

- (1) One mole of an ideal monatomic gas doubles its temperature and doubles its volume. What is the change in entropy of the gas?
- (2) 1 kg of ice at 0°C melts to become water at 0°C . What is the change in entropy of the ice?
- (3) Suppose you mix 1 kg of water at 0°C with 1 kg of water at 100°C . What is the change in entropy for this mixing process?
- (4) You have just made your first million. It also happens that the world has a terrible energy crunch at this time, and efficient engine development is all the rage. An inventor approaches you and suggests that you invest in his engine which works between 30°C and 100°C because it has an efficiency of 70%. Do you invest? Why or Why not?
- (5) Show that:
- (a) U is a function of temperature only
 - (b) $C_v = 3/2R$
- and the other features of ideal gases.

Entropy and the Carnot Cycle

There are many ways to talk about entropy, ranging from information theory, languages, computer science to physics. We'll here concentrate on the physics formulation, specifically pertaining to thermodynamics.

We first need to define the state function Entropy (which is a measure of efficiency of heat flow) is given by:

$$\Delta S = \frac{Q}{T}$$

Strictly said, this applies only to a small amount of heat added to a system at a constant temperature. In general, as temperature changes over a range, you would have to add up individual changes as:

$$\Delta S = \sum_{i \text{ steps}} \frac{Q_i}{T_i}$$

Since entropy is a state function, the change in entropy will be zero for any closed reversible path. If the path is not reversible, then the change is greater than zero. I'll later show you examples of this.

Calculus version:

$$\Delta S = \int_i^f \frac{dQ}{T}$$

where dQ indicates a small amount of Q.

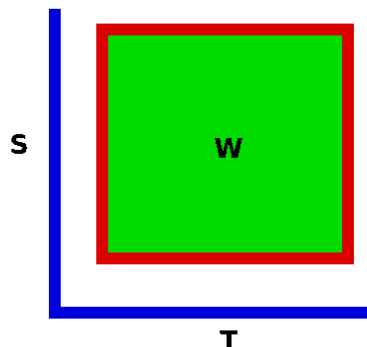
I'll later show you how to calculate some entropies.

Now, it is important to realize that the area enclosed by a closed T-S plot represents work. Let's assume a small closed cyclic change occurs in a system at a temperature T. A small amount of heat will be added to the system. From the first law and the definition of entropy, we then have

$$\Delta S = \frac{Q}{T} = \frac{\Delta U + W}{T} = \frac{W}{T}$$

ΔU is zero because the cycle is closed. We thus have:

$$T(\Delta S) = W$$



It's not much harder to show this in other ways but I think I've shown my point.

Calculation of entropies for different processes (**non-calculus**)

When we calculate the entropy changes for an ideal gas, it is useful to use the first law:

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

Here, we have in general: $\Delta U = n c_v (\Delta T)$ so long as we're talking about an ideal gas.
We also have that the work is given by:

$$W = P \Delta V$$

Thus, if we wanted to calculate Q, we have:

$$Q = n c_v \Delta T + n R T \left(\frac{\Delta V}{V} \right)$$

As it stands, this can't be calculated in general for any process (because you don't know how T varies when it multiplies the last term). However, dividing by T gives:

$$\frac{Q}{T} = n c_v \left(\frac{\Delta T}{T} \right) + n R \left(\frac{\Delta V}{V} \right)$$

You can now use the useful approximation to obtain:

$$\Delta S = n c_v \ln \left(\frac{T_f}{T_i} \right) + n R \ln \left(\frac{V_f}{V_i} \right)$$

Calculation of entropies for different processes (**calculus**)

$$dQ = n c_v (dT) + n R T \frac{dV}{V}$$

where dQ indicates a small amount of Q.

Divide by T

(it is an integrating factor because it allows you to integrate just one variable at a time)

$$\frac{dQ}{T} = n c_v \left(\frac{dT}{T} \right) + n R \left(\frac{dV}{V} \right)$$

$$\Delta S = \int \frac{dQ}{T} = n c_v \int \left(\frac{dT}{T} \right) + n R \int \left(\frac{dV}{V} \right)$$

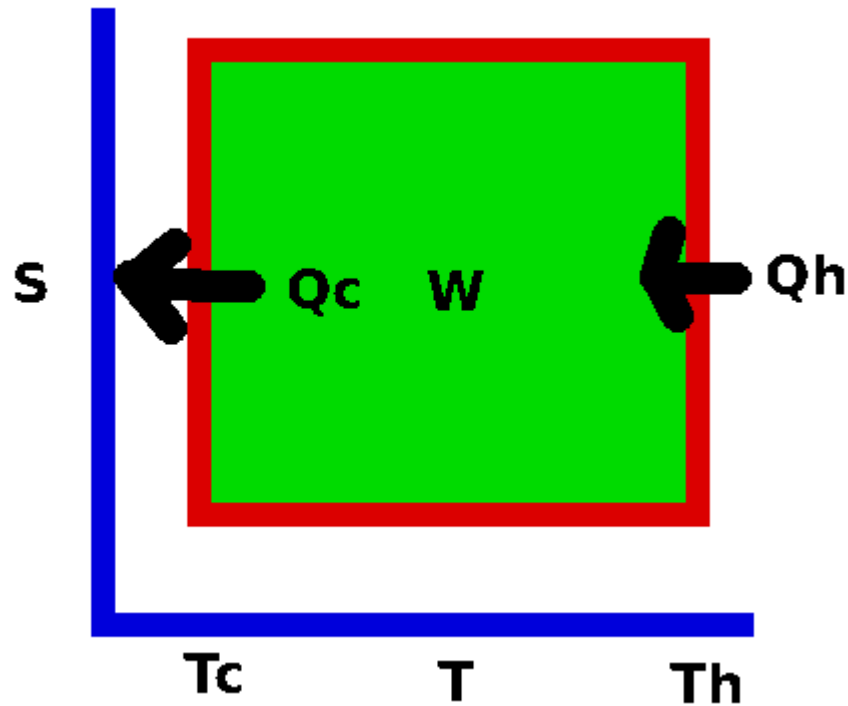
so:

$$\Delta S = n c_v \ln \left(\frac{T_f}{T_i} \right) + n R \ln \left(\frac{V_f}{V_i} \right) .$$

This is completely independently of the process that the gas went through, so long as the process is reversible. This is nice although you probably want to work out specific examples for the different processes.

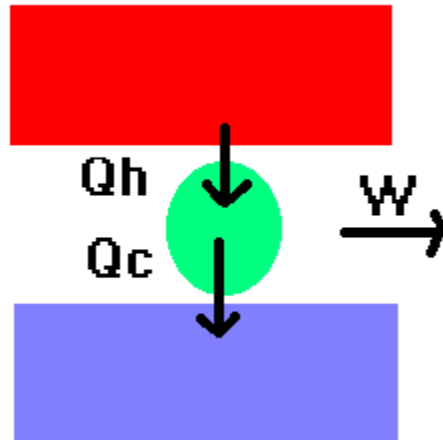
Now, as promised, I'll use entropy to show the Carnot cycle to be the most efficient cycle possible. How?

Remember that for an adiabatic process, $Q=0$ which, in this case, will give a vertical line on a TS plot. For an isothermal process, we end up needing to connect the two ends of these lines which then gives us a square for the Carnot cycle. It looks like the one I've shown before. Let's see where Q_h and Q_c become involved:



What you want to do to make the most efficient engine possible is to maximize the area (green stuff) for a given length of red (and you must have Q_c present). The shape that gives this is the rectangle which is the Carnot cycle. At least that is my simplified version of why the Carnot cycle is the most efficient cycle possible.

Heat Engine diagram



Heat engines work like the diagram shows. Another statement of the second law of thermo is you have got to reject some heat to a cold reservoir (you can't convert heat directly into work without losing some heat in the process). It is perhaps less obvious why this is true but I like the analogy of a battery: the cold reservoir is the - terminal, the + terminal is the hot reservoir and a light bulb is connected between the two. Both terminals must be connected in order for the bulb to light. Here, if you do work you have extracted some heat from the gas that did work and thus, you automatically have a colder gas left or something like that.

It's also impossible to have energy go from cold to hot without doing work. (this is the impossible refrigerator).

Interestingly enough, although we don't have the time to explore this completely, another statement of the second law of thermodynamics is that the entropy of the universe increases in all processes. I'll show you this in the context of mixing two fluids.

(1) One mole of an ideal monatomic gas doubles its temperature and doubles its volume. What is the change in entropy of the gas?

Solution:

$$\Delta S = n c_v \ln\left(\frac{T_f}{T_i}\right) + n R \ln\left(\frac{V_f}{V_i}\right)$$

For a monatomic gas, $C_v = 3/2 R$ we have:

$$\Delta S = 1 \frac{3}{2} R \ln\left(2 \frac{T_i}{T_i}\right) + 1 R \ln\left(2 \frac{V_i}{V_i}\right) = \frac{5}{2} R \ln(2) = 14.5 \frac{\text{J}}{\text{K}}$$

Notice that I don't need to talk about the path (so long as it is reversible) to answer this question.

(2) 1 kg of ice at 0°C melts to become water at 0°C. What is the change in entropy of the ice?

Solution:

Start with:

$$\Delta S = \frac{Q}{T_m}$$

But if you use $T=0^\circ\text{C}$, you're just about as wrong as you can hope to be. You must work in K here. The solution?

$$\Delta S = \frac{mL_f}{273} = \frac{3.33 \times 10^5}{273} = 1219.9 \frac{\text{J}}{\text{K}}$$

(3) Suppose you mix 1 kg of water at 0°C with 1 kg of water at 100°C. What is the change in entropy for this mixing process?

Non-calculus

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = mc \left(\left(\frac{\Delta T_1}{T_1} \right) + \left(\frac{\Delta T_2}{T_2} \right) \right) = 4186 \left(\ln \left(\frac{323}{273} \right) + \ln \left(\frac{323}{373} \right) \right) = 4186 (0.1681 - 0.14393) = 101.5 \frac{\text{J}}{\text{K}}$$

Calculus

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = mc \left[\int \frac{dT_1}{T_1} + \int \frac{dT_2}{T_2} \right] = 4186 \left(\ln \left(\frac{323}{273} \right) + \ln \left(\frac{323}{373} \right) \right) = 4186 (0.1681 - 0.14393) = 101.5 \frac{\text{J}}{\text{K}}$$

(4) You have just made your first million. It also happens that the world has a terrible energy crunch at this time, and efficient engine development is all the rage. An inventor approaches you and suggests that you invest in his engine which works between 30 °C and 100°C because it has an efficiency of 70%. Do you invest? Why or Why not?

Solution: If you calculate

$$\epsilon_c = 1 - \frac{T_c}{T_h} = 1 - \frac{30}{100} = 0.7 \Rightarrow 70\%$$

and then invest, you've just lost your first million to a scam artist.

If you calculate:

$$\epsilon = 1 - \frac{303}{373} = 1 - 0.81 = 0.1888 \Rightarrow 18.8\%$$

and then don't invest, you're just seen the value of my physics course.

You will probably want to be sure to recommend that this guy visit your competition.

Note: each year when I use this problem, it gets closer and closer to being true!

(5) Show that:

(a) U is a function of temperature only

(b) $C_v = 3/2 R$

and the other features of ideal gases.

The kinetic theory of an ideal gas envisions point particles bouncing off of a wall and not interacting with each other. The force exerted by one molecule on the wall is given from Newton's law as:

$$F = \frac{\Delta p}{\Delta t}$$

The time between successive collisions for a box of length L is:

$$\Delta t = \frac{2L}{v_x}$$

for a one dimensional box.

The change in momentum is given by:

$$\Delta p = 2m v_x$$

If we permit the time between collisions to be accepted (in fact it is the time of collision that we should use however this is corrected by a closer examination), we'll use that t and p in the force equation to get:

$$F = \frac{2m v_x}{2L/v_x} = \frac{1}{L} m v_x^2$$

In general, the particle has equal amounts of velocities in the x , y and z directions. Thus,

$$v_x^2 = v_y^2 = v_z^2 = \frac{1}{3} v^2$$

where v is the magnitude of the velocity of the molecule.

We can thus find that for a 3-d box,

$$F = \frac{1}{3L} m v^2$$

Since we're interested in pressure, and since the wall of interest has an area $L \times L$, we find:

$$P = \frac{F}{L^2} = \frac{1}{3L^3} m v^2 = \frac{1}{3V} m v^2$$

Multiply by the volume V to get:

$$PV = \frac{1}{3} m v^2 = \frac{2}{3} \left(\frac{1}{2} m v^2 \right) = \frac{2}{3} \langle KE \rangle$$

We in general have N atoms present to give additions as:

$$PV = \frac{2}{3} N \langle KE \rangle$$

Compare this to the IDG:

$$\frac{2}{3} N \langle KE \rangle = NkT \Rightarrow T = \frac{2}{3} \frac{\langle KE \rangle}{k}$$

This means that the temperature and the average kinetic energy of an atom are connected as shown. But, the kinetic energy is indeed the internal energy of the ideal gas so thus, the internal energy of an ideal gas depends only upon temperature. (N is constant).

We can write this as:

$$U = N \langle KE \rangle$$

and thus, we find the exact functional dependence:

$$U = \frac{3}{2} NkT$$

How does U change with temperature?

$$\frac{\Delta U}{\Delta T} = \frac{3}{2} Nk$$

In terms of moles:

$$Nk = nR$$

so,

$$\frac{\Delta U}{\Delta T} = \frac{3}{2} nR = nc_v$$

Thus, we have the result:

$$c_v = \frac{3}{2} R$$

Notice the 3 .. it is very suggestive. Indeed, there are 3 degrees of freedom and we have 3 (1/2R) contributions to C_v . Suppose that we have a diatomic molecule. The rotational modes have 3 degrees of freedom but only 2 of these modes are capable of storing energy for a true point-particle system. This would add: 2/2 R to C_v .

If the molecule can also vibrate, we have additional considerations. There are 2 ways the molecule can vibrate and this adds an additional 2/2 R to C_v .

Thus, we have potentially:

$$c_v = \underbrace{\frac{3}{2} R}_{\text{translational}} + \underbrace{\frac{2}{2} R}_{\text{rotational}} + \underbrace{\frac{2}{2} R}_{\text{vibrational}}$$

But some of the modes will “freeze out” at low temperatures. Thus, we have the conclusion:

$\frac{1}{2} R$ is added to C_v for each degree of freedom which is realized in a system.

Here is an important quote regarding the vibrational contribution (From “Modern Physics for Scientists and Engineers,” 3rd. Edition (2006) (Brooks/Cole Publishers), page 301.

How many degrees of freedom does this add? One may be tempted to say just one, because of the potential energy $\frac{1}{2}\kappa(r-r_0)^2$, where κ is the spring’s force constant, r the separation between atoms, and r_0 the equilibrium separation between the atoms. But another degree of freedom is associated with the vibrational velocity $\frac{dr}{dt}$, because the vibrational kinetic energy is $\frac{1}{2}m\left(\frac{dr}{dt}\right)^2$.