CH 12
The Laws of Thermodynamics

Work in thermodynamic processes

Energy can be transferred to a system, or object, in two ways.

1) By heat exchange
2) Having work done on the system

We will define a system as the material that is absorbing or giving off energy. For example, a volume of gas.

Work done on a gas

$W = -F\,\Delta y \quad = -PA\,\Delta y$ see fig. 12.1

$A\Delta y = \Delta V$

$W = -P\,\Delta V$

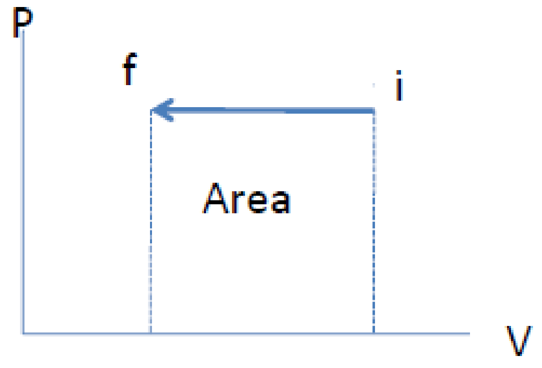
Positive work is done on a gas when it is compressed ($\Delta V < 0$).

If $\Delta V > 0$, then the work on the gas is negative. The gas did work on the environment.

Isobaric process

Isobaric processes occur when the pressure is held constant.

P-V diagram



Area = P $(V_f - V_i)$ = PΔV

The area under the curve in the PV diagram is equal in magnitude to the work done on the gas.

See figure 12.4 for more examples of P-V diagrams.

1^{st} Law of Thermodynamics

- Relates changes in internal energy to the energy transfers due to work and heat.

- “If a system undergoes a change from an initial state to a final state, where Q is the heat, W is the work, the change in internal energy is:

$$\boxed{\Delta U = U_f - U_i = Q + W}$$

- From Ch. 10 (for monatomic ideal gas)

  $U = 3/2\ nRT$ $\Delta U = 3/2\ nR\Delta T$

do example 12.3

Molar specific heat at constant volume

The specific heat of a gas per mole when the volume is held fixed.

$C_v = 3/2\ R$

$\Delta U = nC_v\Delta T$

Also have the molar specific heat at constant pressure. (for an Isobaric process)

$C_p = C_v + R$

for ideal gas $C_p = 5/2\ R$

$$\boxed{Q = nC_p\Delta T}$$

this is found by applying the 1st Law of TD and substituting in for ΔU and W.

Adiabatic process

Adiabatic means no heat transfer.

If you let a gas expand fast enough, there is no time for energy to leave the gas as a loss of heat.

The system is thermally insulated ($Q = 0$).

$$\Delta U = Q + W = W$$

$$\boxed{PV^{\gamma} = \text{constant}}$$

γ = adiabatic index

$\gamma = C_p/C_v$

Isovolumetric (isometric) process

Constant Volume

No work is done.

$$\Delta U = Q + W = Q + 0$$

$$\Delta U = Q$$

$$\boxed{Q = nC_v\Delta T}$$

Isothermal process

Isothermal process, no change in temperature.

$\Delta U = Q + W$

$\Delta U = 0$

$$\boxed{Q = -W}$$

$PV = nRT$ $P = nRT/V$

Work done on the environment:

$$W_{env} = nRT \ln (V_f/V_i)$$

More P-V diagrams

Look at the different curves based on the type of process.

Constant pressure or volume processes are straight lines.

Constant temperature or adiabatic processes are curves.

http://en.wikipedia.org/wiki/Cyclic_process

Heat engines and the 2nd Law of Thermodynamics

Heat engines take in energy by heat and partially convert that energy to other forms.

electrical energy (power plant)

mechanical energy (internal combustion engine)

Heat engines carry some working substance through a cyclic process.

Cyclic process – after one cycle the substance is back to its initial point on the P-V diagram.

1. Heat energy is taken from a source at high temperature.
2. Work is done by the engine.
3. Energy is expelled by heat to a source at lower temperature.

For a complete cyclic process, $\Delta U = 0$

$\Delta U = Q + W \quad \Rightarrow \quad Q_{net} = -W = W_{eng}$

negative work is done on the engine

<u>Work</u>

$Q_{net} = |Q_h| - |Q_c|$

If the working substance is a gas, the work done by the engine for a cycle is the area enclosed by the curve representing the process on a P-V diagram.

Figure 12.12

Efficiency

- Thermal efficiency is defined as the work done, divided by the heat absorbed during one cycle.
- e = $\frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$

do example 12.10

Heat engines take heat from a hot source, produce work and expels excess heat to a cooler source.

Heat can’t naturally flow from cold source to hot source.

Heat pumps and refrigerators remove heat from a cooler source to make colder. (see fig 12.14)

Heat pumps do work on a gas to increase the energy, then that warmer energy is expelled.

2nd Law of Thermodynamics limits the efficiencies of engines.

No heat engine can absorb energy from a reservoir and use it **entirely** for work output.

100% efficiency is **impossible**.

This is why perpetual motion machines do not exist.

There is **always** some wasted energy.

Reversible and irreversible processes.

In a reversible process, every state along the path, on the P-V diagram is an equilibrium state.

The system can return to its initial conditions by going along the same path in the opposite direction.

Otherwise the process is irreversible.

Reversible processes occur slowly.

The slow isothermal compression showed in figure 12.16 is a reversible process.

Carnot Engine – theoretical engine

Carnot Engine operates in an ideal reversible cycle. (Carnot cycle).

See fig. 12.17, 12.18

The efficiency of a Carnot engine puts an upper limit on the efficiencies of all real engines.

For a Carnot engine

$$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$$

For a Carnot Engine efficiency

$$e_c = 1 - T_c/T_h$$

T_c and T_h are the temperatures of the hot and cold reservoirs.

Carnot engines are not real. they would have to run infinitely slowly to perform reversible processes. Thus the power would be zero.

Entropy

Entropy is a quantitative description of the disorganization of a system.

1 kg of water has more entropy than 1kg of ice because in the water the molecules are not organized into a regular crystal lattice.

2nd Law of Thermodynamics stated as entropy:

The total entropy of a system in any physical process cannot decrease, but it can increase. (Also entropy can stay the same, but we need to be very careful to achieve this.)

Law of entropy predicts that most processes are irreversible.

Irreversible processes **will not naturally** occur in the **opposite** direction.

Mix hot water with cold water. You get a mass of water at some intermediate temperature.

The water will never naturally un-mix into separate volumes of hot and cold water again.

Throw a glass ball against a wall. It shatters. Becomes more disorganized.

Entropy

Deck of cards example:

Start with an organized deck. All the cards are in numerical order…

If you shuffle them, they get disorganized.

Shuffle again, they get more disorganized.

The entropy of the deck of cards is increased.

Easy to disorganize things, but it takes considerable effort and lots of luck to organize them.

As universe ages: As all the total chemical reactions and physical processes occur, the total entropy increases.