

Answers to Practice Test Questions 6

Entropy and Free Energy

1. Enthalpy of formation (and free energy of formation) is the enthalpy change (and free energy change) involved in producing a compound from its elements in their standard states. Since hydrogen gas is an element in its standard state, its enthalpy of formation (and free energy of formation) is zero.

Entropy is derived from the number of possible microstates (positional and energetic) for a molecule, and is measured in comparison to a perfect crystal of the substance at 0 K. There are many more ways to distribute energy in a sample of hydrogen gas under standard conditions (298 K) than there are in a sample of crystalline hydrogen at 0 K. As such, S° for hydrogen has a positive value – not zero.

2. A negative standard molar free energy of formation indicates that formation of a compound from its constituent elements is spontaneous.

A positive standard molar free energy of formation, on the other hand, indicates that the compound will (kinetics allowing) spontaneously decompose to its constituent elements. This also means that, under standard conditions, it won't even form in the first place.

For a compound with a positive value for $\Delta_f G^\circ$ to exist, it would therefore have to form under nonstandard conditions and have a relatively high kinetic barrier to decomposition under standard conditions. Thus, most compounds which actually exist have negative values for $\Delta_f G^\circ$.

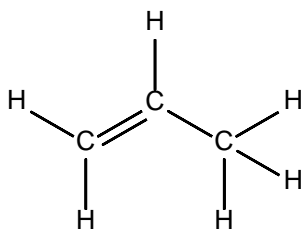
Please note that the terms “exothermic” and “endothermic” do not apply to free energy (they refer to enthalpy). It is entirely possible for a reaction/process to be endothermic and still spontaneous. If that weren't the case, you wouldn't be able to boil water.

3. $\Delta_r S > 0$

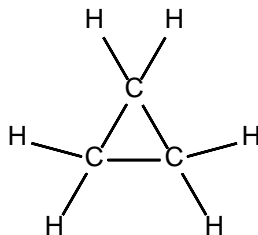
A solid decomposes to a solid and a gas. Since gases tend to have much larger (more positive) entropy values than solids or liquids, any reaction which generates a gas from solids/liquids should have a positive entropy change.

4.

(a)



propene



cyclopropane

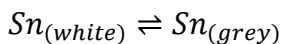
- (b) Propene should (and does) have a larger entropy at room temperature. It is possible to rotate about the C-C single bond, giving a large number of possible rotational microstates for the CH₃ group of each propene molecule. In cyclopropane, the three carbon atoms are locked into a triangle, so there is only one equivalent microstate.

Both molecules also have microstates associated with position of the gas molecules in the sample (both location and orientation) and energies of the gas molecules in the sample. Because we are talking about gases, we do not need to consider the ordering effect of intermolecular forces.

- (c) Condensation of a gas to either a liquid or solid always has a negative entropy change.

5.

- (a) **Step 1: Write a balanced chemical equation for the reaction**



- Step 2: Calculate the standard free energy change for the reaction**

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = \Delta_f G^\circ(Sn_{(grey)}) - \Delta_f G^\circ(Sn_{(white)})$$

$$\Delta_r G^\circ = 0.13 \frac{\text{kJ}}{\text{mol}} - 0 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_r G^\circ = 0.13 \frac{\text{kJ}}{\text{mol}}$$

- Step 3: Use standard free energy change to assess spontaneity under standard conditions**

$\Delta_r G^\circ > 0$ therefore forward reaction is not spontaneous

- (b) A spontaneous reaction is one that is thermodynamically favourable.

A spontaneous reaction may, however, have a high activation energy and be kinetically unfavourable. This is likely the case for the conversion of grey tin to white tin under standard conditions.

6.

(a) $\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$

$$\Delta_r H^\circ = 2 \Delta_f H^\circ(\text{CO}_{(g)}) - [\Delta_f H^\circ(\text{CO}_{2(g)}) + \Delta_f H^\circ(\text{C}_{(graphite)})]$$

$$\Delta_r H^\circ = 2 \left(-110.5 \frac{\text{kJ}}{\text{mol}} \right) - \left[\left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r H^\circ = 172.5 \frac{\text{kJ}}{\text{mol}}$$

(b) $\Delta H > 0$ (calculated in part (a); reaction is endothermic)

$\Delta S > 0$ (two moles of gas are formed for every one mole of gas reacted)

$\Delta G = \Delta H - T\Delta S$ In order for the reaction to be spontaneous ($\Delta G < 0$), $T\Delta S$ must be greater than ΔH . Since both ΔH and ΔS are positive, this will occur when T is large. Thus, the reaction will be spontaneous at high temperatures (or, at least, above a threshold temperature).

7.

(a) There are 50 sites to which the NO can stick, and the molecule can be in one of two possible orientations at each site, so the total number of microstates is $\Omega = 2 \times 50 = 100$.

$$\text{Thus, } S = k_B \ln \Omega = k_B \ln(100) = 4.61 k_B$$

(b) After dissociation, the N atom can be on any of 50 sites. Once we have picked a site for the N atom, there are 49 remaining possible sites for the O atom.

$$\text{The total number of microstates is therefore } \Omega_{\text{after}} = 50 \times 49 = 2450.$$

The change in entropy is therefore:

$$\Delta S = S_{\text{after}} - S_{\text{before}} = k_B \ln(2450) - k_B \ln(100) = k_B \ln\left(\frac{2450}{100}\right) = 3.20 k_B$$

8. All three reactions are spontaneous under standard conditions therefore all have $\Delta G^\circ < 0$.

Given that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, if ΔS° is negative then ΔG° can only be negative if ΔH° is negative (i.e. if the reaction is exothermic).

(a) $P_{4(s)} + 5O_{2(g)} \rightarrow P_4O_{10(s)}$ 5 moles of gas to 0 moles of gas therefore predict $\Delta S^\circ < 0$

Since $\Delta S^\circ < 0$ and $\Delta G^\circ < 0$, it is safe to predict that $\Delta H^\circ < 0$.

It is therefore reasonable to predict that this reaction is exothermic.

(b) $H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$ 2 moles of gas to 2 moles of gas therefore cannot predict sign of ΔS°

We cannot predict the sign of ΔH° with certainty.

(c) $2O_{3(g)} \rightarrow 3O_{2(g)}$ 2 moles of gas to 3 moles of gas therefore predict $\Delta S^\circ > 0$

We cannot predict the sign of ΔH° with certainty.

9.

(a) $\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$

$$\Delta_r H^\circ = [2 \Delta_f H^\circ(\text{BF}_3(\text{g})) + 3 \Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))] - [\Delta_f H^\circ(\text{B}_2\text{O}_3(\text{s})) + 6 \Delta_f H^\circ(\text{HF}(\text{g}))]$$

$$\Delta_r H^\circ = \left[2 \left(-1137.0 \frac{\text{kJ}}{\text{mol}} \right) + 3 \left(-285.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[\left(-1272.8 \frac{\text{kJ}}{\text{mol}} \right) + 6 \left(-271.1 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r H^\circ = -232.0 \frac{\text{kJ}}{\text{mol}}$$

(b) $\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$

$$\Delta_r S^\circ = [2 S^\circ(\text{BF}_3(\text{g})) + 3 S^\circ(\text{H}_2\text{O}(\text{l}))] - [S^\circ(\text{B}_2\text{O}_3(\text{s})) + 6 S^\circ(\text{HF}(\text{g}))]$$

$$\Delta_r S^\circ = \left[2 \left(254.12 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 3 \left(69.91 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right] - \left[\left(53.97 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 6 \left(173.78 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right]$$

$$\Delta_r S^\circ = -378.68 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

(c) Since ΔH° and ΔS° are both negative, ΔG° will only be negative at low temperatures (since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$). Therefore, the reaction will be favoured below a threshold temperature.

The temperature at which the reaction is neither favoured in the forward nor reverse direction is the temperature at which $\Delta G^\circ = 0$:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$T = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{\Delta_r S^\circ}$$

$$T = \frac{\left(-232.0 \frac{\text{kJ}}{\text{mol}} \right) - \left(0 \frac{\text{kJ}}{\text{mol}} \right)}{\left(-378.68 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$T = 612.7 \text{ K}$$

So, the reaction is favoured at temperatures below 612.7 K.

10.

(a) Entropy is a measure of our ignorance of the microstate of the system. If there are more microstates consistent with the observed macrostate, the entropy is higher: $S = k_B \ln \Omega$

In this case, the microstates are the individual passwords.

(b) You would need at least three English words. (*Four unrelated words is usually recommended.*)

Method (i) $\Omega = 94^8 = 6.1 \times 10^{15}$

$$S = k_B \ln \Omega = \left(1.380649 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) \ln(6.1 \times 10^{15}) = 5.0 \times 10^{-22} \frac{\text{J}}{\text{K}}$$

Method (ii) $\Omega = 250000^x = (2.5 \times 10^5)^x$

If $x = 1$, $\Omega = 2.5 \times 10^5$

If $x = 2$, $\Omega = 6.25 \times 10^{10}$

If $x = 3$, $\Omega = 1.6 \times 10^{16}$

$$\text{For } x = 3, S = k_B \ln \Omega = \left(1.380649 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) \ln(1.6 \times 10^{16}) = 5.1 \times 10^{-22} \frac{\text{J}}{\text{K}}$$

11.

- (a) The entropy of a substance is determined by the number of microstates that can correspond to the observed macrostate (according to the formula $S = k_B \ln \Omega$ where Ω is the number of possible microstates).

The entropy of vaporization for a substance refers to the difference in entropy values between the liquid and gas phases at the same temperature (in this case, the boiling point): $\Delta_{vap} S^\circ = S^\circ(gas) - S^\circ(liquid)$

Since the temperature of the gas and liquid is the same, the average kinetic energy of the particles is the same and the distribution of energy levels is the same. So, vaporization will not change the number of energy-level-based microstates. Therefore, the entropy of vaporization must be due to a change in the number of position-based microstates.

Since the entropy of vaporization of ethanol is a significantly larger positive value (compared to the other substances), this indicates that the number of position-based microstates increases by a greater amount from the liquid phase to the gas phase of ethanol (compared to the other substances). This implies either that the gas phase of ethanol has substantially less order (compared to the other substances) or that the liquid phase of ethanol has substantially more order (compared to the other substances) or both.

The order that limits the number of position-based microstates is due to intermolecular forces. Since intermolecular forces are relevant in the liquid phase and much less so in the gas phase (ideal gas model = no significant intermolecular forces in ideal gas), it can be expected that the reason for the anomalous entropy of vaporization value for ethanol is that ethanol experiences unusually strong intermolecular forces in the liquid phase.

Ethanol can hydrogen bond! This is a particularly strong type of intermolecular force which is not present in any of the other substances listed in the table. It increases the order of the liquid ethanol, limiting the number of possible microstates (since the ethanol molecules will be restricted to a limited number of relative orientations which permit maximum hydrogen bonding). When the ethanol vaporizes, the hydrogen bonding is no longer significant. As a result, there is a greater decrease in the order of ethanol when it vaporizes (compared to the other substances) and therefore the entropy of vaporization of ethanol is substantially greater than 85 kJ/mol.

- (b) **Step 1: Convert temperature into Kelvin**

$$T = 59.3 \text{ }^\circ\text{C} = 332.45 \text{ K}$$

Step 2: Calculate enthalpy of vaporization

$$\Delta S = \frac{q_{rev}}{T} \text{ and, at constant pressure, } q_{rev} = \Delta H \text{ therefore } \Delta_{vap} S = \frac{\Delta_{vap} H}{T}$$

$$\Delta_{vap} H = T \Delta_{vap} S$$

$$\Delta_{vap} H = (332.45 \text{ K}) \left(88.61 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 29.46 \frac{\text{kJ}}{\text{mol}}$$

Step 3: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

12.

(a) There are more moles of gas in the reactants (3 moles) than in the products (2 moles); therefore, the reaction is NOT entropy-favoured.

(b) If the reaction were exothermic then it would be favoured by enthalpy ($\Delta H < 0$).

To be thermodynamically favoured, a reaction must have $\Delta G < 0$ where $\Delta G = \Delta H - T\Delta S$.

If $\Delta H < 0$ and $\Delta S < 0$, then $\Delta G > 0$ at temperatures which are high enough that $T\Delta S$ is more negative than ΔH . This reaction will NOT be thermodynamically favoured at those temperatures. It will only be thermodynamically favoured at temperatures low enough that $T\Delta S$ is less negative than ΔH .

(c) If the reaction were endothermic then it would not be favoured by enthalpy ($\Delta H > 0$).

To be thermodynamically favoured, a reaction must have $\Delta G < 0$ where $\Delta G = \Delta H - T\Delta S$.

If $\Delta H > 0$ and $\Delta S < 0$, then $\Delta G > 0$ at all temperatures. So, the reaction will not be favoured under any conditions.*

**This is not 100% true since entropy changes with reaction conditions – temperature, in particular (as does enthalpy, but to a lesser extent). Thus, if it were possible to find a set of reaction conditions (temperature, pressure, etc.) at which the enthalpy or entropy values changed enough to make it favoured by one of those properties, it would then be possible for the reaction to be thermodynamically favoured under *those* conditions. Of course, this is a moot point for this reaction since it is exothermic anyway. And we didn't expect you to wax philosophical to this degree on the test.*

13. Ammonia gas, NH_3 , is synthesized from hydrogen and nitrogen gas.

(a) $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$

(b) $\Delta_r S < 0$, since fewer gaseous molecules are produced than consumed and, therefore, fewer microstates are available on the product side.

(c) For a spontaneous process, the entropy of the universe has to increase. The entropy of the reaction (system) can decrease in a spontaneous process as long as the entropy increase in the surroundings will compensate for that decrease. $\Delta_r S$ is not a measure of spontaneity; $\Delta_r G$ is.

14.

(a) Method A $\frac{1}{2}\text{O}_{2(g)} + \text{F}_{2(g)} \rightarrow \text{OF}_{2(g)}$ or $\text{O}_{2(g)} + 2\text{F}_{2(g)} \rightarrow 2\text{OF}_{2(g)}$

Method B $\frac{1}{2}\text{O}_{2(g)} + 2\text{F}_{(g)} \rightarrow \text{OF}_{2(g)}$ or $\text{O}_{2(g)} + 4\text{F}_{(g)} \rightarrow 2\text{OF}_{2(g)}$

(b) I would expect both reactions to have negative entropy changes. In Method A, 1.5 moles of gas react to form 1 mole of gas. In Method B, 2.5 moles of gas react to form 1 mole of gas. Since gases have large entropy values, reactions which have more moles of gaseous reactants than gaseous products generally have negative entropy changes.

(c) **Method A**

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{OF}_{2(g)}) = 41.9 \frac{\text{kJ}}{\text{mol}}$$

This reaction has a positive standard molar free energy change, so it is not spontaneous under standard conditions.

Method B

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{OF}_{2(g)}) - \left[\frac{1}{2} \Delta_f G^\circ(\text{O}_{2(g)}) + 2 \Delta_f G^\circ(\text{F}_{(g)}) \right]$$

$$\Delta_r G^\circ = 41.9 \frac{\text{kJ}}{\text{mol}} - \left[\frac{1}{2} \left(0 \frac{\text{kJ}}{\text{mol}} \right) + 2 \left(61.91 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r G^\circ = -81.9 \frac{\text{kJ}}{\text{mol}}$$

This reaction has a negative standard molar free energy change, so it is spontaneous under standard conditions.

Method B appears to be the better choice.

If you used the balanced equations with whole numbers, your calculated standard free energy values would be twice as large, but the signs (and therefore the conclusions) would be the same.

15.

(a) **Step 1: Calculate standard enthalpy change from standard enthalpies of formation**

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = \left[\Delta_f H^\circ(\text{HC} \equiv \text{CH}_{(g)}) + 3 \Delta_f H^\circ(\text{H}_{2(g)}) \right] - 2 \Delta_f H^\circ(\text{CH}_{4(g)})$$

$$\Delta_r H^\circ = \left[\left(226.7 \frac{\text{kJ}}{\text{mol}} \right) + 3 \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] - 2 \left(-74.81 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r H^\circ = 376.3 \frac{\text{kJ}}{\text{mol}}$$

Step 2: Calculate standard entropy change from standard entropy values

$$\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$\Delta_r S^\circ = \left[S^\circ(\text{HC} \equiv \text{CH}_{(g)}) + 3 S^\circ(\text{H}_{2(g)}) \right] - 2 S^\circ(\text{CH}_{4(g)})$$

$$\Delta_r S^\circ = \left[\left(200.9 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 3 \left(130.7 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right] - 2 \left(186.3 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$$

$$\Delta_r S^\circ = 220.4 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Step 3: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

$\Delta_r S^\circ$ is positive which makes sense since this is a reaction in which 2 moles of gaseous reactants give 4 moles of gaseous products.

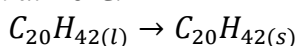
- (b) The system is at equilibrium when $\Delta G = 0$. The temperature at which this occurs can be calculated:

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

$$T = \frac{\Delta_r H - \Delta_r G}{\Delta_r S} = \frac{(376.3 \frac{\text{kJ}}{\text{mol}}) - (0 \frac{\text{kJ}}{\text{mol}})}{220.4 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1707 \text{ K} = 1434 \text{ }^\circ\text{C}$$

Given that ΔH and ΔS are both positive, the reaction will only be spontaneous at temperatures above 1434 $^\circ\text{C}$. This explains why the elaborate heat source is necessary.

16. Overall approach: Calculate $\Delta S_{\text{universe}}$ at 20 $^\circ\text{C}$ since, if $\Delta S_{\text{universe}} > 0$ then the reaction below can proceed in the forward direction at 20 $^\circ\text{C}$.



Since $\Delta_r H$ for the reverse reaction (fusion) is $+68.6 \frac{\text{kJ}}{\text{mol}}$, $\Delta_r H$ for the reaction as written (solidifying) is $-68.6 \frac{\text{kJ}}{\text{mol}}$.

Step 1: Calculate ΔS_{system}

For this part of the calculation, use the temperature at which $\text{C}_{20}\text{H}_{42}$ freezes/melts since that's the temperature at which the phase change occurs (and at which the entropy changes significantly).

The enthalpy change for freezing ought to be (and is) negative since heat is released when the liquid solidifies.

When a liquid solidifies, it becomes more ordered, so expect a negative entropy change for the system.

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta_r H}{T}$$

$$\Delta S_{\text{system}} = \frac{(-68.6 \frac{\text{kJ}}{\text{mol}})}{(37+273.15)\text{K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\Delta S_{\text{system}} = -221 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Step 2: Calculate $\Delta S_{\text{surroundings}}$

For this part of the calculation, use the temperature of interest since that's the temperature at which the surroundings are absorbing the heat from the solidifying substance.

The enthalpy change for the surroundings is positive since the surroundings are absorbing heat.

When the surroundings absorb heat, the number of energetic microstates increases, so expect a positive entropy change for the surroundings.

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta_r H}{T}$$

$$\Delta S_{\text{surroundings}} = \frac{(+68.6 \frac{\text{kJ}}{\text{mol}})}{(20+273.15)\text{K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\Delta S_{\text{surroundings}} = +234 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Step 3: Calculate $\Delta S_{universe}$

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

$$\Delta S_{universe} = \left(-221 \frac{J}{mol \cdot K}\right) + \left(+234 \frac{J}{mol \cdot K}\right)$$

$$\Delta S_{universe} = +13 \frac{J}{mol \cdot K}$$

Therefore, eicosane solidifies at 20°C since $\Delta S_{universe} > 0$ for that reaction at that temperature.

17. The Second Law of Thermodynamics states that “the entropy of the universe increases in any spontaneous process”.

The argument is flawed because it only addresses the entropy of the system and ignores the entropy of the surroundings. Reactions/processes in which the entropy of the system decreases are still allowed as long as the increase in the entropy of the surroundings increases by a greater amount.

This argument implies that water should never freeze; however, we know that this is not the case. While the water molecules become more ordered as the water freezes in a freezer, heat is given off into the surroundings, increasing the energy of the molecules in the air and therefore increasing the number of different ways in which that energy could be distributed between the air molecules. This is a net increase in the entropy of the universe despite being a decrease in the entropy of the system (the water/ice).