

CLUTCH

www.clutchprep.com

CONCEPT: THERMOCHEMICAL PROCESSES

_____ is the branch of physical science concerned with heat and its transformations to and from other forms of energy.

In terms of a chemical reaction, you will learn that depending on certain conditions they can occur or not:

- A reaction that requires no outside energy source is classified as a **natural** process and is _____.
- A reaction that requires a continuous energy source to happen is classified as an **unnatural** process and is _____.

EXAMPLE 1: Which of the following statements is not true?

- The reverse of a spontaneous reaction is always non-spontaneous.
- A spontaneous reaction always moves towards equilibrium.
- A highly spontaneous reaction can occur at a fast or slow rate.
- It is possible to create a non-spontaneous reaction.

PRACTICE: Which of the following statements is/are true?

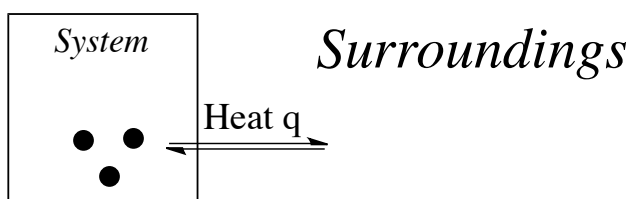
- The rusting of iron by oxygen is a non-spontaneous reaction.
- The addition of a catalyst to a reaction increases spontaneity.
- The movement of heat from a cold object to a hot object is a non-spontaneous reaction.
- The diffusion of perfume molecules from one side of a room to the other is a non-spontaneous reaction.
- None of the above.

CONCEPT: FIRST LAW OF THERMODYNAMICS

Recall that our system represents the chemical reaction, while the surroundings represent everything else. In terms of systems there are 3 major types.

- A(n) _____ system involves the transferring of both matter and energy between system and surroundings.
- A(n) _____ system involves the transferring of neither matter and energy between system and surroundings.
- A(n) _____ system involves the transferring of only energy between system and surroundings.

The **First Law of Thermodynamics** states that energy cannot be created nor destroyed, but only converted from one form to another.



$$\Delta U = \Delta E = q + w$$

$$q = \Delta H \text{ (enthalpy)}$$

$$w = - P\Delta V$$

ΔU or $\Delta E =$

$q =$ * For q : (+) when system _____, _____, _____, heat or energy.
 (-) when system _____, _____, _____, _____ heat or energy.

$w =$ * For w : (+) when work done _____ system _____ the surroundings. Key word: volume _____ .
 (-) when work done _____ system _____ the surroundings. Key word: volume _____ .

CONCEPT: ENTROPY AND SPONTANEOUS REACTIONS

The _____ Law of Thermodynamics states that molecular systems tend to move spontaneously to a state of maximum randomness or disorder.

This disorder is also called *entropy* and uses the variable _____.

In general, as we move from a

solid	→	liquid	→	gas
-------	---	--------	---	-----

 then entropy will _____ and its sign will be _____.

Conversely, if we move from a

gas	→	liquid	→	solid
-----	---	--------	---	-------

 then entropy will _____ and its sign will be _____.

EXAMPLE 1: Which should have the highest molar entropy at 25°C?

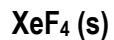
- a) Ga (l)
- b) Ga (s)
- c) Ga (g)
- d) All of them have the same molar entropy.

EXAMPLE 2: Which substance has greater molar entropy.

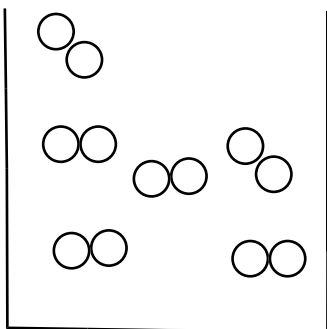
- a) CH₄ (g) **or** CCl₄ (l)
- b) Ne (g) **or** Xe (g)
- c) CH₃OH (l) **or** C₆H₅OH (l)

PRACTICE: ENTROPY AND SPONTANEOUS REACTIONS (CALCULATIONS 1)

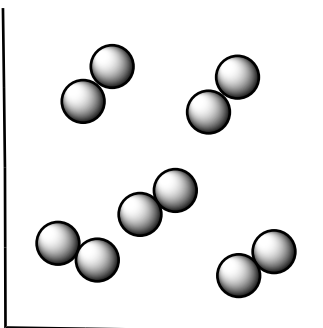
EXAMPLE 1: Arrange the following substances in the order of increasing entropy at 25°C.



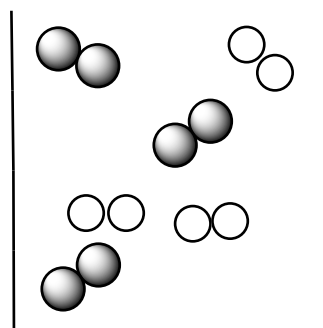
EXAMPLE 2: Containers A and B have two different gases that are allowed to enter Container C. Based on the image of Container C what is the sign of entropy, ΔS° .



A

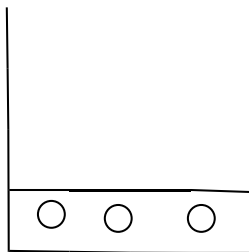


B

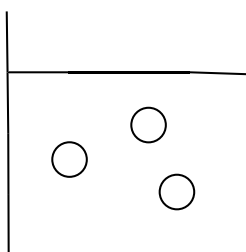


C

PRACTICE: An ideal gas is allowed to expand at constant temperature. What are the signs of ΔH , ΔS & ΔG .



A



B

PRACTICE: ENTROPY AND SPONTANEOUS REACTIONS (CALCULATIONS 2)

EXAMPLE: Consider the spontaneous fusion of ice at room temperature. For this process what are the signs for ΔH , ΔS , and ΔG ?

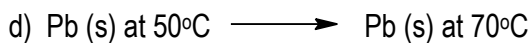
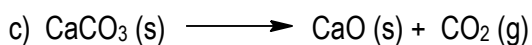
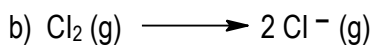
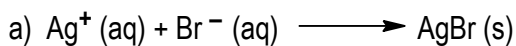
- | | ΔH | ΔS | ΔG |
|----|------------|------------|------------|
| a) | + | + | + |
| b) | - | + | 0 |
| c) | - | + | - |
| d) | + | + | - |
| e) | - | - | - |

PRACTICE: Consider the freezing of liquid water at 30°C . For this process what are the signs for ΔH , ΔS , and ΔG ?

- | | ΔH | ΔS | ΔG |
|----|------------|------------|------------|
| a) | + | - | + |
| b) | - | + | 0 |
| c) | - | + | - |
| d) | - | - | + |
| e) | - | - | - |

PRACTICE: ENTROPY AND SPONTANEOUS REACTIONS (CALCULATIONS 3)

PRACTICE 1: Predict the sign of ΔS in the system for each of the following processes:



PRACTICE 2: For each of the following reactions state the signs of ΔH (enthalpy) and ΔS (entropy):

a) Fusion of Ice.

b) Sublimation of CO_2 .

c) Vaporization of aqueous water.

d) Deposition of chlorine gas.

e) Condensation of a water vapor.

CONCEPT: CALCULATING ENTROPY OF A SYSTEM

The *2nd Law of Thermodynamics* states in terms of a system the entropy of a system increases spontaneously.

- Besides the system we also have our _____ and together they form the total _____.

Thus, to calculate the total entropy change, ΔS_{Total} , we use the following equation:

$$\Delta S_{\text{Total}} =$$

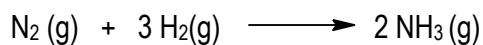
So if,

$\Delta S_{\text{Total}} > 0$, the reaction is _____

$\Delta S_{\text{Total}} < 0$, the reaction is _____

$\Delta S_{\text{Total}} = 0$, the reaction is _____

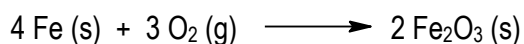
EXAMPLE 1: Calculate the standard entropy (in kJ) of reaction at 25°C for the following reaction:



The standard molar entropies of N_2 , H_2 and NH_3 are $191.5 \frac{\text{J}}{\text{K mol}}$, $130.6 \frac{\text{J}}{\text{K mol}}$ and $192.3 \frac{\text{J}}{\text{K mol}}$ respectively.

PRACTICE: CALCULATING ENTROPY OF A SYSTEM (CALCULATIONS 1)

EXAMPLE: The oxidation of iron metal is given by the following reaction:



a) Calculate the ΔS_{system} if the standard molar entropies of Fe, O₂ and Fe₂O₃ are $27.3 \frac{\text{J}}{\text{K} \cdot \text{mol}}$, $205.0 \frac{\text{J}}{\text{K} \cdot \text{mol}}$ and $87.4 \frac{\text{J}}{\text{K} \cdot \text{mol}}$ respectively.

b) Calculate the $\Delta S_{\text{surroundings}}$ if the reaction is spontaneous at 25°C. The standard molar enthalpy of Fe₂O₃ is $-824.2 \frac{\text{kJ}}{\text{mol}}$.

c) Calculate the ΔS_{Total} and determine if the reaction is spontaneous or non-spontaneous under standard-state conditions?

PRACTICE: Diethyl ether (C₄H₁₀O₂, MW = 90.1 g/mol) has a boiling point of 35.6°C and heat of vaporization of 26.7 kJ/mol. What is the change in entropy (in kJ/K) when 3.2 g of diethyl ether at 35.6°C vaporizes at its boiling point?

PRACTICE: CALCULATING ENTROPY OF A SYSTEM (CALCULATIONS 2)

EXAMPLE 1: The normal boiling point of liquid propane is 231 K. What is the enthalpy of vaporization of liquid propane?

CONCEPT: GIBBS FREE ENERGY

Chemists are generally interested in the system (the reaction mixture) rather than the surroundings. In order to define the free energy of a chemical system they use the following equations:

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

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

If $\Delta G < 0$, the reaction is _____

If $\Delta G > 0$, the reaction is _____

If $\Delta G = 0$, the reaction is _____

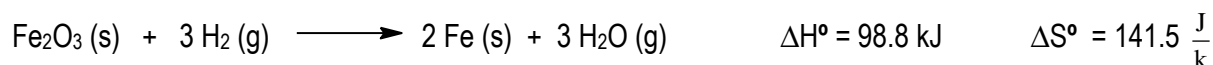
EXAMPLE 1: Which of the following statements is true for the following reaction?



- a) The reaction is spontaneous at all temperatures.
- b) The reaction is spontaneous at low temperatures.
- c) The reaction is spontaneous at high temperatures.
- d) The reaction is non-spontaneous at all temperatures.

PRACTICE: GIBBS FREE ENERGY (CALCULATIONS 1)

EXAMPLE: The reduction of iron(III) oxide with hydrogen produces iron metal and can be written as follows:



a) Is this reaction spontaneous under standard-state conditions at 25°C? If not, at what temperature will it become spontaneous?

PRACTICE 1: If ΔG is small and positive which of the following statements is true?

- a) The forward reaction is spontaneous and the system is far from equilibrium.
- b) The forward reaction is spontaneous and the system is near equilibrium.
- c) The reverse reaction is spontaneous and the system is far from equilibrium.
- d) The reverse reaction is spontaneous and the system is near equilibrium.

PRACTICE 2: Nitrogen gas combines with fluorine gas to form nitrogen trifluoride according to the reaction below at 25°C:



Calculate ΔG° and state if the reaction favors reactants or products at standard conditions.

- a) $\Delta G^\circ = -332 \text{ kJ}$; the reaction favors the formation of reactants.
- b) $\Delta G^\circ = -166 \text{ kJ}$; the reaction favors the formation of products.
- c) $\Delta G^\circ = -166 \text{ kJ}$; the reaction favors the formation of reactants.
- d) $\Delta G^\circ = -332 \text{ kJ}$; the reaction favors the formation of products.

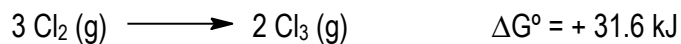
PRACTICE: GIBBS FREE ENERGY (CALCULATIONS 2)

EXAMPLE: For mercury, $\Delta H_{\text{vap}} = 58.5 \frac{\text{kJ}}{\text{mol}}$ and $\Delta S_{\text{vap}} = 92.9 \frac{\text{J}}{\text{k} \cdot \text{mol}}$ at 25°C. Does mercury boil at 350°C and 1 atm pressure?

EXAMPLE: The chemical reaction, $2 \text{NO}_2\text{Br} (\text{g}) \longrightarrow 2 \text{NO}_2 (\text{g}) + \text{Br}_2 (\text{g})$, has a $\Delta S^\circ = 135 \frac{\text{J}}{\text{mol} \cdot \text{k}}$ and $\Delta H^\circ = 926 \frac{\text{kJ}}{\text{mol}}$. Calculate the temperature when $K_{\text{eq}} = 4.50 \times 10^5$.

PRACTICE: GIBBS FREE ENERGY (CALCULATIONS 3)

EXAMPLE 1: Calculate ΔG_{rxn} at 25°C under the conditions shown below for the following reaction.



The partial pressures of Cl_2 and Cl_3 are 0.83 atm and 4.9 atm respectively.

EXAMPLE 2: For the reaction: $\text{N}_2 (\text{g}) + 2 \text{O}_2 (\text{g}) \rightleftharpoons 2 \text{NO}_2 (\text{g})$, $\Delta G^\circ = 75,550 \frac{\text{J}}{\text{mol}}$ at 175 K and $\Delta G^\circ = 41,875 \frac{\text{J}}{\text{mol}}$ at 225 K.

Calculate ΔS° and ΔH° for the reaction.