

Thermodynamics

Okay, thermodynamics is actually a really interesting subject and there are a lot of people who just do thermo, it's a big deal in science and engineering. In this kind of a chemistry course you just barely touch on the subject. Thermo comes close to describing how nature works, at least macroscopically. Natural processes are a balance between nature's contradictory desires to minimize energy and maximize entropy (randomness). This is what the chaos theory stuff in Jurassic Park was about. The park owner jackass-richguy thought he could control all of the variables in his system. He just operated on the minimization of energy principle and ignored nature's other side. So a guy wrote an allegorical book about how nature will bite you in the ass when you do this, and Steven Spielberg made dinosaurs to get the job done. Anyway, as I said, you'll just touch on thermo here but it has crunchier roots than most science.

First Law of Thermodynamics --> Energy Bookkeeping

For a closed system (no mass in or out)

$$\Delta E = q - w$$

Diagram illustrating the First Law of Thermodynamics equation: $\Delta E = q - w$. Arrows point from the terms to their meanings: ΔE is labeled "change in Internal Energy", q is labeled "heat energy", and w is labeled "work energy".

(You guys aren't assumed to know calculus so you can't really do a lot with this equation.)

You can do a couple of easy things though:

- For constant pressure processes $w = p(V_2 - V_1)$. You can calculate the work of expansion.
- Also adiabatic means no heat transfer: $q = 0$

In those special cases, adiabatic ($q = 0$) and isobaric (constant pressure) processes obey:

$$\Delta E = p(V_2 - V_1)$$

- Or, you can be given q and w for any old process and just plug them in.

Now, the sign conventions for q and w are really important because in lots of problems you will just be given numbers and if you don't know whether to make them positive or negative you're screwed.

If the First Law is written as $\Delta E = q - w$ (that's the way I was taught), then

- if heat is absorbed q is positive, if heat is evolved q is negative
- if the volume increases (expansion) w is positive, if the volume decreases (contraction) w is negative.

If the First Law is written as $\Delta E = q + w$ (that's not the way I was taught but is popular), then

- if heat is absorbed q is positive, if heat is evolved q is negative (same as the other one)
- if the volume increases (expansion) w is negative, if the volume decreases (contraction) w is positive.

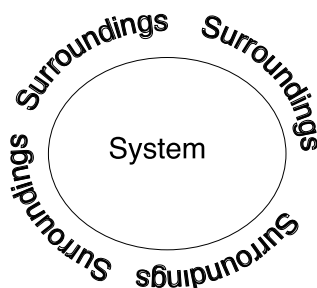
The other Two Thermodynamic Laws

The Second Law of Thermodynamics (This thing can be tough to use but that's kind of nice on this level because you're only expected to know how to use it in a very limited way.)

Second law: Spontaneous natural processes are accompanied by an increase in the entropy of the universe.

So, to tell if a process may be spontaneous, you can keep track of the entropy of the universe. If it increases the process may be spontaneous.

Now, keeping track of the change in entropy that a process will exact on the universe is no small task as you may imagine. To do this you need to break up the universe into two points of view--the system and the surroundings.



$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- Often times ΔS_{system} is just calculated from standard entropies of the reactants and products--using the familiar procedure of adding up the entropy of the products and subtracting from it the entropy of the reactants.
- $\Delta S_{\text{surroundings}}$ in turn can loosely be calculated at constant temperature from

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surr}}}{T} = \frac{-\Delta H_{\text{rxn}}}{T}$$

(The - sign is because of the perspective change. A reaction system loses heat, exothermically, and that's negative. But the surroundings see that as a heat gain and that's positive.)

The second law is used to debunk perpetual motion machines. You take a look at them and calculate a ΔS_{univ} . Perpetual motion machines try to make the universe do things that it doesn't want to and homey don't play that.

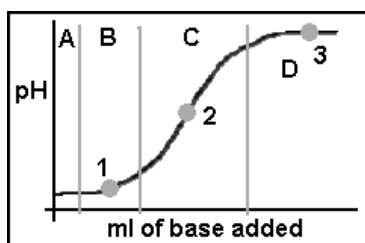
The Third Law of Thermodynamics

The third law says that at 0 Kelvin a completely ordered pure crystal has zero entropy.

This is used as a reference for calculating entropies for substances. Consider it the definition of zero entropy.

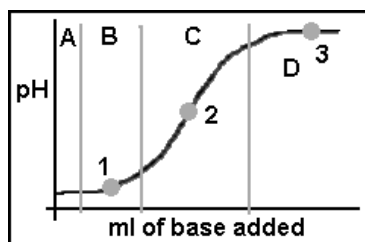
Student Packet: 7.4: Laws of Thermodynamics: AssessMe questions

- 1) Which of the following is true for all zero order reactions?
- A) $E_a = 0$.
 B) $k = 0$.
 C) Reactant concentration does not change with time.
 D) The rate is independent of time.
 E) I'm clueless
- 2) Which of the following pairs yields a straight line when plotted for a first order reaction?
- A) $[A]$ vs. t B) $\log [A]$ vs. t C) $1/[A]$ vs. t D) $[A]$ vs. $1/t$ E) I'm clueless
- 3) The first law of thermodynamics states that:
- A) matter is neither created nor destroyed
 B) the rate of change of temperature of a metal is proportional to the temperature of the metal
 C) energy is conserved in closed systems
 D) 0 K is the lowest possible temperature
 E) I'm clueless
- 4) An increase in entropy implies
- A) an increase in order B) an increase in disorder
 C) a decrease in temperature D) a decrease in volume E) I'm clueless
- 5) In which region is the undissociated acid (HA) the predominate species in solution?



- A) region A
 B) region B
 C) region C
 D) region D
 E) I'm clueless

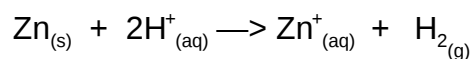
- 6) In which region(s) is the dissociated acid (A^-) the predominate species in solution?



- A) region A and B
 B) region B and C
 C) region C and D
 D) region D
 E) I'm clueless

Student Packet: 7.4: Laws of Thermodynamics: ShowMe questions

- 1) How does entropy change in the following systems?
- A) Solid melts
 - B) Solid Sublimes
 - C) Vapor is converted to solid
 - D) Vapor condenses as a liquid
 - E) Liquid boils
- 2) What is the entropy change if a material is slowly heated from 0 to 2K, which required 0.20 J?
- 3) A gas is enclosed in a piston. The temperature of the surroundings are increased such that the gas gains 50 J of heat energy. The piston is not allowed to move. What are q, w, and ΔU ?
- 4) Consider the reaction:



This is an exothermic reaction, releasing 152.4 kJ per mole Zn. If this reaction took place inside a piston at STP, what is the change in internal energy if 1 mole of Zn is reacted?

Student Packet: 7.4: Laws of Thermodynamics: TestMe questions

- 1) What is the change in entropy for the freezing of 1 mole water of 0°C?
 $\Delta H_{\text{fus}} = 6.0 \text{ kJ}$
- A) 2.2 J/K
B) 6 J/K
C) 22 J/K
D) 6,000 J/K
E) unable to be determined with given information
- 2) A gas is cooled and loses 70 J of heat. At the same time, it contracts, and work is done on the system equal to 30 J. What is the change in internal energy?
- A) +100 J B) +40 J C) no change D) -40 J E) -100 J
- 3) Which of the following thermodynamic functions are associated only with the first law of thermodynamics?
- I. S (entropy)
II. E (energy)
III. H (enthalpy)
IV. T (temperature)
- A) I only B) II only C) III & IV only D) I & IV only E) II & III only
- 4) Which of the following reactions have a positive change in entropy?
- A) $\text{PCl}_{3(l)} + \text{Cl}_{2(g)} \rightarrow \text{PCl}_{5(s)}$
B) $2\text{HgO}_{(s)} \rightarrow 2\text{Hg}_{(l)} + \text{O}_{2(g)}$
C) $2\text{H}_{(g)} \rightarrow \text{H}_{2(g)}$
D) $\text{U}_{(s)} + 3\text{F}_{2(g)} \rightarrow \text{UF}_{6(s)}$
E) $\text{NH}_{3(g)} + \text{HCl}_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$
- 5) An ideal gas undergoes an isothermal compression. If $q = -50 \text{ J}$, what are ΔU and w ?
- A) $w = 0$, $\Delta U = -50 \text{ J}$
B) $w = 50 \text{ J}$, $\Delta U = 0$
C) $w = -50 \text{ J}$, $\Delta U = 0$
D) $w = 50 \text{ J}$, $\Delta U = -100 \text{ J}$
E) $w = 0$, $\Delta U = 50 \text{ J}$