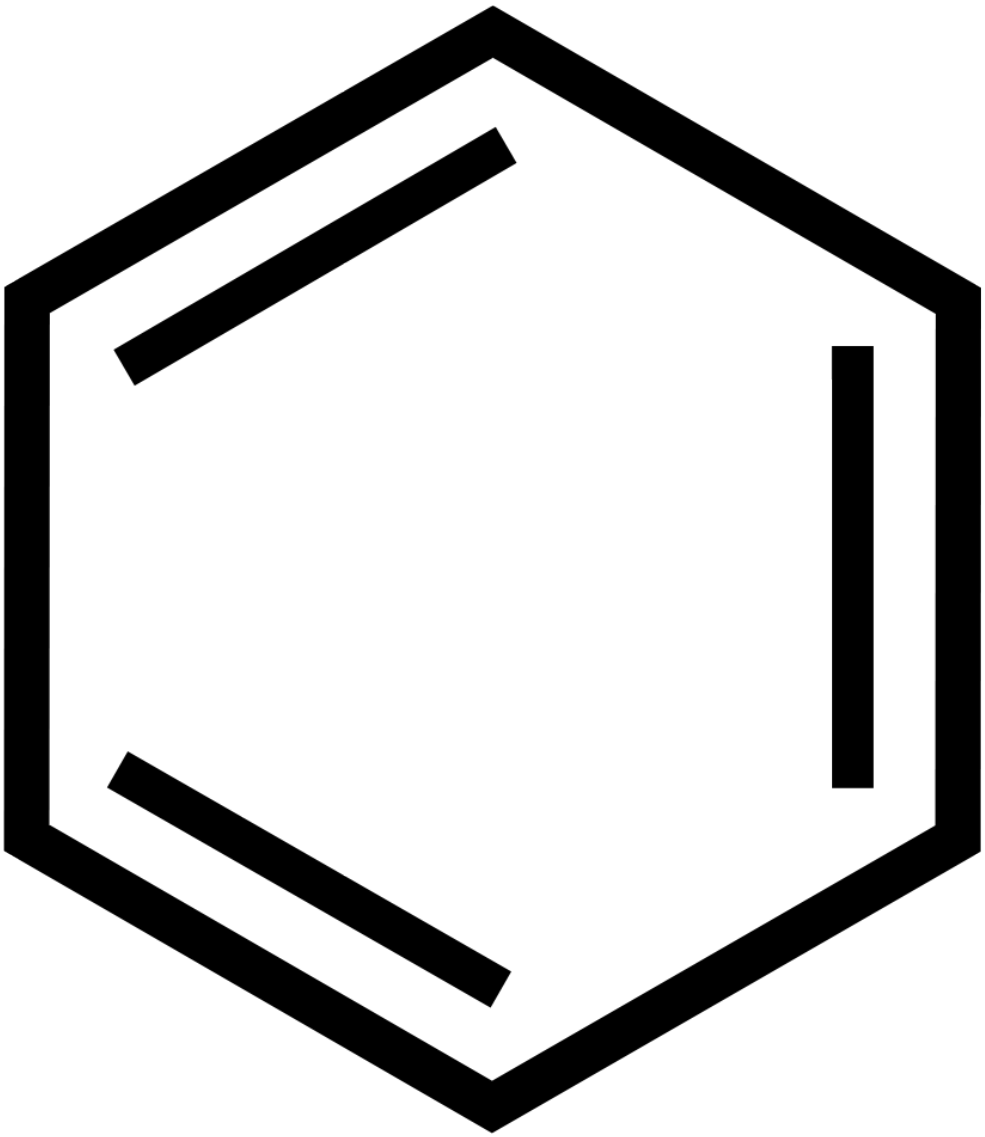

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CONCEPT: THERMOCHEMICAL PROCESSES

_____ 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?

a) The reverse of a spontaneous reaction is always non-spontaneous.

b) A spontaneous reaction always moves towards equilibrium.

c) A highly spontaneous reaction can occur at a fast or slow rate.

d) It is possible to create a non-spontaneous reaction.

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

a) The rusting of iron by oxygen is a non-spontaneous reaction.

b) The addition of a catalyst to a reaction increases spontaneity.

c) The movement of heat from a cold object to a hot object is a non-spontaneous reaction.

d) The diffusion of perfume molecules from one side of a room to the other is a non-spontaneous reaction.

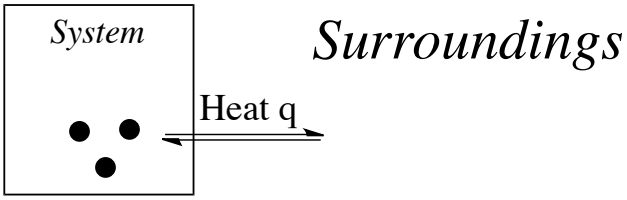
e) None of the above.

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.



$\Delta U = \Delta E = q + w$ $q = \Delta H$ (enthalpy) $w = -P\Delta V$

Δ**U** or Δ**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 25ºC?

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) CH_4 (g) **or** CCl_4 (l)

b) Ne (g) **or** Xe (g)

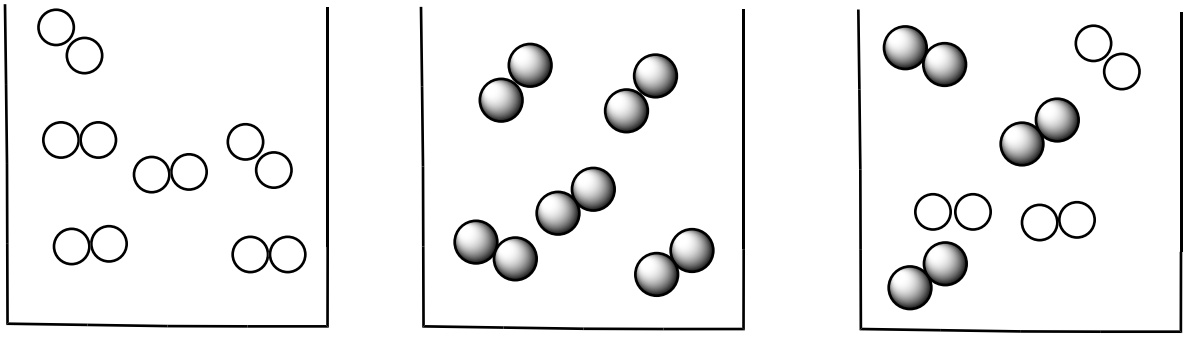
c) CH_3OH (l) **or** C_6H_5OH (l)

PRACTICE: ENTROPY AND SPONTANEOUS REACTIONS (CALCULATIONS 1)

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

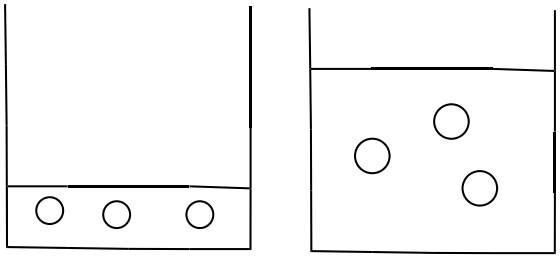
XeF_4 (s) **HI (g)** **BaO (s)** **H_2 (g)** **Hg (l)** **Br_2 (l)**

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^o.



A **B** **C**

PRACITCE: An ideal gas is allowed to expand at constant temperature. What are the signs of Δ**H**, Δ**S** & Δ**G**.



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 30ºC. 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:

a) $Ag^{+}(aq) + Br^{-}(aq) \longrightarrow AgBr(s)$

b) $Cl_2(g) \longrightarrow 2\,Cl^{-}(g)$

c) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

d) Pb (s) at 50°C $\longrightarrow$ Pb (s) at 70°C

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, $\Delta S_{\textbf{Total}}$, 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 25ºC for the following reaction:

$$N_2\,(g) + 3\,H_2(g) \longrightarrow 2\,NH_3\,(g)$$

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

PRACTICE: CALCULATING ENTROPY OF A SYSTEM (CALCULATIONS 1)

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

$$4\ Fe\ (s)\ +\ 3\ O_2\ (g) \longrightarrow 2\ Fe_2O_3\ (s)$$

a) Calculate the ΔS_{system} if the standard molar entropies of Fe, O_2 and Fe_2O_3 are 27.3 $\frac{J}{k \cdot mol}$, 205.0 $\frac{J}{k \cdot mol}$ and 87.4 $\frac{J}{k \cdot mol}$ respectively.

b) Calculate the $\Delta S_{surroundings}$ if the reaction is spontaneous at 25ºC. The standard molar enthalpy of Fe_2O_3 is – 824.2 $\frac{kJ}{mol}$.

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

PRACTICE: Diethyl ether ($C_4H_{10}O_2$, MW = 90.1 g/mol) has a boiling point of 35.6ºC 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 35.6ºC vaporizes at its boiling point?

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?

$N_2O_4\ (g) \longrightarrow 2\ NO_2\ (g)$ $\Delta H^\circ = -57.1$ kJ $\Delta S^\circ = 175.8$ kJ

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:

$$Fe_2O_3\,(s) + 3\,H_2\,(g) \longrightarrow 2\,Fe\,(s) + 3\,H_2O\,(g) \qquad \Delta H^{o} = 98.8\ kJ \qquad \Delta S^{o} = 141.5\ \frac{J}{k}$$

a) Is this reaction spontaneous under standard-state conditions at 25ºC? 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 25ºC:

$$N_2\,(g) + 3\,F_2\,(g) \longrightarrow 2\,NF_3\,(g) \qquad \Delta H^{o} = -249.0\ kJ \qquad \Delta S^{o} = -278\ J/K$$

Calculate ΔG^{o} and state if the reaction favors reactants or products at standard conditions.

a) ΔG^{o} = **-** 332 kJ; the reaction favors the formation of reactants.

b) ΔG^{o} = **-** 166 kJ; the reaction favors the formation of products.

c) ΔG^{o} = **-** 166 kJ; the reaction favors the formation of reactants.

d) ΔG^{o} = **-** 332 kJ; the reaction favors the formation of products.

PRACTICE: GIBBS FREE ENERGY (CALCULATIONS 2)

EXAMPLE: For mercury, ΔH_{vap} = 58.5 $\frac{kJ}{mol}$ and ΔS_{vap} = 92.9 $\frac{J}{k \cdot mol}$ at 25ºC. Does mercury boil at 350ºC and 1 atm pressure?

EXAMPLE: The chemical reaction, 2 NO_2Br (g) $\longrightarrow$ 2 NO_2 (g) + Br_2 (g), has a ΔS^o = 135 $\frac{J}{mol \cdot k}$ and ΔH^o = 926 $\frac{kJ}{mol}$. Calculate the temperature when K_{eq} = 4.50 x 10^5.

PRACTICE: GIBBS FREE ENERGY (CALCULATIONS 3)

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

$$3\ Cl_2\ (g) \longrightarrow 2\ Cl_3\ (g) \qquad \Delta G^o = +\ 31.6\ kJ$$

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

EXAMPLE 2: For the reaction: $N_2\,(g) + 2\ O_2\,(g) \rightleftharpoons 2\ NO_2\,(g)$, $\Delta G^o = 75,550\ \frac{J}{mol}$ at 175 K and $\Delta G^o = 41,875\ \frac{J}{mol}$ at 225 K.

Calculate ΔS^o and ΔH^o for the reaction.