

Entropy

1. What is a spontaneous process?

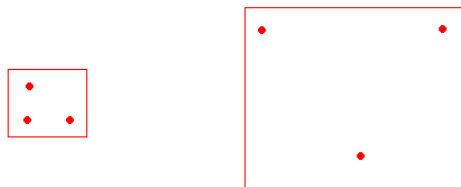
A process that requires no external assistance to occur.

2. True or False: Spontaneous reactions are fast.

False. Diamond → Graphite is spontaneous but it happens very slowly. Spontaneity is no indication of speed.

3. What is entropy?

Scientists wondered why some reactions were spontaneous. Entropy is what they decided to call the reason for spontaneity. Ultimately entropy is a measure of disorder related to positional probability. How many ways something can be placed in space.



The larger box is associated with greater entropy as there are more locations that the gas particles could be arranged relative to one another. Greater positional probability relates to greater disorder.

Entropy also represents the amount of energy in a system not available for useful work.

4. Why do things tend toward disorder?

- a. There are more paths to disorder.
If you think about a deck of cards. There are far more ways to have a disorganized deck than organized one. This is why if you were to toss a deck of cards in the air... you would in all likelihood not have them fall in the "correct" order.
- b. Less energy required to be disordered.
If you consider your own bedroom. Why is it that it is so easy for a mess to develop? Because it takes so much more work to maintain and keep it clean. Laziness and entropy go well together 😊.

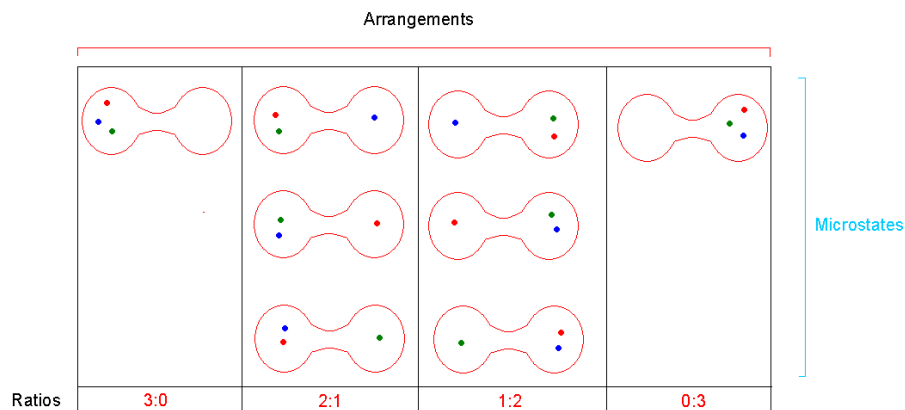
5. What state of matter has the highest entropy?

When we think about the main states of matter we have solid, liquid and gas. Solids are rigid structures that hold the atoms in the bonds firmly in place. The atoms/molecules in the structures typically have only a vibrational energy associated with them. Liquids are far less structured in that the atoms/molecules are able to move around. There are still forces though, that inhibit the extent of motion. Gases on the other hand are free agents. There is no need to interact with another atom/molecule to maintain the gaseous state – thus gases have the highest entropy of all the states of matter.

6. Determine the sign of ΔS :

- a. $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ $+\Delta S$: gain entropy with the solid to gas transition
- b. $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$ $-\Delta S$: lose entropy with loss of moles of gas.

7. What is an arrangement versus a microstate?



An arrangement represents the number of ways a system can be set so that one arrangement is distinct from another. In the picture above the ratio 3:0, 2:1, 1:2 and 0:3 represent the four different possibilities.

A microstate, on the other hand, represents the number of ways that a particular arrangement can be reorganized so that it has the same overall “big picture” (macroscopic) appearance.

Microscopically, however, there is a difference. If one were able to distinguish one particle from another you would have the situation illustrated above. In this example, there is only one way (or one microstate) associated with all the particles on the left and none on the right. There are, however, three variations when 2 particles are on the left and one is on the right. This is because there are three possibilities for which particle is on the right and which two are paired up.

8. There are multiple equations for entropy. The first relates it to the number of microstates a system has:

$$S = k_b \ln \Omega$$

$$k_b = 1.381 \times 10^{-23} \text{ J/K (Boltzmann's constant)}$$

Ω = number of microstates

- a. Why is this not a very useful equation?

Actual gas samples (with multiple molecules of gas) have far too many microstates to account for.

9. What would the change in entropy be for the following system change?



To solve this problem you need to remember that

$$\Delta S = S_F - S_I = (k_b \ln \Omega)_F - (k_b \ln \Omega)_I = (k_b \ln 1) - (k_b \ln 3) = -k_b \ln 3$$

The value of 1 for the final arrangement comes from the fact that it has only 1 microstate. The value of 3 for the initial arrangement comes from the fact that has 3 microstates.

10. What are the 3 additional equations for entropy, and in which case do you use each?

- a. Constant Temperature

$$\Delta S_T = nR \ln \left| \frac{V_2}{V_1} \right| = \frac{q_{\text{reversible}}}{T}$$

$$\Delta S_T = nR \ln \left| \frac{P_1}{P_2} \right| = \frac{q_{\text{reversible}}}{T}$$

- a. Constant Pressure

$$\Delta S_p = n C_p \ln \left| \frac{T_2}{T_1} \right|$$

b. Constant Volume

$$\Delta S_v = n C_v \ln \left| \frac{T_2}{T_1} \right|$$

11. One mole of an ideal gas with a volume of 1.0L and a pressure of 5.0 atm is allowed to expand isothermally into an evacuated bulb to give a total volume of 2.0L. Calculate w and q .

Remember that isothermal means that $\Delta T = 0$. In reactions where $\Delta T = 0$, $\Delta E = 0$ as well. Because $\Delta E = 0$, $q = -w$. The next thing we need to look at in this question is the fact that the expansion happened into an evacuated bulb. An evacuated bulb means that there were no forces countering the gases expansion... it was allowed to freely expand, i.e. it was a free expansion. In a free expansion there is no work. Thus $q = -w = 0$.

12. The molar heat capacities for CO_2 at 298.0K are

$$C_v = 28.95 \text{ J/molK}$$

$$C_p = 37.27 \text{ J/molK}$$

The molar entropy of CO_2 gas at 298.0 K and 1.000 atm is 213.64 J/mol K

- a. Calculate the energy required to change the temperature of 1.000 mol of CO_2 from 298.0K to 350.0K, both at constant volume and at constant pressure.

The energy required to change the temperature of a substance is q .

Because we are looking at both the constant volume and constant pressure conditions we will have to use two different equations.

$$q_V = nC_V\Delta T$$

$$q_P = nC_P\Delta T$$

All we need to do is take the information provided us in the question and plug it into the equations.

$$q_V = (1.000 \text{ mol})\left(28.95 \frac{\text{J}}{\text{mol K}}\right) (350\text{K} - 298\text{K}) = \boxed{1505.4 \text{ J}}$$

$$q_P = (1.000 \text{ mol})\left(37.27 \frac{\text{J}}{\text{mol K}}\right) (350\text{K} - 298\text{K}) = \boxed{1938.0 \text{ J}}$$

As we would expect, there is more energy required under constant pressure conditions than under constant volume conditions.

- b. Calculate the molar entropy of CO₂ gas at 350.0K and 1.000 atm.

If you compare these conditions to those described above – “The molar entropy of CO₂ gas at 298.0 K and 1.000 atm is 213.64 J/mol K” – we can see that the pressure remained constant so, to solve we will use

$$\Delta S_P = nC_P \ln \left| \frac{T_2}{T_1} \right|$$

All we need to do is plug in the given information.

$$\Delta S_P = (1.000 \text{ mol})\left(37.27 \frac{\text{J}}{\text{mol K}}\right) \ln \frac{350}{298} = 5.99 \frac{\text{J}}{\text{K}}$$

Be very careful in questions like these. You are being asked to solve for the molar entropy of the CO₂, not for the change in entropy.

Unlike E and H where we only look at the changes in each... we can look at the entropy of a given system.

In order to complete this question, we need to add the ΔS that we determined to the molar entropy value given in the question.

$$S = 213.64 \frac{\text{J}}{\text{K}} + 5.99 \frac{\text{J}}{\text{K}} = \boxed{219.6 \frac{\text{J}}{\text{K}}}$$

- c. Calculate the molar entropy of CO_2 gas at 350.K and 1.174 atm.

If you compare these conditions to those of part b (CO_2 gas at 350.0K and 1.000 atm) we can see that the temperature remained constant so, to solve we will use

$$\Delta S_T = nR \ln \left| \frac{P_1}{P_2} \right|$$

Now we just have to plug in and solve.

$$\Delta S_T = (1.000 \text{ mol}) \left(8.3145 \frac{\text{J}}{\text{mol K}} \right) \ln \left| \frac{1.000 \text{ atm}}{1.174 \text{ atm}} \right| = -1.33 \frac{\text{J}}{\text{K}}$$

Remember that this question asked for the molar entropy of CO_2 , not change in entropy so...

$$S = 219.6 \frac{\text{J}}{\text{K}} + (-1.33 \frac{\text{J}}{\text{K}}) = \boxed{218.3 \frac{\text{J}}{\text{K}}}$$

13. Calculate the entropy change for a process in which 3.00 mol of liquid water at 0°C is combined with 1.00 mol of water at 100.0°C in a perfectly insulated container. (Assume the molar heat capacity of water is constant at 75.3J/Kmol)

In this question it is important to note that there are 2 systems here – the hot system and cold system - and they will not have the same change in

entropy. We need to find the change of entropy in each system and then add up those values to find the net change in entropy for the process.

$$\Delta S_{\text{process}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}}$$

To answer this question we will use

$$\Delta S = nC \ln \left| \frac{T_2}{T_1} \right|$$

Unless you are dealing with a gaseous substance, you do not have to worry about C_p or C_v . It is just, simply, C . Let's plug the given information into the equation...

$$(3.00 \text{ mol}) \left(75.3 \frac{\text{J}}{\text{mol K}} \right) \ln \frac{T_2}{273\text{K}} = \Delta S_{\text{cold}}$$

$$(1.00 \text{ mol}) \left(75.3 \frac{\text{J}}{\text{mol K}} \right) \ln \frac{T_2}{373\text{K}} = \Delta S_{\text{hot}}$$

As you can see, we are missing a rather important piece of information, the final temperature. How are we supposed to get that value?

If you consider what has been done in this question – a hot system and cold system have been mixed. Does this remind you of anything? Hopefully it is reminding you of calorimetry calculations. In which case the following relationship is established

$$q_C = -q_H$$

and, for each system, we can use the equation

$$q = nC\Delta T$$

Combining these two ideas we get

$$n_C C \Delta T = - n_H C \Delta T$$

As you can see this equation incorporates temperature – this will then lead us to the value we are looking for. All we need to do is plug in the given information

$$(3.00 \text{ mol}) (\cancel{C}) (T_F - 273 \text{ K}) = -(1.00 \text{ mol}) (\cancel{C}) (T_F - 373)$$

both systems are liquid water. This means they have the same value of C, so they cancel out.

$$T_F = 298 \text{ K}$$

Now we are able to plug into the 2 entropy equations and solve

$$(3.00 \text{ mol}) \left(75.3 \frac{\text{J}}{\text{mol K}}\right) \ln \frac{298 \text{ K}}{273 \text{ K}} = 19.79 \frac{\text{J}}{\text{K}}$$

$$(1.00 \text{ mol}) \left(75.3 \frac{\text{J}}{\text{mol K}}\right) \ln \frac{298 \text{ K}}{373 \text{ K}} = -16.9 \frac{\text{J}}{\text{K}}$$

Now that we have determined how each system's entropy has changed, we can find the overall entropy change for the process

$$\Delta S_{\text{process}} = 19.79 \frac{\text{J}}{\text{K}} + -16.9 \frac{\text{J}}{\text{K}} = \boxed{2.9 \frac{\text{J}}{\text{K}}}$$

14. When changes in state happen under isobaric conditions. What relationship is established?

Because these processes are assumed to be occurring at constant pressure,

$$\Delta H = q.$$

15. What are the changes of state for each of the following?

- a. Fusion is when a solid \rightarrow liquid
- b. Vaporization is when a liquid \rightarrow gas.
- c. Sublimation is when a solid \rightarrow gas
- d. Condensation is when a gas \rightarrow liquid
- e. Freezing is when a liquid \rightarrow solid
- f. Deposition is when a gas \rightarrow solid

16. The equation to find the change in entropy during a state change are:

At the melting point and boiling point of a substance, the two states are present at equilibrium with one another. Remember that equilibrium processes are synonymous with reversible processes.

Additionally, these processes are reversible at these specific melting/boiling point temperatures; which mean that they are tantamount to an isothermal process at the point of state change.

Finally, remember that we have established that $\Delta H = q$ when these constant pressure phase changes occur. All of these factors lead us to the following equations.

a.
$$\Delta S_{\text{fusion}} = \frac{q_{\text{reversible}}}{T} = \frac{\Delta H_{\text{fusion}}}{T_{\text{melting point}}}$$

b.
$$\Delta S_{\text{vaporization}} = \frac{q_{\text{reversible}}}{T} = \frac{\Delta H_{\text{vaporization}}}{T_{\text{boiling point}}}$$

$$\Delta S_{\text{sublimation}} = \frac{q_{\text{reversible}}}{T} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sublimation point}}}$$

c.

17. A sample of ice weighing 1.00 mol, initially at a temperature of -30.0°C , is heated to 140.0°C at a constant pressure of 1.00 atm. Calculate q , w , ΔH , ΔE , and ΔS . For the process. The molar heat capacities (C_p) for solid, liquid, and gaseous water are 37.5 J/mol K, 75.3 J/mol K, and 36.4 J/mol K respectively. The enthalpies of fusion and vaporization are 6.01 kJ/mol and 40.7 kJ/mol, respectively. Assume ideal gas behavior.

When performing these calculations, it is a very good idea to consider every step of the process. Let's list what is happening:

1.	$\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(s)}$	(243K \rightarrow 273K)
2.	$\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$	(273K)
3.	$\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(l)}$	(273K \rightarrow 373K)
4.	$\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$	(373K)
5.	$\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(g)}$	(373K \rightarrow 413K)

The reason that we need to consider all of the steps, is because each phase has its own heat capacity associated with it. Additionally there are special equations for dealing with the phase changes. Let's first solve for q . Remember that because we are performing this process at constant pressure $q = \Delta H$.

We will consider the equation needed for each of the steps:

1.	$q = nC_{\text{solid}}\Delta T = \Delta H$
2.	$q = n(\Delta H_{\text{fusion}}) = \Delta H$
3.	$q = nC_{p, \text{liquid}}\Delta T = \Delta H$
4.	$q = n(\Delta H_{\text{vaporization}}) = \Delta H$
5.	$q = nC_{p, \text{gas}}\Delta T = \Delta H$

Now all we have to do is plug all the information into the equations to determine the heat gained in each step.

1. $\Delta H = q = (1.00 \text{ mol})(37.5 \frac{\text{J}}{\text{mol K}})(273\text{K} - 243\text{K}) = 1125 \text{ J}$

2. $\Delta H = q = (1.00 \text{ mol})(6010 \frac{\text{J}}{\text{mol}}) = 6010 \text{ J}$

3. $\Delta H = q = (1.00 \text{ mol})(75.3 \frac{\text{J}}{\text{mol K}})(373\text{K} - 273\text{K}) = 7530 \text{ J}$

4. $\Delta H = q = (1.00 \text{ mol})(40700 \frac{\text{J}}{\text{mol}}) = 40700 \text{ J}$

5. $\Delta H = q = (1.00 \text{ mol})(36.4 \frac{\text{J}}{\text{mol K}})(413\text{K} - 373\text{K}) = 1456 \text{ J}$

Lastly we sum up all the values of q that we have solved for to determine q for the entire process.

$$\Delta H = q = 1125 \text{ J} + 6010 \text{ J} + 7530 \text{ J} + 40700 \text{ J} + 1456 \text{ J} = 56800 \text{ J}$$

$$56800 \text{ J} \frac{\text{kJ}}{1000 \text{ J}} = \boxed{56.8 \text{ kJ}}$$

We are going to go through these same steps for each of the values we are calculating.

Let's look at work next.

1. There is no work for this transition as the solid would not have changed by any appreciable volume.
2. There is no work for this transition as the solid to liquid transition would not have changed by any appreciable volume.
3. There is no work for this transition as the liquid would not have changed by any appreciable volume.
4. There would be work for this phase change. There would be a rather large change in volume going from liquid to gas. We will use the formula: $w = -P\Delta V = -P(V_g - V_l)$

We are going to assume that the volume of the liquid is insignificant compared to the volume of the gas. So we can rework the equation to $w = -PV_g = -nRT_g$

5. There would also be work in this step as there would be an expansion of the gas. So we will once again use $w = -P\Delta V = -nR\Delta T$

Let's plug in the data for each point

1. $w = 0$
2. $w = 0$
3. $w = 0$

$$w = -(1 \text{ mol})\left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right)(373\text{K}) = -30.6 \text{ L atm}$$

4.
$$30.6 \text{ L atm} \frac{0.101325 \text{ kJ}}{\text{L atm}} = -3.10 \text{ kJ}$$

$$w = -(1 \text{ mol})\left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right)(413\text{K} - 373\text{K}) = -3.28 \text{ L atm}$$

5.
$$-3.28 \text{ L atm} \frac{0.101325 \text{ kJ}}{\text{L atm}} = -0.33 \text{ kJ}$$

Lastly we sum up all the values of work that we have solved for to determine w for the entire process.

$$w = (-3.10 \text{ kJ}) + (-0.33 \text{ kJ}) = \boxed{-3.43 \text{ kJ}}$$

Solving for the value of ΔE is pretty easy at this point. Remember that

$$\Delta E = q + w$$

Because we have already solved for the q and w of this process, we can just plug our information into this equation and solve.

$$\Delta E = (56.8 \text{ kJ}) + (-3.43 \text{ kJ}) = \boxed{53.4 \text{ kJ}}$$

Lastly, let's solve for entropy, following the same guidelines laid out.

1.
$$\Delta S = nC_{p, \text{solid}} \ln \left| \frac{T_2}{T_1} \right|$$

2.
$$\Delta S = \frac{\Delta H_{\text{fusion}}}{T_{\text{melting point}}}$$

3.
$$\Delta S = nC_{p, \text{liquid}} \ln \left| \frac{T_2}{T_1} \right|$$

4.
$$\Delta S = \frac{\Delta H_{\text{vaporization}}}{T_{\text{boiling point}}}$$

5.
$$\Delta S = nC_{p, \text{gas}} \ln \left| \frac{T_2}{T_1} \right|$$

Let's plug in the data for each point

1.
$$\Delta S = (1.00 \text{ mol}) \left(37.5 \frac{\text{J}}{\text{mol K}} \right) \ln \left| \frac{273 \text{ K}}{243 \text{ K}} \right| = 4.37 \frac{\text{J}}{\text{K}}$$

2.
$$\Delta S = \frac{6010 \text{ J}}{273 \text{ K}} = 22.0 \frac{\text{J}}{\text{K}}$$

3.
$$\Delta S = (1.00 \text{ mol}) \left(75.3 \frac{\text{J}}{\text{mol K}} \right) \ln \left| \frac{373 \text{ K}}{273 \text{ K}} \right| = 23.5 \frac{\text{J}}{\text{K}}$$

4.
$$\Delta S = \frac{40700 \text{ J}}{373 \text{ K}} = 109.1 \frac{\text{J}}{\text{K}}$$

5.
$$\Delta S = (1.00 \text{ mol}) \left(36.4 \frac{\text{J}}{\text{mol K}} \right) \ln \left| \frac{413 \text{ K}}{373 \text{ K}} \right| = 3.71 \frac{\text{J}}{\text{K}}$$

Lastly we sum up all the values of work that we have solved for to

determine w for the entire process.

$$\Delta S = (4.37 \frac{\text{J}}{\text{K}}) + (22.0 \frac{\text{J}}{\text{K}}) + (23.5 \frac{\text{J}}{\text{K}}) + (109.1 \frac{\text{J}}{\text{K}}) + (3.71 \frac{\text{J}}{\text{K}}) = \boxed{162.7 \frac{\text{J}}{\text{K}}}$$

18. For mercury, the enthalpy of vaporization is 58.51 kJ/mol and the entropy of vaporization is 92.92 J/molK. What is the normal boiling point?

So in this question we are dealing with three factors, $\Delta H_{\text{vaporization}}$, $\Delta S_{\text{vaporization}}$, and $T_{\text{boiling point}}$. What we need to do, is think of an equation, that relates these three values. That equation is:

$$\Delta S_{\text{vaporization}} = \frac{\Delta H_{\text{vaporization}}}{T_{\text{boiling point}}}$$

Based on the information given we can plug in the values of $\Delta H_{\text{vaporization}}$ and $\Delta S_{\text{vaporization}}$ and solve for $T_{\text{boiling point}}$.

$$T_{\text{boiling point}} = \frac{\Delta H_{\text{vaporization}}}{\Delta S_{\text{vaporization}}} = \frac{(58510 \frac{\text{J}}{\text{mol}})}{(92.92 \frac{\text{J}}{\text{K mol}})} = \boxed{629 \text{ K}}$$

19. What do the following signs/values of ΔS_{univ} indicate?

- a. + : **spontaneous**
- b. - : **non-spontaneous**
- c. 0 : **at equilibrium**

20. What sign of $\Delta S_{\text{surroundings}}$ would be assigned for

a. Exothermic: $+ \Delta S_{\text{surroundings}}$

b. Endothermic: $- \Delta S_{\text{surroundings}}$