

CPC 022

DAY 5

Thermodynamics

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Sir James Dewar was responsible for the development of the Dewar flask. This flask is a container that keeps its contents at a steady temperature. Dewar flasks are used to keep hot and cold substances. Many medicinal containers are modeled on this flask.

- **Thermodynamics, and introduction**

Thermodynamics

Thermodynamics is the study of energy and energy transfer.

Before we get into the details, let's look at some words and the particular way that scientists use them.

The BIG ONE is **Energy**

This is a tough one...what is it?

It has something to do with motion and something to do with heat...but again precisely what?

Is light energy?

Is a moving baseball a form of energy or is the fact that the baseball was moving a manifestation that it contains energy?

What does it mean to "contain" energy?

These questions are fundamental and very hard to sort out.

- **Energy**

What Exactly Is Energy?

At a certain level, the only honest answer to this question is: we are clueless. This is a bit of an overstatement but not that far from the truth. We can't say that energy looks like this, or has a color, or weighs this much or even always acts in some particular way. Remember, from class, the Richard Feynmann anecdote about the lady and the blocks—asking; "what is energy" is like asking where are the blocks. Just as the blocks might be anywhere and might even be hidden, so it also seems that energy can take on many forms, some of them extremely subtle and difficult to detect.

A useful starting point for understanding energy is to understand its various manifestations and transformations, and that is what we will embark on in the next few pages.

- **Kinetic energy**

Energy is often associated with motion

A moving object has more energy than a stationary one. The faster it is moving the more energy it has.

We call this form of energy kinetic energy:

$$K = \frac{1}{2}mv^2$$

Where K = kinetic energy

m = mass

v = speed

- **Potential energy**

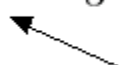
Energy is often associated with position

The higher above the earth's surface an object is, the more energy it has. An object hanging from a spring has more energy when the spring is stretched than when it just hangs there.

We call energy that depends on position the potential energy and use the letter " U " to represent it.

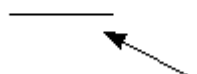
We define gravitational potential energy as:

$$U_g = mgh$$

 This is a subscript

We define elastic potential energy as:

$$U_e = \frac{1}{2}kx^2$$

 What does this mean?

x = amount a spring is stretched.

" k " is called the force constant, and refers to the stiffness of the spring--the stiffer the spring the higher the value of k .

- **Mechanical energy**

Mechanical Energy

The **mechanical energy of an object is simply the sum of its potential and kinetic energy.**

$$ME = U + K$$

- **Work**

Work

We can increase an object's mechanical energy by doing **work** on it.

An object decreases its mechanical energy by doing work on something else.

To do work you must **exert a force** on an object and do so over a distance.

- No force, no work.
- No distance traveled, no work.

- **Internal energy**

An object can contain energy even if it is not moving and even if it is not above the surface of the earth. This is called the object's internal energy.

A pot of boiling water sitting idly on the stove contains a lot of energy...more than an identical room-temperature pot of water sitting right next to it. Neither pot is moving. And the hot pot is at the same

height as the cold pot. So the hot pot doesn't have more mechanical energy than the cold pot.

- We say the hot pot has more **internal energy**.

Internal Energy (2)

Where does internal energy come from?

- **Internal Energy comes from the kinetic and potential energies of the atom and molecules that make up an object.**
 - The kinetic energies are in random directions and we do not see the object as a whole move.
 - The potential energies are electrical in nature and are stored in the electrons that make up the atoms and molecules of our object.
 - **Heat**

Heat

Internal energy is transferred from one substance to another via heat.

Heat (or q) is always associated with the process of internal energy transfer, just as work is always associated with a change in mechanical energy.

- **Temperature**

Temperature

We are all familiar with the idea of temperature on an experiential level. When we say something is hot, we mean that it has a high temperature. But **temperature is not the same as heat**.

What temperature really is, is this:

- It is the amount of internal energy divided by the number of places we have to store that energy.
- These "places" are called "modes"... this is not a very satisfying definition but we can think of it this way: the more molecules we have, the more modes we have.

For any substance, the temperature is proportional to the internal energy per molecule. Substances that contain more internal energy per molecule are said to be at higher temperature.

- **A mid-lecture summary**

Summary

Let's review the concepts we have discussed so far

- E = Energy, the sum of the mechanical and internal energies of an object.
- ME = Mechanical energy, the energy associated with the overall position and movement of an object...the sum of it's potential and kinetic energies.
- K = The kinetic energy = $1/2 mv^2$.
- U = Potential energy arising from position or configuration of an object...can originate in gravity, elasticity (spring) or electronic effects.
- w = Work, mechanical energy added or subtracted from an object due to a force acting over a distance.
- q = Heat, internal energy added to or subtracted from an object.
- IE = Internal energy...the sum of the kinetic and potential energies of the atoms and molecules excluding those of the object as a whole (ME).
- T = Temperature: a measure of the internal energy per molecule of a substance.

E , ME , K , U , w , q , IE , and T

Confused?

See if you can, from memory, explain them in writing.

Don't try to memorize their definition...try to understand what they mean.

- **The Laws**

The Laws

- (0) It is possible to establish a temperature scale.
- (1) Energy can neither be created nor destroyed, however, it can be changed from one form to another.
- (2) In any spontaneous change, the disorder of an isolated system will increase. We call this disorder **entropy**.
- (3) It is possible to establish an absolute zero for entropy.

- **Law zero**

Why does this have to be a law?

Isn't the establishment of a temperature scale self-evident?

Read this only in an emergency

- **First law**

What is energy?

What does "conservation" mean?

How do we know it is conserved or do we just **believe** this?

Didn't we say that energy can be converted into mass and vice-versa?

- **Second Law**

What is disorder really?

Is it mathematical?

How do scientists define it?

Every time I straighten up my room or think a clever thought I am making things more orderly...doesn't this violate the second law?

- **Law three**

Say what?

What is meant by an absolute zero of entropy? From the thermodynamic standpoint, the most orderly thing possible would be something that could only exist in one state, with no other states accessible to it.

The only such object would be a "perfect crystal" (one without any inclusions or defects), provided that it was held at zero degrees absolute.

In fact the formal statement of the third law, one that most scientists use, is "The entropy of a perfect crystal, at absolute zero, is zero." How is this statement equivalent to the one we gave in class?

The Laws

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- **Entropy: everything goes in one direction**

Entropy

My favorite card game, **FIFTY-TWO PICKUP**, is a classic illustration of the concept of entropy. What makes the game so much fun is that the cards never land all face up arranged by number according to suite, even if they started out that way. They are always "disorderly".

Scrambled eggs also remind me of entropy (ever see eggs spontaneously unscramble?), as do sand castles being washed away by the ocean.

More Entropic Musings:

Entropy is time's arrow...we would not have a sense of time were it not true that everything goes preferentially in one direction (greater disorder).

Heat Death of Universe: When everything achieves the same temperature there will be total thermodynamic disorder and the universe will stop running.

- **Chemical reactions and heat**

Thermodynamics and Chemistry

The energy that we measure from a chemical reaction is called the **Enthalpy** and is symbolized by ΔH . In an exothermic reaction you get a negative ΔH .

In an endothermic reaction you get a positive ΔH .

Exothermic? Endothermic?

An exothermic reaction is when heat is released. The reaction feels "hot".

An endothermic reaction is when heat is absorbed. The reaction feels "cold".

- These properties (exothermic and endothermic) are also used to describe physical processes such as solution and phase changes. Thus when you dilute concentrated sulfuric acid in water, the process is said to be exothermic, and the evidence of this is that the flask you are using becomes hot to the touch.

- **Chemical bonds and heat**

Thermodynamics and Chemical Bonds

Breaking bonds costs energy.

Making bonds releases energy.

In a chemical reaction we break bonds in our reactants, and form new bonds in our products.

When it costs more energy to break the bonds, than what we get back when the new bonds are formed, the reaction is **endothermic**.

When we get back more energy from the newly formed bonds than we had to put in to break the bonds in the reactants, then the reaction is **exothermic**.

- **Spontaneity**

Two factors will determine whether a chemical reaction is spontaneous or not:

Enthalpy change = ΔH

Entropy change = ΔS

If a reaction is exothermic, it tends to be spontaneous (ΔH is negative).

If the entropy of the products is bigger than the reactants...this tends towards spontaneity as well (ΔS is positive).

This means there are 4 possibilities.

(1) Exothermic,
greater disorder--
always spontaneous.
(ΔH is negative and
 ΔS is positive)

(2) Endothermic,
greater order--never
spontaneous. (ΔH is
positive and ΔS is
negative)

(3) Endothermic,
greater disorder
(ΔH is positive and
 ΔS is positive)

(4) Exothermic,
greater order (ΔH is
negative and ΔS is
negative)

- 3 and 4 must be decided on a case-by-case basis

- **Many physical processes are also accompanied by emission or absorption of heat**

Physical Processes

Thermodynamics applies to physical processes as well as to chemical processes. The two areas of primary interest are:

- The solution process
- Phase changes

○ Solutions

Thermodynamics of Physical Processes: Solutions

The solution process can be accompanied by either the emission or absorption of heat. In addition, it is likely to be accompanied by entropy changes:

1. The ions in a crystalline solid increase in entropy when they leave the structure of the crystal and wander aimlessly about in solution;
2. The water molecules, because they hydrate the ions in solution, decrease in entropy; the presence of the ions "organizes" them so that several of them surround each ion.
3. Obviously 1 and 2 work at cross purposes, and so each solute/solvent pair must be evaluated case-by-case to discover whether the entropy increases or decreases.

Everything we said about spontaneity, the mutual contributions of enthalpy and entropy, applies to solutions. The cold pack...the solution of NH_4NO_3 in H_2O , is a good example of this. The process takes place spontaneously in spite of the fact that ΔH is positive and thus endothermic.

This is because the increase in disorder due to the breaking up of the orderly solid NH_4NO_3 crystal lattice outweighs the endothermicity.

○ **Phase changes**

Thermodynamics of Physical Processes: Phase Changes

Phase Changes

1.) Fusion $S \longrightarrow L$

2.) Evaporation $L \longrightarrow G$

3.) Sublimation $S \longrightarrow G$

**All
Endothermic**

4.) Freezing $L \longrightarrow S$

5.) Condensation $G \longrightarrow L$

6.) Deposition $G \longrightarrow S$

**All
Exothermic**

Question: If melting (fusion) is endothermic, why is it that an ice cube spontaneously melts?

**Thermodynamics of Physical Processes: Phase Changes
(2)**

Each phase change has a characteristic heat associated with it such as:

- Heat of fusion
- Heat of vaporization

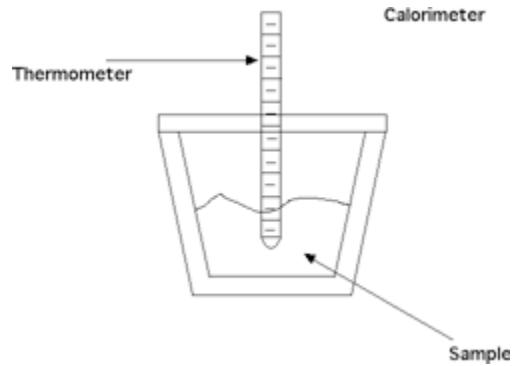
These are sometimes referred to as "latent heats" such as:

- Latent heat of fusion
- Latent heat of vaporization

- **We can measure heat using a calorimeter**

How do we measure heat

We use an insulated vessel called a calorimeter.



We calculate heat using the specific heat equation:

$$Q = ms\Delta T$$

m = mass

s = specific heat

ΔT = change in temperature

- **We need to use the specific heat equation to make this work**

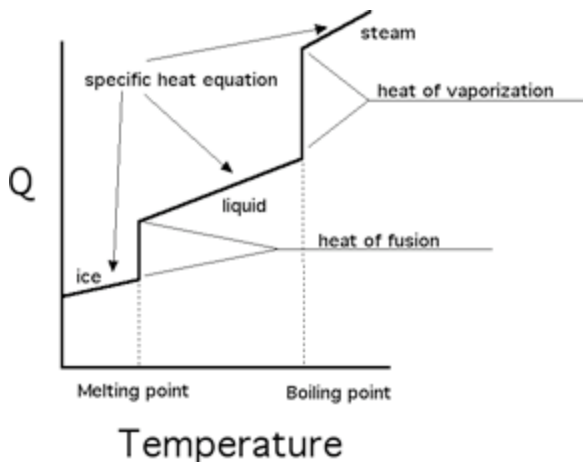
Heating a solid

When we heat a solid we see a steady temperature increase. This is what we would expect from the specific heat equation:

$$Q = ms\Delta T$$

All this equation says is that, every time we add some heat (Q), the temperature (T) goes up a little. This works until we hit a phase change. At a phase change, the temperature stops going up until we have added all the heat of fusion (if we are going from solid to liquid) or all the heat of vaporization (if we are going from liquid to gas).

Suppose we added heat to a solid, e.g. ice, and kept adding heat until we had converted the ice to liquid water, and then to steam. If we plotted our results, we would expect to get a graph like this:



- Note relative sizes of heat of vaporization and fusion.

Note that specific heats for ice, liquid and steam are all different, and so the slopes of the lines are all different.