

1. Find/borrow a coin and flip it four times.
 - a) Record how many times the coin lands “heads up”.

Results here will vary between 0 and 4 for number of times it lands “heads up”.

- b) Is the outcome you obtained what you would have initially predicted? Briefly explain.

When flipping a coin four times, you would expect the coin to land an equal number of times heads up and tails up. For ONE individual performing this experiment, we could expect significant variation in the outcomes (with number of times heads up varying between 0 and 4). For a large group such as our class, we’d expect a distribution of results to emerge, with the most likely result to be $n = 2$ (2 flips landing heads up), $n = 1$ or 3 to be less likely, and $n = 0$ and 4 to be even less likely.

2. **Good question.** If all students in the class flip a coin four times, calculate the entropy associated with the MOST and LEAST likely outcomes. ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$).

As discussed in Question 1, the most likely outcome is $n = 2$ for heads up flips. There are six possible variations that lead to this result:

HHTT, TTHH, HTHT, THTH, HTTH, THHT

Therefore, there are six equivalent microstates ($W = 6$). The entropy associated with this is:

$$S = 1.38 \times 10^{-23} \ln(6) \text{ J K}^{-1} = 2.47 \times 10^{-23} \text{ J K}^{-1}$$

The LEAST likely outcome is $n = 0$ or $n = 4$ and the entropy will be the same with each of those. For example, with $n = 0$, only one microstate can describe this result (TTTT).

The entropy associated with this is:

$$S = 1.38 \times 10^{-23} \ln(1) = 0$$

3. HFC-134a (CH_2FCF_3 ; molar mass = 102.0 g mol^{-1} , boiling point = -27°C , $\Delta H_{\text{vap}} = 22.0 \text{ kJ mol}^{-1}$) is a common liquid refrigerant. It vaporizes using heat from the refrigerator, thereby cooling its contents, and is later condensed into a liquid with the help of a pump.
- a) Determine the entropy change (ΔS) in J K^{-1} for the reversible vapourization of 102.0 g of HFC-134a at its boiling point (at a constant pressure of 1 atm).

The vapourization process occurs at constant T and P (with $T = -27^\circ\text{C} = 246 \text{ K}$, and $P = 1 \text{ atm}$) and is done reversibly. Under these conditions, the change in entropy is given by

$$\Delta S = \frac{q_{p,\text{rev}}}{T} = \frac{n\Delta H_{\text{vap}}}{T} = \left(\frac{102 \text{ g}}{102 \text{ g mol}^{-1}} \right) \frac{22.0 \text{ kJ mol}^{-1}}{246 \text{ K}} = 0.0894 \text{ kJ K}^{-1} \\ = 89.4 \text{ J K}^{-1}$$

- b) If the heat in part a) comes from a refrigerator whose contents (the surroundings) are at a temperature of 4°C , determine ΔS_{surr} in J K^{-1} for the vapourization process.

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr,rev}}}{T_{\text{surr}}} = \frac{-q_p}{T_{\text{surr}}} = \frac{-n\Delta H_{\text{vap}}}{T_{\text{surr}}} = - \left(\frac{102 \text{ g}}{102 \text{ g mol}^{-1}} \right) \frac{22.0 \text{ kJ mol}^{-1}}{277 \text{ K}} \\ = -0.0794 \text{ kJ K}^{-1} = -79.4 \text{ J K}^{-1}$$

- c) Determine $\Delta S_{\text{universe}}$ for this process.

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}} = 89.4 \text{ J K}^{-1} - 79.4 \text{ J K}^{-1} = 10.0 \text{ J K}^{-1}$$

4. **Good question.** While performing an experiment, a CHEM 154 student cools the refrigerator from Question 3) to -35°C . Use the second law of thermodynamics to prove the refrigerator cannot operate by having HFC-134a absorb heat from the contents of the refrigerator under these conditions.

T_{surr} is now -35°C (238 K) and ΔS is still 89.4 J K^{-1} as determined in part a) but now the entropy change for the surroundings is

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr,rev}}}{T_{\text{surr}}} = \frac{-q_p}{T_{\text{surr}}} = \frac{-n\Delta H_{\text{vap}}}{T_{\text{surr}}} = - \left(\frac{102 \text{ g}}{102 \text{ g mol}^{-1}} \right) \frac{22.0 \text{ kJ mol}^{-1}}{238 \text{ K}} \\ = -0.0924 \text{ kJ K}^{-1} = -92.4 \text{ J K}^{-1}$$

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}} = 89.4 \text{ J K}^{-1} - 92.4 \text{ J K}^{-1} = -3.0 \text{ J K}^{-1}$$

$\Delta S_{\text{universe}}$ is negative, therefore this process is non-spontaneous.

There is a flaw with the solution above (or rather it makes an assumption not stated in the problem). For a challenge, see if you can find it. *Hint:* think about how Question 13 in Worksheet 4 might apply here.

5. Calculate ΔS° for the formation of 1 mol of solid Fe_2O_3 (rust!) from its elements given the following information:

Species	S_m° (J mol ⁻¹ K ⁻¹)
Fe(s)	27.28
O ₂ (g)	205.10
Fe ₂ O ₃ (s)	87.40



$$\Delta S^\circ = S^\circ(\text{Products}) - S^\circ(\text{Reactants})$$

$$= 1 \text{ mol} \times S_m^\circ(\text{Fe}_2\text{O}_3)$$

$$- \left[2 \text{ mol} \times S_m^\circ(\text{Fe}) + \left(\frac{3}{2}\right) \text{ mol} \times S_m^\circ(\text{O}_2) \right]$$

$$= 87.40 \text{ J K}^{-1} - \left[2(27.28 \text{ J K}^{-1}) + \left(\frac{3}{2}\right) 205.10 \text{ J K}^{-1} \right] = -274.81 \text{ J K}^{-1}$$

6. Consider the reaction: $\text{N}_2\text{O}_4\text{(g)} \rightarrow 2 \text{ NO}_2\text{(g)}$ $\Delta H^\circ = 58.03 \text{ kJ}$ $\Delta S^\circ = 176.7 \text{ J K}^{-1}$

- a) Calculate the temperature at which the reaction is at equilibrium under standard conditions (assume ΔH° and ΔS° do NOT vary with temperature).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

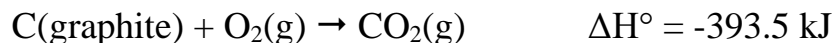
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{58030 \text{ J}}{176.7 \text{ J K}^{-1}} = 328 \text{ K}$$

- b) Explain what happens to the spontaneity of the reaction when the temperature is above or below that calculated in part a).

When the temperature is more than 328 K, the entropy term ($T\Delta S$) will be larger than the enthalpy term (ΔH); therefore, ΔG will be negative and the reaction will be spontaneous.

When the temperature is less than 328 K, the enthalpy term (ΔH) will be larger than the entropy term ($T\Delta S$); therefore, ΔG will be positive and the reaction will be non-spontaneous (in other words, it will be spontaneous in the reverse direction)

7. As part of your continued efforts to pay your CHEM 154 tuition bill by making diamonds from graphite, you have been studying the reaction:



In order to solve the key mysteries and create your diamonds, you need to determine the Gibbs energy of formation (ΔG_f°) for $\text{CO}_2(\text{g})$ using the following data (measured at 298 K):

$$S_m^\circ(\text{graphite}) = 5.7 \text{ J mol}^{-1} \text{ K}^{-1} \quad S_m^\circ(\text{O}_2) = 205.0 \text{ J mol}^{-1} \text{ K}^{-1} \quad S_m^\circ(\text{CO}_2) = 213.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

Using Gibbs' energy of formation the change in Gibbs energy can be found for the reaction using

$$\begin{aligned} \Delta G^\circ &= 1 \text{ mol} \times \Delta G_f^\circ(\text{CO}_2) - [1 \text{ mol} \times \Delta G_f^\circ(\text{C}) + 1 \text{ mol} \times \Delta G_f^\circ(\text{O}_2)] \\ &= 1 \text{ mol} \times \Delta G_f^\circ(\text{CO}_2) \end{aligned}$$

With the information provided, we can also calculate the change in entropy for the reaction as

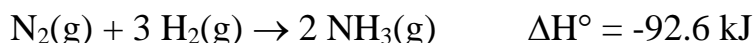
$$\begin{aligned} \Delta S^\circ &= 1 \text{ mol} \times S_m^\circ(\text{CO}_2) - [1 \text{ mol} \times S_m^\circ(\text{C}) + 1 \text{ mol} \times S_m^\circ(\text{O}_2)] \\ &= 213.6 \text{ J K}^{-1} - [5.7 \text{ J K}^{-1} + 205.0 \text{ J K}^{-1}] = 2.9 \text{ J K}^{-1} \end{aligned}$$

Finally, we know that at constant temperature $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ which when used with the information above gives

$$\begin{aligned} \Delta G^\circ &= 1 \text{ mol} \times \Delta G_f^\circ(\text{CO}_2) = \Delta H^\circ - T\Delta S^\circ = -393.5 \text{ kJ} - (298 \text{ K})(2.9 \text{ J K}^{-1}) \\ &= -394.4 \text{ kJ} \end{aligned}$$

This then gives $\Delta G_f^\circ(\text{CO}_2) = -394.4 \text{ kJ mol}^{-1}$.

8. **Good question.** Determine whether the reaction below is spontaneous using the data provided (measured at 298 K). Assume the system is in thermal equilibrium with the surroundings at 25 °C and the pressure is constant at 1 bar.



Species	S_m° (J mol ⁻¹ K ⁻¹)
N ₂ (g)	191.6
H ₂ (g)	130.6
NH ₃ (g)	192.5

First use the supplied information to calculate the change in entropy for the reaction as

$$\begin{aligned} \Delta S^\circ &= S_m^\circ(\text{Products}) - S_m^\circ(\text{Reactants}) \\ &= 2 \text{ mol} \times S_m^\circ(\text{NH}_3) - [1 \text{ mol} \times S_m^\circ(\text{N}_2) + 3 \text{ mol} \times S_m^\circ(\text{H}_2)] \\ &= (2)(192.5 \text{ J K}^{-1}) - [(1)(191.6 \text{ J K}^{-1}) + (3)(130.6 \text{ J K}^{-1})] \\ &= -198.4 \text{ J K}^{-1} \end{aligned}$$

One approach is to calculate ΔG° so that

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92.6 \text{ kJ} - (298 \text{ K})(-198.4 \text{ J K}^{-1}) = -33.5 \text{ kJ}$$

so the reaction is spontaneous as written under these conditions. Another approach is to calculate $\Delta S_{\text{universe}}$ directly, that is

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr,rev}}}{T_{\text{surr}}} = \frac{-q_p}{T} = -\frac{(-92.6 \text{ kJ})}{298 \text{ K}} \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = 310.7 \text{ J K}^{-1}$$

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}} = -198.4 \text{ J K}^{-1} + 310.7 \text{ J K}^{-1} = 112.3 \text{ J K}^{-1}$$

The reaction is spontaneous because the change in entropy of the universe is positive. Note that $-T\Delta S_{\text{universe}} = \Delta G^\circ$ as it should be (showing that these two approaches are just two different ways of expressing the Second Law).

9. Please watch <https://www.youtube.com/watch?v=IZaGmUGBdC0> or recall the frozen flask demo in class showing the result of mixing two solids – $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and NH_4Cl . The mixture of the two solids in the beaker is defined as our system. You will be asked to make observations about the different things going on with this reaction.
- a) What is happening to the consistency of the mixture as stirring occurs? What were the phases of the two reactants? Based on what you observed in the demo, what do you think the phase(s) of the products are?

The two reactants were solids. As they were mixed and stirred the mixture become more “soup like” as it was becoming a liquid.

- b) The reaction creates a strong odour as it proceeds. Does that help you identify any of the products of the reaction? What phase is the product that produces the smell?

The strong smell likely corresponds to ammonia gas.

- c) Based on the above, what do you think the SIGN of the entropy change is for the overall reaction? Can you speculate on the MAGNITUDE of the entropy change at all?

2 solids becoming liquid and gas. Entropy change will be positive and potentially quite large.

- d) Note what is being described about the temperature as the reaction proceeds. Is heat flowing into the system or out of the system? What is the sign of enthalpy for this reaction?

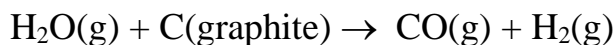
The flask gets very cold so heat will flow into it (the system). This means the enthalpy is positive so the reaction is endothermic.

- e) Is the reaction spontaneous? If so, what drives the spontaneity of this reaction – enthalpy, entropy or both? Explain and justify your answer. (Note: Mixing is NOT influencing the spontaneity of the reaction, it is merely speeding up the kinetics...)

Once two chemicals were mixed the reaction proceeded spontaneously. Therefore, ΔG is negative. As discussed above, ΔH is positive and ΔS is positive. That means $T\Delta S > \Delta H$ must be true to make the overall ΔG negative.

The process is entropy driven, by the formation of a large number of liquid H_2O molecules and the gaseous ammonia.

10. **Good Question.** Under standard conditions, determine the temperature above which the reaction below will favour the formation of products. (Assume the values of ΔH° and ΔS° in the table do not change with temperature)



	ΔH_f° (kJ mol ⁻¹)	S_m° (J mol ⁻¹ K ⁻¹)
H ₂ O (g)	-241.8	188.7
C(graphite)	0	5.7
CO(g)	-110.5	197.9
H ₂ (g)	0	130.6

$$\begin{aligned} \Delta H^\circ &= [1 \text{ mol} \times \Delta H_f^\circ(\text{CO}) + 1 \text{ mol} \times \Delta H_f^\circ(\text{H}_2)] \\ &\quad - [1 \text{ mol} \times \Delta H_f^\circ(\text{H}_2\text{O}) + 1 \text{ mol} \times \Delta H_f^\circ(\text{C})] = 131.3 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= [1 \text{ mol} \times S_m^\circ(\text{CO}) + 1 \text{ mol} \times S_m^\circ(\text{H}_2)] \\ &\quad - [1 \text{ mol} \times S_m^\circ(\text{H}_2\text{O}) + 1 \text{ mol} \times S_m^\circ(\text{C})] = 134.1 \text{ J K}^{-1} \end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{and at equilibrium } \Delta G^\circ = 0 \text{ giving a temperature of}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{131.3 \times 10^3 \text{ J}}{134.1 \text{ J K}^{-1}} = 979 \text{ K}$$

Above 979 K the formation of products will be favoured because for those temperatures, $\Delta G^\circ < 0$.