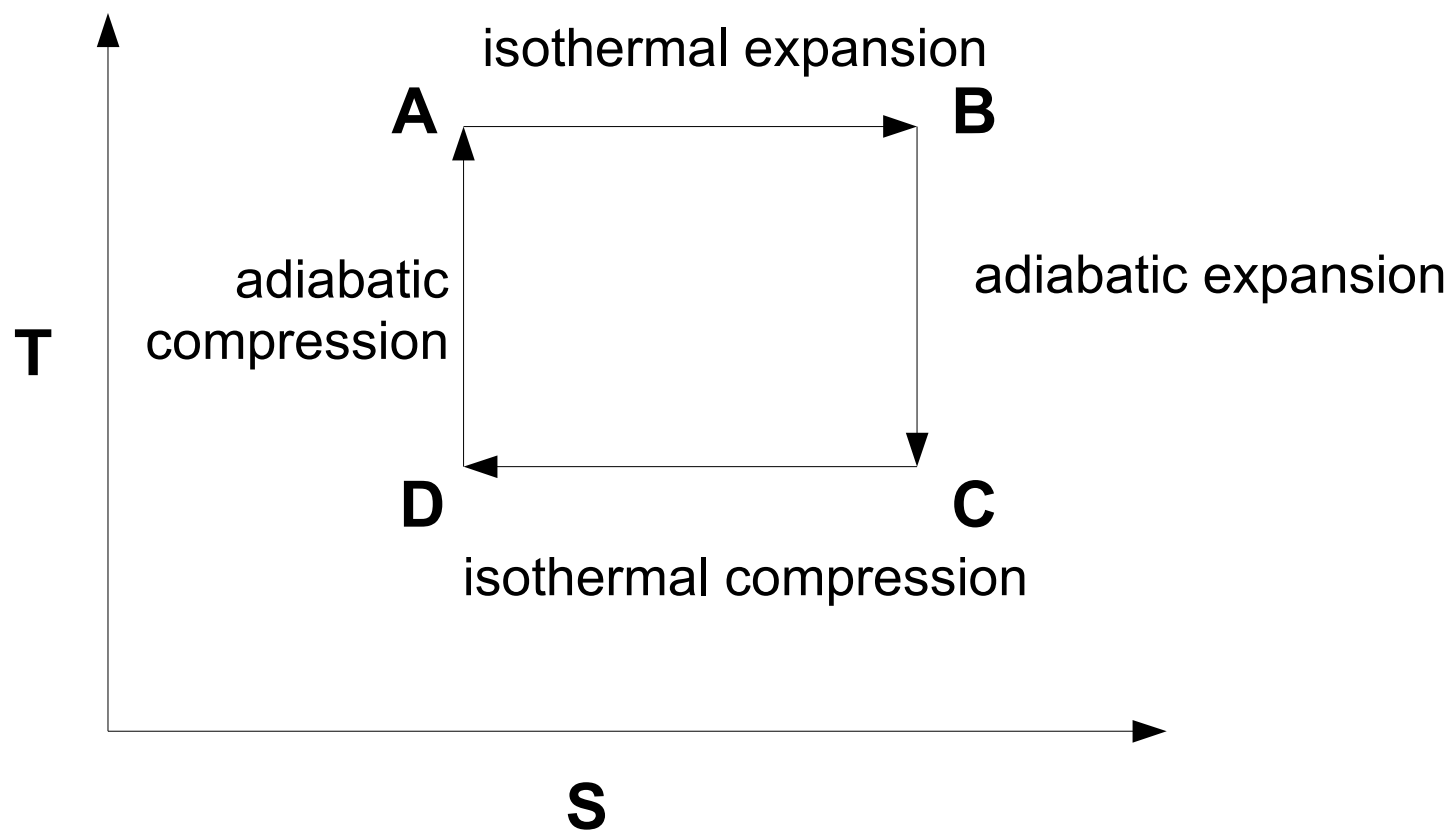
The Carnot cycle works in four steps:

4. Adiabatic compression of the gas.

In the last step the surrounding does more work on the gas compressing it and causing it to heat up to the temperature of the hot reservoir.

At the end of this step, the gas is in the same state that it started in.

Carnot cycle





Carnot cycle

There are two approaches to maximise the thermodynamic efficiency of heat engines:

1. lowering the temperature of the cold reservoir.
2. raising the temperature of the hot reservoir.

The first option is much more costly than the second option, so most industrial processes try to work at high temperatures.



Carnot cycle

Examples:

Typical power plants working with overcritical steam work at 550°C (the hot reservoir) and 100°C for the condenser. This corresponds to an efficiency of 55%. The remaining 45% of thermal energy from fossil fuel or geothermal energy have to be released in order to increase the entropy of the surroundings.



Carnot cycle

Examples:

Typical four-stroke car engines work between 3200K, the temperature caused by burning petrol in the engine, and 1400K, the temperature of the exhaust gas as it exits the cylinder. This corresponds to an efficiency of only 56%. In practice, this efficiency is even lower. Typically around 25%.

Room for systematic improvement of efficient car engines...



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