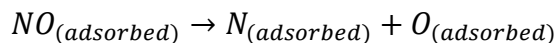


Practice Test Questions 6

Entropy and Free Energy

- Hydrogen gas has $\Delta_f H^\circ = 0 \frac{\text{kJ}}{\text{mol}}$ and $\Delta_f G^\circ = 0 \frac{\text{kJ}}{\text{mol}}$, but its $S^\circ = 130.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}$.
The enthalpy and free energy values are zero; why isn't the entropy value also zero?
- The vast majority of compounds in a table of thermodynamic data have a negative value for the standard molar free energy of formation. Why?
- Predict the sign of the entropy change for the reaction below. Briefly, justify your answer.
$$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$$
- There are two isomers of C_3H_6 . Both are gases under standard conditions.
 - Draw the Lewis structure of each isomer.
 - Which isomer would you expect to have a larger entropy under standard conditions? (*assuming the same volume of sample*) Why?
 - What would be the sign of the entropy change for the condensation of either of these gases?
- There are two allotropes of tin: white tin and grey tin.
 - Is the reaction converting white tin to grey tin spontaneous at 25 °C and 1 bar?
 - Both white tin and grey tin are stable at 25 °C. How can this be consistent with the statement that the conversion of one allotrope to the other is spontaneous at 25 °C? In other words, what does it mean for a reaction to be spontaneous?
Note that this part of the question doesn't imply which allotrope is converted to the other!
- Consider the following reaction:
$$\text{CO}_{2(g)} + \text{C}_{(\text{graphite})} \rightarrow 2 \text{CO}_{(g)}$$
 - Calculate ΔH° for the reaction:
 - Under what conditions would you expect this reaction to be spontaneous? Explain your reasoning.

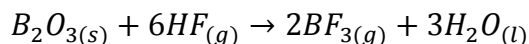
7. Atoms and molecules can adsorb (stick) onto metal surfaces. For diatomic molecules, we often find that one end of the molecule sticks to the surface while the other points away from the surface. Once adsorbed, further chemical processes can take place. This is often important in catalysis. Recently, research into catalysis by metals has emphasized the creation of very small metal particles because of the large surface area which can be obtained for a given mass of metal.
- (a) Suppose that we have a metal particle with 50 surface sites to which molecules can stick. A molecule of NO adsorbs onto this surface. If it is equally likely that either end of the NO molecule initially sticks to the surface, what is the entropy of this system (NO molecule stuck to metal surface via one atom)? *Express your answer as a multiple of k_B .*
- (b) After the initial adsorption, the NO molecule dissociates and both the N and O atoms end up adsorbed to the surface. After dissociation, the N and O atoms diffuse independently over the surface, each occupying a site:



What is ΔS for this process? *Express your answer as a multiple of k_B .*

8. Which of the following reactions, all of which are spontaneous under standard conditions, can you safely predict to be exothermic under standard conditions? Briefly, explain your reasoning.
- (a) $P_{4(s)} + 5 O_{2(g)} \rightarrow P_4O_{10(s)}$
- (b) $H_{2(g)} + F_{2(g)} \rightarrow 2 HF_{(g)}$
- (c) $2 O_{3(g)} \rightarrow 3 O_{2(g)}$

9. Consider the following reaction:



- (a) Calculate the enthalpy change for this reaction under standard conditions.
- (b) Calculate the entropy change for this reaction under standard conditions.
- (c) At what temperatures is this reaction favoured in the forward direction if all reactants and products have activities of 1? *Your answer must either be:*
- *a temperature range (including values and showing how they were determined),*
 - *“at all temperatures” (including explanation), or*
 - *“at no temperature” (including explanation).*

10. As discussed in class, entropy is often used in information theory. Among other uses, the entropy of a string of characters can be used to determine the strength of a password, i.e. how hard it would be to guess it. Consider two different ways to generate a password:
- Select eight random characters from the upper- and lower-case letters, numerals, and punctuation (a total of 94 characters).
 - Select a series of English words (e.g. onetwothreefourfive)*. There are about 250 000 words in English.

* *onetwothreefourfive* would be a really bad choice for an actual password ☺

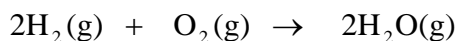
- What does entropy measure that makes it useful for determining the strength of a particular method for generating passwords?
- How many English words would you have to use so that the entropy of a password generated using method (ii) was higher than that of one generated using method (i). Show your calculations.

11. Consider the following table which gives the entropies of vaporization of a number of substances at their respective normal boiling points:

Substance	$\Delta_{\text{vap}} S_m^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$
Br ₂	88.61
CS ₂	83.7
Decane (C ₁₀ H ₂₂)	85.1
Dimethyl ether (CH ₃ OCH ₃)	86
Ethanol (CH ₃ CH ₂ OH)	110.0

- Note that all of the values in this table, except for that of ethanol, are around 85 J K⁻¹ mol⁻¹. This is known as Trouton's rule. Why is ethanol an exception to Trouton's rule? Your discussion should consider in detail the meaning of entropy and the physical factors that determine the value of the entropy of vaporization.
- Bromine boils at 59.3 °C. Calculate the enthalpy of vaporization of bromine at its boiling point. Report your answer in kJ/mol.

12. Consider the following reaction:



- Is this reaction entropy-favoured? Why or why not?
- If this reaction was exothermic, would it be thermodynamically favoured at all temperatures? Why or why not?
- If this reaction was endothermic, would there be any conditions under which it would be thermodynamically favoured? If yes, what would they be? If not, why not?

13. Ammonia gas, NH_3 , is synthesized from hydrogen and nitrogen gas.
- Write a balanced reaction equation for this synthesis. Include states of matter.
 - Predict the sign of the entropy change in this reaction. Provide an explanation for your answer.
 - Does your answer to part (b) explain that the reaction is spontaneous? Provide a brief explanation for your answer.

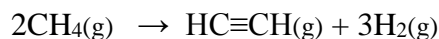
14. You wish to prepare oxygen difluoride (a gas). You are considering two methods for preparation of oxygen difluoride:

- Reaction of molecular oxygen with molecular fluorine (Method A)
- Reaction of molecular oxygen with atomic fluorine (Method B)

Due to equipment limitations, you must perform your reaction under standard conditions.

- Write a balanced reaction equation for each method.
- For each method, indicate whether you would expect the reaction to have a positive or negative entropy change. Justify your answers.
- For each method, determine whether or not the reaction will be spontaneous under standard conditions.

15. Acetylene, $\text{HC}\equiv\text{CH}$, can be manufactured from methane, CH_4 . Methane gas is passed through a chamber where it is exposed to a 1.5-metre-long electric arc discharge. Hydrogen is also produced:



- Calculate $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for this reaction.
- Why does this reaction require such an elaborate heat source? Estimate the temperature at which this reaction becomes spontaneous as part of your explanation. *Assume that $\Delta_r H$ and $\Delta_r S$ do not vary with temperature.*

16. Eicosane ($\text{C}_{20}\text{H}_{42}$) has a melting point of 37°C and an enthalpy of fusion of 68.6 kJ mol^{-1} . Using the second law of thermodynamics, show that liquid eicosane will solidify at 20°C .

17. Certain groups argue that life cannot have originated without help from a higher being. One of their arguments is as follows:

“In order for large biological molecules to form from smaller molecules (like CH_4 , H_2O and CO_2), you must violate the second law of thermodynamics. This is a universal law of decay and states that no process can create order from chaos.”

This argument misrepresents the second law of thermodynamics. State the real Second Law of Thermodynamics, and explain why this argument is flawed.

Your personal opinion on the origin of life is not relevant to this question. Please focus on this particular argument only.